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Electrically Conductive Structured Polymer Blends

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ELECTRICALLY CONDUCTIVE STRUCTURED POLYMER BLENDS

Principal Investigator M Narkis
Grantee Institution Technion - Israel Institute of Technology
Haifa, Israel

Collaborator M Kozlowski
Institution Polymark - Research, Development and Consulting Center
Wroclaw, Poland

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Electrically Conductive Structured Polymer Blends

M Narkis and A Siegmann
Israel

and

M Kozlowski
Poland

This final report reflects the collaborative research efforts both, in Poland and in Israel The two teams have maintained close collaboration throughout the three project years, aiming at the complementary efforts The Polish's team extended visits to Israel have greatly contributed to both, analyzing the data produced and outlining and updating future objectives In addition, experimental techniques and methods were compared and exchanged

The report was prepared in two main sections, the Israeli and the Polish one follows

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Electrically Conductive Structured Polymer Blends

M Narkis, R Tchoudakov, O Breuer and A Siegmann
Departments of Chemical and Materials Engineering
Technion - Israel Institute of Technology
Haifa, Israel 32000

Executive Summary

Polymer blends are presently being in the forefront of polymer science and technology and their further developments are only limited by creativity and imagination Their applications are as both, structural and/or functional materials Electrically conductive materials are of increasing industrial interest Smart blending namely, structuring of immiscible polymer blends containing a conductive filler, leads to conductive systems of unique structure and properties and of scientific and technical interest

The present project was designed to develop model systems, using conventional polymer processing methods and commodity polymers, and to better understand the general rules controlling the structure and properties of electrically conductive immiscible blends The structure and conductivity of numerous blends consisting of a series of immiscible polymer pairs and a conductive carbon black (CB), which were prepared by different routs, were investigated The polymer pairs were selected based on their thermodynamic properties and melt blended with CB The effects of matrix composition, i e , type of polymers and their relative content, and CB loading on the blends morphology and electrical conductivity were investigated The use of proper blend composition enabled to attain conductivity at very low CB content, an order of magnitude lower than that estimated by the classical percolation theories This could be achieved through the formation of a co-continuous matrix phase morphology and the preferential location of the CB particles in the dispersed phase or at the interphase area The control the composition of the systems and their thermodynamic and kinetic characteristics and the selection of a proper processing method enables one to design low CB content electrically conductive blends

The project's results and conclusions were presented in international conferences and published in scientific journals The results were of great interest and importance as the development and the understanding of conductive blends are concerned Moreover, the project's results are quite general and can be further applied to other systems and for different applications All goals were accomplished including also training of scientists and engineers, know-how and technology transfer and a fruitful international collaboration Both, the project and the collaboration are scheduled to continue

It is our pleasure to acknowledge the financial support of the project by the CDR program

Research Objectives

The technology of polymer blends for structural and functional applications is rapidly developing Electrically conductive plastics have become of great interest, especially for the electronic industry The demand for conductive plastics increases as the electronic industry is becoming larger and more sophisticated Polymer blends seem to be the optimal solution for the production of conductive plastics Therefore the science and technology of these blends is of great importance and will continue to be in the foreseen future Structured electrically conductive blends are innovative in nature and combine modern approaches of polymer physics, polymer physical chemistry and polymer engineering These type of blends enable to tailor make systems exhibiting desired optimal properties, through the detailed preferred distribution of the dispersed conductive filler in a designed multi-phase polymer morphology

The overall objective of the project was to develop model compounds of electrically conductive immiscible blends having unique electric/dielectric properties and stable structures towards conventional thermoplastic melt processing operations This research topic is at the forefront of polymer science and technology, as evident by the recent literature publications [1 - 10] The present project has contributed significantly to the state-of-art in the area, to better understanding the general rules controlling the structure and properties of electrically conductive immiscible polymer blends and to the advancement of their technology and applications Its contribution is not limited to conductive systems but rather general to the field of polymer blends

Methods and Results

To develop the understanding and general rules of the composition - processing - structure and behavior relationships of electrically conductive immiscible polymer blends several, different in nature material systems were selected to be blended with a conductive grade of carbon black (CB) The selection was based on thermodynamic and kinetic considerations, using commodity polymers The processing methods used were all based on conventional processing equipment

The processing - structure - conductivity relationships for the various selected systems were investigated

Experimental

Materials

Polypropylene (PP) - VC15-15P, Neste, Finland (Tm=173 C)
Copolyamide (Ny) - Nylon 6/6 9, EMS, Switzerland (Tm=132 C)
HIPS - Galirene HT 88-5, Carmel Olefins, Israel
LLDPE - Dowlex NG 5056 and Dowlex 2552E, Dow Chemicals
SIS - Quintac 3421 (14% PS), Japan
Carbon Black (CB) - Ketjenblack EC, Akzo Nobel Chemicals

Blends Preparation

All blends were prepared by melt mixing the dry blended CB and polymer components in a Brabender Plastograph equipped with a 50 cm^3 cell, at the typical processing temperature of the polymer components, for 15 minutes The resulting blends were subsequently compression molded to obtain 3 mm thick plaques Alternatively, selected systems were injection molded, using an Arburg 220/150 molding machine combined with a standard ASTM mold

Characterization

The resistivity measuring method of CB loaded polymers and blends depended on the sample geometry Compression molded samples were cut into 5 cm in diameter discs Their volume resistivity was measured (DIN 53596) using a Keithley Electrometer 614 and a high voltage supplier For samples with low level resistivity a Sorensen power supply, model QRD 60-1,5 was used Injection molded bars were measured according to ASTM D991, known as the "four point method"
The blends phase morphology was studied by both optical microscopy and electron microscopy An Olympus optical microscope was used to observe

microtomed samples A Jeol JSM 5400 scanning electron microscope (SEM) was employed to investigate freeze-fractured and microtomed surfaces
The rheological behavior of the studied systems was investigated using a capillary rheometer coupled with an Instron testing machine, equipped with a capillary 2" long and 0 05" in diameter The rheometer was operated at temperatures identical to those used for the processing

Results and Discussion

Polypropylene/Polyamide/CB Blends

The effect of CB on the conductivity of the individual polymers is very different The percolation threshold for the PP and Ny are 2 5 and larger than 13 phr, respectively (Fig 1), compared to literature values of 2 and 25 wt%, respectively [1,11,3,12,13] This difference stems from interfacial phenomena, resulting in different CB dispersion in the two polymers The interfacial energy plays an important role in the conductive paths formation, the greater the surface tension of the matrix polymer the higher is the percolation threshold It should be recalled that conductive paths (segregated structures), rather than homogeneous dispersions, are formed in systems in which the matrix/CB interfacial energy is high Therefore, the formation of CB/CB interface in such systems is energetically advantageous, leading to the formation of conducting networks However, in systems the polymer readily wets the CB particles, they are completely dispersed Hence, percolation can be achieved only at high CB loading For both, PP and Ny, the conductivity data and the morphological observations agree with the correlation between the surface tension of the matrix polymer and the resistivity of the CB-loaded composites [2]

The resistivity of PP/Ny/CB blends for different matrix composition and different CB loadings (e g Fig 2) does not obey any "additivity rule", but rather exhibits a complex behavior Moreover, the mixing sequence seems to significantly affect the blends resistivity Optical microscopy observations show that the PP/Ny matrix consists of two phases and that the CB is preferentially located in the Ny phase (Fig 3) This location of the CB was observed for all mixing sequences Thus, when PP

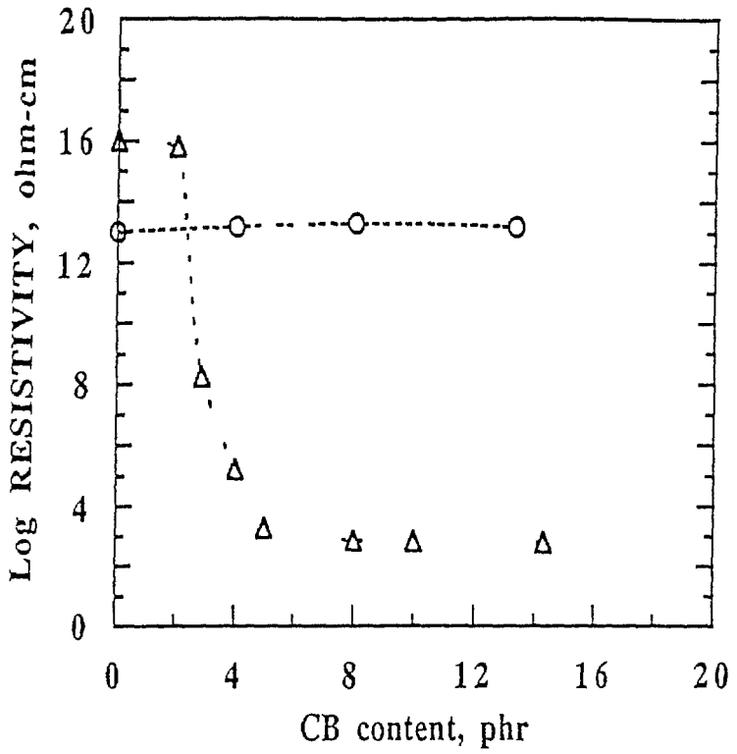

Fig 1 The resistivity of PP ( ) and Ny ( ) vs CB content

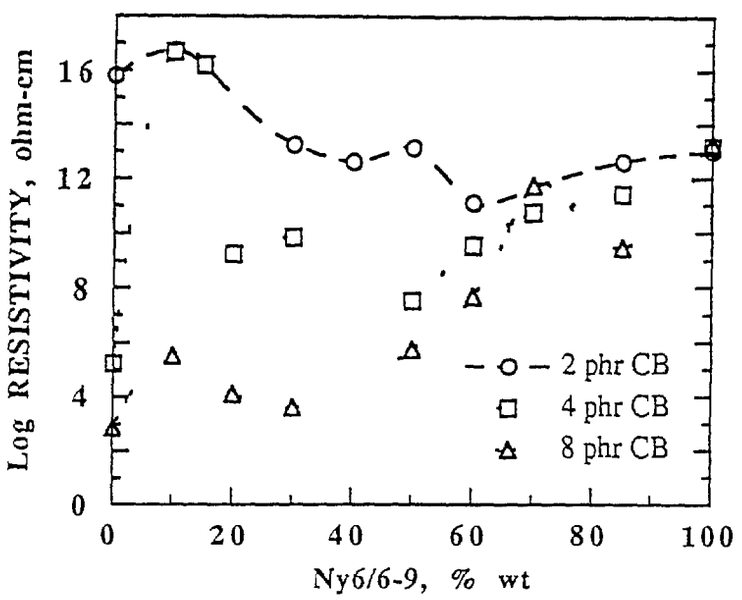

Fig 2 The resistivity of PP/Ny/CB blend vs Ny content

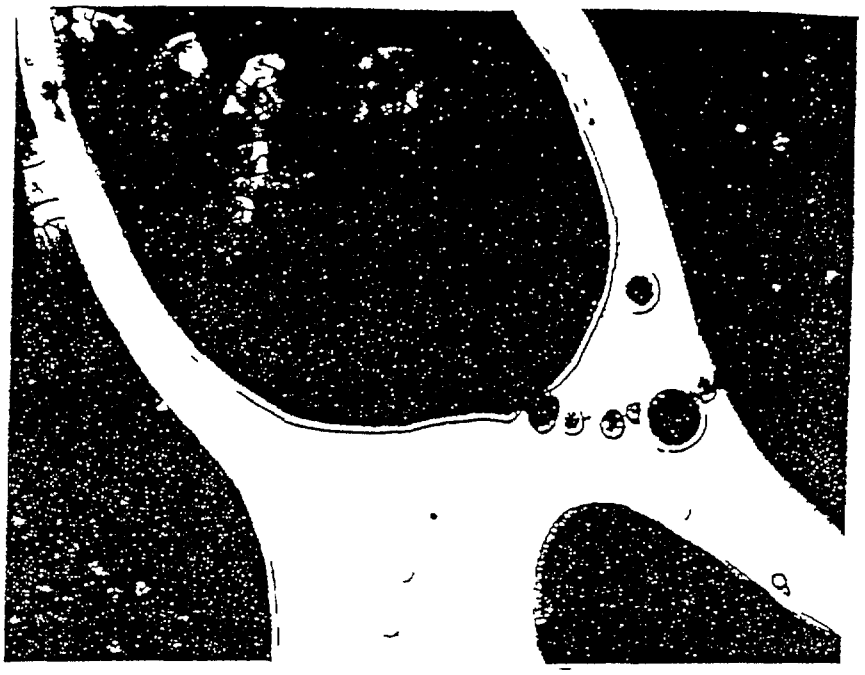

Fig 3 An Optical micrograph of the phase morphology of a PP/Ny/CB blend (Ny+CB - dark phase PP - white phase)

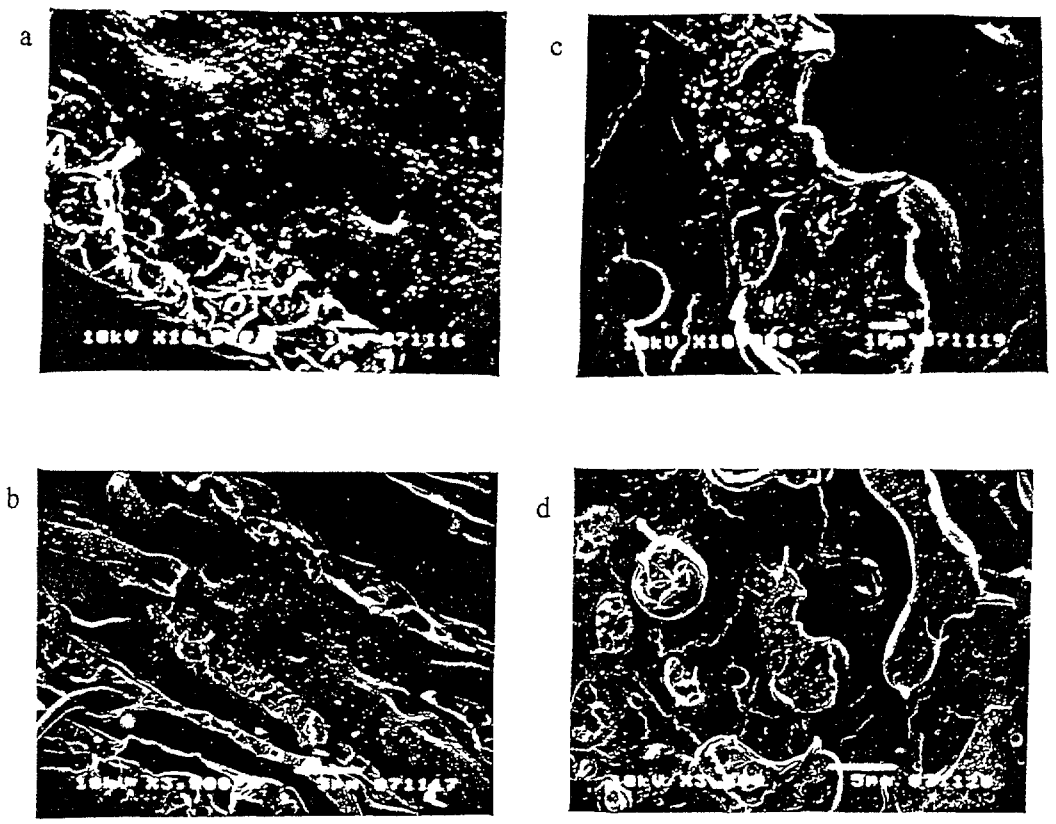

Fig 4 SEM micrographs of freeze-fractured 70HIPS/30LLDPE + 2 phr CB extruded at low shear rate parallel to flow, high (a) and low (b) magnification, transverse to flow, high (c) and low (d) magnification.

and CB are mixed first the CB is being transferred during blending from the PP to the Ny phase, for all blends composition

The PP/Ny/CB blends turn from insulating to conductive if the dispersed Ny phase forms a continuous phase and the CB particles within the Ny phase form a conductive network These conditions are met at Ny and CB contents above certain critical values Interestingly, the addition of CB makes the Ny phase continuous at a surprising low Ny content Hence, a co-continuous phase morphology in which a "double percolation" occurs leads to conductive PP/Ny/CB blends On the basis of these considerations the complex effects of the blends composition on the electrical conductivity can be explained

HIPS/LLDPE/CB Blends (Figures 4 & 5)

The effect of shear level on the structure and resultant resistivity of CB-containing high impact polystyrene/linear low density polyethylene (HIPS/LLDPE) extrudates produced by a capillary rheometer, as a function of blend composition and CB content, was studied The data were compared to results obtained by various processing methods such as compression molding, extrusion and injection molding The conductivity of systems consisting of a single polymer matrix is more sensitive to shear rate than in the case of HIPS/LLDPE matrices Increased temperature tends to increase resistivity at high shear rates, and has practically no effect at low shear rates Capillary entrance effects determine the CB structure and resultant resistivity of the extrudates Apparently, combined effects of CB location and flow-induced structuring, may explain the enhanced conductivity of some of the extrudates

HIPS/SIS/CB Blends

The morphology of high impact PS / tri-block copolymer styrene-isoprene/styrene / CB blends is of interest due to the unique structure of the matrix polymers and the blends potential as a conductive system

The fracture surfaces of HIPS/CB blends exhibit CB particles well dispersed in the PS matrix, leaving the rubber particles, which turn the PS into a HIPS, free of CB (Fig 6) Fracture surfaces of HIPS/SIS blends (Fig 7) show a multi-phase

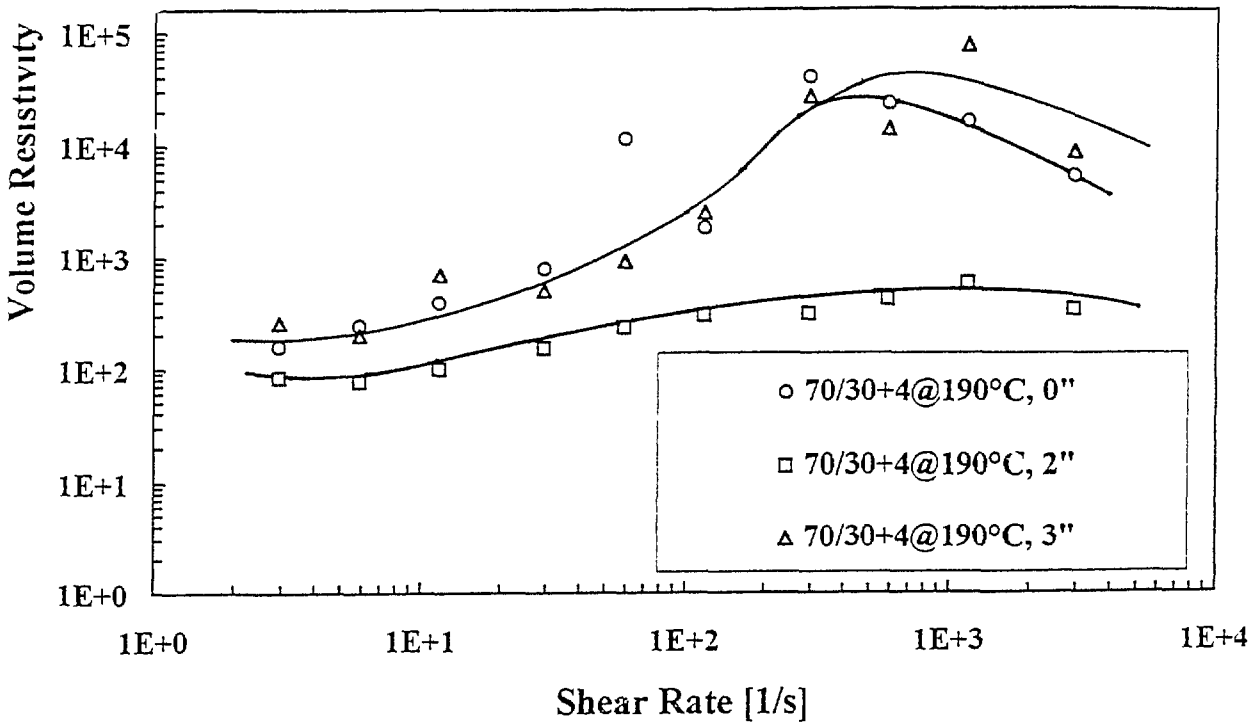

Fig 5 Resistivity vs extrusion shear rate of 4 phr CB containing 70HIPS/30LLDPE extrudates, at various capillary lengths, at 190°C

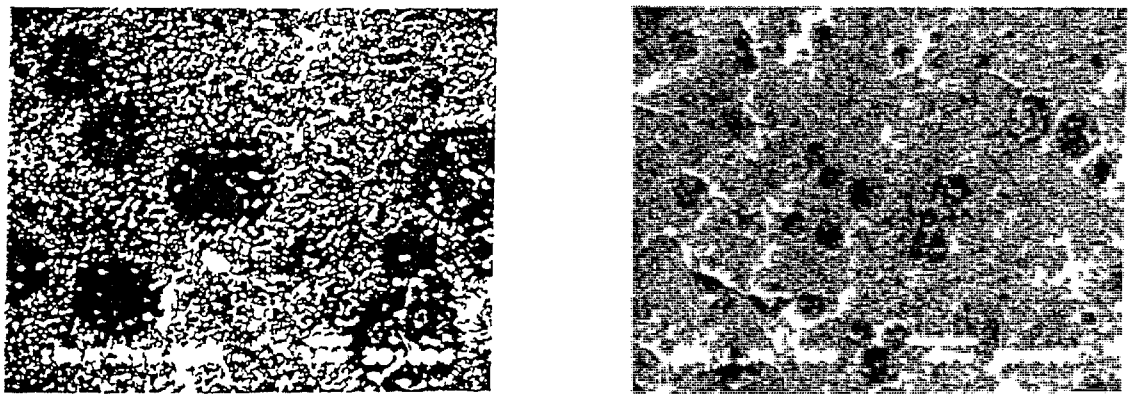

Fig 6 A SEM micrograph of a HIPS/CB(6 phr) blend

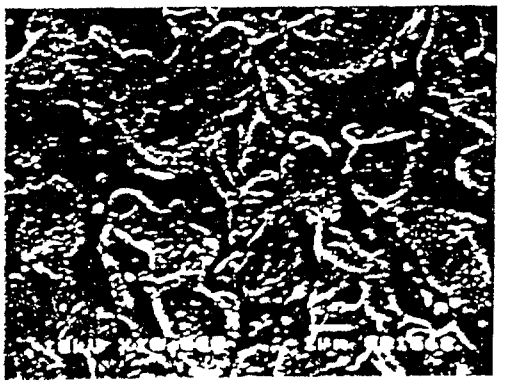

Fig 7 A SEM micrograph of a 80/20 HIPS/SIS blend

morphology with good interphase adhesion Upon increasing the SIS content a co-continuous phase structure is formed When CB is added to this blend, it is preferentially located in the HIPS

HIPS/ LLDPE/CB Blends

The volume resistivity of the individual HIPS, LLDPE and LL25 (a lower viscosity LLDPE) as a function of CB is depicted in Fig 8 HIPS exhibits the lowest percolation threshold (similar to that of PS) of these polymers This in spite the fact that the surface tension of PE is lower than that of HIPS, which has also some level of polarity This can be explained by the ability of HIPS to enhance some particle disintegration, however the HIPS/CB interactions are not strong enough to disperse CB uniformly within the matrix, as in polyamide-CB systems (shown above) Thus, an optimal structure producing conductive network at extremely low CB content is formed

The use of different viscosity PEs shows that the viscosity plays an important role in the dispersive mixing process, which consists of particle incorporation within the polymer liquid, deagglomeration, aggregate fracturing distribution and flocculation Thus, a high viscosity liquid may induce good dispersion, whereas the opposed effect of particle flocculation is more pronounced in a low density medium [14] The HIPS/LLDPE viscosity ratio affects also their blend morphology Both, the phase inversion composition and the dispersed particle size are affected

When CB is added to the HIPS/LLDPE blend, it is preferentially located in the PE phase, mainly on top of the PE phase surface [15,16] This location reflects the intermediate levels of CB interactions with both polymers The percolation threshold of these blends is generally at a very low CB content (Fig 9) Already a blend containing 15 wt% PE percolates at just 1 wt% CB This low percolation content is due to the CB location at the interphase area and due to the PE phase morphology namely, elongated particles, which enable the double percolation effect Although the blends percolate at about the same CB content as the HIPS (already very low) however, the resistivity values of the blends is several orders of magnitude lower than that of HIPS/CB systems

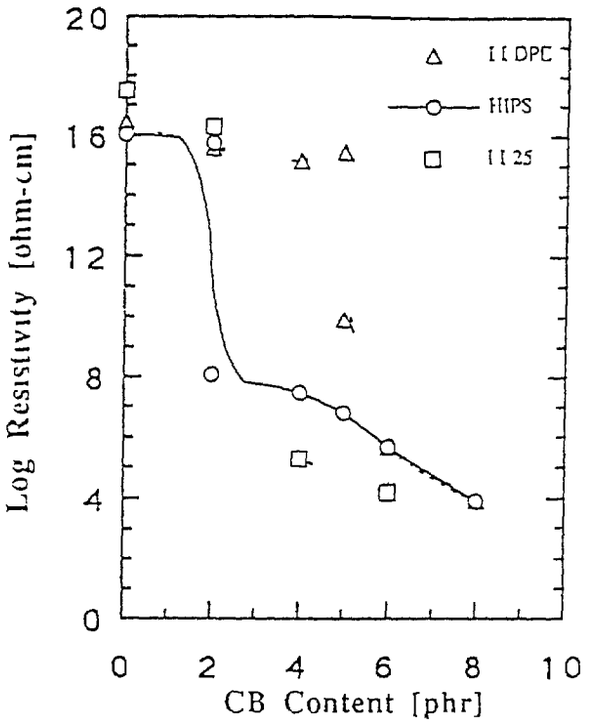

Fig 8 The resistivity of LLDPE, HIPS and LL25 vs CB content

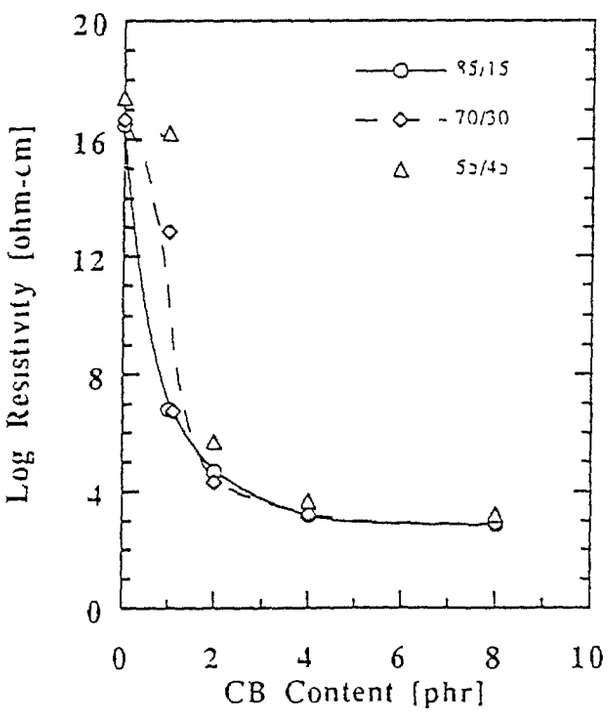

Fig 9 The resistivity of HIPS/LLDPE blends vs CB content

Fig 10 A SEM micrograph of a 70/30 HIPS/LCP blend

The rheological behavior of the two neat polymers is affected differently by the addition of CB The viscosity of HIPS increases while that of the LLDPE is unaffected by the incorporation of low CB loadings This difference is probably due to the different interactions between the CB particles and the two polymers The rheological behavior of the blends is affected by both, polymer matrix composition, CB content and matrix phase morphology, mainly whether dispersed or co-continuous one

HIPS/LCP/CB Blends

Blends containing liquid crystalline polymers (LCP) are of special interest due to both, their phase morphology and rheology The incorporation of LCP into HIPS results in significant reduction in the melt viscosity, becoming less significant at high shear rates It should be noticed that the addition of CB to HIPS results in a viscosity increase, which is a limiting factor in processing of highly CB loaded polymers The morphology of the rheometer extrudates is quite interesting Elongated LCP particles, rather than spherical, are dispersed in the HIPS matrix (Fig 10), their L/D ratio increases with shear rate In HIPS/LCP/CB blends the CB is located in the LCP phase, decreasing the LCP particle size

Conclusions

Studying the various immiscible polymer blends containing CB allows to draw the following main conclusions

1 Thermodynamic and kinetic considerations determine the phase morphology and thus the electrical conductivity of the blends

2 The relative surface energy of the components is a major factor in determining the blends morphology and the CB location

3 CB is preferentially located in the higher surface tension polymer

4 CB is dispersed homogeneously in a high surface tension polymer and segregates, forming a conductive network, in a low surface tension polymer

5 CB affects the matrix polymers rheology at a level depending on the CB/polymer interactions

6 Electrical conductivity in low CB content blends is attained in blends fulfilling the following conditions CB is located in or on the dispersed phase, the dispersed phase forms a continuous structure, the CB content is higher than the critical content required for percolation in the dispersed phase

7 Co-continuous morphologies enable the blends to percolate at low CB content

8 The processing method and conditions affect the blends morphology and their conductivity

These general main conclusions may serve as guide-lines for the tailor-making of economically and technologically feasible electrically conductive blends, based on commodity polymers Moreover, they may be used to design various functional blends other than conductive ones

Impact, Relevance and Technology transfer

The field of electrically conductive plastics, electrostatic dissipating (EDS) and anti-static (AS) materials, has recently been developed tremendously While it was in its infancy stage in 1992, when our R&D proposal was submitted, it is now a developed field and a variety of commercial materials with various levels of sophistication is available Nevertheless, there is still room for new, unique materials, which will be developed by scientists having a good background in polymer science and engineering, in the general field of conductive plastics and most importantly those who understand the need in ESD and AS materials of the electronic industry and are creative and have good imagination Along these lines it is clear that our approach of studying electrically conductive immiscible polymer blends has proven itself A new area, relevant to ESD and As materials, focuses on polymer systems containing intrinsically conductive polymers, such as polyaniline and polypyrolle The Israeli team has been already active in this field since 1995 and able to produce several interesting scientific publications and also results having a commercial potential The Polish team is exploring opportunities to enter this new field With the background gained through the AID project, the Polish team has now excellent skills for execution of a project related to intrinsically conductive plastics The relations of the two teams are excellent and include mutual visits and frequent e mail correspondence The Polish scientists are informed that the Israeli

team will gladly participate in a new project focusing on intrinsically conductive plastics and will bring to the project its expertise gained since 1995

Poland is well known as a country making significant steps to become a developed country in general and specifically also in plastics, carbon black and compounds thereof It is anticipated that the know-how gained based on the AID project may contribute to the relevant industrial development progress providing that suitable contacts are established In Israel, the AID project has served as a partial basis for a new project of developing electrically conductive composites which has the potential to materialize into an industrial project The in-depth understanding gained coupled with recent market studies are presently serving to work out new ideas for collaboration with local industry

Project Activities/Outputs

Conference Presentations

1 M Narkis, R Tchoudakov and A Siegmann, "Electrically Conductive Polymer Blends Containing Low Concentration Carbon Black", 2nd Intern Conf on Carbon Black, Mulhous (1993)

2 A Siegmann, D Benderly, M Narkis, R Tchoudakov and O Breuer, "Structuring Phenomena in Reinforced/Filled Immiscible Polymer Blends", The Eur Phys Soc Conf , Eindhoven (1994)

3 R Tchoudakov, O Breuer, M Narkis and A Siegmann, "Conductive Polymer Blends", ANTEC'95, Boston (1995)

4 M Narkis, T Tchoudakov, O Breuer and A Siegmann, "Conductivity and Morphology of Immiscible Polymer Blends with Low Carbon Black Loading", IUPAC Intern Symp on Polymer Morphology and Electrical Properties, Lodge (1995)

5 O Breuer, R Tchoudakov, M Narkis and A Siegmann, "Segregated Structures in Electrically Conductive Immiscible Polymer Blends", The 24th Israel Polymer and Plastics Conf , Tel Aviv (1995)

6 R Tchoudakov, O Breuer, M Narkis and A Siegmann, "Conductivity/Morphology Relationship in Immiscible Polymer Blends HIPS/SIS/Carbon Black", ANTEC'97, Canada (1997)

7 O Breuer, R Tchoudakov, Y Haba, Y Nachmias, M Narkis, A Siegmann, M Zilberman and G Titelman, "Electrically Conductive Polymer Blends", The 8th Materials Eng Conf , Beer Sheva (1997)

8 R Tchoudakov, M Narkis and A Siegmann, "Conductivity - Morphology Relationship in Immiscible Polymer Blends of the HIPS/SIS/CB Type", The 26th Israel Polymer and Plastics Soc Conf , Tel Aviv (1997)

Publications

1 "Conductive Polymer Blends with Low Carbon Black Loading Polypropylene/Polyamide", R Tchoudakov, O Breuer, M Narkis and A Siegmann, Polym Eng Sci , **36**, 1336 (1996)

2 "Conductive Polymer Blends with Low Carbon Black Loading Polypropylene/Polycarbonate", R Tchoudakov, O Breuer, M Narkis and A Siegmann, Polym Networks Blends, **6**, 1 (1996)

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4 "Conductive Polymer Blends with Low Carbon Black Loading High Impact Polystyrene/Thermoplastic Elastomer (Styrene-Isoprene-Styrene)", R Tchoudakov, M Narkis and A Siegmann, Polym Eng Sci , **37**, 1928 (1997)

Training

The program enabled to train a new immigrant from Russia and a several graduate students

Project Productivity

The project has accomplished, in our opinion, all goals included in the research proposal for the present grant

Future Work

The project has lead already to further studies of various immiscible blend systems, including electrically conductive systems It has expanded to systems containing intrinsically conductive polymers rather than just carbon black Research proposal were submitted to the Israel Ministry of Science and to the German-Israel Bi-National Science Foundation (GIF) The collaboration with the Polish partner will continue, depending on available support

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Conductive Polymer Blends With Low Carbon Black Loading Polypropylene/Polyamide

R TCHOUDAKOV O BREUER *and* M NARKIS*

Department of Chemical Engineering

and

A SIEGMANN

Department of Materials Engineering
Technion Israel Institute of Technology
Haifa 32000 Israel

The electrical resistivity and morphology of polypropylene/nylon (PP/Ny) immiscible blends incorporated with carbon black (CB) were studied CB was found to be preferentially located in the Ny phase or upon the Ny/PP interface Blends with a co-continuous phase morphology depicted especially low resistivity values due to a "double percolation" effect The blend preparation sequence tends to affect the phase morphology thus influencing the system s resistivity Polymer polarity and crystallinity are important factors determining the blend s morphology which relates directly to the electrical resistivity obtained

INTRODUCTION

One of the current goals of materials research is to create new materials with properties tailored to a particular application and to understand the physical processes that determine the end properties At present there is a great need to produce polymeric materials with relatively higher conductivity than is currently available without compromising the desirable mechanical and processing properties

The conduction mechanism of polymer/conductive filler systems is not yet fully established The effect of the polymer and filler characteristics on the conductivity of their mixtures especially the critical composition at which a dramatic resistivity change occurs i e the insulative-conductive transition are of special interest The common explanation for such a drastic change in the resistivity/filler content curves is related to the filler mode of dispersion In the low content region the filler incorporated in the form of small particles (aggregates or agglomerates) of different shapes is homogeneously distributed in the insulating matrix where adjacent filler particles are far apart With increasing filler content larger agglomerates of the filler particles are formed in which particles are in "contact " At a certain critical filler content the growing agglomerates reach a size that makes large scale "contact" possible forming a compact one two or three-dimensional network of the conducting phase within the insulating matrix The first appearance of the network results in a transition depicted by a drastic decrease in the resistivity of the mixture Following the initial formation of the conductive network and upon the sharp transition completion additional filler causes the resistivity of the mixture to gradually further decrease because of a slight improvement of the conductive network quality More important for the production of an optimized conductive mixture i e compounds showing a drastic resistivity decrease at a minimal amount of filler are the physical and sometimes chemical factors determining the formation of the conductive networks

The conductive network formation is currently explained in terms of the percolation theory Lux (1) in his recent extended review depicts a number of models that were proposed to explain the conductivity of mixtures on the basis of different factors such as volume fraction of the conductive phase the specific conductivity of the filler particles the probability of the development of at least a one-dimensional conductive network and the interfacial interactions at the boundary between the individual filler particles and the polymeric matrix Lux concludes that currently no existing model is able to explain all of the different results of experimental studies Furthermore no model is able to account for the extensive influence of different processing methods on the percolation process

To whom correspondence should be addressed

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A new dynamic interfacial theory of the sudden increase of conductivity in heterogeneous polymer systems was recently developed by Wessling (2 3) His major conclusion is that the conductivity increase phenomenon is actually a "phase transition" the conductive phase is suddenly converted at least partially from a fully dispersed to a flocculated stage The critical content at which this phase transition occurs is crucially dependent on the properties of the interphase between a conductive particle and the matrix polymer molecules and the temperature as well

Interesting results are reported by Carmona (4) and Miyasaka *et al* (5) relating the surface tension of polymers to the critical filler concentration of carbon black (CB) in polymer compositions They concluded that an excess energy due to the formation of CB/polymer interfaces plays the most important role When this excess energy reaches a "universal" value independent of polymer used the CB particles coagulate forming networks in the composite They have suggested that because of the CB surface properties the critical carbon content corresponding to the conductivity jump is related to the matrix polymer s polarity the higher the polarity of a given polymer the larger the critical content is The main assumption of their model is that CB particles begin to coagulate at an iso-interfacial energy state of the polymer which is analogous to the iso-free volume state for the glass transition temperature

According to Jurado *et al* (6) the percolation phenomenon observed for polypropylene samples at low CB contents is related to the wetting behavior and microstructure of the PP matrix It was found also that the non percolative samples seem to show a tunnelling effect as a conduction mechanism and percolative samples manifest a metallic behavior

The conduction mechanism for CB loaded natural rubber was studied (7–10) using current-voltage measurements and an electron spin resonance method for natural rubber compounds (7) The results are consistent with a model of electron-hopping transport with traps playing a prominent role the trap distribution depending on type of CB in the matrix Elastomer-CB surface interactions were reviewed in detail (11) and the existence of a chemical linkage between CB and typical rubbers was recognized Oono (12) studied the distribution of CB in rubber by the Fraunhofer diffraction method He found that under 40 phr CB isolated aggregates were distributed in the rubber and at 40 phr they began to partially form networks This CB content corresponds to the abrupt change of physical properties including conductivity of the filled rubber

Many authors have reported the electrical properties of CB-filled polyethylene (PE) (13–15) It has been established (13 14) that crosslinked compounds containing mixtures of two types of CB have shown good conductivity reproducibility and switching properties Segregated PE CB systems exhibit unusual electrical and dielectrical properties with relatively high conductivities at very low filler loadings (0 25% to 0 65% v/v CB) (15)

Conductivity of polymer blends containing CB i e three-component blends was investigated mainly for blends of elastomers (16) The existence (17) or absence (18) of CB migration within the multi-phased system during blending is discussed in terms of the affinity of different elastomers for CB Less has been reported on the conductivity of immiscible polymer blends filled with CB The electrical conductivity in addition to the parameters discussed above for single polymer/CB systems is expected to depend on the nature of the polymers comprising the blends and on the phase morphology of the systems Conductivity of low density polyethylene/natural rubber (LDPE/NR) blends loaded with CB (19) did not vary monotonously as a function of the blends composition Addition of only 10% LDPE to NR resulted in a sharp drop in the resistivity and the lowest value was obtained for 60%NR/40%LDPE blend containing 4% to 10% CB probably because of a specific structuring of the immiscible three-component system The resistivity of these blends is lower than the corresponding values for the individual components at the same CB loading

A model PE/PS blend system filled with CB was recently studied (20) It was noted that for CB in a semicrystalline polymer (PE) the percolation threshold was significantly lower compared to an amorphous matrix (PS) This could result from both the lower surface tension of PE than that of PS and the higher actual CB content in the semicrystalline PE because of the preferential location of the CB particles in the amorphous phase The percolation threshold was reduced even more when CB was located in the minor phase of a co-continuous PE/PS blend A more interesting situation corresponds to a system in which the CB was selectively located at the interface of a co-continuous PE/PS blend In the latter two cases the conductive phase network was continuous with the actual CB content in that phase probably much higher than the nominal content

Lee (21) has shown that the conductivity of a filled polymer system can be improved by the addition of a second polymer of lower viscosity The latter reduces the melt viscosity of the matrix and consequently reduces the breakdown of the CB structure Honeycomb-like conductive pathways through incompatible plastic/rubber blends at relatively low CB contents were obtained because of preferential accumulation of CB in one phase (22)

Sumita *et al* (23) showed that for roller mixed HDPE/PMMA blends a majority of the CB was located in the interfacial region around the HDPE phase while for HDPE/PP blends the CB appeared mainly in the HDPE matrix This preferential CB distribution was attributed to the interfacial tension and spreading coefficients The resulting high electrical conductivity of these systems depends on the percolation of CB within the CB rich phase and on a degree of continuity of this phase known as the "double percolation" concept It seems that these two factors do not provide a

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complete explanation for the preferential CB localization in the interfacial region or in one polymer only

Presently CB loaded polypropylene/polyamide blends with a low CB content were studied the initial results presented in (24) The effects of polyblend composition blending procedure and the components nature on the compounds electric conductivity and structure were investigated

EXPERIMENTAL

The polymers used to study the PP/Nylon/CB blends were polypropylene VC15-15P Neste Finland (T_m = 173°C) and copolyamide 6/6 9 EMS Switzerland This copolyamide (Ny 6/6-9 - a 1 1 random copolymer) is unique in its relative low melting temperature (132°C) and low degree of crystallinity both values much lower than for conventional polyamides The carbon black used in this study was Ketjenblack EC Akzo with a surface area (N_2) of 929 m^2/g and a diameter of 300 nm

PP/Ny blends containing different loadings of CB (phr) were prepared by dry blending of polymer granules with CB in a blender followed by melt mixing in a Brabender Plastograph (200°C 50 rpm) Ny was previously dried in a vacuum oven at 70°C overnight All blend ratios described relate to percentage by weight In order to investigate the influence of the blending procedure on the properties of the blends three modes of ingredient incorporation were studied addition of CB to the polymer blend (PP + Ny) + CB CB compounding with PP followed by Ny addition (PP + CB) + Ny or CB compounding with Ny followed by PP addition (Ny + CB) + PP The resulting blends were subsequently compression molded at 200°C to obtain 3 mm thick plaques

The volume resistivity of disc-shaped samples 5 cm in diameter was measured (DIN 53596) using a Keithley Electrometer 614 and a high 240A voltage supply For samples with a low resistivity level a Sorensen power supply (model QRD 60-1 5) was used Silver or nickel paint was applied to ensure contact between sample and electrodes namely to eliminate the contact resistance

The blends phase morphology was studied using an Olympus optical microscope Samples ~50 mm thick cut of the plaques using a microtome were placed between two glass slides and observed using regular Nomarsky or cross-polarized optics Hot stage microscopy was used to observe structural changes in the samples during heating up to melting followed by cooling to ambient temperature

The blends phase morphology was also studied using a Jeol 5400 scanning electron microscope (SEM) Two types of surfaces of each sample were investigated namely freeze fractured and microtomed surfaces The latter enables observation of CB particles in the dispersed phase by looking at sliced cross sections

RESULTS AND DISCUSSION

Individual Polymers

The effect of CB content on the volume resistivity of the individual polymers is depicted in *Fig 1* (these samples were prepared in the same manner as their blends) The neat Ny exhibits a relatively low resistivity in comparison to the neat PP because of the high polarity of the Ny amide groups A characteristic drop in resistivity is observed for the loaded PP at 2 5 phr while for Ny there is no change in resistivity up to 13 phr CB content Literature reports of percolation thresholds (2 3 5 19 21) for PP and Ny are 2 wt% and more than 25 wt% CB respectively Although data refers to CB types other than Ketjenblack the difference is nevertheless significant According to Wessling (2 3) this is due primarily to interfacial phenomena resulting in different CB dispersion in the two polymers Accordingly the interfacial energy also plays an important role in the conductive path formation in the CB loaded polymer the greater the surface tension of the matrix polymer the higher is the percolation threshold Conductive bridges are formed when the system achieves a minimum surface energy by forming cohesive contacts In systems that have a high matrix/CB interfacial energy the formation of a CB/CB interface is energetically advantageous leading to formation of a conducting network However in a system that readily wets the CB the same particles at the same level of loading are completely dispersed Hence higher concentrations are needed to achieve the state of network formation

There is a significant difference in CB distribution in PP and Ny as seen in *Fig 2* for example in systems containing 4 phr CB In PP a chain-like structure of

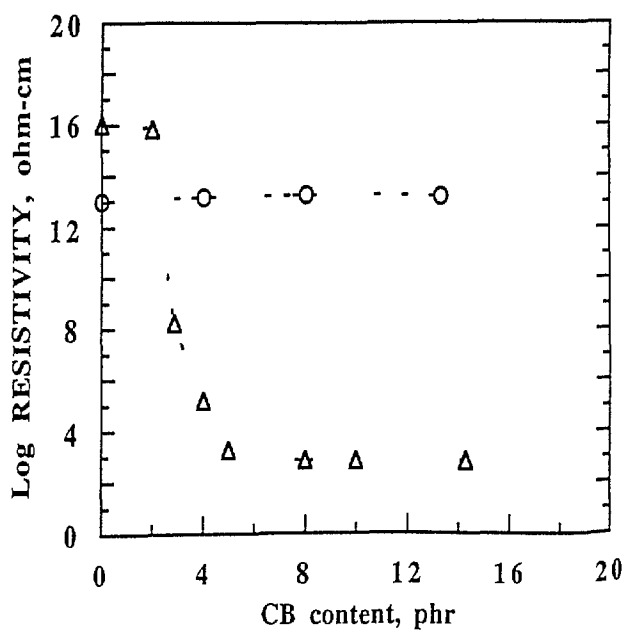

Fig 1 Resistivity vs CB content for neat PP (Δ) and neat Ny (O)

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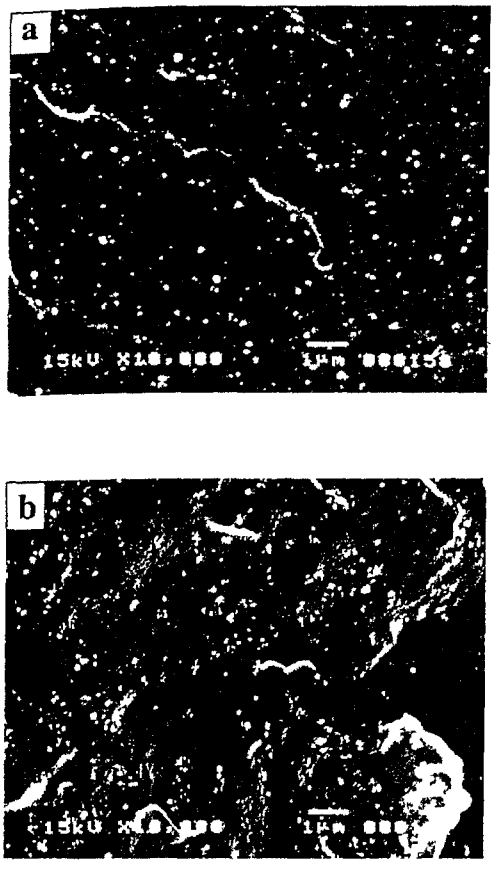

Fig 2 SEM micrographs of Ny a and PP b with 4 phr CB

CB agglomerates is clearly observed whereas in Ny the CB at the same content is distributed more uniformly. This demonstrates clearly the difference in the interaction of CB particles with the PP or Ny matrix Ny is characterized by a very high surface tension and polarity compared to that of PP (5) Both conductivity data and morphological observations agree with the presently accepted notion regarding the high correlation between the surface tension of the polymer matrix and the resistivity of CB-loaded composites (4)

Polymer Blend Conductivity

The resistivity of PP/Ny/CB blends for different Ny contents of 2 4 and 8 phr CB is depicted in *Fig 3* It should be noted that none of the blends shown has a resistivity that obeys any "additivity rule " The resistivity of the blends at a given CB concentration changes with composition in a rather complex manner for all CB loadings and all sequences of CB addition Interestingly a clear effect of the mixing order is seen The (Ny + CB) + PP blends prepared by first blending molten Ny and CB followed by compounding with PP (*Fig 3c*) have the highest resistivity values relative to those of blends of identical compositions prepared by the other two mixing procedures

The resistivity of blends with either 4 or 8 phr CB (above the percolation threshold for PP) varies with Ny content similarly for the first two mixing procedures (PP + CB) + Ny and (PP + Ny) + CB (*Figs 3a* and *3b*)

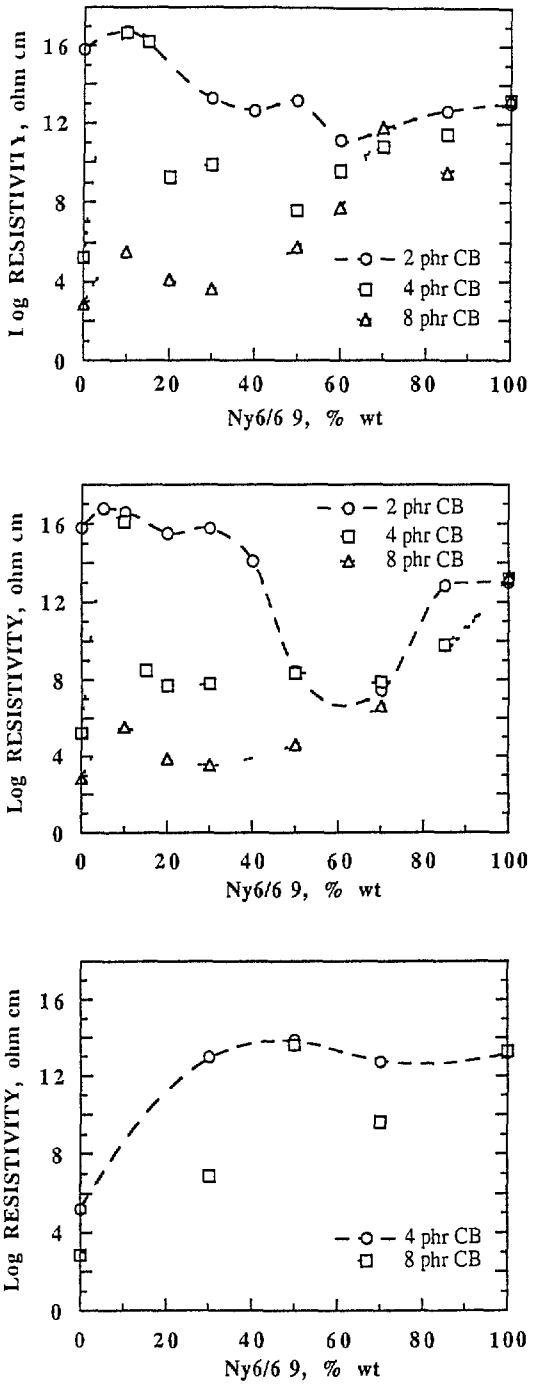

Fig 3 Resistivity vs Ny content in polymer blends with different CB concentrations a (PP + Ny) + CB b (PP + CB) + Ny c (Ny + CB) + PP

A local resistivity maximum is observed in the blends containing 4 phr CB upon the addition of 10% Ny followed by a resistivity decrease at an Ny content of 20% The resistivity of the 4 phr CB content blends containing 20% to 70% Ny is nearly constant and then gradually increases up to the resistivity of Ny Blends containing 8 phr CB behave in a similar manner with lower resistivity values The (Ny + CB) + PP mixing procedure results in specimens of relatively high resistivity

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The resistivity of blends with 2 phr CB (below the percolation threshold for PP) varies with Ny content in a different manner compared to blends containing 4 or 8 phr CB At 2 phr CB a resistivity decrease well below the value of both individual polymers is observed for the (PP + CB) + Ny blend exhibiting a remarkable minimum at 50% to 60% Ny (*Fig 3b*) almost 10 and 6 orders of magnitude lower than the resistivity of PP and Ny respectively Similar results were observed for other blends such as PP/PS (20) or HDPE/PMMA (23) emphasizing the tendency of blends to enhance con ductivity above that of the individual polymers This provides an opportunity to produce semiconductive or conductive materials based on polymer blends with a very low conductive filler concentration

The complex character of resistivity variation with composition for PP/Ny blends will be further discussed in conjunction with the results of SEM and optical microscopy investigation

Polymer Blend Morphology

Some light micrographs of unfilled PP/Ny blends are shown in *Fig 4* and of CB loaded blends in *Figs 5* and *6* A two phase morphology is clearly observed as expected both by regular Nomarsky optics (*Fig 4a*) and cross-polarized optics (*Figs 4b* and *4c*) The latter makes it possible to identify the PP phase because of its high crystallinity compared to the dark practically amorphous Ny phase Upon heating up to the PP melt ing temperature higher than that of Ny both molten phases appear dark in cross-polarized lenses at less than full cross position the phases are clearly seen (*Fig 4b*) *Figure 4c* depicts the phase morphology after reducing the temperature below the melting point of PP *Figure 5* shows micrographs of blends with differ ent CB loadings using Nomarsky optics Two distinct phases are observed one is a light transparent phase and the other is black It should be noted that samples of individual polymers with 1 phr CB only are already dark in the optical microscope field because of the presence of CB and the thickness of the sample Com parison with *Fig 4a* enables the conclusion that the dark phase contains CB and is identified as the Ny phase As expected the phase structure shown in *Fig 5* changes with composition *Figure 6* shows a (PP + Ny) + CB blend with 2 phr CB (PP/Ny = 70/30) below and above PP melting Since Ny constitutes the dis persed phase it is clear from *Fig 6b* that CB is located solely within the Ny phase Similar optical studies have shown that the CB is located preferentially in the Ny phase for all the studied PP/Ny blends irrespective of the sequence of CB addition to the polymers Thus in the (PP + CB) + Ny blends CB particles are being transferred during blending from the PP to the Ny phase

More details regarding the blends morphology were obtained by SEM observation of freeze fractured and room temperature microtomed surfaces methods which complement each other and give a clear picture of the CB distribution in the present immiscible systems (*Figs 7–12*) Two phases are clearly observed in all blends often with particles of the continuous phase occluded within particles of the dispersed phase (a phase within a phase within a phase) As evident from *Fig 7* in agreement with the optical studies the CB is located in one phase namely in the Ny phase independently of the sequence of blending

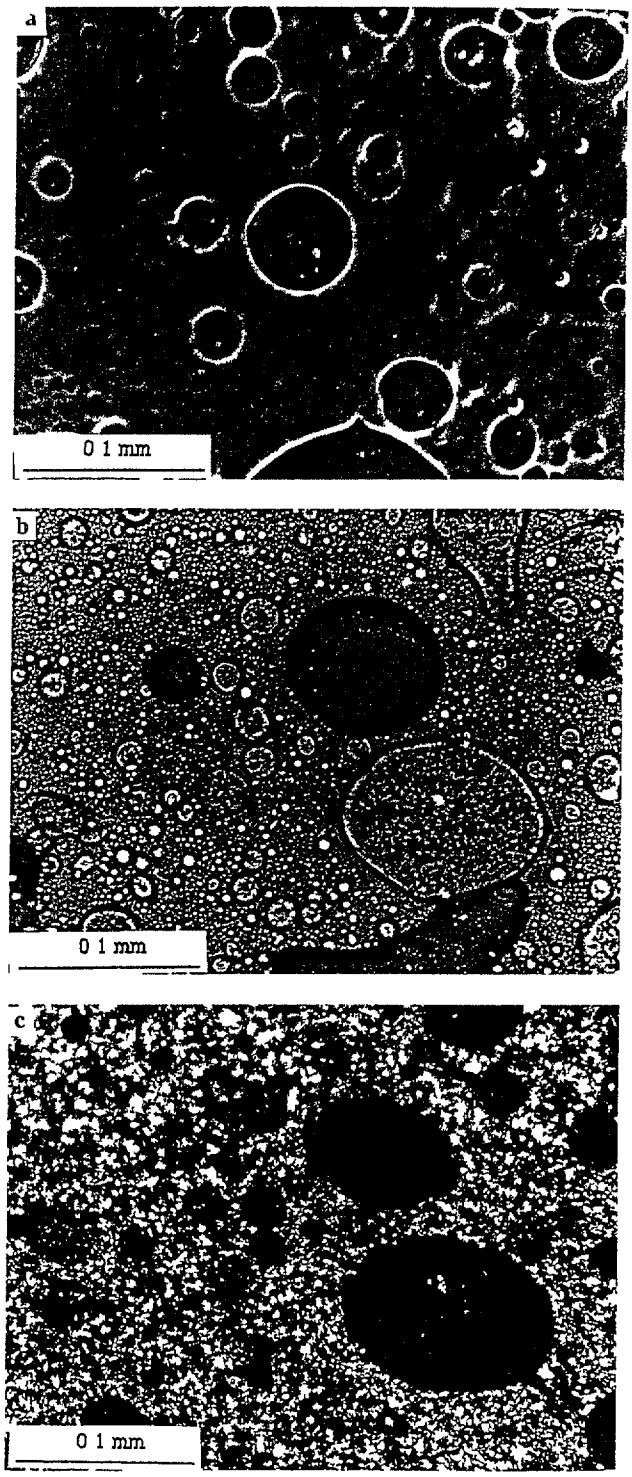

Fig 4 Optical micrographs of PP/Ny blends (PP/Ny = 70/30) a Nomarsky optics b c cross polarized optics b molten state 180°C c after cooling

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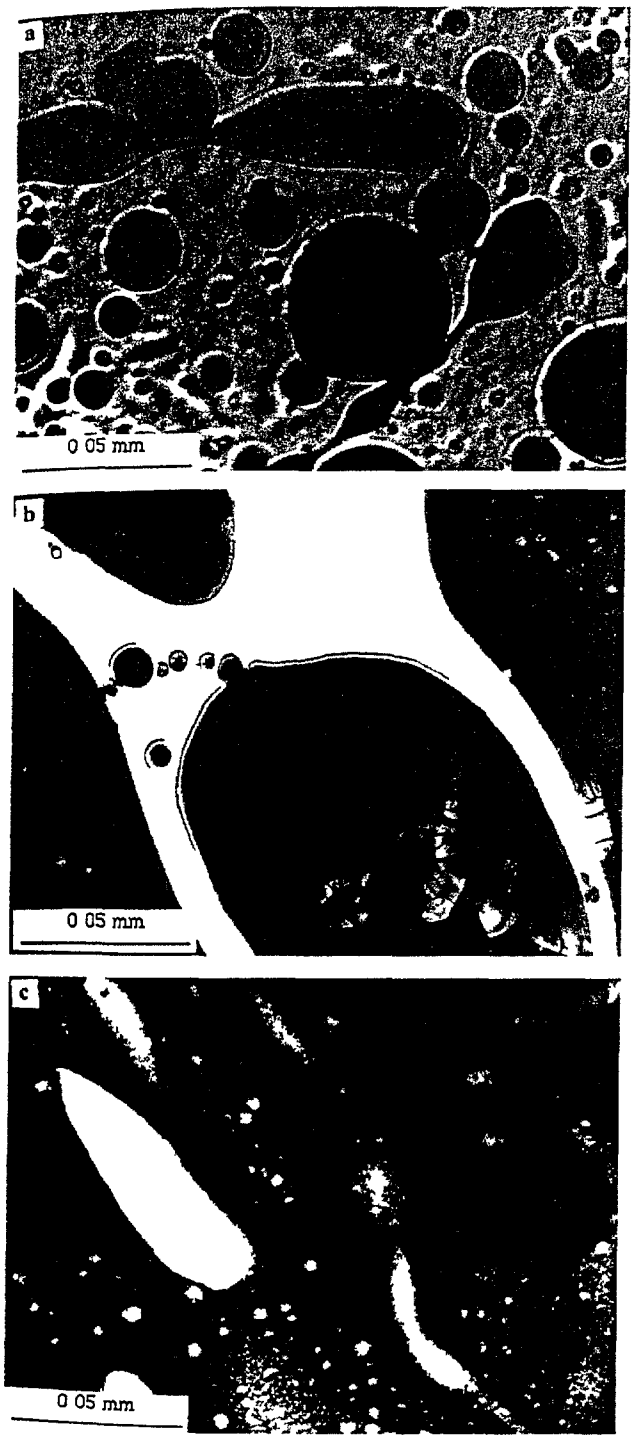

Fig 5 Optical micrographs of (PP + Ny) + CB blends Nomarsky optics a PP/Ny = 70/30 1 phr CB b PP/Ny = 50/50 2 phr CB c PP/Ny = 30/70 4 phr CB

This further supports the conclusion of CB transfer from PP to Ny for the sequence (PP + CB) + Ny This CB redistribution stems from the higher affinity of CB to Ny than to PP because of a higher surface tension and polarity of Ny compared to PP (5)

It is important to note that during Ny addition in the (PP + CB) + Ny blends CB transfers initially to the surface of the Ny phase namely for low CB contents

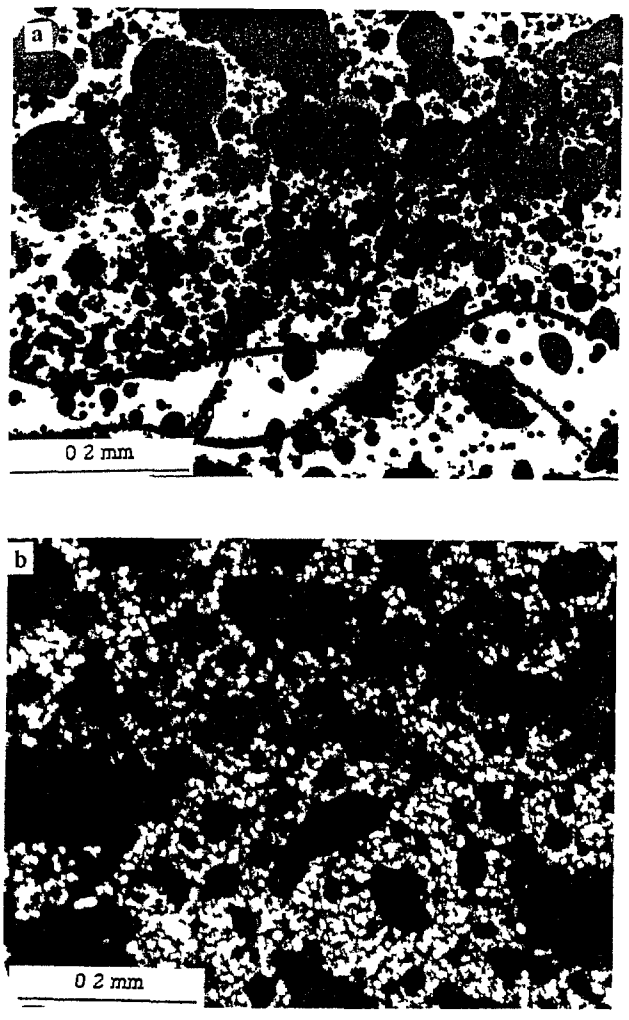

Fig 6 Optical micrograph of a (PP + Ny) + CB blend with 2 phr CB (PP/Ny = 70/30) cross polarized a molten state 175°C b after cooling

a majority of the CB remains located in a thin Ny outer layer (*Fig 8*) The resistivity minimum on the (PP + CB) + Ny curve with 2 phr CB (*Fig 3b*) shows that for the blends with a co continuous two phase structure (50% to 70% Ny) even 2 phr CB are sufficient to form a conductive layer located at PP/Ny interfaces It is suggested that during the first PP/CB mixing step CB forms in PP a chain-like structure Then upon Ny addition to the PP/CB molten blend the CB agglomerates are being transferred retaining their shape in the new phase which interacts strongly with CB *Figure 7* depicts the differences in the CB distribution in the Ny phase for the three blending methods appearing agglomerated and dispersed less uniformly for the (PP + CB) + Ny mixing procedure (*Fig 7b*) Other mixing modes result in a homogeneous CB distribution The small resistivity value of the (PP + CB) + Ny blends compared to the other identical composition blends (*Fig 3a–c*) may therefore be explained by the transfer of agglomerated CB from PP to Ny

It should be pointed out that complete CB transfer takes place in (PP + CB) + Ny blends containing as

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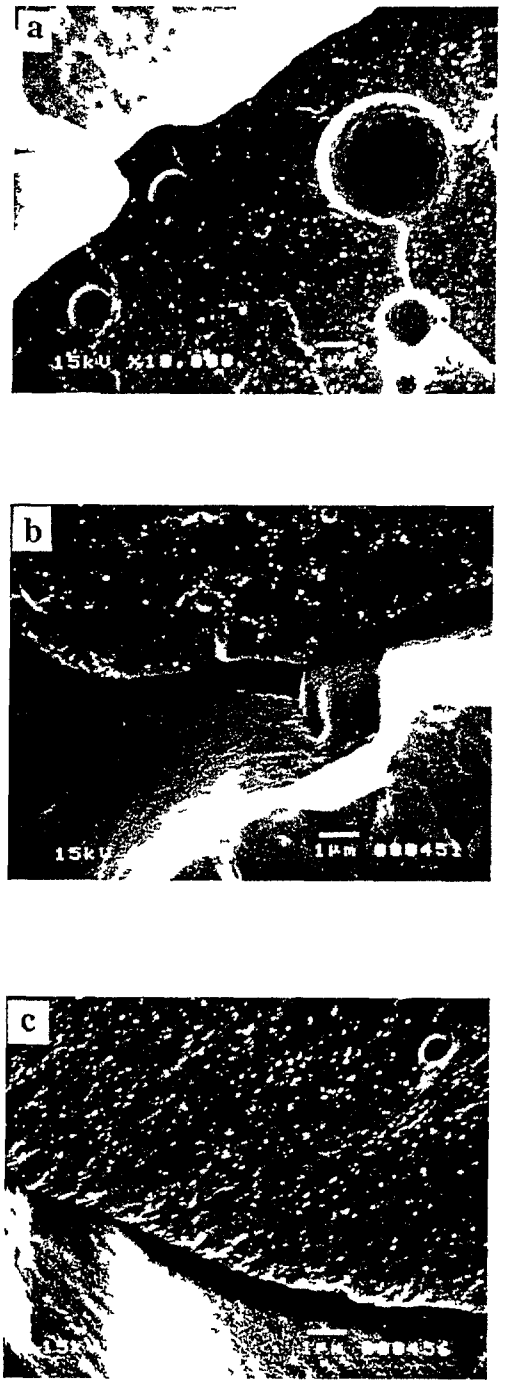

Fig 7 SEM micrographs of microtomed 50/50 PP/Ny blends with 2 phr CB a (PP + Ny) + CB b (PP + CB) + Ny c (Ny + CB) + PP

little as 10% Ny even at 8 phr CB content (*Fig 9*) In other blends at the same composition (PP + Ny) + CB with 8 phr CB a part of the CB appears also in the PP phase It is assumed that at the same CB content agglomerated CB particles occupy less space than in

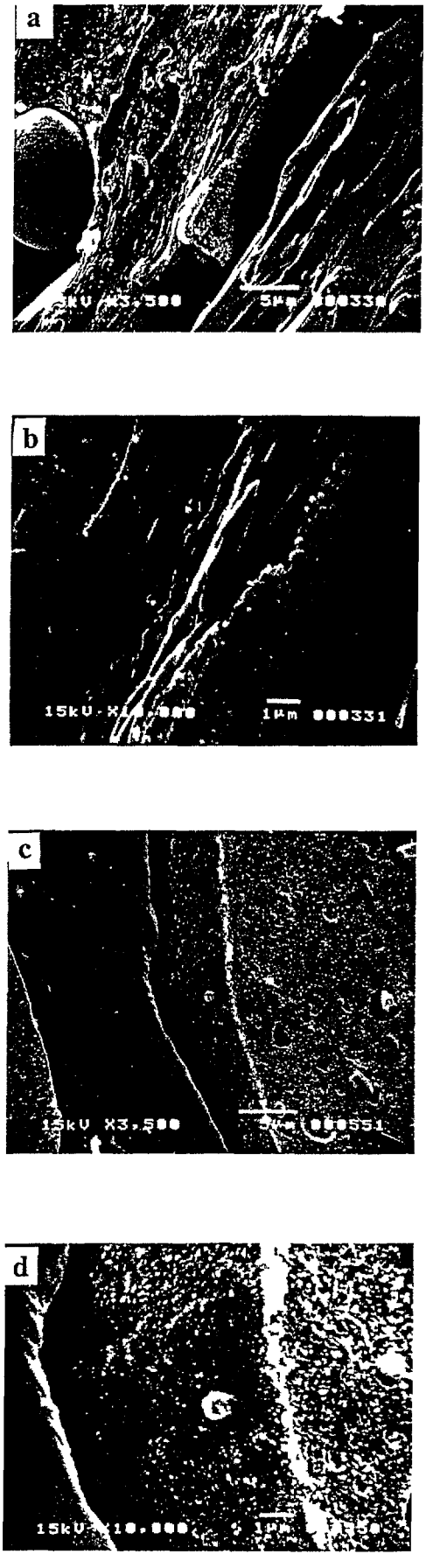

Fig 8 SEM micrographs of microtomed (PP + CB) + Ny blends a b PP/Ny = 30/70 2 phr CB c d PP/Ny = 80/20 4 phr CB

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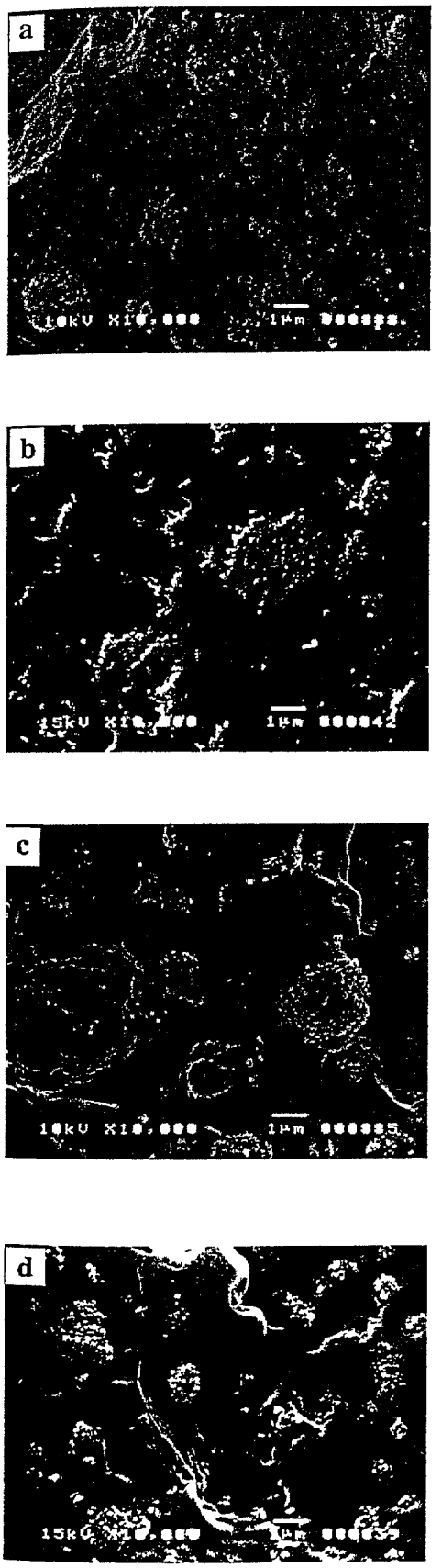

Fig 9 SEM micrographs of 90/10 PP/Ny blends with 8 phr CB a b (PP + Ny) + CB c d (PP + CB) + Ny a c freeze fractured surface b d microtomed surface

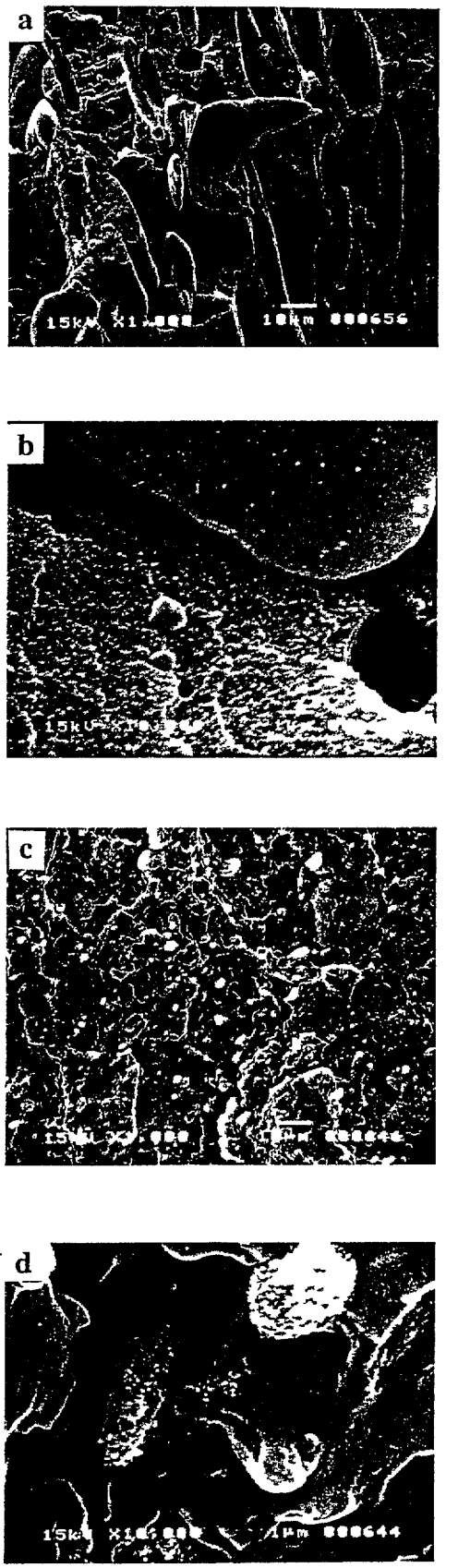

Fig 10 SEM micrographs of freeze fractured surfaces (PP + CB) + Ny blends with 4 phr CB a b PP/Ny = 80/20 c d PP/Ny = 90/10

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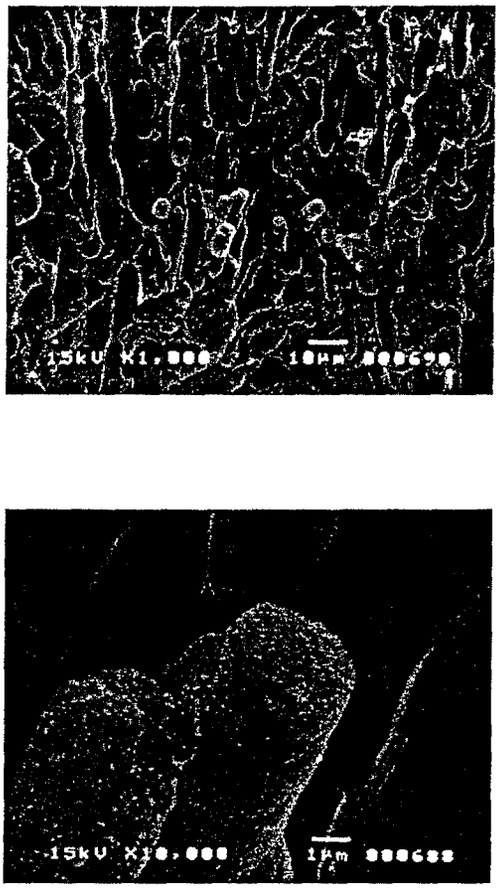

Fig 11 SEM micrographs of freeze fractured surfaces (PP + CB) + Ny blends with 4 phr CB PP/Ny = 70/30

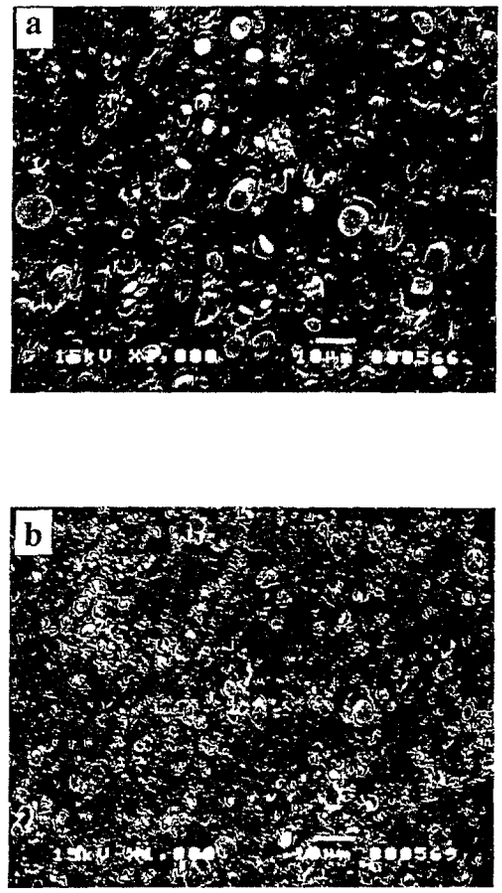

Fig 12 SEM micrographs of microtomed 90/10 PP/Ny blends with 4 phr CB a (PP + Ny) + CB b (PP + CB) + Ny

uniform individually dispersed particles Thus 10% Ny in the (PP + CB) + Ny blend with 8 phr CB is sufficient for complete wetting of already agglomerated CB particles in PP and insufficient for wetting of the respective (PP + Ny) + CB blend

Another parameter should be noted that relates to the shape of the dispersed Ny particles Blends with 10% Ny exhibit spherical particles while higher Ny contents provide elongated particles that develop into co-continuous structures as Ny content is increased (*Fig 10*) Therefore the presence of a local maximum on the resistivity vs Ny content curves at 10% Ny (*Fig 3a–b*) is suggested to be related to the spherical shape of the dispersed phase particles which are in capable of forming a network throughout the contin uous phase As CB is fully transferred to the Ny the addition of a small amount of Ny to the blend results in CB-containing Ny spherical particles that are dis persed in the PP matrix At Ny contents above 20% resistivity is reduced drastically by 7 to 8 orders of magnitude corresponding to the development of an elongated structure of the dispersed Ny phase which provides the basis for a conducting network

An additional significant parameter that should be taken into consideration is the amount of CB added It is known (25 26) that the higher the CB content the finer the dispersed particles as depicted in *Fig 9c* and *Fig 10d* This is found to be true for all mixing modes At 2 phr CB the dispersed Ny particles are large and far apart providing no opportunity for the CB agglom erates within them to approach each other and form a conducting network Only at 50% Ny content a co-continuous morphology is formed and conducting paths are made available At higher CB contents such as 4 and 8 phr the particle size is greatly reduced Thus Ny is finely dispersed and the blend s resistivity is reduced at 20% Ny because of the elongated particle structure (*Fig 10*) The effect of increased CB content is of such significance that even a co-continuous structure is obtained at a relatively low Ny percentage (30%) as depicted in *Fig 11* for a 70/30 PP/Ny blend It may be noted as well that the size of the dispersed Ny particles differs in the (PP + CB) + Ny and (PP + Ny) + CB blends (*Fig 12*) The particles are significantly smaller when Ny is blended into a PP/CB mixture than when blended with the neat PP first or when CB is mixed in the (PP + Ny) + CB sequence This could result from the increased viscosity of the CB-contain ing PP which requires Ny dispersion in viscous media thus creating different mixing conditions

Studying the effect of blending time for the (PP + CB) + Ny with 4 phr CB (PP/Ny = 80/20) blend (after Ny addition into the Brabender preblended PP with CB) shows an insignificant increase of resistivity with

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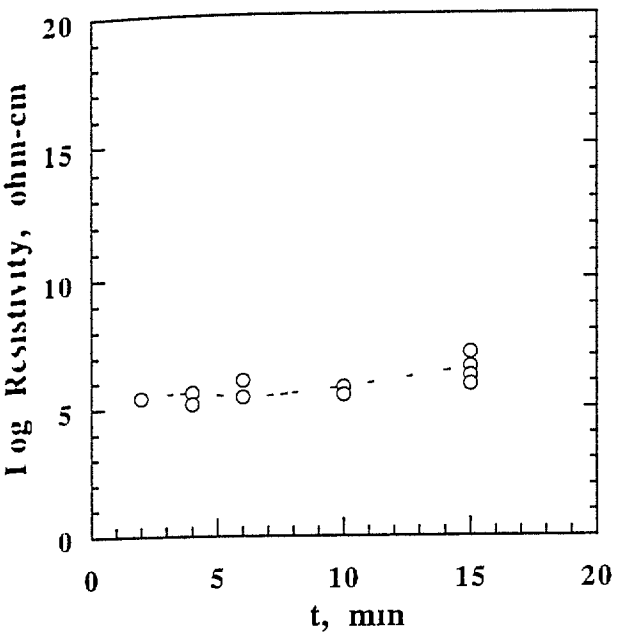

Fig 13 Resistivity vs mixing time for a (PP + CB) + Ny (PP/Ny = 80/20) blend with 4 phr CB

increasing mixing time (*Fig 13*) The SEM micrographs of samples blended for 1 to 15 min show that CB is always located in the Ny phase and that all of the blends morphology is similar Thus surprisingly the CB particles transfer from the PP to the Ny phase is very rapid Hence when all CB particles are already thoroughly wetted in the Ny phase additional mixing only causes small changes in the dispersed phase morphology which has no influence on the blends resistivity This very quick process of particles being transferred from one phase to the other in spite of the high polymer viscosity indicates the predominating thermodynamic effects compared to kinetic ones

CONCLUSIONS

Interesting low electrical resistivities were measured for the CB containing PP/Ny blends Of special interest are blends with a co-continuous phase morphology in which a "double percolation effect occurs where the CB is located either at the Ny/PP interface or within the Ny phase The CB particles form network structures within or alongside the continuous Ny phase The two phase polymer morphology in the PP/Ny immiscible blend and the preferential localization of the CB particles in the minor Ny phase cause the effective CB content to be significantly higher than its nominal value Hence conductive polymer systems can be achieved at rather low CB loadings lower than required for turning a single polymer into a conductor

The much stronger affinity of CB to Ny than to PP results in the preferential location of CB in the Ny phase rather than its homogeneous distribution in the system Moreover CB particles transfer during melt mixing at a surprisingly high rate from the PP to the Ny phase

The sequence of blend preparation PP/Ny or PP/CB initially affect not only the CB particles location in or alongside the Ny phase but also the phase morphology of the polymer components In the (PP + CB) + Ny blends the dispersed Ny particles are significantly smaller than in blends prepared by the other routes Both polymer phase morphology and preferred location of CB affect the system s resistivity

All observed results may be explained taking into consideration the interactions between CB and polymers which are correlated with the surface tension of the examined polymers A significant difference in polarity and crystallinity of the polymer components is also reflected in the end properties of the blends A complementary system polypropylene/polycarbonate/CB in which PC the dispersed phase is highly viscous in the molten state amorphous in the solid state and less polar than Ny will soon be reported (27)

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Conductive Polymer Blends with Low Carbon Black Loading Polypropylene/Polycarbonate

R Tchoudakov, O Breuer, and M Narkis*

Department of Chemical Engineering Technion Israel Institute of Technology Haifa 32000 Israel

A Siegmann

Department of Materials Engineering Technion Israel Institute of Technology Haifa 32000 Israel
* To whom correspondence should be addressed

Carbon black CB loaded immiscible polypropylene/polycarbonate blends exhibit low resistivity values at low CB contents CB is preferentially located in the PC phase which is dispersed throughout the PP matrix in the form of numerous small particles encountering one another and forming conductive networks A co continuous structure is not essential for promoting low resistivity apparently the interfacial properties of CB/polymer pairs in combination with the polymers individual features polarity crystallinity viscosity influence the blend morphology which in turn affects the electrical resistivity

Keywords Blends Carbon Black Electrical Conductivity Polycarbonate Polypropylene

INTRODUCTION

Increasing attention is currently given to incorporation of carbon black, CB, into incompatible polymer blends A number of recent publications dealing with such conductive blends[1 15] reported that their conductivity may be much higher than that of their individual constituents at the same CB loading, and that high levels of conductivity may be achieved at surprisingly low CB loadings As high content of CB tends to diminish polymer mechanical properties, increase polymer melt viscosity, and cause extreme dusting, an opportunity to lower the filler amount is advantageous [1]

The enhancement of conductivity is suggested to be due to the formation of honeycomb-like conductive pathways through the blend due to preferential accumulation of CB in one of the phases or at their interface [1] Main points of interest are the CB location in the studied polymer blends and the correlation between their electrical conductivity and morphology The CB location in the blend is determined by a combination of complex properties including mixing procedure relative polymer viscosity and the polymer s ability to wet and adhere strongly to the filler

Various mixing sequences may be used when blending components together through masterbatching or simultaneous mixing of all ingredients [2-4] This affects the blend morphology, the CB location, and the resultant blend conductivity CB may stay in the phase to which it is initially added or may transfer from one phase to another The transfer depends on the polarity of the polymer and its affinity to CB, resulting in a preferential CB location The domain size of the dispersed phase is strongly affected by the manner in which the CB is introduced into the blend[4 5] and by the mixing energy input [5]

The viscosity of the components and the ratio between their viscosity values is of great importance and affects the morphology generated during mixing, resulting in either a dispersed phase or co-continuous morphology [6] Increased CB content was found to reduce the size of the dispersed phase [7 9] Thus, there is a direct correlation between the mixing sequence and the resultant morphology, due to CB s tendency to increase the phase viscosity

It is well known that CB drastically reduces the electrical resistivity when added to a polymer matrix The critical amount of CB necessary to build up a conductive network and, accordingly, to make the material conductive is referred to as the percolation threshold [10] An additional term is the "double percolation threshold", referring to percolation in incompatible polymer blends This is affected by the percolation of the CB in the filler-rich phase and by the structural continuity of this phase in the blend [10-13] This notion is further expanded to a multiple percolation theory in multi-phased blends [14]

In the recent study,[15] PP/Ny blends of co-continuous phase morphology exhibited appreciable conductivity at low CB content However, in this case, CB content is lower than the percolation threshold required for the dispersed Ny phase, where it is usually located in PP/Ny blends Percolation in this PP/Ny blend was observed at a very low CB content, with the CB located alongside the Ny continuous phase It was also shown that the sequence of blend preparation, PP+Ny or PP+CB first, affects not only the CB particles preferential location, in or alongside the Ny phase, but also the two polymer phase morphology In the (PP+CB)+Ny blends the dispersed Ny particles are significantly smaller than in blends prepared by the other routes Thus it was established that both polymer phase morphology and CB location affect the systems resistivity

Presently, the behavior of PP blends with PC, less polar than Ny, with low CB contents is studied Morphology and conductivity were determined for blends of different

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composition and different sequences of ingredient incorporation

EXPERIMENTAL

The polymers used to study the conductive blends of PP/PC, were Polypropylene VC15-15P, Neste, Finland (T_m=173°C) and Polycarbonate Lexan 103-GE (T_g=149°C, T_m=225°C) All blend ratios described relate to percentage by weight Carbon black Ketjenblack EC by Akzo was used in this study

Polyblends of PP with PC containing 1-4 phr CB were prepared by melt mixing in a Brabender Plastograph equipped with a 50 cm^3 cell The temperature of the mixer was increased from 235 to 250°C with increase of the PC content in the blends due to difficulties in processing blends with high PC content The influence of the blending procedure on the properties of the blends was investigated by using three modes of ingredients incorporation addition of CB to the polymer blend, (PP+PC)+CB, CB compounding with PP followed by PC addition, (PP+CB)+PC, or CB compounding with PC followed by PP addition, (PC+CB)+PP Prior to processing the polymer granules were ground and PC was dried at T=120°C The resulting blends were subsequently compression molded at 240°C to obtain 3 mm thick plaques

The volume resistivity of disc-shaped samples, 5 cm in diameter, was measured according to DIN 53596 using a Keithley Electrometer 614 and a high (240 A) voltage supply For samples with low level resistivity a Sorensen power supply, model QRD 60-1,5 was used Silver or nickel paint was used to ensure contact between sample and electrodes, namely, to eliminate the contact resistance All samples were of approximately 3 mm thickness

The blends phase morphology was studied using a Jeol 5400 scanning electron microscope, SEM Two types of surfaces of each sample were investigated namely, freeze fractured and microtomed surfaces

Influence of mixing time on blends resistivity was carried out only for (PP+CB)+PC blends in the following manner PP was blended with CB in the Brabender for 6-7 minutes, then PC was gradually added to this mixture during 5 minutes The 15 minutes required for mixing all blend components together was measured upon completion of the PC addition

RESULTS AND DISCUSSION

The influence of CB content on the volume resistivity of the individual polymers is shown in Figure 1 These samples were prepared under the same conditions as their blends A characteristic drop in resistivity is observed for both CB loaded polymers, being more drastic for loaded PP The percolation threshold for PP occurs at a lower CB content compared to that for PC These results

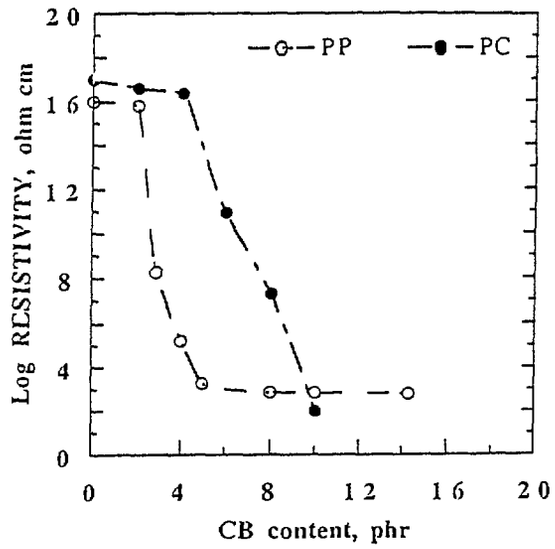

Figure 1 Resistivity vs CB content for individual polymers

are in accordance with data of Miyasaka,[16] who found that the critical CB content at the percolation threshold tends to increase with the polymer surface tension The surface tension of PP is lower than that of PC, i e 29 and 50 dyne/cm [17 18]

Figure 2 shows the resistivity of different compositions of PP/PC blends for various modes of CB incorporation A complex resistivity-composition relationship is observed for all these blends For all PP/PC ratios it appears that the (PP+CB)+PC blends have especially low resistivity, lower than that of blends with similar compositions but mixed by other sequences A significant minimum in resistivity is observed at 30% PC content for 2 phr CB containing blends at both mixing procedures depicted in Figure 2a (The (PC+CB)+PP mixing sequence with 2 phr is of no interest and therefore not shown, taking into consideration that PC percolates above 4 phr CB content) It should be noted that both individual polymers at this level of loading exhibit high resistivity values Thus, addition of 15-20% PC leads to a significant decrease in the CB-filled PP phase resistivity This implies that a certain CB redistribution takes place in the PP/PC blends containing 30% PC In blends with 4 phr CB as depicted in Figure 2b, the addition of PC does not enhance conductivity in a significant manner due to the fact that PP+4 phr CB is already conductive at this CB content Similar resistivity changes were recently reported for (PP+CB)+Ny blends containing 2 phr CB [15] This minimum was explained by the existence of a co-continuous phase morphology with a majority of the CB located at the interface The reason for the changes presently ob-

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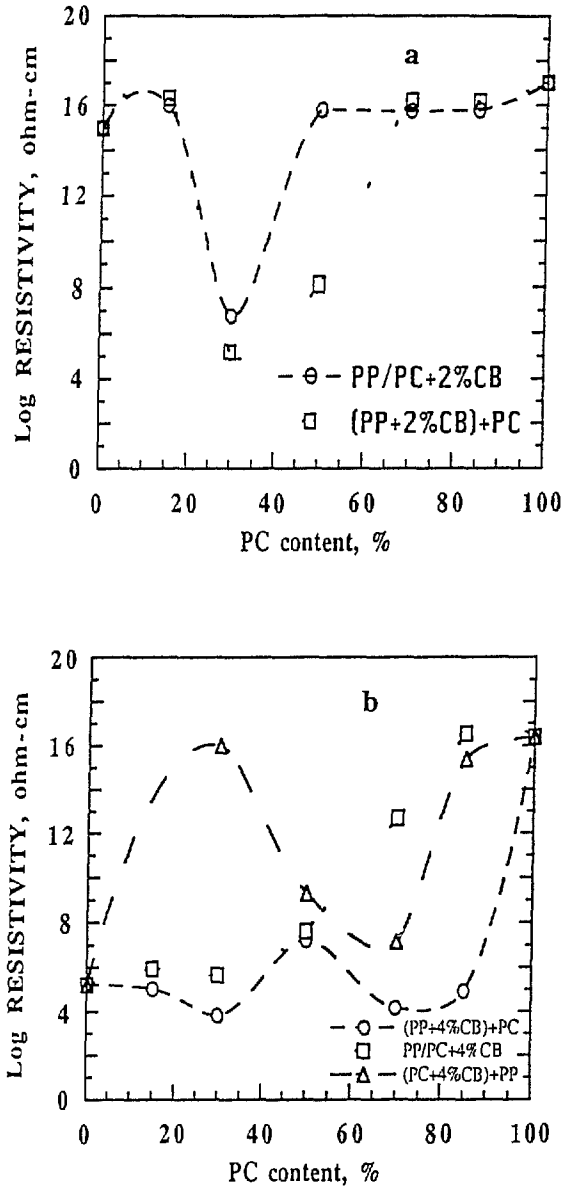

Figure 2 Resistivity vs PC content for PP/PC blends with CB a 2phrCB b-4phrCB

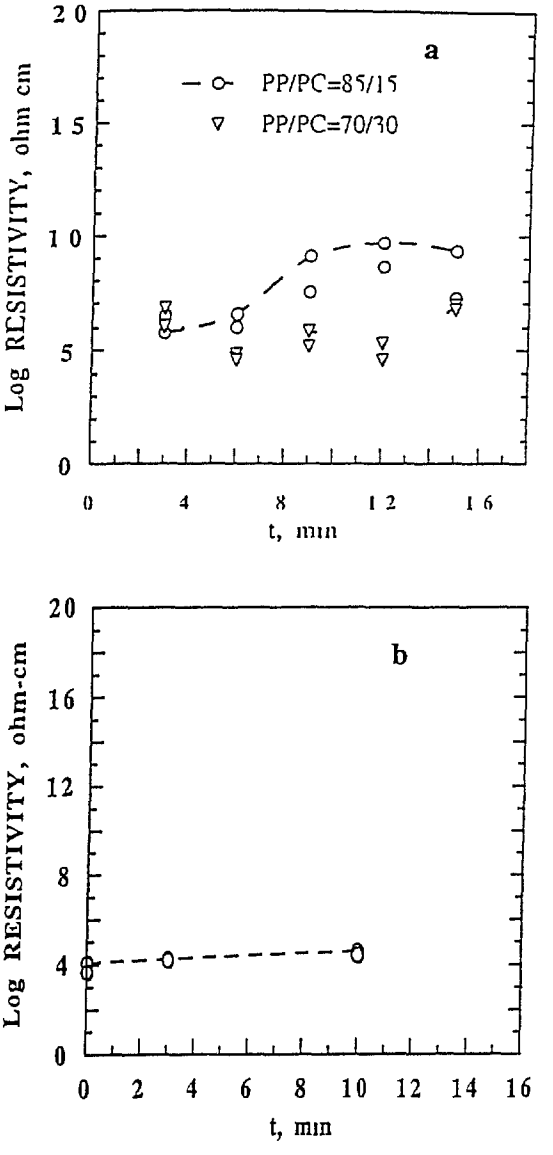

Figure 3 Resistivity vs mixing time for (PP+CB)+PC blend with 4 phr CB a constant rate 54 rpm b step I 54 rpm step II 18 rpm

served in PP/PC blends will be discussed in relation to the SEM observations of the blends structure

The influence of mixing time on resistivity of (PP+CB)+PC blends with 4 phr CB is shown in Figure 3 Blends were prepared either at a constant mixing rate of 54 rpm (Figure 3a) or stepwise mixing PP with CB at 54 rpm and then mixing in PC with the ready PP/CB mixture at 18 rpm (Figure 3b) For blends prepared at a constant rate, there were no changes in resistivity after a short mixing time, up to 6 min After this period, the 85/15 blend exhibits an increase of resistivity with mixing time and the 70/30 blend s resistivity remains constant No influence of the mixing time on the resistivity of the same samples prepared by the stepwise mode (Figure 3b) was observed

SEM micrographs of blends with different PC contents are shown in Figures 4-9 It is clearly seen that the CB distribution in each polymer is not uniform and CB agglomerated chains may be distinguished (Figure 4) This may be interpreted according to the well-known notion[19] that for these, CB-loaded polymers, CB particle cohesive contacts are preferred to CB-polymer adhesion The higher percolation threshold of CB in PC may also be attributed[8] to the higher PC viscosity relative to that of PP at the experimental conditions

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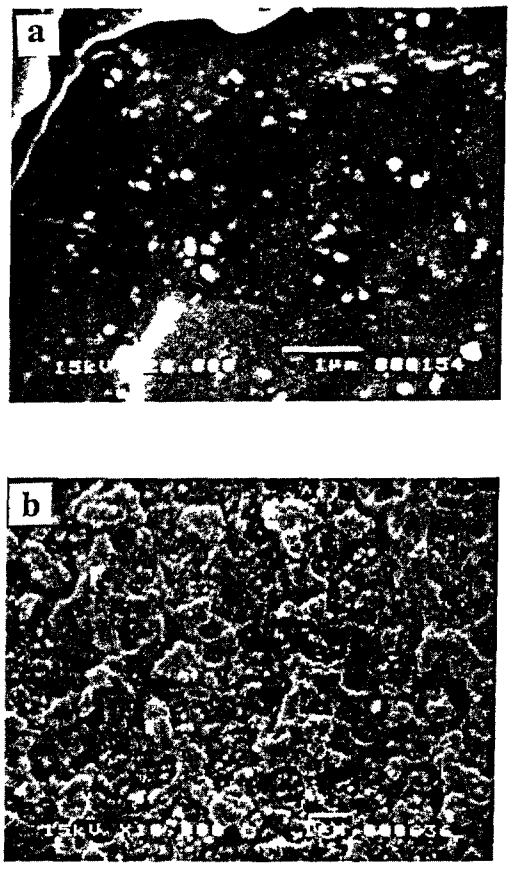

Figure 4 SEM micrographs of individual polymers with 4 phr CB freeze fractured surfaces a PP b-PC

It is evident from the SEM micrographs that CB is always located in the PC phase for all studied blends (Figures 5-9) CB transfer takes place from the PP to the PC phase for the (PP+CB)+PC blends This transfer takes a certain time, depending on blend composition and blending rate It is clearly seen that mixing for 3 minutes at a constant high rate of 54 rpm is sufficient for the full transfer of 4 phr CB from PP into the PC phase for the 30% PC blend (Figure 9c-d) For the 15% PC blend mixing for the same period is insufficient, not allowing a complete CB transfer, with CB residues left in the PP phase (Figure 9a-b) After 9 minutes of mixing, however, CB in all studied blends was already located in the PC phase only, concentrating mainly in a thin layer close to the domain's surface A quite different morphology was observed for samples, prepared by the two steps process at different mixing rate In this case, CB was located in a thin layer of the PP phase close to the interface (Figure 9 e-f) independently of the mixing time within the studied limits Hence, there is a strong influence of mixing conditions on morphology and the CB redistribution in the (PP+CB)+PC blends The formation of separate diffuse interfacial zones was observed also for SBR/BR blends,[5] in which no significant migration of CB from one rubber phase to the other was observed In the presently studied PP/PC blends, CB is transferred during mixing from the PP phase to a second more polar polymer, which is characterized by a higher surface tension This transfer is faster in the case of PP/Ny blends[15] than in PP/PC ones, at the same experimental conditions The Ny surface tension is close to that of PC,[17] but its viscosity is much lower than that of PC during processing Thus such

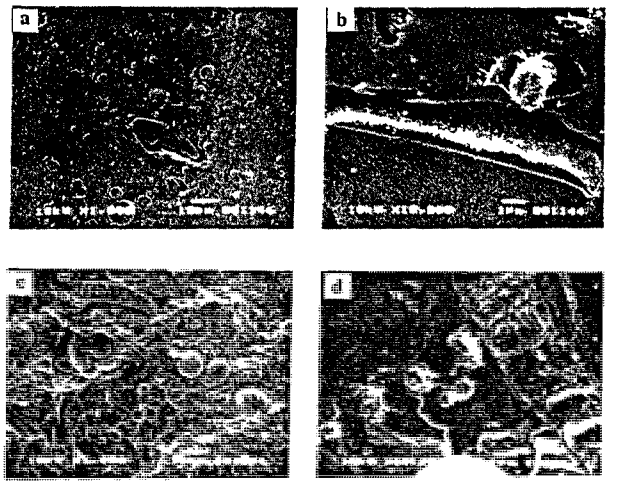

Figure 5 SEM micrographs of (PP+PC)+CB blend with 2 phr CB PP/PC=85/15 a b microtomed surfaces c d freeze fractured surfaces

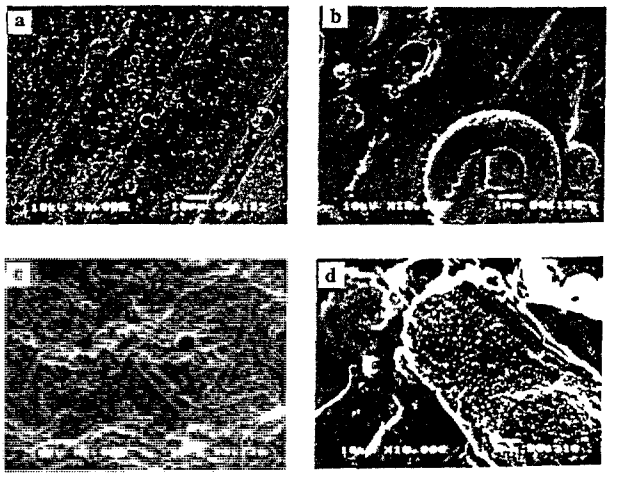

Figure 6 SEM microgaphs of (PP+CB)+PC blend with 2 phr CB PP/PC=85/15 a b-microtomed surfaces c d freeze fractured surfaces

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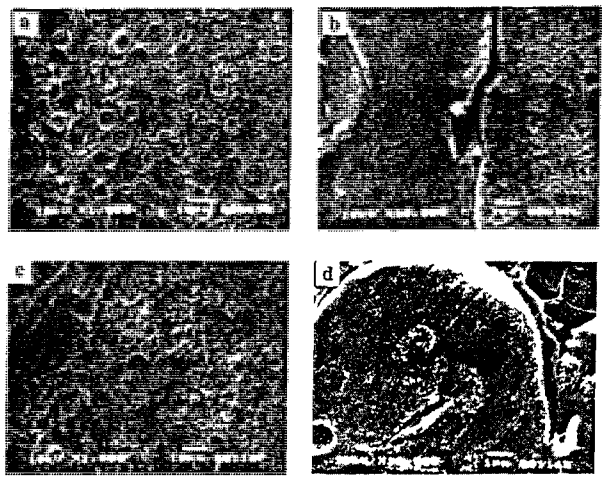

Figure 7 SEM micrographs of PP/PC=70/30 blends with 2 phr CB microtomed surfaces a b-(PP+PC)+CB c d (PP+CB)+PC

factors as polarity of polymers, sequence of ingredients incorporation, the rate of mixing and polymer viscosity determine the CB localization in polymer blends, their morphology and thus their conductivity

Direct structure-conductivity relationships were observed for the PP/PC/CB systems As evident from Figures 5-8, the dimensions of the dispersed PC phase particles are smaller and their dispersion is more uniform for all (PP+CB)+PC blends compared to blends prepared by other mixing sequences These two factors, combined with the preferential CB location at the surface layer of the PC particles, are responsible for the observed lower resistivity of the (PP+CB)+PC blends Upon increasing the PC minor phase content in the blends, a significant increase of the number of PC dispersed particles is perceived (Figures 5-7) In the 30% PC blend, the number of dispersed phase particles becomes sufficient to provide conductive paths throughout the blend, even with as low content as 2 phr CB, resulting in a remarkably low resistivity Further PC addition to the blend leads to a growth of the PC phase dimensions and simultaneously CB is observed not only on the surface, but also within the phase itself SEM studies show that the larger the dimen-

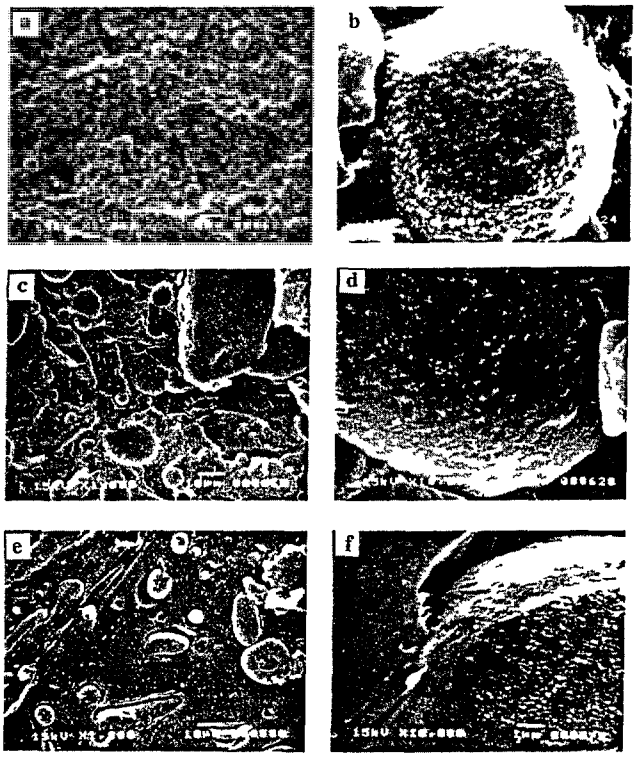

Figure 8 SEM micrographs of PP/PC=70/30 blends with 4 phr CB a b-(PP+CB)+PC c d e f (PC+CB)+PP a b c d freeze fractured surfaces e f microtomed surfaces

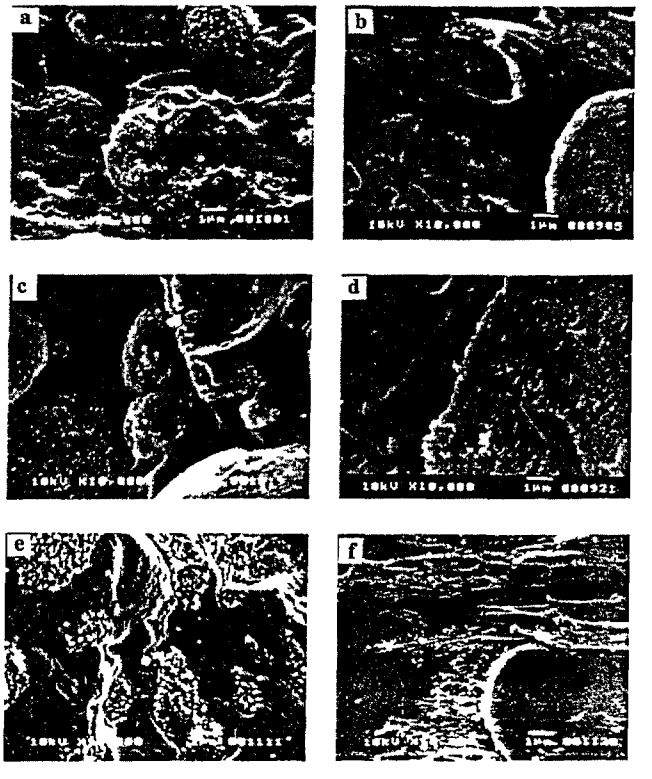

Figure 9 SEM micrographs of (PP+CB)+PC blends with 4 phr CB at a different rate of mixing a b PP/PC=85/15 constant rate 54 rpm c d PP/PC=70/30 constant rate 54 rpm e f PP/PC=70/30 step I 54rpm step II 18rpm a c e-freeze fractured surfaces b d f microtomed surfaces

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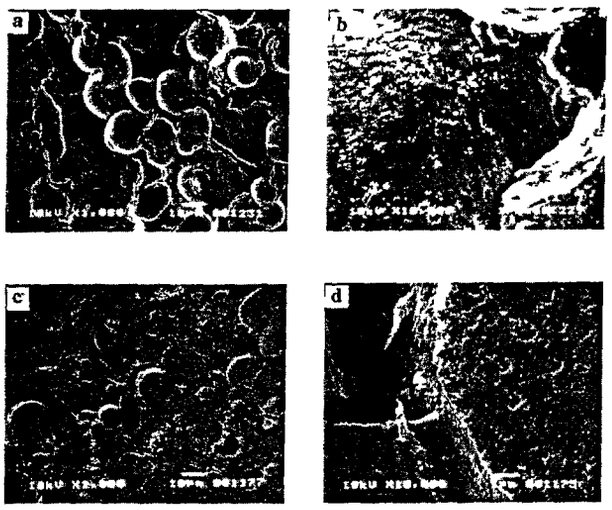

Figure 10 SEM micrographs of 50/50 (PP+CB)+PC blends with 2 phr CB a b freeze fractured surfaces c d microtomed surfaces

sions of the PC dispersed particles, the higher the tendency of CB to penetrate them Thus, the smaller PC particles appear to have a higher CB concentration on their surfaces (Figure 10) These changes in morphology of the blend, with increasing PC content, are the reason for the observed resistivity minimum at 30% PC for blends with 2 phr CB

An increase of CB content in the blends induces a decrease in the dimensions of the dispersed particles, as was previously reported [5,7,8,15] For PP/PC blends, containing 4 phr CB, the dispersion of 15% PC in the PP phase is so fine, that the PC content provides the blend with an already a high conductivity, close to that of PP with the same CB content The blend retains its conductivity level up to 50% PC in (PP+PC)+CB blends and up to 70% PC in (PP+CB)+PC blends It should be emphasized that for these blends the effective CB content in the PC phase is higher than the nominal one and it is beyond the percolation threshold for the PC/CB composition

In accordance with the above results, an explanation may be found for the exceptional behavior exhibited by the (PC+CB)+PP blend containing 4 phr CB (as depicted in Figure 2b) At 80-100% PC, the effective CB content in PC is lower than the minimum necessary to obtain percolation resulting in high blend resistivity levels Resistivity is drastically reduced at 70% PC content due to the higher effective CB loading which enables percolation The 30% PP contained in this composition does not diminish the essential structure which provides a conductive network This conductive network is retained at 50/50 blend, where co-continuity prevails, however, increasing the PP content beyond this level results in PC transformation into a dispersed form, which causes a

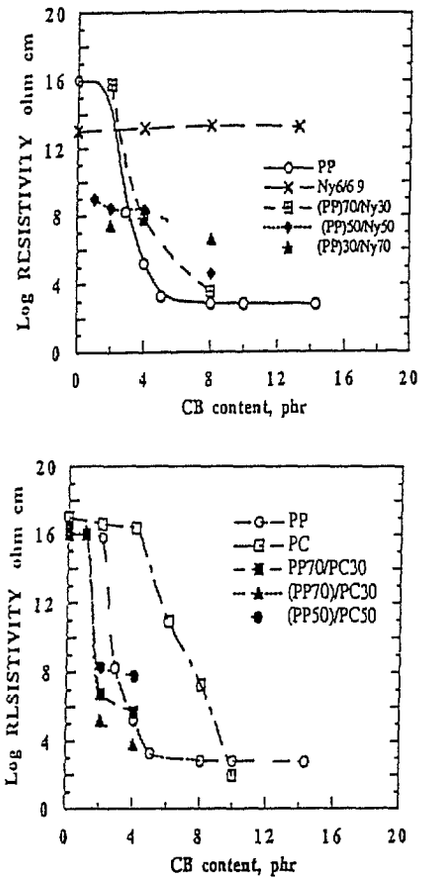

Figure 11 Resistivity vs CB content for PP blends with Ny(a) and PC(b)

significant rise in resistivity The particle size of the dispersed PC is found to be higher in the (PC+CB)+PP mixing sequence than in the other modes, therefore increasing the distance between adjacent particles and lowering the opportunity for conductive network formation

Comparison of the results for PP/PC and PP/Ny blends shows a certain difference in resistivity vs composition For the PP/Ny blends,[15] the differences in behavior between the (PP+CB)+Ny and (PP+Ny)+CB blends are greater than between the (PP+CB)+PC and (PP+PC)+CB ones Increased PC content in blends with 2 phr CB provides a great enhancement of the blend s conductivity in comparison to that of PP/CB or PC/CB compositions at the same CB content For PP/PC blends containing 4 phr CB almost no change in blend resistivity is measured up to 50% PC compared to that of PP with 4 phr CB On the contrary, for PP/Ny blends, a small amount of Ny addition to PP/CB compositions (4-8 phr CB) leads to a certain increase of the initial resistivity followed by a decrease in resistivity of blends with above 20% Ny content However, the resistivity of these blends

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is always higher compared to that of PP/CB composition with the same CB content Only for blends of the (PP+CB)+Ny sequence containing 2 phr CB and 50-70% Ny a significant decrease in resistivity is observed, down to a value which corresponds to that of the same composition, containing 4 phr CB

It is interesting to analyze the data of the studied blends, presented in the form of percolation curves depicted in Figure 11, in which parentheses note initial CB incorporation within PP All blends exhibit a shift in the percolation threshold compared to the individual polymers These shifts are larger for the PP/PC blends compared to those for the PP/Ny blends In any case, the percolation thresholds of the blends are lower than that of the component with the lowest value A clear distinction between the PP/Ny and PP/PC systems is observed in the shape of the dispersed phase in the blends at the percolation threshold For PP/Ny blends with low CB content, the extreme decrease in resistivity occurs at a certain Ny content, at which the separate dispersed Ny particles are deformed into elongated form, which is the beginning of the co-continuous stage of the blend This phenomenon is in partial agreement with the double percolation concept in conductive polymer blends [10 13] However, for PP/Ny blends, as was mentioned above, a majority of the CB is located near the Ny phase surface It is therefore impossible to compare the real CB content in the Ny phase with its percolation threshold For PP/PC blends, a significant decrease in resistivity was observed at a lower PC content compared to that of Ny The PC phase is distributed in the form of numerous small separated particles, which is sufficient for the formation of conductive pathways throughout the blend Therefore, the percolation threshold in the PP/PC blend does not depend on continuity of the CB-rich phase as was proposed in the recent concepts,[10-13] and double percolation is not always necessary to obtain conductivity in CB loaded polymer blends

CONCLUSIONS

Low CB content PP/PC blends exhibit low resistivity values, similar to those observed for the PP/Ny systems Conductivity has been found to occur at low PC contents in comparison to Ny - thus, co-continuity in phase morphology is not a necessary condition in this case Apparently, PC distributes throughout the blend in the form of minute particles, which are sufficiently numerous to encounter one another and originate conductive pathways

In the PP/PC blends, CB was preferentially located in the PC phase due to a stronger affinity to it Upon melt mixing, CB was induced to transfer from PP to PC as to Ny, with lower rates of transfer

The melt mixing procedure polymer ratio, and CB loading and susceptibility affect the phase morphology and preferential CB location, which determine the blend resistivity level When PC content is sufficient to allow for the formation of sufficiently dispersed PC particles with CB located on their surface, conductivity is enhanced

Studies of PP/Ny and PP/PC blends stress the significance of the interactions between CB and polymer in determining the conductivity level of the blend In particular, polymer polarity was found to affect CB transfer from the PP phase to the more polar Ny or PC phase Electrical properties of CB-filled polymer blends may be tailored by taking into consideration the CB-polymer interfacial properties in combination with the polymers individual features

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Segregated Structures in Carbon Black-Containing Immiscible Polymer Blends: HIPS/LLDPE Systems

O BREUER,[1] R TCHOUDAKOV,[1] M NARKIS,[1] A SIEGMANN[2]

Departments of [1]Chemical Engineering and [2]Materials Engineering Technion-Israel Institute of Technology, Haifa 32000, Israel

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ABSTRACT The structure/electrical resistivity relationship in CB loaded immiscible HIPS/LLDPE blends was studied Effects of CB content and location, dispersed polymer phase size and shape, dispersed phase viscosity, and processing procedures were examined The elongated dispersed phase in CB-containing blends is essential for promoting conductivity in formulations prepared by melt mixing and compression molding However, the same formulations proved highly resistive when injection-molded, due to orientation and excessive shearing © 1997 John Wiley & Sons Inc J Appl Polym Sci **64** 1097–1106 1997

INTRODUCTION

Polymer blends assume an important role in CB-filled polymer systems due to the tendency of the filler to accumulate preferentially in certain regions within the multi-phase matrix [1] This induces the formation of segregated structures whereupon CB may form a network,[2] enhancing the electrical conductivity and reducing the critical CB content essential for percolation The practical advantages of low CB loadings in terms of processing, cost, and mechanical properties are apparent[3,4], however, the complexity introduced by multi-phase polymer systems, their structure and properties, demands an in-depth understanding of the behavior of such systems and additional caution in material design

The fact that material properties as well as processing parameters influence the electrical conductivity has already been established in CB-filled one-component matrices Polymer properties such as surface tension, viscosity, and degree of crystallinity are to be considered in addition to the processing conditions as factors determining the resulting conductivity level [5–8]

Correspondence to M Narkis
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Some immiscible polymer blend systems have already been studied,[9–13] yielding the following general results

- CB locates preferentially within the phase in which it has a higher percolation threshold, being usually the polymer of higher surface tension value This effect is so significant that occasionally migration of CB from one phase to another may be observed during melt mixing when the filler is initially incorporated within the polymer of lower polarity
- The phase morphology and CB location determine the blend resistivity level The double percolation concept, requiring continuity for the CB network, has been introduced and found necessary to obtain conductivity in CB-loaded polymer blends
- The percolation threshold and resistivity values of the blend are lower than those depicted for the corresponding CB-filled individual polymers

In this study a high-impact polystyrene/linear low-density polyethylene (HIPS/LLDPE) system was investigated This constitutes a typical immiscible polymer blend in which the former com-

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ponent is an amorphous matrix and the latter serves as a semicrystalline dispersed phase An emphasis will be made on effects concerning the dispersed phase viscosity and the processing procedure The structure/electrical resistivity relationship will be studied with regard to former results obtained for polypropylene/polyamide[9] and polypropylene/polycarbonate[10] blends

EXPERIMENTAL

The principal polymers used in this study were HIPS, Galirene HT 88-5 (MFI = 5 g/10 min, Carmel Olefins, Israel) and LLDPE, Dowlex NG 5056 (MFI = 1 g/10 min, Dow) An additional low-viscosity grade of LLDPE, Dowlex 2552E (MFI = 25 g/10 min), was used as well, and referred to in the text as LL25 All blend ratios described relate to percentage by weight Carbon black (CB) Ketjenblack EC-300, (Akzo), was used in this study

All polymers and blends were prepared by melt mixing the dry-blended CB and polymer components in a Brabender Plastograph equipped with a 50 cm^3 cell at 190°C for ~ 15 min The resulting blends were subsequently compression molded at 190°C to obtain 3-mm-thick plaques An alternative processing method used for some selected formulations was injection molding, prepared by an Arburg 220/150 injection molding machine combined with a standard ASTM mold In order to obtain well-mixed samples, the processing stages were as follows initially, dry-blending the components in the desired ratios, injection molding, grinding the product, and subsequently remolding it

The resistivity measuring method of CB-loaded polymers and blends depended on the geometry of the samples produced by the specific processing mode Compression-molded samples were cut into disks, 5 cm in diameter, and their volume resistivity was measured (DIN 53596) using a Keithley Electrometer 614 and a high 240A voltage supply For samples with low-level resistivity a Sorensen power supply, model QRD 60-1,5 was used Injection-molded bars were measured according to ASTM D991, known as the "four point method" Nickel paint was applied to ensure contact between the sample and electrodes

The blend phase morphology was studied by both optical and electron microscopy An Olympus optical microscope was used to observe 50 μm-thick microtomed samples These samples were

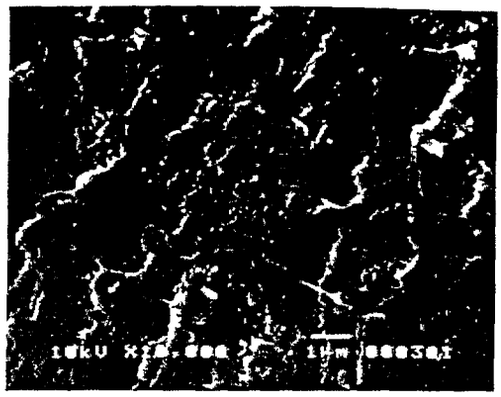

Figure 1 SEM micrograph of microtomed HIPS + 2 phr CB

studied by regular Nomarsky optics A Jeol JSM 5400 scanning electron microscope (SEM) was employed for investigating freeze-fractured and microtomed surfaces All SEM samples were gold sputtered prior to observation

RESULTS AND DISCUSSION

Individual Polymers

Observation of CB dispersion within the polymer matrices was usually conducted through SEM upon cryogenically fractured surfaces Polystyrene samples are difficult to investigate due to the presence of excessive crazing in the brittle fractured surface, the craze tips hindering recognition of CB particles A microtomed sample, such as in Figure 1, produces a more coherent picture HIPS reveals circular regions unoccupied by CB These areas probably correspond to the cross-linked polybutadiene phase dispersed within polystyrene due to their size (~ 1 μm) and the fact that CB does not penetrate them CB particles seem very small within the HIPS matrix, detached from it and nonuniformly dispersed, promoting the formation of a conductive network LLDPE exhibits a typical ductile fracture surface, of smoother texture in comparison to HIPS In the 2 phr sample [Fig 2(a)] CB particles are randomly dispersed in the matrix, too distant for conductive pathways to be formed The 6 phr CB sample [Fig 2(b)] shows that CB is usually located in oval cavities larger than the particles themselves These gaps may be caused by poor adhesion between the filler and the matrix or result from the nonuniform topography obtained upon the fracture surface due to polymer ductility

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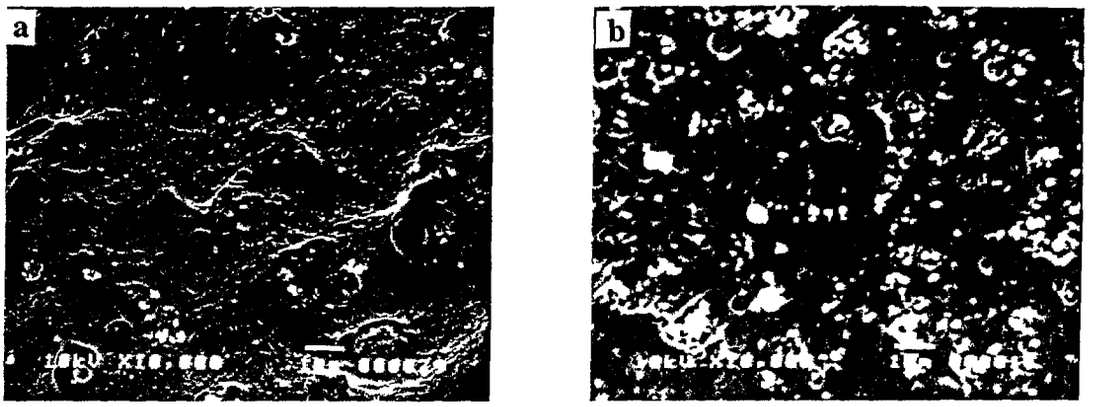

Figure 2 SEM micrographs of freeze fractured (a) LLDPE + 2 phr CB, (b) LLDPE + 6 phr CB

LLDPE of low viscosity, LL25, was studied as well The fracture surface differs greatly from the smooth texture of the former sample, appearing much more complicated and ductile (Fig 3), rendering the CB very difficult to distinguish The addition of CB even in small content results in a more brittle behavior

The volume resistivity of the HIPS, LLDPE, and LL25 as a function of CB content is depicted in Figure 4 The percolation threshold of HIPS is the lowest of these polymers, at 2 phr CB

The LL25 percolates at ~ 4 phr CB, whereas the high-viscosity LLDPE threshold is obtained at 6 phr CB Understandably, polymer viscosity plays an important role in the dispersive mixing process, which consists of particle incorporation within the liquid, deagglomeration, aggregate fracturing, distribution by flow, and flocculation The viscosity of the suspending liquid undergoing mixing exerts hydrodynamic forces upon the agglomerates, competing with the cohesive forces within them Thus, a high-viscosity liquid may induce agglomerate rupture and fracturing of aggregates, whereas the opposed effect of particle flocculation is more pronounced in a low-viscosity medium [14] Seemingly, the higher-viscosity LLDPE disperses CB more uniformly, reducing particle size and inhibiting floccular configurations The lower-viscosity LLDPE tends to exert lower shear stresses on the agglomerates, causing less structural degradation, along with reduced resistance to reagglomeration, enabling the CB aggregates to approach one another more easily and form conductive networks

The effect of surface tension and polarity of polymers on the critical volume fraction in various CB-filled thermoplastics has been well established [5 15] An increase in surface tension increases the percolation threshold, favoring CB uniform

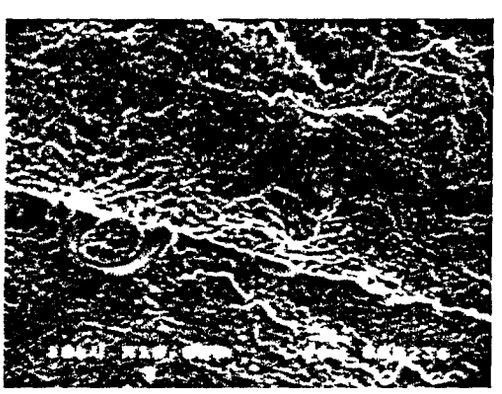

Figure 3 SEM micrograph of freeze fractured LL25 + 2 phr

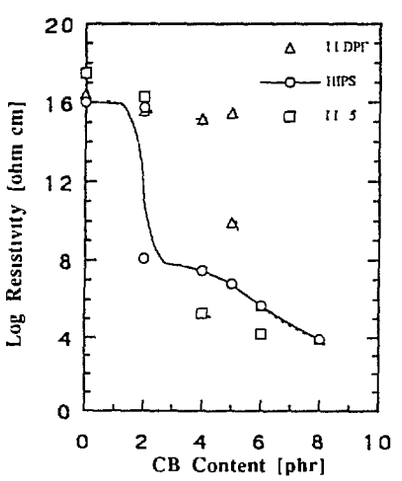

Figure 4 Resistivity of individual polymers versus CB content

dispersion within the polymeric matrix Carmona[15] depicts polystyrene (PS) as demanding a higher CB content than polyethylene or polypropylene in order to percolate, inconsistently with observations obtained in this study and previous ones [9,10] CB-loaded HIPS has a low percolation threshold, at an approximate loading of 2 phr CB (Fig 4) This value is especially low in light of the fact that polystyrene has a higher surface tension than either PP or PE (~ 41, 30, 36 dyne/cm at 20°C, respectively) [16] Apart from its higher surface tension, polystyrene also has some extent of polarity (0 168) as opposed to PP and PE (0 0) These facts lead us to expect a higher percolation threshold for PS due to its higher surface tension and polarity

Apparently PS is a polymer of intermediate surface tension in comparison to PP and LLDPE on one hand, and to polyamide on the other hand Its slight polar nature differs from that of polar polyamides resulting from aromatic pi-orbitals and polar functional groups, respectively Polystyrene is also known to be weakly basic (its electron donor parameter, $\gamma^{(-)} = 1\ 1$ dyne/cm[17]), enabling interactions with the CB surface, acidic in nature [18] Thus, CB in HIPS exhibits a more uniform distribution, compared to the segregated structures viewed in PP and PE This intermediate nature could enhance some particle breakage, which is sufficient to provide conductive bridges However, interactions are not strong enough to cause severe agglomerate degradation and disperse CB uniformly within the matrix (as in polyamide–CB systems), which would diminish conductivity Thus, what seems to be an optimal structure, which produces a conductive network at an extremely low CB content, is formed The two-phase nature of HIPS, known to have < 10 wt % dispersed crosslinked rubber particles, was found not to have a direct effect on the percolation threshold, as a similar general-purpose polystyrene was measured having the same percolation threshold

Polymer Blends

The neat blends were studied at proportions of 95/5, 85/15, 70/30, and 55/45 with HIPS serving as the matrix and LLDPE as the dispersed phase The neat blends exhibit a typical behavior where the dispersed phase is very small for the 95/5 blend (1 μm order of value), slightly larger for the 85/15 blend [Fig 5(a)] and co-continuous for the 70/30 [Fig 6(a, b)] and 55/45 blends Phase inversion is therefore obtained at about a 70/30 composition, whereupon a co-continuous structure is observed This does not correlate with the simple model developed by Jordhamo, Manson, and Sperling[19] for predicting phase inversion and the point of co-continuous network formation, according to melt viscosity ratio of the components

Favis and Chalifoux[20] observed a correlation between this prediction and phase viscosity ratio as obtained either by Brabender torque values or viscosities measured by capillary rheometer for the neat polymers at a shear rate corresponding to that within the Brabender mixing chamber For the present HIPS/LLDPE system, torque values predict phase inversion at approximately 50% (by volume) LLDPE, whereas rheological values of melt viscosity as well as MFI data at 190°C (5 g/10 min for HIPS versus 1 g/10 min for LLDPE) forecast phase inversion at an even higher LLDPE content

It has already been stated[21] that the position and shift of the region of dual-phase continuity are not consistent with predictions based exclusively on composition and viscosity ratio For mobile interfaces in which adhesion between phases is poor, as in the present case, the morphology of immiscible blends appears to be controlled by a series of effects such as interfacial tension, viscosity ratio, and level of shear stress, in this order of significance

An additional effect may result from the subinclusions of HIPS within LLDPE, when the latter transforms from a spherical dispersed phase at a 85/15 composition to a continuous structure at 70/30 Continuous regions of LLDPE serve as a matrix for HIPS, constituting a type of blend within a blend,[22] resulting in an effective higher-volume fraction for LLDPE than the nominal one This could explain, at least partially, the significant shift in the phase inversion point to a lower minor phase content than the predicted value from the Jordhamo equation

When comparing the dispersed-phase size and distribution of the blend containing high- and low-viscosity LLDPE [Fig 7(a, b)], it is apparent that the former is of smaller droplet size, while the latter has larger droplets and is of wider distribution Two opposing processes taking place throughout the blending should be considered mixing (involving continuous breakdown of the dispersed particles) versus coalescence (upon which dispersed particles approach one another and eventually collide, the matrix material between them being removed) [21,23] Coalescence time

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Figure 5 SEM micrographs of freeze fractured 85HIPS/15LLDPE (a) Neat blend, (b) 2 phr CB-loaded blend

is highly dependent on the dispersed-phase viscosity, which implies rapid fusion of particles of low viscosity [14] The final morphology of a blend is a result of the dynamic processes of break-up of large droplets and coalescence of the smaller ones during mixing Apparently, in blends with low-viscosity LLDPE, both processes of droplet breakup and coalescence occur more rapidly,

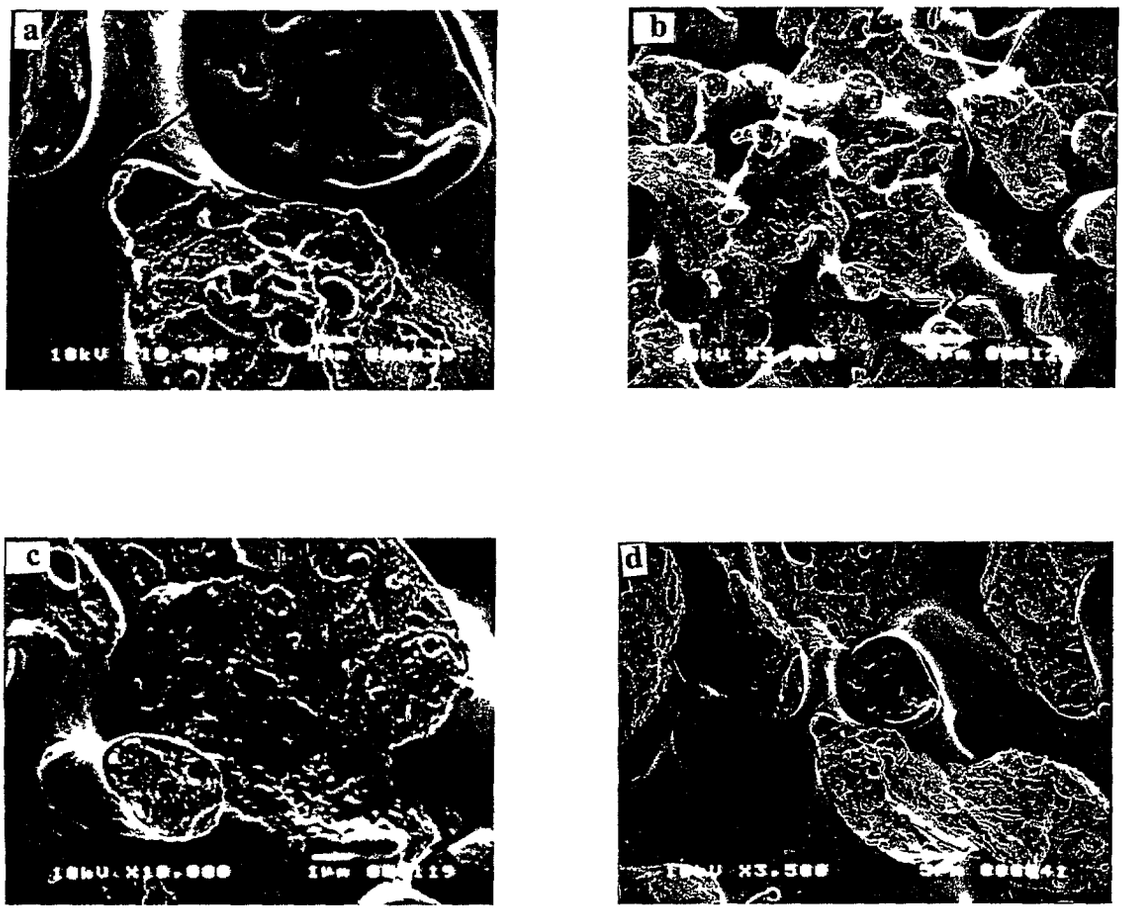

Figure 6 SEM micrographs of freeze-fractured 70HIPS/30LLDPE blend (a, b) Neat blend at 2×, (c, d) 2 phr CB loaded blend at 2×

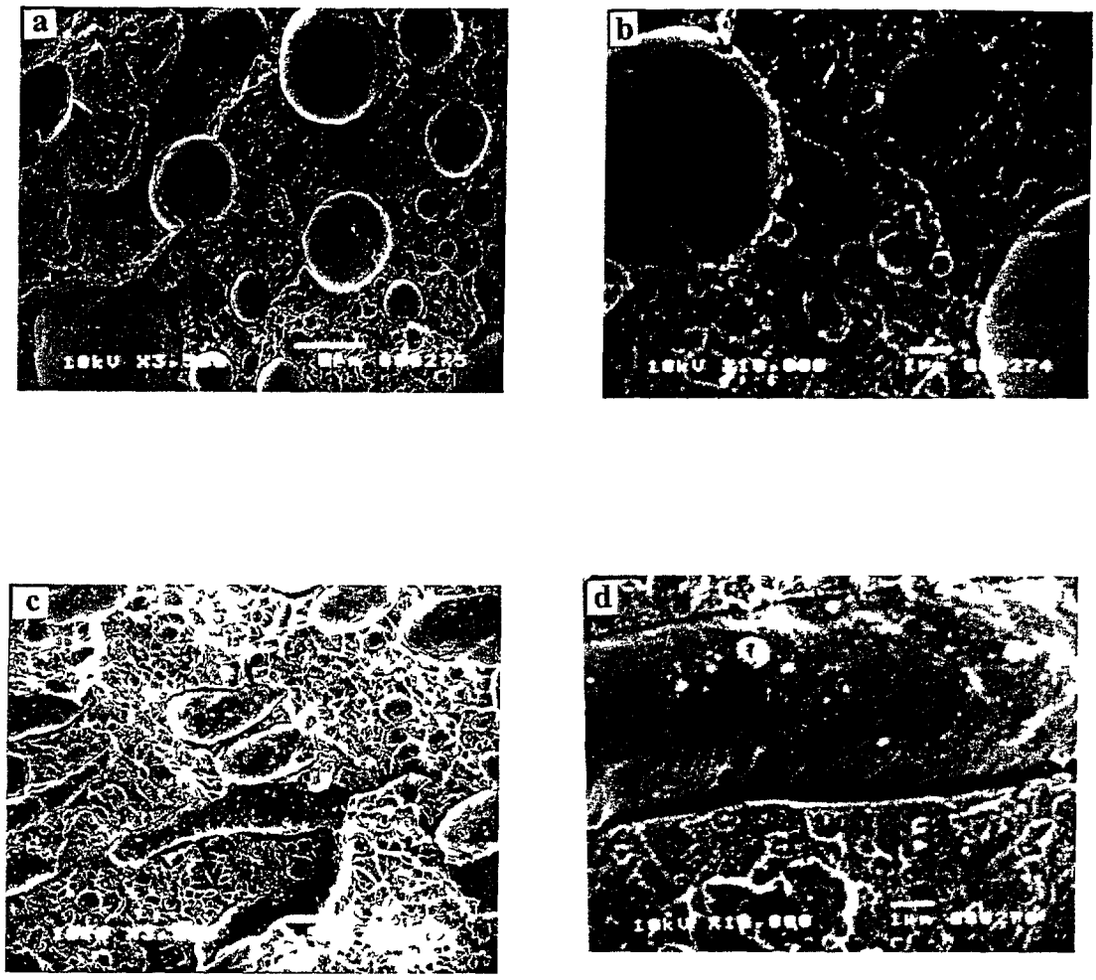

Figure 7 SEM micrographs of freeze-fractured 85HIPS/15LL25 (a, b) Neat blends at 2×, (c, d) 1 phr CB loaded blend, at 2×

which may explain the wide distribution of particle size depicted in the 85/15 blends of HIPS with low-viscosity LLDPE

Addition of CB to the HIPS/LLDPE systems is accompanied by its preferential location in the LLDPE, as depicted in Figures 5(b) and 6(c, d) SEM micrographs reveal that CB is usually positioned upon the surface of the LLDPE dispersed phase, and less incorporated within it The CB particles are clearly seen on the surface, and tiny cavities corresponding to them are stationed upon the HIPS surface The higher percolation threshold of the individual LLDPE in comparison to HIPS implies the tendency of CB to locate preferentially within LLDPE, as observed previously [9 10] Interaction of CB with both polymers, of intermediate nature in the case of HIPS and weak for LLDPE, may promote CB location in the interfacial region When utilizing LL25, the low viscosity enables CB penetration within the dispersed phase, so that mixing dynamics comes into effect

CB usually alters the morphology significantly, depending on the initial blend structure The 95/5 blend loaded with 2 phr CB has a dispersed LLDPE phase of tiny dimensions, resulting in difficulty to recognize the CB within it CB is distributed throughout the matrix in this case, and the dispersed LLDPE phase consists of tiny particles which have no significant effect on the CB location The 85/15 blend, composed of spherical dispersed LLDPE particles in the neat case (Fig 7) exhibits a change both in size and in shape, developing an elongated dispersed-phase structure upon CB addition [Fig 5(b)] The dispersed phase becomes smaller, but as the dimensions are reduced the number of particles increases, creating numerous CB-coated LLDPE cylinders, as depicted in Figures 5 and 7 The reduction in dis

persed phase size and its change in shape has been previously reported[9 10] and has been attributed to friction between CB and the dispersed polymer The higher viscosity of the dispersed droplets upon CB addition is expected to affect the resulting morphology, according to Min, White, and Fellers,[24] deformation should be less pronounced In practice, since CB tends to locate more on the dispersed particle surface than within it, the interface between the dispersed and continuous phases may become less mobile Friction between the CB-coated dispersed particles and the matrix may cause deformation leading to elongated structures, contrary to the description by Min These maintain their rodlike structure with no apparent droplet breakup as obtained in the neat case This phenomenon occurs in both types of LLDPE As to the 70/30 and 55/45 blends, co-continuity prevails, as in the neat case The co-continuous structure of the CB-loaded blends is finer than that of the unloaded ones, resulting in an enhanced network (Fig 6) The 55/45 composition is of coarser structure than the 70/30 one

The resistivity curves of the CB-loaded blends are depicted in Figures 8 and 9 The 95/5 blend (Fig 9) percolates at ~ 1 phr CB, slightly less than the individual HIPS, which percolates at 2 phr The dispersed LLDPE particles are very small and of minor quantity, so that this blend acts similarly to the individual HIPS The dispersed LLDPE phase is not necessarily penetrated by CB and conductivity in this case results from the effective CB content in HIPS The 85/15 blend demonstrates a percolation threshold at

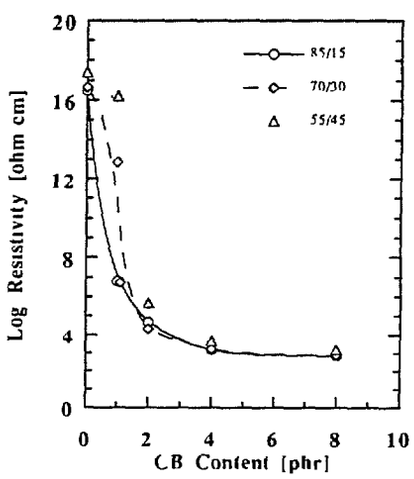

Figure 8 Resistivity versus CB content of various HIPS/LLDPE blends

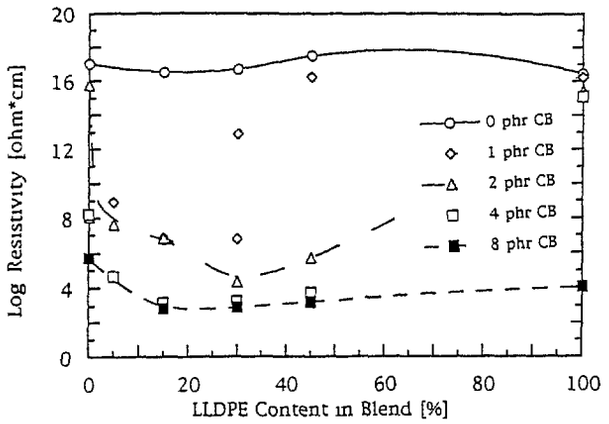

Figure 9 Resistivity as a function of LLDPE content in HIPS/LLDPE blends, for various CB loadings

< 1 phr CB (Fig 8), due to the tendency of CB to locate itself in the LLDPE phase, and the elongated dispersed phase structure obtained in this case Thus, CB is concentrated in the LLDPE (mainly upon its interface) in an effective content highly above the polymer's percolation point, and the elongated configuration creates loci of contact between the dispersed domains, leading to the observed conductivity The 70/30 composition has a slightly higher percolation threshold (Fig 8) and is slightly less conductive (Fig 9), although co continuous Due to the higher LLDPE content than in the former case, it has a smaller effective CB loading in it and thus conductivity is slightly diminished, as seen in Fig 9 This demonstrates that extended configurations that contact each other enhance the formation of a network and double percolation may be realized, leading to a reduced percolation threshold This takes place for the 55/45 blend as well, which has a percola tion point similar to the individual HIPS at 2 phr CB For most blend compositions, the percolation point is not greatly reduced in comparison to the individual HIPS matrix, perhaps due to the fact that HIPS alone percolates at a low CB content However, the magnitude of the resistivity is decreased by approximately four orders of magnitude, which is indeed a significant enhancement This may be attributed to the unique morphology obtained in the blend systems, in which the CB is preferentially placed upon the LLDPE phase surface Thus, the concentration of CB particles upon the interface greatly promotes conductivity, in comparison to conductivity values typical of CB dispersed within a single matrix, even above the percolation point

Blending the ingredients by a different mixing

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sequence does not practically produce different resistivity values or morphology, as described elsewhere [9-11] Upon incorporating CB into HIPS prior to LLDPE addition, results were indistinguishable from the standard method used

HIPS/LLDPE blends in which low-viscosity LLDPE is used generally exhibit a behavior similar to the one described above (Fig 10) CB tends to penetrate the LLDPE phase more in this case, due to its lower viscosity The lower percolation values exhibited for all blend ratios stems from the lower percolation point of the lower-viscosity LLDPE No unique morphology was obtained, however, coarsening of the dispersed phase due to the accelerated coalescence has led to a more gradual formation of a co-continuous structure Thus, a higher dispersed-phase content resulting in a 70/30 composition is necessary to obtain lower resistivity in this case (Fig 11)

Processing Effects

Injection-molded samples were tested for morphology and resistivity data The samples consisted of HIPS + 8 phr CB, 85 HIPS/15 LLDPE + 4 phr CB, and 70 HIPS/30 LLDPE + 4 phr CB The electrical resistivity of these samples was measured by the four point method (specified above) and was proved to be relatively high (above 10^8 ohm/cm) even for samples that were of low resistivity by the former compression-molding processing method

SEM micrographs of HIPS/LLDPE + CB blends depict, as expected, significant differences

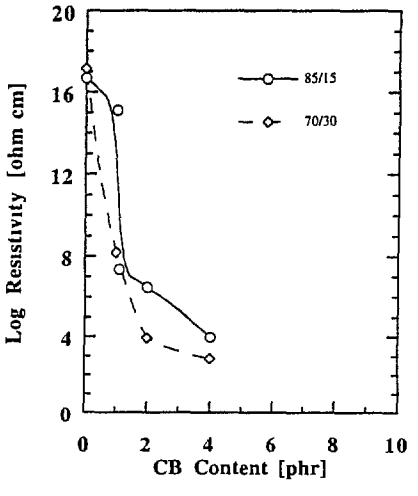

Figure 10 Resistivity versus CB content of various HIPS/LL25 blends

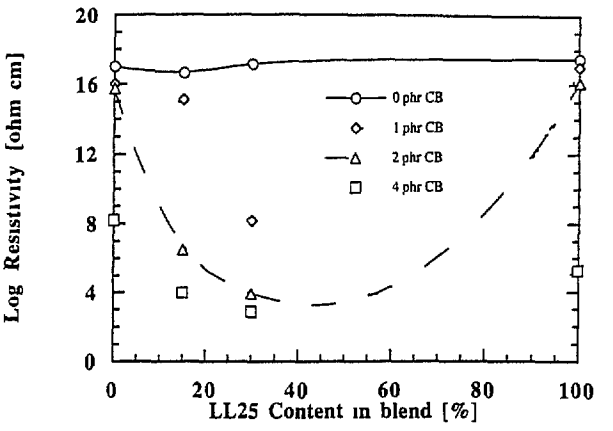

Figure 11 Resistivity as a function of LL25 content in HIPS/LL25 blends, for various CB loadings

between the directions parallel and transverse to flow Within the CB-loaded 85/15 HIPS/LLDPE blend [Fig 12(a, b)], the dispersed PE phase becomes highly extended, obtaining cylindrical structures of relatively low diameter (~ 1 μm) and widely distributed lengths of a few microns CB is located within the dispersed phase, more so than for the former processing method, in which CB was upon the interface The 70/30 formulations are relatively similar (Fig 13), however, structures are more co-continuous in the direction parallel to flow and the dispersed phase is of irregular, rather than circular, cross-section

Morphological observations provide some insight as to why injection-molded samples are insulative The high orientation of the dispersed phase within the matrix causes an orderly sequence of cylindrical structures, however, these hardly come into contact In the case of Brabender mixing, extended structures were observed as well, but these were randomly oriented, overlapping to provide a well-established conductive network Even the 70/30 blend, with a slight tendency toward co-continuity in the direction parallel to flow, is insufficiently continuous CB penetrates the dispersed phase in injection-molded samples more thoroughly than in the Brabender mixed ones, presumably due to the significantly high shear rates involved in the injection molding process followed by rapid solidification in the mold This may constitute an additional reason for the higher CB contents required for percolation, and the corresponding higher resistivity values

The higher shear rate exercised in injection molding definitely has an effect on agglomerate degradation and destruction of chainlike tendencies—this is apparent by the fact that the 8 phr

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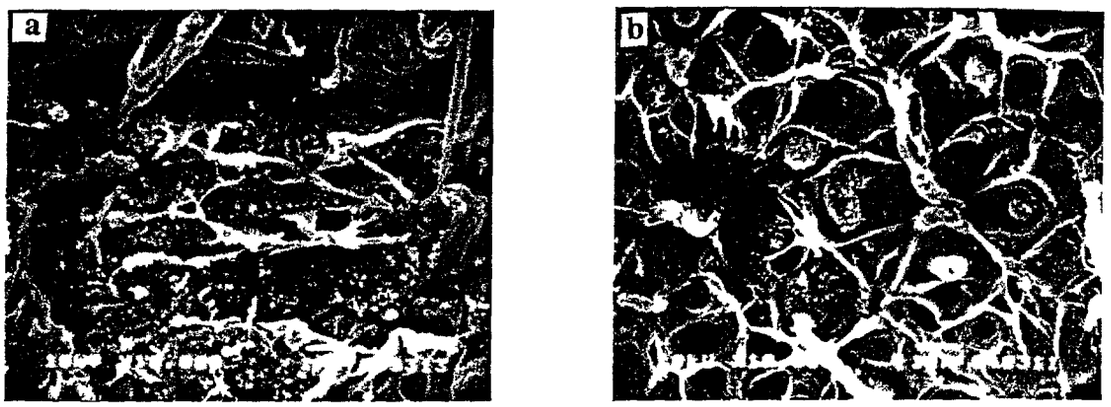

Figure 12 SEM micrographs of microtomed samples of injection molded 85HIPS/15LLDPE+ 4 phr CB (a) parallel to flow, (b) transverse to flow

loaded HIPS is insulative when injection molded However, SEM micrographs are insufficient to depict this clearly, due to the very small CB agglomerate size involved

Several authors have related to the increased resistivity of CB-loaded injection-molded polymer systems[4 25 26] due to orientation and degradation of agglomerates by shearing Webling[27] attributed this to kinetic effects, whereupon thermodynamically stable cohesive structures of CB chains cannot be restored within the time scale of the injection molding process

It is therefore clear that two competitive processes are implemented during injection molding, when deformation comes into effect the destruction of CB structures formed during the compounding step versus their tendency to reconstruct by shearing In this case, the former effect prevails, due to the rapid rate of the injection molding process Thus, this procedure results in highly deformed structures in the high-resistivity injection-molded samples, in comparison to Brabender mixing combined with compression molding, where much lower resistivities are obtained

CONCLUSIONS

As was previously shown[9 10] the CB percolation thresholds in the individual polymers vary from one matrix to another, based on effects of surface tension, polarity, and viscosity An emphasis has been placed on HIPS, unique in its combination of a relatively high surface tension and low percolation threshold, yielding an optimal network structure at low CB contents CB percolates in LLDPE at a higher content than in HIPS, and locates preferentially in LLDPE (or upon its surface) in HIPS/LLDPE systems The location depends upon a balance between CB-polymer interactions, mixing kinetics and viscosity effects Blends exhibit lower percolation thresholds and

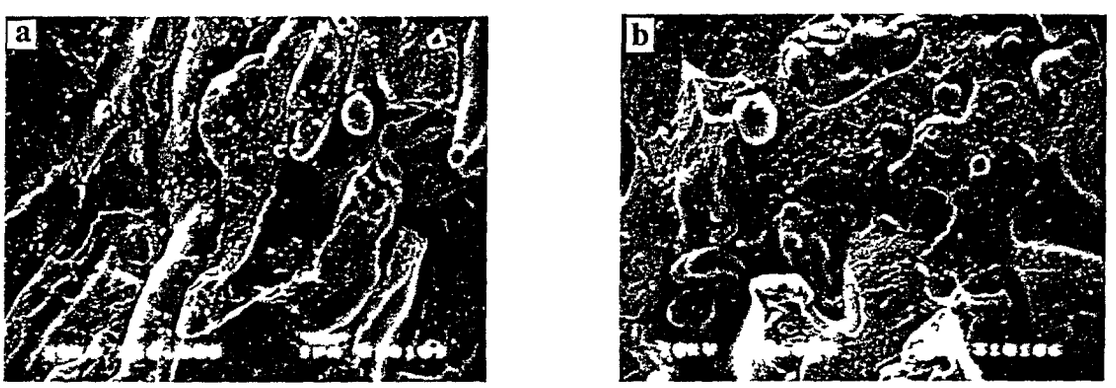

Figure 13 SEM micrographs of freeze fractured samples of injection molded 70HIPS/30LLDPE+ 4 phr CB (a) parallel to flow, (b) transverse to flow

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lower resistivity values than those depicted for the individual polymers

Double percolation is implemented in these systems through formation of overlapping extended structures of the dispersed LLDPE phase in which CB is located primarily on its surface In HIPS/LL25 a higher dispersed phase content is needed to provide a more well-developed co-continuous network, as blend structure is coarser CB enhances the networking effect by reducing the dispersed phase size and elongating it, generating a fine honeycomb-like structure

Injection molding severely diminishes conductivity compared to conductive blends processed by Brabender mixing followed by compression molding This is attributed to high shear rates, orientation, and rapid kinetics involved in injection molding, which induce the formation of noncontinuous highly deformed dispersed-phase structures in which CB agglomerates disintegrate and only partially reagglomerate

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Conductive Polymer Blends With Low Carbon Black Loading High Impact Polystyrene/Thermoplastic Elastomer (Styrene-Isoprene-Styrene)

R TCHOUDAKOV O BREUER *and* M NARKIS

Dept of Chemical Engineering

and

A SIEGMANN

Dept of Materials Engineering
Technion—Israel Institute of Technology
Haifa 32000 Israel

Electrical resistivity and morphology of high impact polystyrene (HIPS)/styrene-isoprene-styrene copolymer (SIS)/carbon black (CB) blends were studied Conductive CB particles locate preferentially within the HIPS phase of the HIPS/SIS blends The blends studied remain conductive as long as HIPS maintains a continuous phase and the effective CB concentration within HIPS surmounts its percolation threshold Thus blends containing 2 phr CB depict significant changes in resistivity with the HIPS/SIS composition transforming from insulative to conductive SIS/CB mixtures exhibit an unusual behavior explained by a physical model suggested in this paper and extended to the HIPS/SIS/CB systems

INTRODUCTION

Polymer blends consisting of two immiscible polymers and a thermoplastic elastomer that contains fragments identical to the homopolymer chains are of specific interest because of possible compatibilization effects in these blends Thus the added block copolymer acts as an alloying agent or a surfactant which contributes to the stabilization of the multiphase structure (1 2) Numerous publications concern the morphology and properties of blends such as polystyrene (PS) with its copolymers (3–6) However almost nothing is reported on such blends loaded with carbon black (CB) Numerous publications concerning elastomer/CB conductive compositions reveal some fundamental parameters determining their conductivity level among them is the CB-polymer interaction (7–10) For CB-loaded polymer blends the conductivity is controlled by the CB content in the blend the blend s morphology and the CB location within the blend (11–15) These elements are the key components of the double percolation concept (16–18) which is currently accepted as the background for understanding the behavior of CB-filled multiphase polymer systems A thermoplastic elastomer mixed with CB being a part of the multiphase conductive system manifests a particular behavior of the blends conductivity (3 19) owing to the thermoplastic elastomer intrinsic microstructure

The subject of this study is the correlation between resistivity and morphology of CB-loaded compositions of a high impact PS (HIPS) and a tri-block copolymer styrene-isoprene-styrene (SIS)

EXPERIMENTAL

The polymers used in this study were the following

- HIPS Galirene HT 88-5 MFI—4 5 Israel Petrochemical Industry
- SIS Quintac 3421 MFI—11 14% PS Japan and
- CB Ketjenblack EC-300 Akzo The Netherland

Sample preparation procedure included melt mixing for 15 min at a speed of 50 rpm in a Brabender plastograph at 190°C followed by a standard compression molding procedure at the same temperature to obtain 3 mm-thick plaques

The volume resistivity of disk-shaped samples was measured according to DIN 53596 by techniques previously specified (11) The blend morphology was studied using a Jeol 5400 scanning electron microscope (SEM) Freeze-fractured and microtomed surfaces (both prepared in liquid nitrogen) were investigated

RESULTS AND DISCUSSION

Figure 1 shows the resistivity of polymer/CB compounds as a function of the CB content It is clearly seen that the SIS/CB percolation value (about 10 phr) is much higher than the corresponding one for HIPS/CB compounds (about 2 phr) As well-established now the critical concentration of a given CB at the percolation threshold in different polymers depends on the polymer/CB interaction Such interactions are related to some polymer characteristics such as surface tension polarity crystallinity and viscosity where surface tension often seems to be the dominant parameter It was shown (20) for a variety of polymers that a higher surface tension leads to a higher critical concentration at the percolation threshold with the exception of only a few polymers Precise surface tension values for the polymers used in this study (HIPS and SIS) are not known Nevertheless relevant surface tension values are as follows PS—40 4 polybutadiene—32–34 polyisoprene—31–34 dyne/cm (21) It is known (21) that the surface tension of copolymers is always lower than the value corresponding to the component of higher surface tension even if the component of the lower surface tension is present in relatively small amounts In the present case PS is the component of higher surface tension value of both polymers—HIPS and SIS In the former the lower surface tension component (butadiene rubber) is the minor component (less than 10%) whereas the specific studied SIS copolymer contains 86% isoprene It is possible to assume according to Wu (21) that the weighted surface tension of HIPS (γ_1) is closer to that of PS than the weighted surface tension of SIS (γ_2) i e $\gamma_1 > \gamma_2$ but the percolation thresholds of these polymers as seen in *Fig 1* are not congruous to the known rule (20)

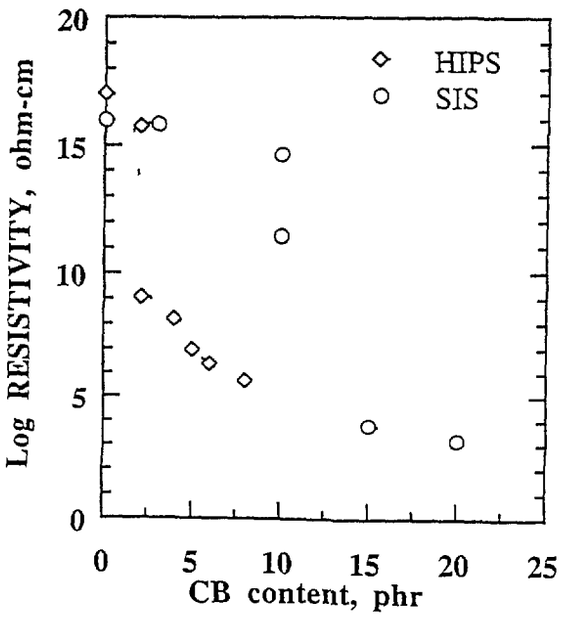

Fig 1 Resistivity vs CB content in HIPS and SIS

Micrographs of the neat polymers and their CB/polymer compositions are shown in *Figs 2–4 Figures 2a* and *2b* depict a typical freeze-fractured surface of HIPS with characteristic contours of a PS matrix fracture and dispersed polybutadiene containing domains The tips of crazes generated during the specimen s freeze fracturing are observed The dispersed domains 1–3 μm in diameter containing a rubber phase are seen more clearly in the micrograph of a microtomed surface (*Fig 2c*) The addition of CB to HIPS does not lead to significant changes in the appearance of the freeze-fractured surface in comparison with that of the neat HIPS (*Fig 3*) Many tiny white particles are present in both micrographs (*Fig 2b* and *Fig 3b*) and it is thus difficult to distinguish between tips of crazes and CB agglomerates The CB dispersion within HIPS can only be determined using mic-

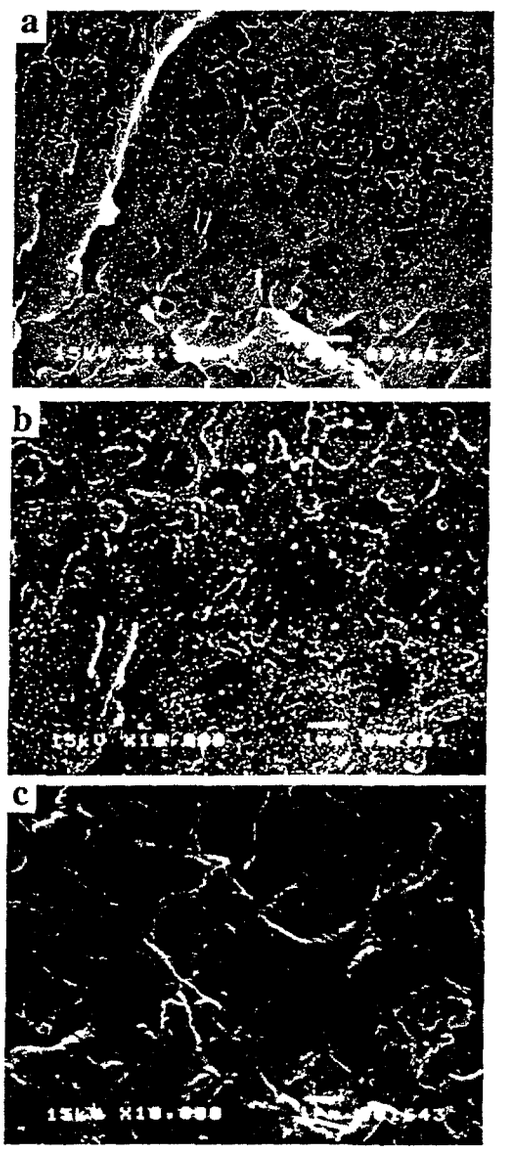

Fig 2 SEM micrographs of neat HIPS (a, b)—freeze fractured surface (c)—microtomed surface

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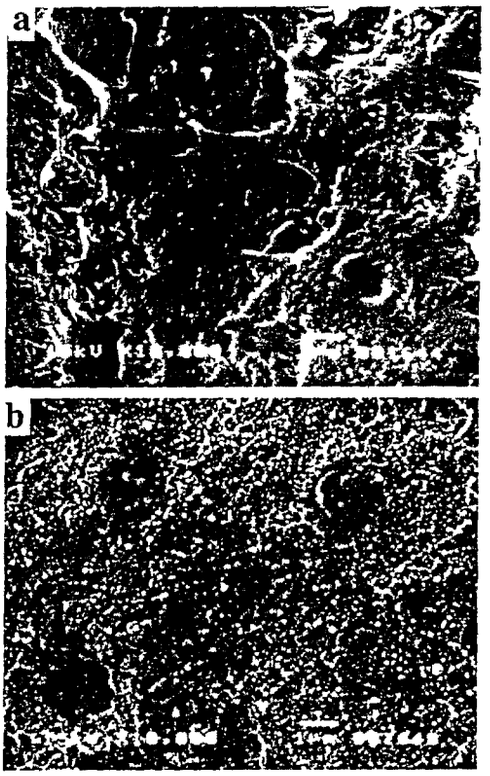

Fig 3 SEM micrographs of CB loaded HIPS (a)—2 phr CB microtomed surface (b)—5 phr CB freeze fractured surface

rotomed rather than fractured surfaces (*Fig 3a*) This micrograph shows a fairly good CB dispersion in only the PS phase while the rubber domains are free of CB The rubber domains in a CB-loaded HIPS look darker and are distinct from the matrix (*Fig 3b*) It should be noted that a careful study of microtomed surfaces assists in viewing these features in freeze fractured surfaces as well

The segregated phase morphology of tri-block sty rene copolymers SIS or SBS was studied elsewhere in detail by TEM (22) Using the presently applied SEM it was impossible to observe SIS samples at sufficiently high magnifications (> ×10 000) Hence only a slight hint of some segregated structure or texture may be visible in the SIS micrographs On the other hand CB addition to SIS is manifested by the appearance of bright particles the quantity of which increases with CB concentration (*Fig 4*) Even taking into consideration a vague CB appearance in the mi crographs the difference in appearance of the CB dispersion within SIS before (10 phr) and after (15 phr) the percolation threshold (*Figs 4 b* and c) is undoubtedly depicted

As already recognized the resistivity of CB-loaded polymer blends is determined by their structure and by the CB concentration and location within the blend It is thus important to study the relationship between the blend s morphology and its resistivity *Figure 5* depicts the effect of SIS content on the blend resistivity at a constant CB concentration in the blend Interestingly blends with 2 phr CB depict a

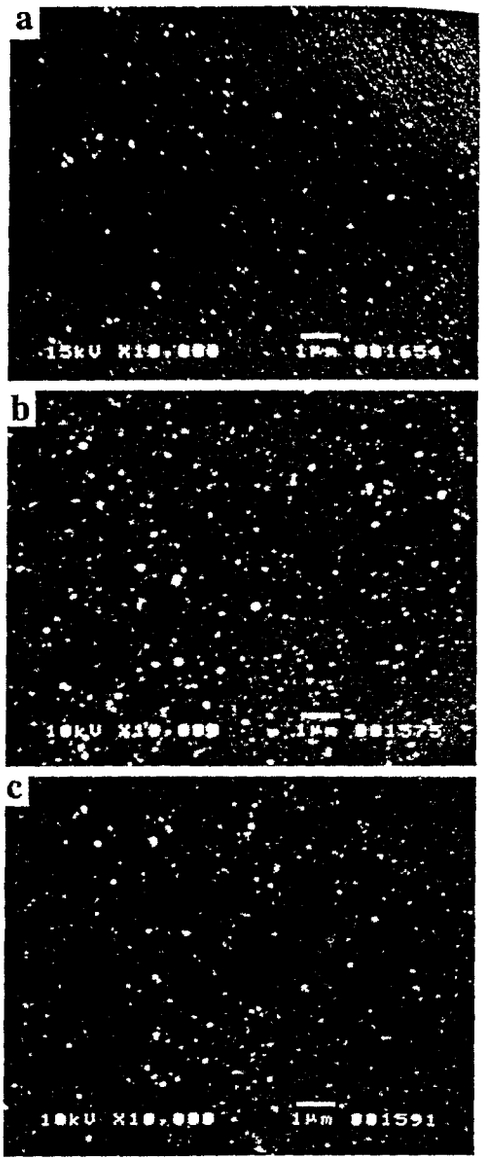

Fig 4 SEM micrographs of CB loaded SIS (a)—3 phr CB (b)—10 phr CB (c)—15 phr CB freeze fractured surface

stronger change in resistivity with blend composition compared to the blends containing 4 phr CB It should be noted however that the resistivity of HIPS containing 4 phr CB is 9 orders of magnitude lower than that of HIPS containing just 2 phr CB The resistivity of the former is practically unaffected by the addition of SIS up to 45 wt% while the 2 phr CB containing blends exhibit a large resistivity reduction for SIS content of 20–30 wt% The morphology of neat and CB-containing blends is shown in *Figs 6–10*

Figure 6 shows freeze fractured surfaces of HIPS/SIS blends containing 5 10 15 20 30 and 45 wt% dispersed SIS phase in the absence of CB At low contents SIS is dispersed in a very fine manner in the blends its particle size is within 0 2–1 μm (*Fig 6a–c*) A co-continuous structure already appears at a blend composition of 80HIPS/20SIS (*Fig 6d*) and the distri-

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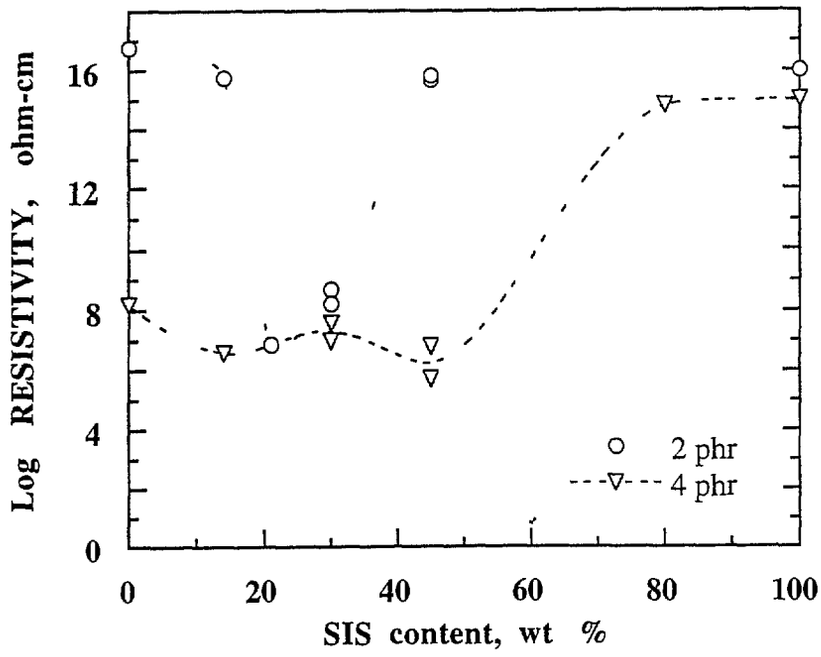

Fig 5 Resistivity vs SIS content for two CB loadings in HIPS/SIS blends

bution of each polymer in the fractured surface is visible (*Fig 6d–e*) At 45 wt% SIS seems to be the major phase of the blend (*Fig 6f*) and HIPS the dispersed phase The two phases seem strongly interconnected as there are no gaps at the interface between the phases characteristic of low interacting components in immiscible polymer blends Note again that the bright tiny details present in the HIPS phase are also visible in the SIS phase This means that to determine the genuine location of CB particles within the blend is not an easy task

Micrographs of freeze fractured surfaces of CB-loaded HIPS/SIS blends are shown in *Fig 7* Rubber-containing domains are clearly seen in the HIPS phase without any traces of CB present For the 55HIPS/45SIS blends many small bright spots are visible in both phases (*Fig 7 c d*) however the number of such details is undoubtedly increased in the HIPS phase only with an increase of CB content from 2 to 4 phr An increase of CB content in the blend leads to a more enhanced contrast in the appearance of the two polymer phases (*Figs 6e* and *7b* and *Figs 6f* and *7c d*)

A clear phase structure together with a well-defined CB location are seen in *Fig 8* which depicts some microtomed surfaces These samples were microtomed immediately after cooling in liquid nitrogen Although this procedure leads to a noticeable surface distortion of the original morphology especially of the SIS phase the two phases appear separate enabling to examine the CB presence within each phase In all these micrographs the SIS phase looks smooth without an evident presence of CB agglomerates On the contrary HIPS contains a lot of the CB well-distinguished agglomerates (*Figs 8b c*) Hence preferential CB location in the HIPS phase of the blend occurs In the filled 55HIPS/45SIS blends CB is almost invisible in the micrographs because in these blends SIS envelopes the CB loaded HIPS domains (*Fig 8d*) It should be noticed that the CB preferential location within the HIPS phase was observed for the samples studied regardless of the sequence of the CB addition to the polymers namely to SIS HIPS or to their blend

Returning to *Fig 5* and recalling the double percolation notion the conductivity of CB-filled HIPS/SIS blends is determined by the conductivity of the CB-rich HIPS phase and its continuity It is clear that SIS addition to a HIPS/CB blend increases the effective concentration of CB in HIPS (constant CB content in the total mixture) Therefore the blend containing 2 phr CB insulative in the absence of SIS becomes relatively conductive upon about 30 wt% SIS addition By further increasing the SIS content a phase inversion occurs whereupon HIPS transforms to the dispersed phase i e continuity of the CB-rich conductive HIPS phase is disrupted and the blend becomes insulative Blends containing 4 phr CB (*Fig 5*) are already conductive in the absence of SIS and no significant change in resistivity with SIS addition is observed HIPS is maintained as a continuous phase probably up to 45 wt% SIS in the blend so that a sharp blend transformation from conductive to insulative is not seen in this range of composition As shown previously (11) an increase of CB content in the blend is accompanied by a decrease of the CB-containing phase dimension Thus it is probable that phase inversion occurs at a higher SIS content for 4 phr CB-containing blend then for that containing 2 phr CB Finally it is interesting to remark that for the previously studied PP/Ny or PP/PC blends (11) the most drastic changes also occurred in compounds with a low CB loading

The most surprising result observed for the HIPS/SIS blends is the fact that the CB preferential location is not in the polymer of higher percolation threshold

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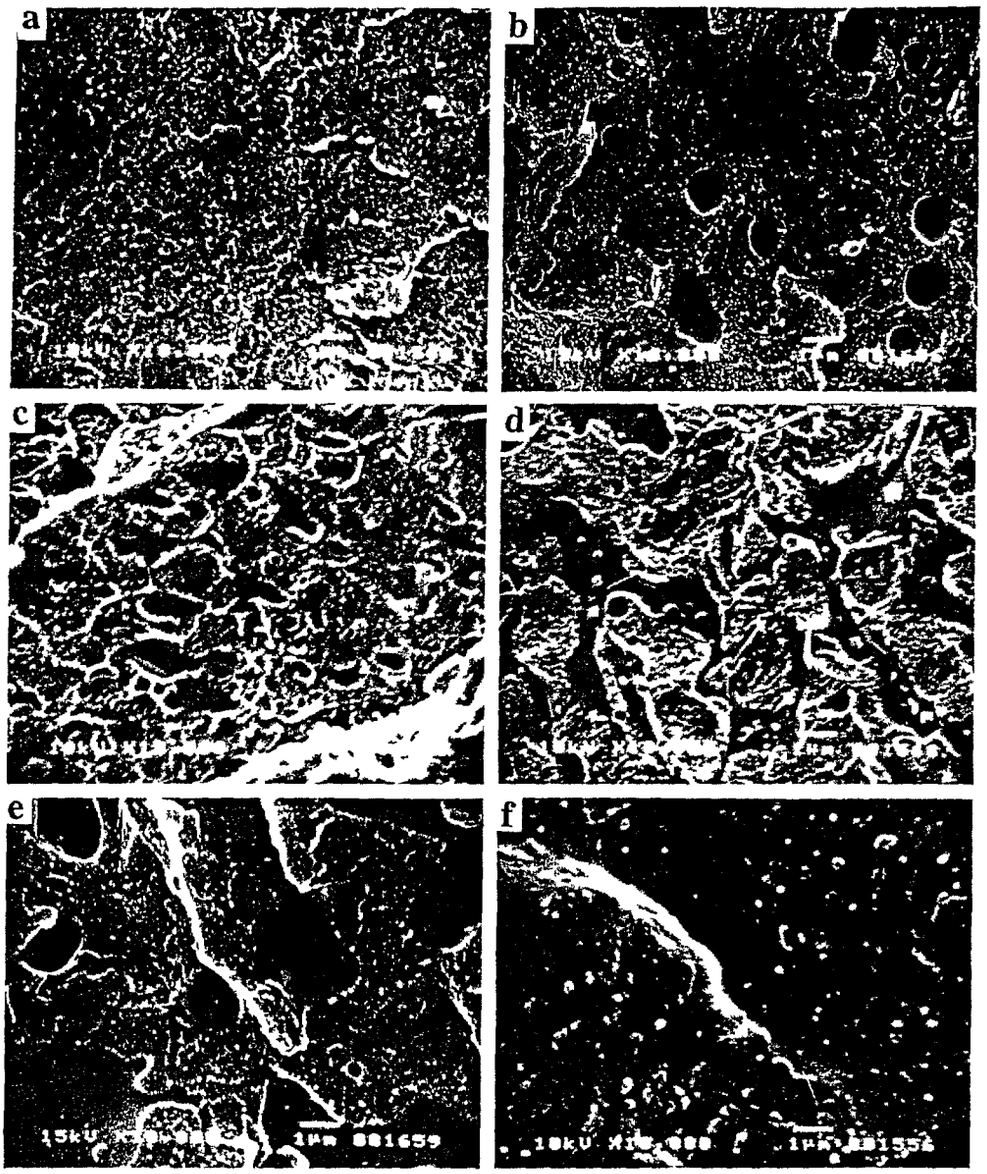

Fig 6 SEM micrographs of HIPS/SIS blends for different blend compositions (a)—95/5 (b)—90/10 (c)—85/15 (d)—80/20 (e)—70/30 (f)—55/45 freeze fractured surface

as was commonly observed for other CB-loaded conductive polymer blends (11–15) It should be again mentioned that the percolation thresholds of these polymers do not follow the known rule namely increasing with their surface tension values (20) In an attempt to explain the relative high percolation CB content in SIS (*Fig 1*) it is rational to assume that the particular SIS triblock copolymer structure may cause an unusual CB distribution It is known that the PS chain ends of such a copolymer are segregated in domains which vary in shape and size according to the PS content It was shown for SBS (23) that the PS domains are of spherical shape about 35 nm in diameter for a 38% PS copolymer These data permit as to propose a model of CB dispersion in the SIS copolymer which helps understand the presently observed results This model is based on the phenomenon of preferential location of CB in PS rather than in SIS An initial SIS structure is schematically depicted in *Fig 9* together with consistent steps of the CB addition It is suggested that the first CB particles incorporated into SIS are engulfed by PS (*Fig 9b*) The CB encapsulated by PS does not contribute to the material s conductivity During subsequent CB addition its particles "saturate" most of the PS domains of the copolymer and the excess CB starts to form a segregated CB morphology in the SIS (*Fig 9c*) Only then the CB percolation within the continuous rubber phase is exceeded and a conductive CB network is formed through the two phase SIS medium (*Fig 9d*) Such a consistent CB dispersion in the SIS medium explains the relatively high CB content necessary to percolate this copolymer and to convert it into a conductive form The CB chain network is observed rather se

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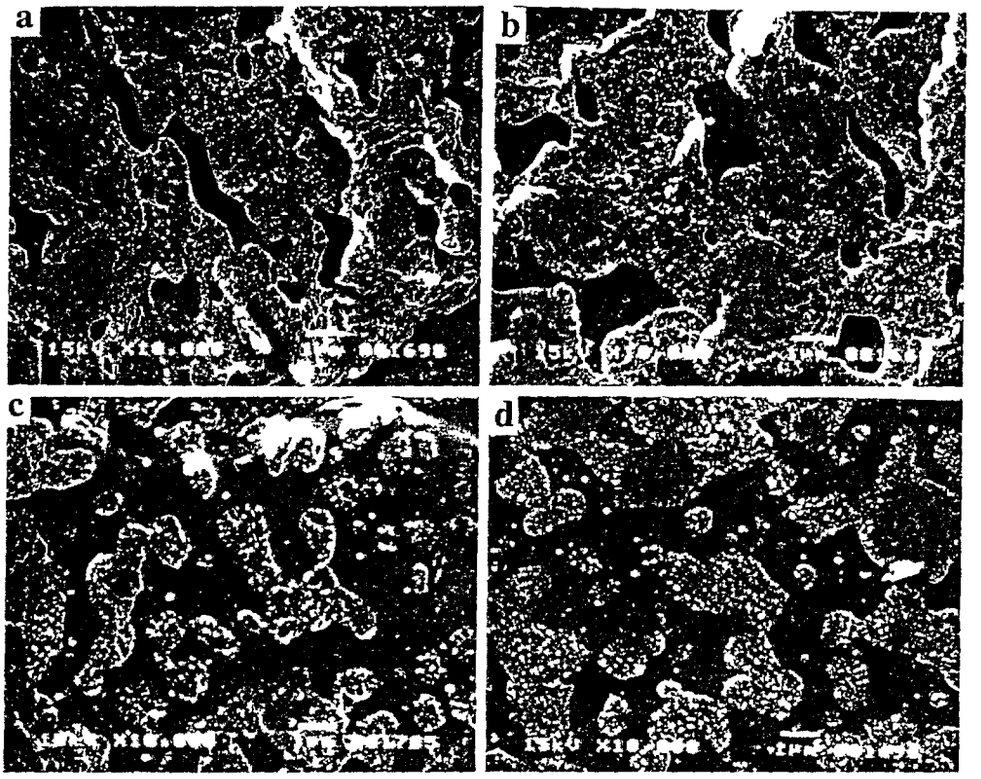

Fig 7 SEM micrographs of HIPS/SIS blends with CB (a)—2 phr CB 85/15 (b)—2 phr CB 70/30 (c)—2 phr CB 55/45 (d)—4 phr CB 55/45 freeze fractured surface

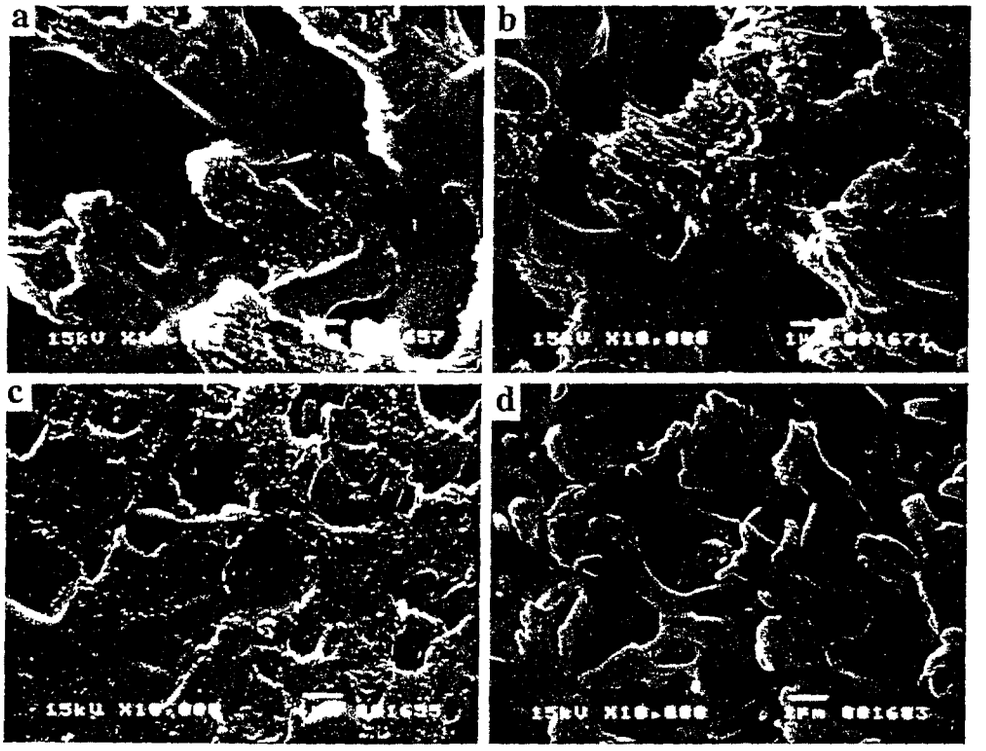

Fig 8 SEM micrographs of HIPS/SIS blends (a)—70/30 without CB (b)—70/30 4 phr CB (c)—85/15 4 phr CB (d)—55/45 4 phr CB microtomed surface

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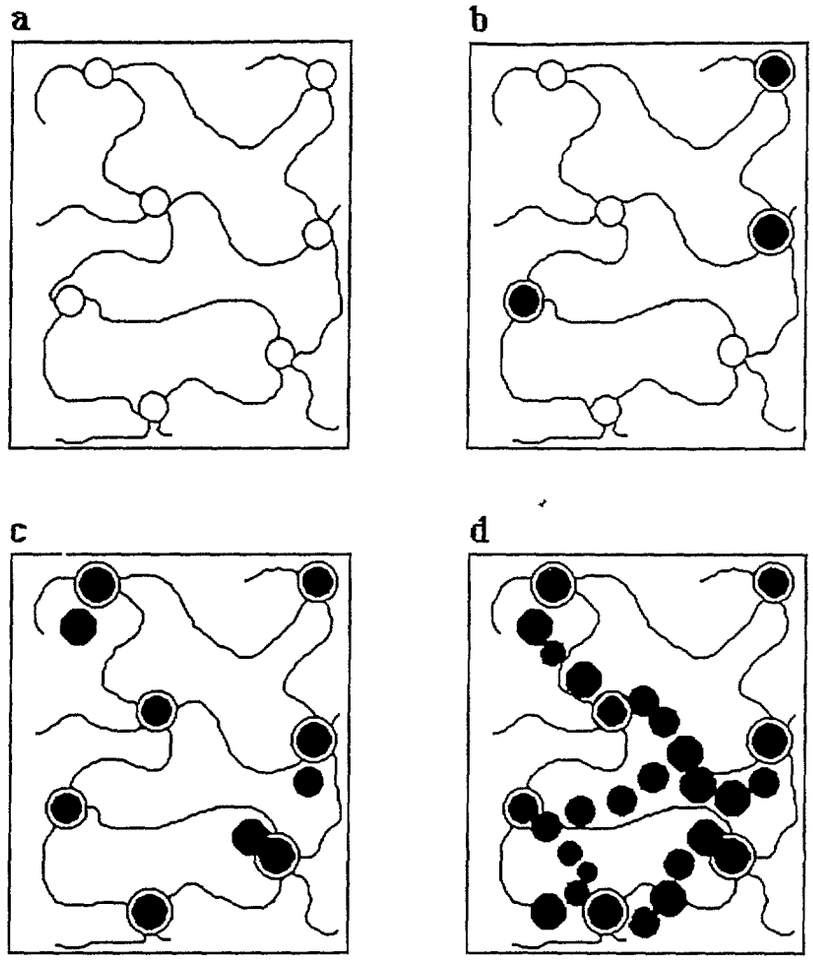

Fig 9 Scheme of CB distribution in SIS (a)—neat SIS (b)—CB encapsulated in the PS domains (c)—PS domains "saturated" with CB excess CB starting to form a segregated morphology in the rubber phase (d)—CB percolation within the rubber is exceeded

curely within SIS after percolation i e at 15 phr CB content (*Fig 4c*) Similarly a small amount of CB added to the HIPS/SIS blends is initially located in the PS phase of HIPS abundant in PS and only thereafter it may be distributed also in the SIS phase

CONCLUSIONS

Low concentrations of CB-loaded HIPS/SIS blends demonstrate interesting conductive properties and unusual morphology The preferential CB location in the HIPS phase occurs in spite of the fact that the percolation threshold of the HIPS/CB composition is much lower than that of the SIS/CB one The blends remain conductive as long as the HIPS phase is continuous and the CB amount exceeds its percolation value A described physical model of CB distribution within the SIS copolymer based on the known rules of preferential location of CB in the phase with higher surface tension is proposed explaining the observed morphology and conductivity as a function of composition

ACKNOWLEDGMENT

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CONDUCTIVITY/MORPHOLOGY RELATIONSHIPS IN IMMISCIBLE POLYMER BLENDS HIPS/SIS/CARBON BLACK

R Tchoudakov, O Breuer and M Narkis, Department of Chemical Engineering and A Siegmann, Department of Materials Engineering, Technion - Israel Institute of Technology Haifa 32000, Israel

Abstract

The morphology and electrical resistivity of high impact polystyrene (HIPS)/thermoplastic elastomer (SIS)/carbon black (CB) based blends were studied Conductive CB-EC fine particles locate preferentially within the HIPS phase of the HIPS/SIS blends, whereas medium thermal black large particles CB-MT do not demonstrate any preference to either phase The studied blends with CB-EC remain conductive as long as HIPS maintains a continuous phase and the effective CB concentration within HIPS surmounts its percolation threshold SIS/CB-EC mixtures exhibit an unusual behavior explained by a suggested physical model which is extended to the HIPS/SIS/CB systems

Introduction

It is generally known, that CB-loaded polymer blends often exhibit a higher conductivity level than either of the component polymers at the same low CB content. This phenomenon is due to the preferential CB location within one of the phases and/or at the interfaces, resulting in segregated phase structures of the blend leading to the double percolation concept [1,2] Usually, block copolymers are added to immiscible polymer blends to function as alloying agents or surfactants which contribute to the stabilization of the multiphase structure [3] There are numerous publications concerning the morphology and properties of blends such as polystyrene (PS) with its copolymers However, almost nothing is reported on such blends loaded with carbon black (CB) especially the conductive CBs In addition, utilization of a block copolymer as the dispersed phase within a PS matrix is also uncommon Various publications concerning conductive elastomer/CB compositions reveal fundamental parameters determining their conductivity level among them the CB-polymer interaction [4 5] A thermoplastic elastomer mixed with CB being a part of the multiphase conductive systems shows a blend conductivity affected by the thermoplastic elastomer intrinsic microstructure [6,7] The subject of this study is the correlation between the morphology and resistivity of CB-loaded compositions of a high impact PS (HIPS) and a tri-block copolymer, styrene-isiprene-styrene, (SIS)

Experimental

The polymers used in this study were HIPS Galirene HT 88-5 MFI - 4 5 Carmel Olefins Israel and SIS Quintac 3421, MFI - 11 14% PS Japan The carbon blacks were CB-EC Ketjenblack EC-300 Akzo Netherlands and CB-MT Thermal black N990 Vanderbilt, characterized by surface area (BET) 950 and 9 m^2/g and particle diameters ~ 30 and (285-500) nm correspondingly

HIPS/SIS/CB blends containing 5-45 wt% SIS and 0-4 phr CB were produced by melt mixing in a Brabender plastograph at 190 °C and subsequently compression molding Their volume resistivity was measured as previously reported [8] The blend morphology was studied using a SEM Jeol 5400 Freeze-fractured and microtomed surfaces (both prepared in liquid nitrogen) were investigated

Results and Discussion

The resistivity of polymer/CB-EC compounds as a function of the CB content is presented in Fig 1a It is clearly seen that the SIS/CB percolation occurs at a rather high critical CB concentration about 10 phr This value is much higher than the corresponding value for HIPS/CB compounds, about 2 phr Figure 1b depicts the effect of SIS content on the blend resistivity at a constant CB concentration in the blend Interestingly blends with 2 phr CB depict a stronger change in resistivivy with blend composition compared to the blends containing 4 phr CB It should be noted however that the resistivity of HIPS containing 4 phr CB is 9 orders of magnitude lower than that of HIPS containing just 2 phr CB The resistivity of the former is practically unaffected by the addition of SIS up to 45 wt% while the 2 phr CB containing blends exhibit a large resistivity reduction for SIS content of 20-30 wt% It is well established that the critical concentration of a given CB at the percolation threshold in different polymers depends on the polymer/CB interaction [9] Such interactions are related to some polymer

characteristics, such as surface tension, polarity crystallinity and viscosity, where surface tension often seems to be the dominant parameter SEM micrographs of the HIPS/CB compounds enable to observe the distribution of CB EC-300 only of microtomed surfaces Their micrographs clearly show that the rubber inclusions 1-3 μm in diameter, do not contain CB Carbon black addition to SIS is manifested by the appearance of bright particles increasing in quantity when CB concentration increases It may be noted that appearance of the CB dispersion within SIS after the percolation threshold resembles a chain-like particles distribution

The morphology of neat and CB-containing blends is shown in Fig 2 The structure of HIPS/SIS blends without CB consists of very fine SIS dispersion at 5 wt% content (particle size 0 2 to 1 μm) up to the co-continuous morphology obtained at about 20 wt% SIS in the blend The two components are strongly inter-connected as there are no visible gaps at the interface between the phases characteristic of low interacting components in immiscible polymer blends It is important to point out again that the bright tiny details present in HIPS are also visible in SIS Therefore to determine the genuine location of CB particles within the blend is not an easy task Rubber inclusions are clearly seen in the HIPS without any traces of CB-EC present A clear phase structure, together with a well-defined CB-EC location are seen only in a microtomed surfaces of the blends The SIS component appears smooth, without an evident presence of CB-EC agglomerates, whilst HIPS contains numerous well-distinguished CB agglomerates (Fig 3c) Hence, preferential CB-EC location in HIPS occurs, contrary to the case of CB-MT addition, which does not demonstrate a preference to either phase The CB-MT large size particles added to these polymers are clearly seen penetrated in both phases (Fig 3d)

Returning to Fig 1b, the conductivity of the CB-filled HIPS/SIS blends is determined by the conductivity of the CB-rich HIPS component and its continuity SIS addition to HIPS/CB-EC blends increases the CB effective concentration in HIPS transforming the insulative HIPS/2phr CB compound in the absence of SIS to relatively conductive upon about 30 wt% SIS addition When the continuity of the CB-rich conductive HIPS is disrupted the blend reverts insulative HIPS compounds with 4 phr CB-EC are conductive in the absence of SIS therefore no significant change in resistivity with SIS addition is observed

The presently reported finding that CB EC is preferentially located in the polymer of lower percolation threshold is exceptional since the opposite is true for most known immiscible polymer blends [8] It is assumed that the particular SIS structure where PS domains are dispersed in the rubber matrix [10] may cause the unusually high CB percolation found in SIS Taking into account the dimensions of CB-EC particles and PS domains within SIS a model of CB-EC dispersion in SIS is suggested (Fig 4) The model is based on the preferential location of CB-EC in PS rather than in polyisoprene which is described by the engulfing of the CB particles by the PS blocks until their saturation This engulfing of CB-EC with the PS blocks isolates the CB particles and therefore does not contribute to the material's conductivity Only when the engulfing process is completed, the excess CB starts its distribution within the polyisoprene phase Therefore SIS becomes conductive when CB-EC percolation the polyisoprene phase has been achieved This explains the relatively high CB-EC content necessary for percolation in SIS and converting it into a conductive form Thus for HIPS/SIS blends, the added CB is first located in the PS phase of HIPS abundant in PS and only thereafter it may be distributed in the SIS component as well Considering the suggested model the absence of preference of CB-MT location within the studied blends is understandable The large size of CB-MT particles hinders its mobility and selective interaction with either the plastic or the rubber phase of the thermoplastic elastomer Thus CB-MT particles are immobilized within the phase in which they have been initially incorporated during the mixing procedure

Conclusions

Low concentration of CB-loaded HIPS/SIS blends demonstrate interesting conductive properties and unexpected morphology The preferred CB-EC location in HIPS occurs in spite of the fact that the percolation threshold of HIPS/CB is much lower than that of SIS/CB The blends are conductive as long as the HIPS component is continuous and the CB contained in it exceeds its percolation value A difference in the distribution of CB-EC and CB-MT within the blends was observed depicting the significance of both CB size and properties and CB/polymer interaction A physical model of CB-EC distribution within the SIS triblock copolymer has been proposed explaining the observed unique morphology and conductivity as a function of composition

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Key words HIPS thermoplastic elastomer electrical conductivity morphology

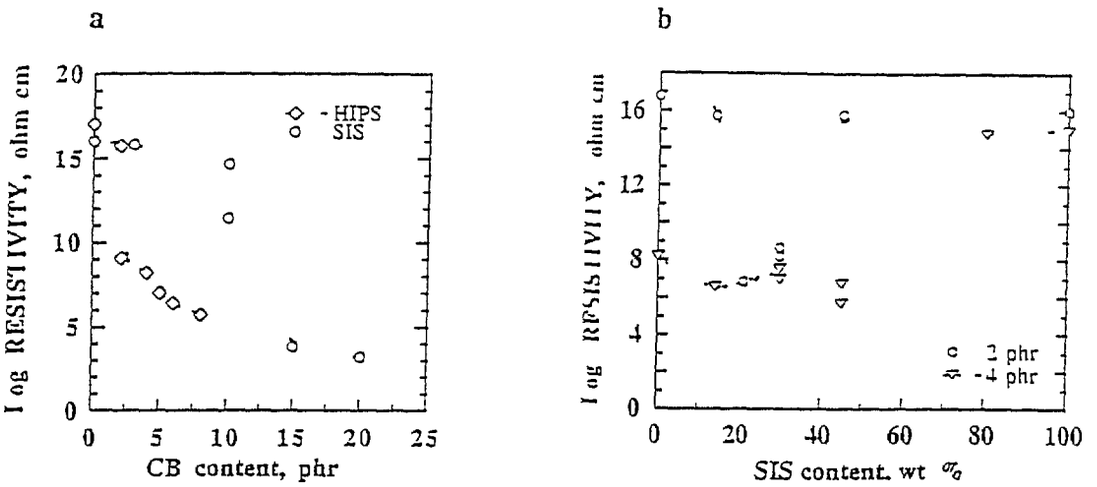

Figure 1 Resistivity vs composition for (a) - individual polymers (b) - blends

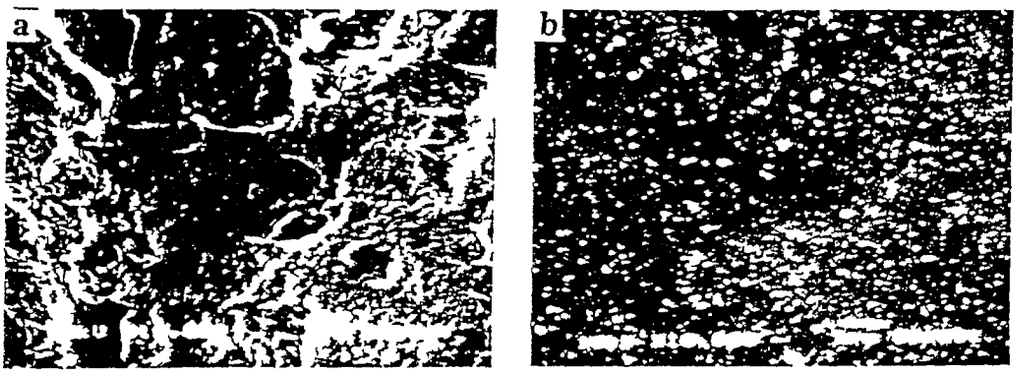

Figure 2 SEM micrographs of the individual polymers with CB-EC (a) HIPS + 2phr CB microtomed surface (b) SIS + 15 phr CB freeze fractured surface

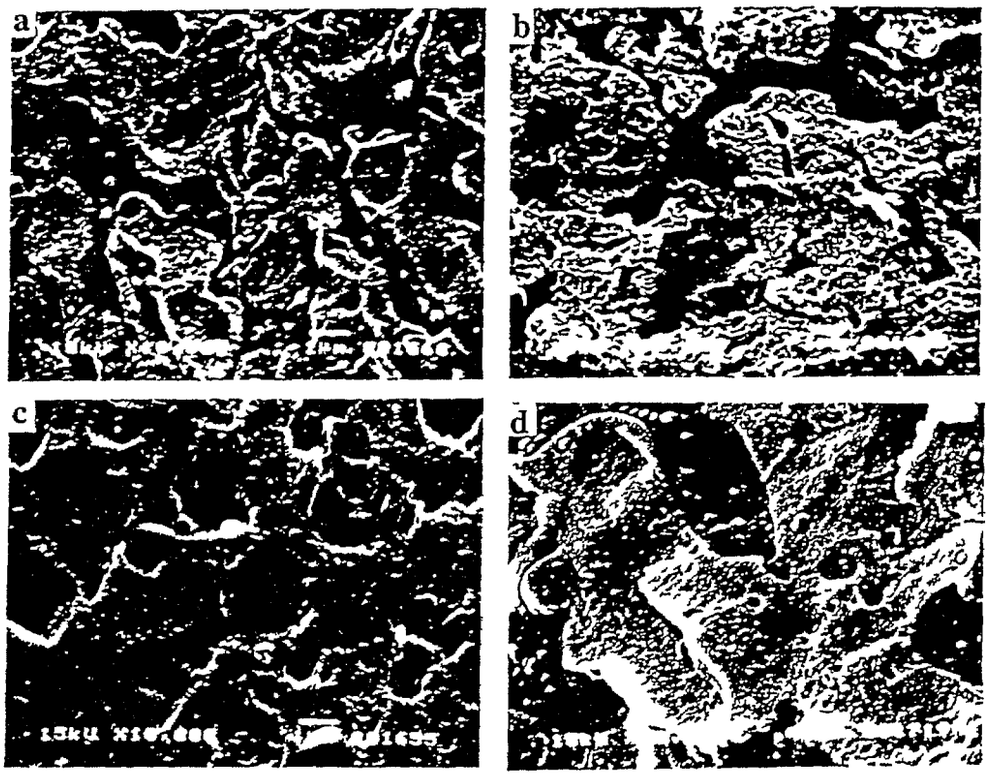

Figure 3 SEM micrographs of HIPS/SIS blends (a) - 80/20, without CB, (b) - 70/30 2 phr CB-EC, (c) - 85/15, 4phr CB-EC, (d) - 70/30, 4 phr CB-MT, (a), (b) (d) - freeze-fractured surfaces (c) - microtomed surface

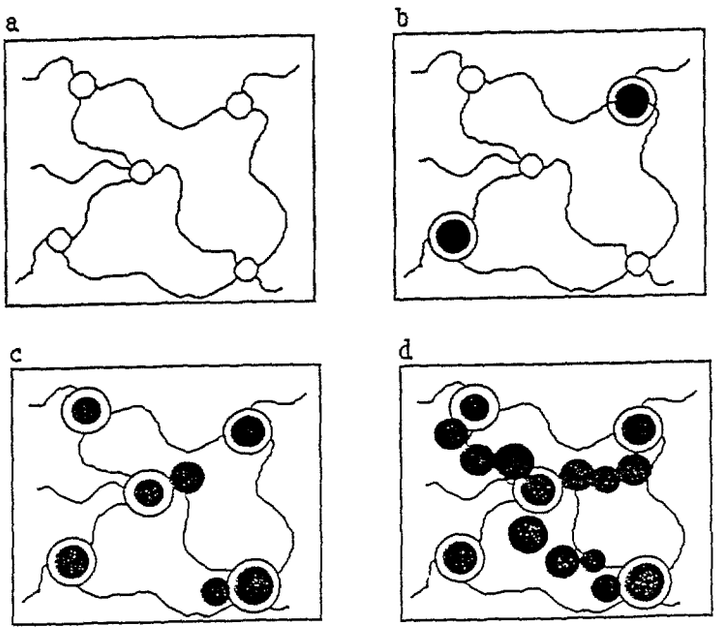

Figure 4 Scheme of CB-EC distribution in SIS (a) - neat SIS (b) CB encapsulation in the PS blocks (c) - PS blocks saturated with CB excess CB starts to appear in the rubber phase (d) CB percolation within the rubber is realized

Research, Development and Consulting Center POLYMAK

FINAL REPORT
Covering Period September 1993 - September 1996

ELECTRICALLY CONDUCTIVE STRUCTURED POLYMER BLENDS

M Kozlowski and A Kozlowska

The report is a collaborative research between
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US-Israel Cooperative Development Research Program

November 1996

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Executive Summary

Polymers have been widely known as highly electroresistive materials Their conductivity is in the range of 10^{13} - 10^{16} [Ω cm], therefore plastics are used as electrical insulators in numerous applications In order to make plastic materials conductive, electrically conductive components may be admixed Usually there are fillers like metal powders, flakes or fibers, carbon blacks and carbon fibers Recently intrinsically conductive polymers, like polyaniline, polyacetylene, polyphenylene and polypyrolle, have focused considerable interest among researchers For practical reason the most widely used filler is still carbon black (CB), as much cheaper and lighter than metallic particles

Depending on a filler content in a composite, one obtains the insulating, antistatic or electrically conductive materials At particular CB-level the familiar insulator-to-conductor transition occurs The classical percolation estimates a critical volume fraction at 0 156 Such high degree of loading brings about deterioration of mechanical properties and increase in the melt viscosity of plastics Thus, searching for a compromise of the conductivity level and mechanical properties, highly sophisticated phase structures have been recently generated, aiming to develop a network of the conductive pathways through the material

Our goal was to develop the model compounds of incompatible polymer blends having unique electric/dielectric and stable structures towards melt processing Upon our three-years study the preparation conditions for highly conductive polymer composites with a low carbon black content have been defined Different polymer grades and blends of virgin polymers in diversity of ratios, different CB-grades and CB-content, as well as mixing technology were among the factors studied, as far as the influence on the conductivity level and morphology is concerned

We concluded that a detailed description of the mixing history (shear stress, residence time) is required for polymer blending, being equally important for the resulted morphology, like the chemical structure and ratio of the components Generation of a disperse, stratified, or co-continuous morphology has been performed in a controlled manner The interpenetrating-type blends and alloys have been proved as the most useful for electrically conductive plastic materials Significant reduction of a filler content was achieved resulting from its selective location in one of the phases, or at interface

Our results, published in international journals and presented at international conferences, have been accepted with interest by the scientific community, adding its own value to a contemporary state-of-the-art

Possible applications of such multicomponent polymer systems include the electrically conductive/dissipative materials for

- packaging foils, foames, tapes,
- antistatic flooring and carpetbackings,
- tubing and ventilation ducts in mining industry, petrochemical plants, hospitals,
- antistatic clothing, hoses,
- semicon cables,
- EMI/RFI shielding

Research Objectives

Research performed under the grant has been focused on the following objectives
- Methods of structuring incompatible polymer blends
- Method for determination of the inversion point based on the electric/dielectric behavior of incompatible blends,
- Carbon black distribution between the phases and at the interface,
- Finding conclusions of general character for other incompatible polymer blends,
- Advancing the scientific and technological levels in the field of structured polymer blends and conductive plastic materials by establishing sound infrastructure in Poland

The objectives of our research have been among the most intensively investigated recent years, since polymer blends exhibit highest dynamics of their consumption among other polymeric materials Nevertheless, there remain still many open questions, as far as their structurization and electrical conductivity is concerned Several laboratories have been involved in a similar approach to ours - finding a possibly low percolation level for the electrically conductive plastic composites by a preferential location of the conductive filler in one of the phases, or at interface [1-10] Our research has added its own value to a contemporary state-of-the art, finding place among the frontiers of science Innovative aspects of our research constitute the model of a morphology evolution under dispersive mixing and application of the multiple percolation concept to the electrically conductive polymer blends, containing a semicrystalline polymer as one of the components

Methods and Results

Materials

Commercial grade polystyrene (PS) from ZCh Oswiecim (Poland) and six grades of low density polyethylene (LDPE) from ZCh Blachownia (Poland), as well as (ethylene-vinyl acetate) copolymer (EVA) Ribolene from Enimont, (styrene-butadiene-styrene) tri-block copolymer (SBS) from Shell and liquid crystalline polymer (LCP) Rodrun LC 3000 from Unitika Ltd were used in the study

Partially hydrogenated poly(styrene-b-isoprene) di-block copolymer Kraton G1701 from Shell Chemicals was added as a compatibilizer

Eight different grades of electrically conductive carbon black were supplied by Akzo Nobel Chemicals (the Netherlands), Cabot Co (USA) and Degussa AG (Germany) All the grades have been declared as highly conductive The most important parameters which influence the CB-electroconductivity have been included in Table 1 The surface area, measured by iodine- or nitrogen-adsorption is a total sum of external- and internal surface areas of the basic carbon particles in the primary aggregates The tendency to aggregation is characterized by the structure of carbon black, measured by Di-Butyl-Phtalate (DBP)-absorption The oxygen-containing organic groups formed at the CB-surface so called "volatiles", act as a barrier for the electron-tunelling effect, hence decreasing conductivity

Table 1 Characteristics of the carbon black grades

CB code	CB grade	DBP ml/100g	IOD mg/g	Density g/l	Volatiles %	Janzen's $\varnothing_c$
	AKZO Nobel Ketjenblack					
1	EC-600JD	490	1 077	107	0 6	2 5
2	EC-300J	327	752	134	0 7	3 7
	Cabot					
3	Vulcan P	115	175	322	1 0	9 8
4	Elftex 160	89	37	436	-	12 3
5	Vulcan XC72	171	284	278	1 5	6 8
	Degussa					
6	Printex XE2	367	1,107	150	0 1	3 3
7	Printex L6	123	-	120	1 2	9 2
8	Printex L	118	-	200	0 8	9 6

Blends Preparation

Polymer components were mixed with carbon black using the Brabender Plasti-Corder mixing unit Composite plaques of approximately 1 mm thickness were compression molded under pressure of 12 MPa for 5 minutes

Segregated blends were prepared by thorough mixing of the powdery components and subsequent compression molding under the same conditions, as used for the melt-mixed blends

Samples for the electrical resistivity and mechanical strength measurements were cut out from the plaques

Measurements

Volume resistivity ρ and surface resistivity ρ_S was estimated according to ASTM D257 We used the three-electrode electrometer arrangement for the DC-measurements of insulation resistance The apparatus used was Keithley 617 Keithley 6512, 2000 Multimeter or Meratronic V 641 depending on the resistivity range Similarly, the voltage level was 100 V or 1 1 V The samples were Al-coated by evaporation prior the measurements

Rheological measurements were performed with the capillary rheometer type MCR 3210 The capillary used was of diameter d = 1 27 mm and length to diameter ratio L/d = 40 The Rabinowitch correction was applied, whereas the Bagley correction was neglected because of the high L/d ratio

The rheological characterization of polymers and CB-composites was also performed using Rheometrics RDSII dynamic spectrometer This is a controlled-strain instrument in which the sample is subjected to shear deformations between two concentric surfaces The sample was subjected to oscillatory or steady motions, using plate-plate geometry of 25 mm diameter In dynamic experiments the shear strain resultant shear stress and phase angle between those were resolved

The dynamic strain sweep mode experiments, performed at frequency of 1 0 rad/s and for strains ranging from 0 3 to 300% provided the strains for which the

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material behaves linearly The dynamic frequency sweep measurements delivered the storage and loss moduli G' and G" at strain of 10% and between frequencies 0 05 to 500 0 rad/s

Tensile tests were performed at room temperature using the FU 1000 eZ machine The cross-head speed was 50 mm/min The tensile modulus of elasticity E, tensile strength σ_T and the elongation at break ε were registered

Morphology inspections were performed by means of scanning electron microscopy (SEM) Freeze-fractured and microtomed surfaces were vacuum-coated with the Au/Pd layer and then observed using the scanning electron microscope JEOL JSM-5400 or Leica S360, operating at 15 kV

Results

The efficiency of particular CB grades, as electrically conductive fillers for PS and LDPE/PS systems, was compared for the melt-mixed composites with 2 wt % and 6 wt % of carbon black Significant improvement in conductivity was found for the composites with Ketjenblack EC-600 JD from Akzo Nobel Chemicals This grade has been chosen for further experiments

Highly conductive materials have been developed using LDPE and PS as the blended polymer matrix for carbon black composites The volume resistivity versus CB-content for the segregated and melt-mixed blends LDPE/PS 50/50, as well as for LDPE and PS, have been summarized in Figure 1 The dependence is of familiar Z-shape for LDPE and PS It is similar for blends, but the percolation treshold $\varnothing_C$ is located at a significantly lower CB-content Segregated-type composites exhibit the dependence of a more asymptotic character (L-shaped)

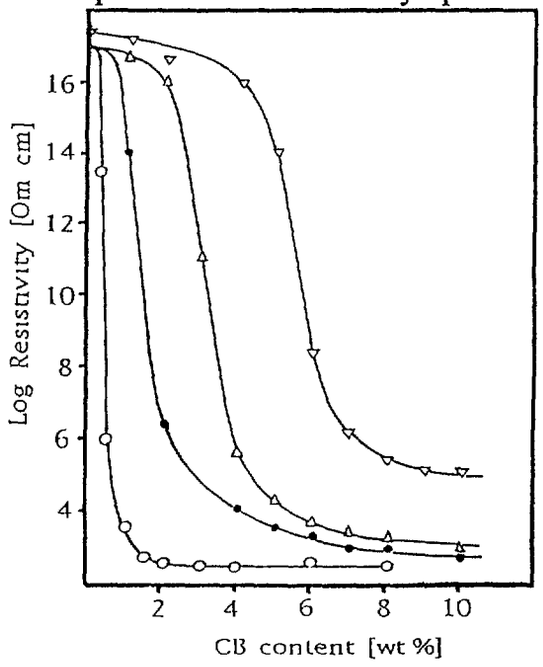

Fig 1 Resistivity of CB composites (▽ - PS matrix, △ - LDPE matrix, ● - LDPE/PS 50/50 melt mixed o - LDPE/PS 50/50 segregated)

Composite based on LDPE/PS 30/70 blend is of interpenetrating structure with the CB percolation treshold below 1 8 wt % Such low percolation level has been explained in terms of the multiple percolation concept

Similar interconnecting morphology has been evidenced for the compatibilized LDPE/PS 50/50 blend, which was of a disperse morphology before addition of the compatibilizer

Segregated blends offer the percolation treshold as low as 0 5 wt % of CB, but poor mechanical strength of such blends is a significant drawback (Table 2)

Table 2 Mechanical properties of PS and LDPE composites with CB

Polymer matrix	CB content %	Tensile modulus MPa	Tensile strength, MPa	Elongation at break, %
PS	0	2,600	54 1	4 6
LDPE	0	230	16 0	70 0
LDPE	6	238	9 8	35 1
LDPE/PS 50/50 melt mixed	1	710	10 0	2 8
LDPE/PS 50/50 melt mixed	6	496	4 0	2 3
LDPE/PS 50/50 segregated	1	306	5 6	4 8
LDPE/PS 50/50 segregated	6	448	1 1	2 9

Rheological measurements have revealed an increase in the melt viscosity of composites with carbon black in comparison to that of polymer blends Only slight dependence on the CB-content was observed within the measured CB-range Melt flow curves have been characteristic for the filled systems - the Newtonian plateau has not been evidenced

PS/SBS composites are less conductive than that based on a LDPE/PS matrix The percolation treshold estimated for PS/SBS 50/50 composite with Ketjenblack EC-600 JD was 7 wt % Similar values were estimated for the composites based on SBS or PS exclusively (7 wt % and 7 5 wt % respectively - Figure 2)

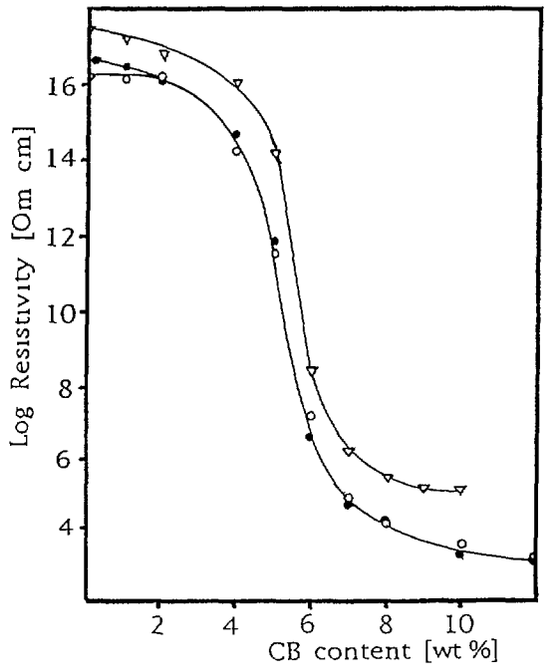

Fig 2 Percolation curves of CB composites based on PS (1), SBS (2) and PS/SBS 50/50 (3)

Polystyrene melt (Fig 3) shows viscoelastic response with elastic modulus dominating withing full scale of frequencies Fig 4 (SBS) demonstrates the classic behavior of a thermoplastic melt with G" dominating at low angular frequency and G' dominating at high frequencies Moreover, SBS melt is of lower viscosity than PS

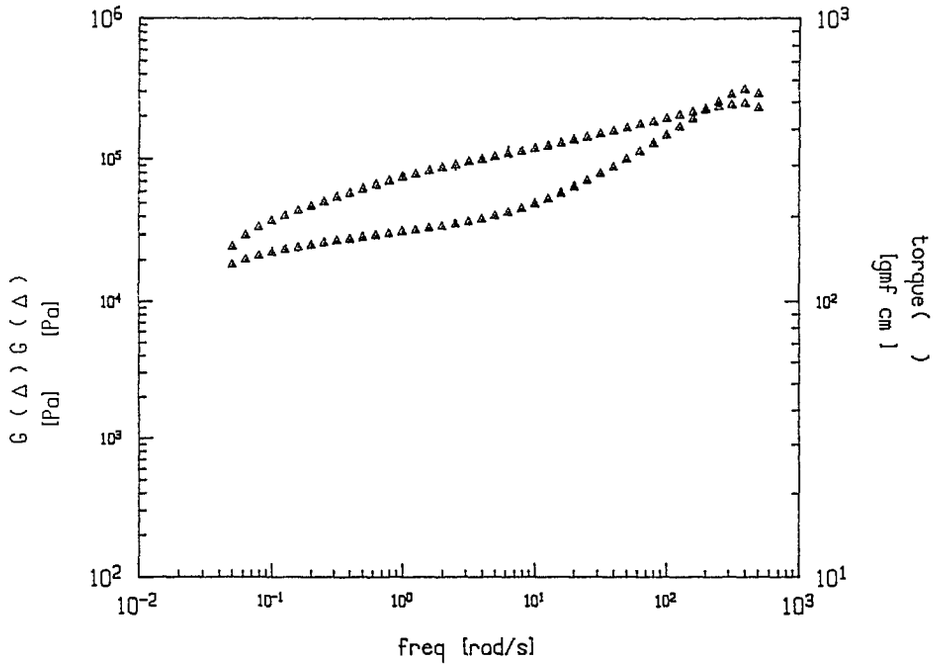

Fig 3 Rheology of polystyrene melt at 150 °C - frequency sweep

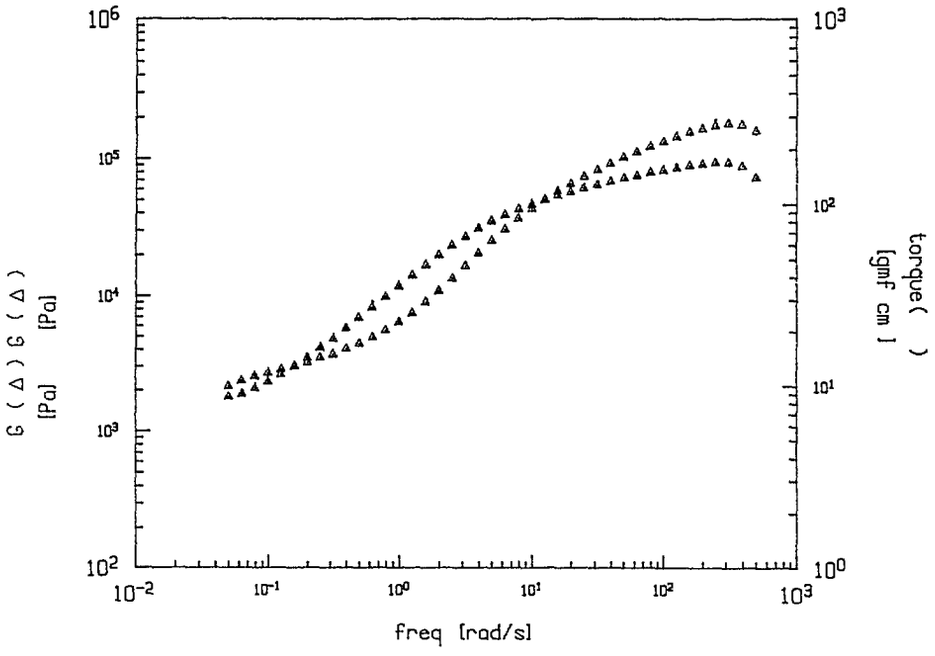

Fig 4 Rheology of SBS melt - frequency sweep

Rheological characteristics of PS/SBS blends and composites depends on a component dominating the system Carbon black caused increase in a melt viscosity and more pronounced elastic response

Tensile properties have been dominated by the major component of composites (Table 3) Deterioration of mechanical strength, observed with addition of a filler, concerns mainly polystyrene We suppose, that the higher tendency to aggregation of CB in PS-matrix in parallel to a week CB-PS interactions caused, that the transmission of a tensile force took place through regions of poor mechanical strength

Table 3 Mechanical properties of PS and SBS composites filled with CB

Polymer matrix	CB content %	Tensile strength MPa	Elongation at break %
PS	0	54 1	4 6
SBS	0	3 1	1221
PS	6	15 1	2 2
SBS	6	3 8	1262
PS/SBS 70/30	6	15 7	6 2
PS/SBS 50/50	6	5 1	48 3
PS/SBS 30/70	6	3 3	359

Composites based on PS/EVA are less conductive than that with PS/LDPE - matrices The percolation treshold for EVA filled with 6 wt % of Ketjenblack EC-600 JD is 6 wt % of CB, whereas for PS/EVA 50/50 composite it is 4 wt % of CB (Fig 5) Higher percolation treshold in ethylene-vinyl acetate copolymer composites in comparison to polyethylene should be related to the chemical composition and morphology Polar vinyl acetate groups in EVA may interact with oxygen containing groups on CB-surfaces Therefore higher affinity of EVA-CB than LDPE-CB may result in a preferred formation of CB-composed conducting pathways in polyethylene

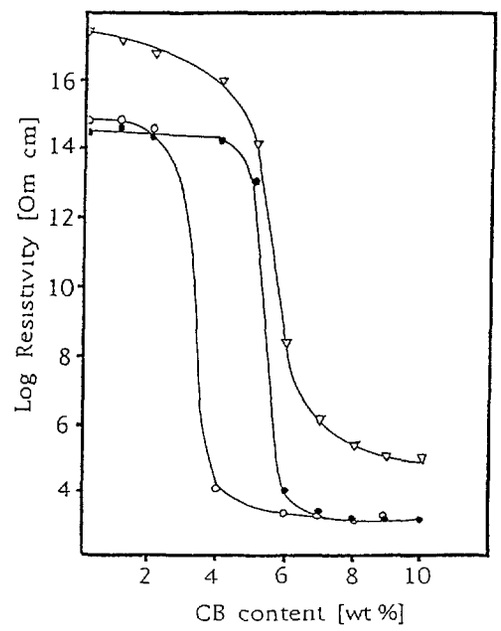

Fig 5 Percolation curves of CB composites based on PS (▽), EVA (●) and PS/EVA 50/50 (o)

Mechanical properties, obtained by the tensile tests of PS and PS/EVA composites, have been presented in Table 4 High tensile modulus and moderate tensile strength make the composites containing 30 - 50 wt % of EVA of commercial potential and confirm their interpenetrating structure, in which every component plays its specific role in favour of the material as a whole

Table 4 Mechanical properties of composites based on PS and EVA

Polymer matrix	CB content %	Tensile modulus, MPa	Tensile strength, MPa	Elongation at break, %
PS	0	2600	54 1	4 6
EVA	0	37 1	23 7	802
PS	6	1504	5 6	2 0
EVA	6	46 7	16 5	754
PS/EVA 70/30	6	824	17 1	3 3
PS/EVA 50/50	6	783	13 9	4 5
PS/EVA 30/70	6	282	8 8	30 4

Viscoelastic response of SBS and EVA has been similar, with slightly higher moduli in case of SBS Both polymers are significantly less viscous and less elastic than PS melt, which finding may be important as far as processing and the resulting blend morphology is concerned

LCP and LCP based blends are conductive at a lower content of the filler than PS alone (Figure 6) Very low percolation treshold, which has been observed for LCP-composite, may be attributed to a self-organisation of the thermotropic polymer chains Such structurization may favour a particular CB particles distribution, thus leading to a formation of conductive pathways through the composite

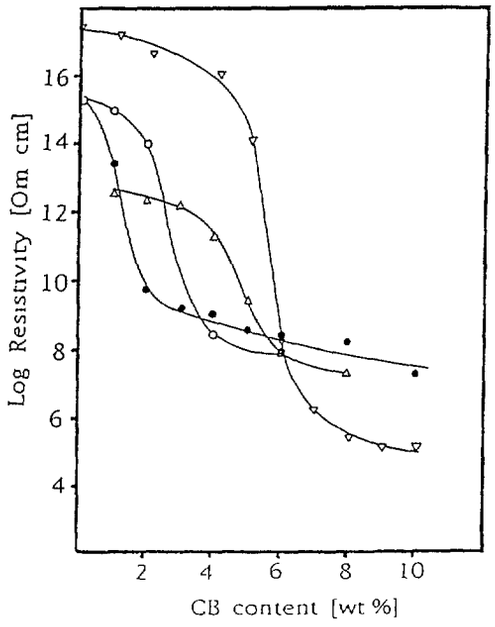

Figure 6 Volume resistivity of composites with different CB content and polymer matrices (▽ - PS, ● - LCP, △ - PS/LCP 90/10, ○ - PS/LCP 50/50)

Liquid crystalline polymer exhibit markedly higher tensile modulus and tensile strength than polystyrene, resulting from the characteristic orientation of LCP macromolecules (Table 5) For PS/LCP blends a decrease in mechanical strength has been observed, which is below additive values This observation suggests rather poor interfacial adhesion The tendency is increasing with decreasing LCP content in PS/LCP blends and composites
Addition of carbon black is of negative influence on tensile properties - both the tensile modulus and tensile strength decrease While increasing the filler content a further drop in mechanical strength was observed

Table 5 Tensile properties of polymers, blends and composites

Polymer matrix	CB content, wt %	Tensile modulus, MPa	Tensile strength, MPa	Elongation at break, %
PS	0	960	24 8	3 4
	6	504	15 1	2 2
LCP	0	1877	35 5	2 8
	2	1139	32 2	1 6
	6	889	35 9	4 1
PS/LCP 50/50	0	1088	19 9	2 2
	2	823	19 5	2 5
	6	718	11 1	1 1
PS/LCP 90/10	2	816	16 4	2 7
	6	477	14 1	4 0

Viscosity of particular LCP systems has been presented on Figure 7 together with viscosity of polystyrene PS melt tends to show Newtonian plateau at low shear, which is vanishing with increasing content of both LCP and carbon black Liquid crystalline polymer melt viscosity markedly decreases with increasing deformation rates This may be attributed to orientation of macromolecules and interlayer slippage within the material Significant increase in a melt viscosity has been noted for carbon black filled melts, proportionally to its content Similarly a linearity of the viscosity curve has been improved with increasing CB loading

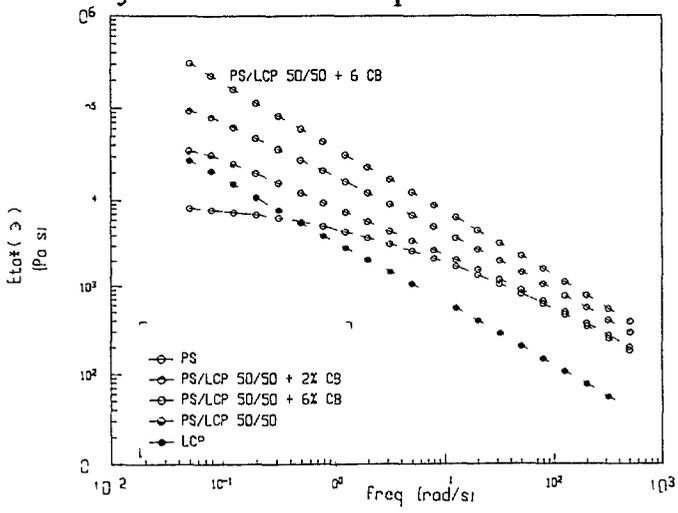

Figure 7 Melt viscosity of polymers and composites at 210°C - frequency sweep

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During reported study a modification of the mixing technology was also performed We compared conductivity of the composites prepared by simultaneous and delayed mixing mode of the components Additionally a pre-mixing of CB into one component followed by blending with a second polymer was introduced Results presented in Table 6 suggest that delayed mixing of components is favourable for high conductivity of a material We suppose the different affinity of carbon black to particular components and melt viscosity differences influence a final distribution of a filler within the phases/on interface

Table 6 Mixing technology influence on resistivity of PS/X 50/50 composites with 6 wt % of Ketjenblack 600-JD

Blend component X	Mode of mixing			Resistivity [Ohm cm]
	simultaneous	delayed		
		PS first	CB in PS	
LDPE */	+	-	-	1 5e+13
	-	+	+	1 7e+14
	-	+	-	1 7e+12
SBS	+	-	-	8 7e+06
	-	+	+	3 7e+08
	-	+	-	3 9e+08
	-	-	-	5 7e+05
	-	-	+	1 2e+08
EVA	+	-	-	4 5e+03
	-	+	+	1 2e+04
	-	+	-	1 0e+02

*/ PS/LDPE composites with 1 wt % of CB

The results obtained during the study period have clearly evidenced, that electrically conductive polymer materials can be produced while conductive filler is introduced to heterogeneous matrix Desirable matrix material is a mixture of thermoplastic polymers, which exhibit specific interpenetrating structure (Fig 8)

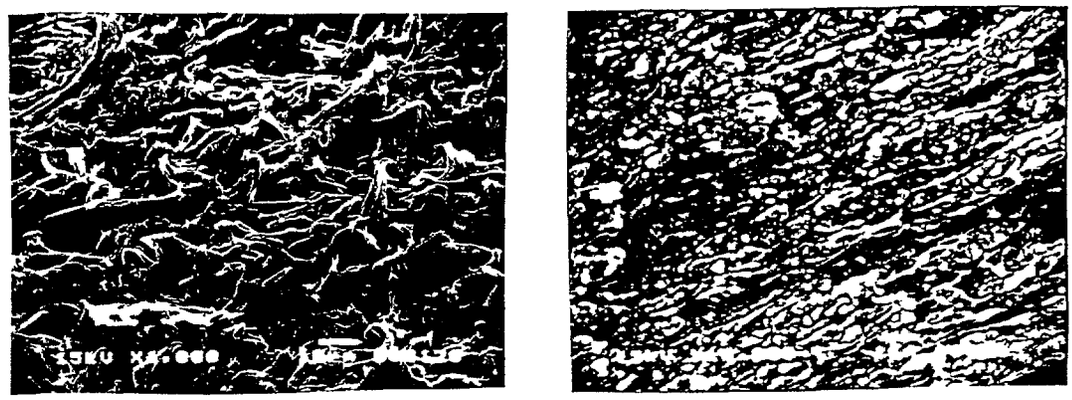

Fig 8 Interpenetrating structure of PS/LDPE blend (on left) and CB composite

Summarising also other mixing technology modifications, one may conclude that the delayed mode of mixing is favourable for high electrical conductivity, especially if the second component is rich in carbon black The second stage of mixing should be short, depending on the nature of component polymers and interfacial characteristics

The resulting structure, schematically shown of Figure 9, gives rise to a high conductivity level of the plastic material

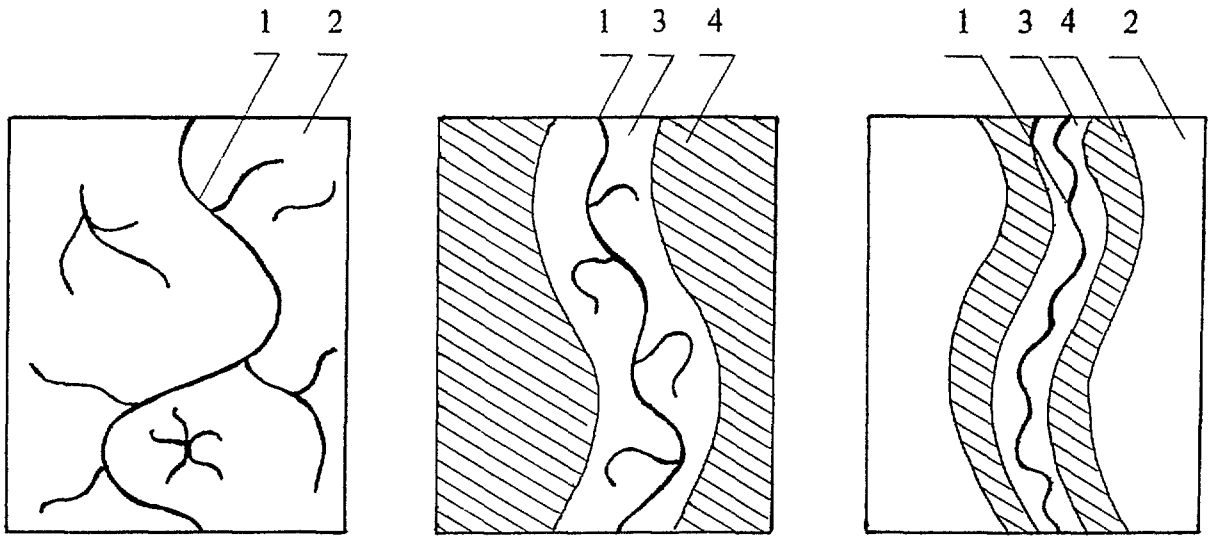

Fig 9 Scheme of carbon black location in amorphous polymer, semi-crystalline polymer and a blend of both (from left to right)
1 - CB, 2 - PS 3 - amorphous phase of LDPE, 4 - crystalline part of LDPE

Conclusions

- Detailed description of a mixing history (shear stress, residence time) is required for polymer blends structurization,
- The interpenetrating-type blends and alloys have been proved as most useful for electrically conductive plastic materials,
- Significant reduction of a filler content was achieved, resulting from its selective location in one of the phases or at interface,
- Using a blend composed of amorphous/crystalline polymers as a matrix for CB composite is advantageous to its high electrical conductivity,
- Delayed mode of mixing is favourable for high electrical conductivity especially if a second component is rich in carbon black

Impact, Relevance and Technology Transfer

The experience gained by scientists performing the project and its results should be exploited in forthcoming years for the sake of Polish science and industry Well trained staff and laboratory equipped with new instruments have been already recognised as frontiers of Polish scientists, being active in a field of electrically conductive plastics Several presentations and consultations given so far resulted in a spreading of knowledge gained by individuals from POLYMAK

to other scientists Cooperation with the Technical University of Wroclaw and the Polish Academy of Science at Lodz has been launched
Looking for implementation of the research results there have been offers presented to several producers of carpet backings and to mining industry Preliminary tests were performed - for large scale trials some financing is needed

Project Activities/Outputs

Papers published during the project period

1 M Kozlowski, "Modelling of the Polymer Blends Morphology", Polym Networks Blends, **3**, 213 (1993)
2 M Kozlowski, "Study on Morphology Development in Dispersive Mixing", Polym Networks Blends, **4**, 39 (1994)
3 M Kozlowski, "The Formation of Interpenetrating Polymer Blends", J Polym Eng , **14**,15 (1995)
4 M Kozlowski, "Structure and Mechanical Properties of Heterogeneous Polymer Blends", J Appl Polymer Sci , **55**, 1375 (1995)
5 M Kozlowski, "Electrically Conductive Structured Polymer Blends", Polym Networks Blends, **5**, 163 (1995)
6 M Kozlowski, A Kozlowska, "Comparison of Electrically Conductive Fillers in Polymer Systems", Macromol Symp , **108**, 261 (1996)
7 M Kozlowski, "Plastics for Electroconductive Applications" Proceedings of the International Conference "Advances in Plastics Technology", Katowice (Poland), November 26-28, 1996

Conference Presentations

1 M Kozlowski, "Percolation in Electrically Conductive Polymer Blends", International Symposium on "Polymer Morphology and Electrical Properties", Lodz (Poland), July 5-7, 1995
2 M Kozlowski, A Kozlowska, "Comparison of Electrically Conductive Fillers in Polymer Systems", EUROFILLERS 95, Mulhouse (France), September 11-14, 1995
3 M Kozlowski A Kozlowska "Electrically Conductive Plastic Materials", International Technology Forum ESSENTIA'96, Prague (Czech Republic), January 8-11, 1996
4 M Kozlowski, "Plastics for Electroconductive Applications", International Conference "Advances in Plastics Technology", Katowice (Poland), November 26-28, 1996
5 M Kozlowski, A Kozlowska, "Percolation in Electrically Conductive Polymer Blends", 1997 Gordon Research Conference on Elastomers, Networks and Gels (submitted)

Training

2 Polish staff were trained on the new measurement techniques at the Technion during their 2-months stay in Israel

Project Productivity

The project did accomplish, in our opinion, all of the goals proposed in our application

Future Work

The project should be continued The recommended research direction is on "Electrically Conductive Structured Polymer Blends Comprising Intrinsically Conductive Polymers" We are ready to perform such research for the US AID Additionally, respective proposal to the National Council for Scientific Research, (Poland) is under preparation

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Modelling of the Polymer Blends Morphology

M Kozlowski
RDCC Polymak' Trentowskiego 21 PL 52 430 Wroclaw Poland

Literature review on morphology modelling in polymer blends has been provided Thermodynamics is of limited applicability because of non equilibrium character of the polymer mixing process - more relevant is hydrodynamics The mixing machinery design and viscoelastic properties of components are of specific importance for anticipation of polymer blends morphology

Types of mixing in different kind of processing machinery have been discussed and flow mechanism studies reviewed. Principles of flow prediction was presented based on the assumption that polymer mixing process is predominantly of dispersive character Viscoelastic and interfacial characteristics of mixed polymers are among the major factors which allow coarse quantification in modelling the heterogeneous systems morphology

Keywords Blend Hydrodynamics Interfacial Tension Microrheology, Miscibility, Mixing, Stress, Structure Viscosity

INTRODUCTION

Polymer alloys and blends (PAB) constitute a special group of plastics which shows the average growth rate twice as high as that of all plastics [1] The reason for such a high difference is unique opportunity to obtain almost an unlimited spectrum of the material properties by blending the polymer components, which is much simpler and less expensive than synthesis of new polymers This opportunity has resulted from recent progress made by scientists in understanding the rules governing the technology of polymer mixing In fact, it is possible to offer plastics of "tailor-made" morphology and properties The interest in designing the highly sophisticated multicomponent polymer systems can be measured, e g by over 20,000 papers on this topic published every year, special IUPAC projects[2] and conferences[3] and by the creation of this Journal itself The state of art on PAB's has been reviewed recently by Utracki [4] Prior to the discussion of different aspects of polymer blending the most important terms have been defined in Table 1

POLYMER-POLYMER MISCIBILITY

The original idea of obtaining the appropriate properties by blending two miscible polymers of complementary characteristics became less attractive as most polymer pairs appeared to be immiscible This results from the thermodynamics of mixing of the macromolecular components The basic rule governing miscibility is a negative free energy of mixing ΔG_m at a given set of temperature and pressure (T and P respectively) and at specific molecular weight of the polymer components

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad [1]$$

where ΔH_m - heat of mixing, ΔS_m - entropy of mixing

The entropy term for long-chain molecules is usually low because of the restricted amount of their possible configurations It follows that a value of ΔH_m is decisive for inequality $\Delta G_m < 0$

According to Huggins and Flory[5] the heat of mixing is proportional to the binary interaction parameter χ_{12} The negative value of χ_{12} promotes a mutual solution of the components - in other words, the attractive forces between mixed polymers - χ_{12} - are larger than forces between macromolecules of the same kind (χ_{11} or χ_{22}) This is a case of strong specific interactions (ionic bonds, hydrogen bonds, etc), the strength of which is inversely proportional to the distance of the bond active centers In general the attractive forces are a function of the bonds density, e g they are related to the interfacial area The attractive forces and the differences of chemical potential of the components on both sides of the interface can be considered a thermodynamic driving force of mixing The opposite are interfacial tension, density differences, low mobility of macromolecules because of high viscosity of polymer melts and the melts elasticity The competition of the tendencies promoting or counteracting the polymer mixing process can be expressed by a diffusivity factor The self-diffusion coefficient in polymers is low For example in the system polyvinyl chloride/polycaprolactam the diffusion constant is only of 10^{-9} m /s at 90 C [6] The thickness of a interface would increase ca 10 μm per day! According to Elmendorp[7] the diffusion will promote homogenization of the miscible polymer blends only when the size is reduced to the order of 10 nm Discussion of the polymer systems behavior in

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terms of the equilibrium thermodynamics needs to take into account the time factor At least in the early stages of a mixing process, the polymer pairs, classified as either miscible or immiscible pairs, form heterogeneous blends As a consequence of a usually long time needed to achieve the thermodynamic equilibrium, most of the morphologies observed in polymer blends are of a nonequilibrium state Therefore every discussion on polymer blends/alloys should strictly specify the characteristics of the mixed components, pressure, temperature and a whole history of the system manufacturing In order to improve the blending efficiency one should try to increase the mobility of macromolecules by compounding the polymers in a molten state or in a solution under intense mixing

LITERATURE REVIEW ON POLYMER MIXING

The mixing technologies and machinery have been widely discussed [8-18] In the course of the blending process one polymer is dispersed in the other Diverse mixing categories specified in Table 1 participate, to a varying degree, in numerous types of the structures of desired size, designed as disperse- or interconnected-type, the dispersive mixing is all-important This category of mixing is determinated by the stress level in a melt [19-20] When stratified morphology is generated, the dominate type is the laminar mixing, determined mainly by the strain history of a melt [21 22] The mixing processes are performed in commonly used batch or continuous mixers There are numerous papers on the study of the mixing mechanism and on a modelling of the flow and mixing in processing equipment An understanding of the mixing mechanism is of high practical value as a basis for the invention of more efficient machinery It involves experiments enabling observations of a flow in real mixers by means of different windows, tracers and other "tricky" methods according to the invention of the researchers

Modelling aims to predict the ultimate flow patterns within the mixing chamber For this purpose one must solve a set of equations of motion for the flow between the mixing elements receiving the pressure and velocity fields The method of simulation applies the Reynolds hydrodynamic lubrication theory As a rule the coordinate system is placed in the rotor which is assumed to be stationary whereas the mixing chamber is considered rotating It has been mentioned that even if the detailed modelling of a flow is obtained with extensive computational efforts the calculations are limited to the relatively simple configurations with numerous simplifications The simulated flow patterns have to be considered as approximations of real streamlines

Discussing the processing equipment used for preparation of the polymer blends and alloys, the roll-mills and internal mixers are worth mentioning among batch mixers Both are of the dispersive mixing type working with high efficiency Roll-mills as pioneers in the thermoplastics processing obtained numerous treatments of the flow analysis Among the more realistic are these of Vlachopoulos *et al*,[23,24] Tokita and White,[25] and Takserman-Krozer *et al*[26] Internal mixers can be assumed as a next step in the progress of a mixing equipment imitating a roll-mill action by the double-flighted rotors, but in a closed chamber They produce higher shear rates allowing faster processing Considering the efforts and achievements both in modelling and in the mixing mechanism studies the groups of Tadmor,[8,11,27-29] White,[14,30,31] and Manas - Zloczower[32,33] should be mentioned

Continuous mixers are commonly represented by the single and twin screw extruders, single and twin shaft mixers and by corotating disc processors The single screw extruders are good extensive mixers but of poor dispersive action The explanation of this has been found from the modelling results obtained by Manas-Zloczower and Tadmor[34] The concept of Passage Distribution Function[35] revealed that most of polymer melt particles does not pass through the only high shear region of the extruder, i e the clearance between the screw flight and the barrel To enhance the dispersive characteristics of the single screw extruders screws with special mixing sections, barrels with pins, etc[36] were developed Among the fundamental studies on modelling of these machines again that of Tadmor *et al*[37], White *et al*,[38] and Elemans[39] should be mentioned

The twin screw extruders are co- or counter-rotating, partially or fully intermeshing Often equipped with a variety of mixing and kneading elements, the screws yield high shear stresses and provide both laminar and dispersive mixing [14,40 41] The flow mechanism studies have been described by Schenkel[42] Kaplan and Tadmor,[43] and Janssen[44] Flow modelling performed for twin screw machines has been reported by Tadmor *et al*,[43-45] White and co-workers[31 46-48] Among practical conclusions the leakage flow role in the mix-

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Table 1 Definitions

POLYMER BLEND (PBL)	mixture of at least two homo- or copolymers
MISCIBLE POLYMER BLEND	PBL whose components are mutually mixed down to the molecular level
COMPATIBLE POLYMER BLEND	popular term indicating commercially attractive PBL usually homogeneous to the eye but immiscible
IMMISCIBLE POLYMER BLEND	PBL exhibiting at least two phases under any conditions
POLYMER ALLOY (PAL)	immiscible PBL with stabilized morphology often generated through modification of interfacial properties
COMPATIBILIZATION	process of the interfacial adhesion promotion resulting in stabilization of PBL morphology
MORPHOLOGY	phase structure of polymer blend
TEXTURE	spatial distribution of the dispersed phase (supradomain morphology)
LAMINAR MIXING	process of the domains deformation in a flow field resulting in the interfacial area increase but without reduction in domain size (other terms extensive mixing, blending)
DISPERSIVE MIXING	process of the dispersed domains breaking down under the stress field Dominating at early stage of mixing, determinated by the domains size and shape (also called. intensive mixing)
DISTRIBUTIVE MIXING	process of domains spatial distribution and disaggregation generated during earlier stages of mixing (also extensive mixing)

ing efficiency was underlined

The corotating disk compounder is an example of recently invented processing machine [49] Its compact construction consists of two disks rotating in a well-fitted barrel By connection of individual chambers in a variety of serial/parallel combinations the processor of desired laminar/dispersive mixing intensity can be designed The mixing mechanism in this kind of processor was investigated by David [50]

PRINCIPLES OF MODELLING

Summarizing the above review one can observe that in every kind of a mixer a specific combination of all mixing modes, listed in Table 1, is realized Diverse intensity of particular components brings about a different dispersion state of the mixture Polymer mixing processes are of dispersive character, dominated by the stress level Therefore, a special attention is given to the zone of stress generation both in a study of the mixing mechanism and in modelling of the process itself It would not be reasonable to attain a high stress level needed for achieving reduction in size of the dispersed component within whole material in a mixing chamber because of high energy demand and the polymer thermo- and mechano-destruction danger Instead, the mixers are designed with small high stress regions These are clearances between the rotor tip or the screw flight and the barrel In between succeeding passages through tight clearances the material is transported to other mixer regions where it undergoes predominantly the laminar and distributive mixing

Another important finding is the key role of randomization for the mixing efficiency Erwin[51] produced evidence that if a blended material is reoriented N-times, the interfacial area ratio is

$$\frac{A}{A_o} = \frac{1}{2}\left(\frac{\gamma}{N}\right)^N \qquad [2]$$

where A, A_o - the final and the initial area, respectively, γ - total shear strain ($\gamma = \gamma t$)

This explains the high efficiency of static mixers and the distinct improvement of dispersive action if the mixing sections are added to the screw extruders

From the reviewed papers one can extract other conclusions

- there is a high complexity of the mixing process, leading to the necessity of randomization of the factors influencing the mixing efficiency
- the process description should use distribution functions referring to the particular elements throughout the mixed volume Among these there are functions describing the composition distribution, strain/stress field, temperature and residence time distribution, and, resulting from the mixing process, the dispersed phase size distribution However such complete description of the processing history of every particle reaching the shaping die and the entire history of a melt leaving the machine, by integration of the particular contributions is too difficult For this reason mean values of the factors influencing the blending process have been widely used

Another complexity is brought about by the three-

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dimensionality of a flow generated by a complex geometry of real mixers and their mode of operating with partially filled mixing elements Therefore, the necessity for the detailed knowledge of the real flow pathlines still arises as an unsolved problem Because the mixing chambers are filled with real polymers (viscoelastic materials), the knowledge of their behavior in the processing conditions is of importance, raising the probability of exact prediction of the blend morphology - the main goal of all studies on mixing and compounding For this reason there exist numerous papers and reviews on the melt rheology-polymer blend morphology relationships [1,9 14,15 19,20,52 81]

MICRORHEOLOGY

Three basic morphologies of PAB's are usually specified

- disperse (droplet- or fibril-type)
- stratified (lamellar- or sandwich-type)
- co-continuous (interlocked)

They are formed depending mainly on volume fraction (ϕ), viscosity ratio of the dispersed and the matrix polymer (λ), interfacial tension (ν) and stress level (σ_{12}) = $\eta\gamma$, where η is matrix viscosity and γ a shear rate In the course of mixing one deals with a motion of the deformable domains of one polymer melt in another

Under the shear/elongational deformations related to flow, the spherical domains undergo the hydrodynamic deforming stresses counterbalanced by the interfacial tension At first the word "counterbalanced" sounds strange, comparing the typical σ_{12} for polymer melts of 10^4 N/m^2 and ν of 10^2 N/m At a sufficiently small diameter (d) of a dispersed droplet the stress resisting deformation ν/d is equal to σ_{12}, indeed In the considered case, the equilibrium diameter d=1 μm The ratio of the stresses $\sigma_{12}d/\nu$ is known as the capillarity number (K) This is related to the classic equation derived by Taylor[81] for the droplet equilibrium deformation into a spheroid of the major (L) and minor (B) axis

The deformation D is expressed by

$$D = \frac{L-B}{L+B} = \frac{\eta\gamma R}{\nu}\left(\frac{19\lambda+16}{16\lambda+16}\right) \qquad [3]$$

where R is the initial droplet radius

The equation derived for Newtonian liquids in a simple shear flow can be applied to two-dimensional planar elongational flow when the shear rate γ is substituted by 2ε

$$D = \frac{2\eta\varepsilon R}{\nu}\left(\frac{19\lambda+16}{16\lambda+16}\right) \qquad [4]$$

where ε is the rate of elongation

According to the theory the droplets burst at a deformation D=0 5

Neglecting the value of a fraction $(19\lambda+16)/(16\lambda+16)$, one obtains an approximated equilibrium droplet diameter

$$d_e = \frac{\nu}{\sigma_{12}} \qquad [5]$$

The dispersed domain will deform along the streamlines of a matrix phase when the shear stress level surpasses the interfacial tension barrier If opposite is the case, the domains will rotate in a shear field and undergo a periodically varying force Cox, extending Taylor's analysis to the time-dependent flows derived an expression for the orientation angle Θ of a deformed droplet [84]

$$\Theta = \frac{\pi}{4} + \frac{1}{2}\arctan\left(\frac{19\lambda\kappa}{20}\right) \qquad [6]$$

There were numerous trials to extend the Taylor's treatment to other two-phase systems having a higher complexity (viscoelastic fluids, complex flow etc) but one has to remember the applicability of both Taylor's and Cox's equations only to small deformations and to restricted λ-values ($\lambda \leq 3\ 8$) For deformation of domains in the systems with $\lambda >> 1$, Cox derived an equation

$$D = \frac{5}{2\lambda}\sin\left(\frac{\gamma t}{2}\right) \qquad [7]$$

Among other reviews of the theoretical analysis of flow and experimental works on deformation of the polymer droplets/fibers in the Newtonian/non-Newtonian fluids under simple shear, hiperbolic, extensional or rotational flows, one can recommend those published in the last decade Grace,[77] Rallison,[88] Bentley *et al* ,[89 90] and Elmendorp [60] In general, the treatment of Taylor and Cox has been confirmed by Mason *et al* [91 93] Karam and Bellinger,[94] Acrivos and Lo [85] Choi and Schowalter [95] Han *et al* ,[96] Flummerfelt *et al* [97 98] These authors pointed out the existence of the critical regions within which the droplets break up occurs They are restricted by the stress level (specified as a

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critical shear stress or critical capillarity number $K_{=}$) or by the viscosity ratio Grace[77] based on an extensive study ($10^{-6} < \lambda < 10^{3}$) on the Newtonian droplets deformation in a simple shear flow, derived an appropriate expression

$$K_{=} = 0\ 16\lambda^{-0\ 6} \qquad [8]$$

He has found that for $\lambda < 3\ 8$ no more fibers are formed

In hyperbolic extensional flows such a limit does not exist As this kind of flow excludes a rotation of droplets, even highly viscous ones can be deformed to any extent

The theoretical and experimental results on the droplets/fibers deformation have limited applicability to polymer systems in case they concern Newtonian liquids The melt elasticity effect has been observed by Van Oene[20] who proposed the equation

$$\nu_o = \nu + \frac{R}{6}(N_{11} - N_{12}) \qquad [9]$$

where ν_o - interfacial tension accounting for a polymer melt elasticity, N_{11}, N_{12} - first normal stress difference for the dispersed phase and the matrix, respectively

The equation regards a difference of the extra shear stresses generated at the interface when a shear flow is imposed in a dispersion of elastic fluids It follows that if the dispersed phase is more elastic than the matrix ($\Delta N_1 > 0$) the interfacial tension increases It means the stability of a dispersion is enhanced By substituting ν_o into Eq 5 one derives

$$d_e = \nu/(\sigma_{12} - \Delta N_1/12) \qquad [10]$$

The practical meaning is that the more elastic the dispersed phase, the larger the equilibrium droplets According to Flummerfelt[99] the elasticity of a continuous phase also causes an increase of the minimum droplet size and an enhanced value of the critical shear rate at which break up occurs

The increasing volume of the minor component enhances the probability that the domains will coalesce The problem has been studied by Van der Vegt and Elmendorp,[100] Tokita,[62] Fortelny and Kovar[101] and Lyngaae-Jørgenson and Valenza[107] The first paper suggested the modification of an expression for the equilibrium droplet diameter

$$d_e^* = d_e(1 + \beta\phi) \qquad [11]$$

where β is a factor depending on conditions of a value 50-200 A more recent equation for the droplet size is[101]

$$d_e = \frac{2\nu}{\eta}\left(\frac{\kappa_c}{\gamma} + \frac{\alpha^*}{f}\phi\right) \qquad [12]$$

where f characterizes the frequency of particle break up, α^* is a coalescence probability of two droplets after their collision The next feature complicating the prediction of the polymer blends morphology is the break up of the liquid fibers embedded in a viscous matrix Surface tension is responsible for the instabilities developed on a fiber and on their growth up to a break up into a line of droplets From the analysis of a sinusoidally distorted fiber, Tomotika[103] concluded that high viscosity of the matrix is unfavorable for the development of the distortion, whereas the surface tension is an accelerating factor Van der Vegt and Elmendorp[100] verified the analysis with experiments They calculated the time to break up of a polymer filament from the equation

$$t_b = \frac{1}{q}\ln\frac{0\ 8R}{\alpha} \qquad [13]$$

where q - coefficient of Tomotika's analysis, R_o - initial filament radius, α - distortion amplitude

The practical meaning of Eq 13 is that when t_b is shorter than the residence time in the processing equipment one can expect transformation of the fibrilar-type morphology into the droplet-mode Recent study by Leal *et al*[87,89] gave evidence that within a broad viscosity ratios $0\ 01 < \lambda < 10$, the fibrilar break up mechanism via sinusoidal distortion is valid only for highly extended fibers (L/B) > 15 For moderately extended fibers 6 <(L/B) < 15 the "end pinching" was observed which develops much faster than Rayleigh disturbances

The study on the surface tension driven break up process in a simple shear and hyperbolic extensional flow has shown that a flow field stabilizes the fiber[98,104] In hyperbolic extensional flow the time for break is proportional to the capillarity number

$$t_b \approx \log K \qquad [14]$$

For possible prediction of the polymer blends morphology based on compounding/processing condi-

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Table 2 Tendencies of the average diameter change and the preferred morphology type as a response on mixing parameters variations (up to 50 vol%)

Increasing value (+)	σ_{12}	γ	δ	λ	ν	ϕ
d	( )	( )	(+)	(+)	(+)	(+)
D (droplets) F (fibers)	F	F	D	D	D	F

tions the experiments performed on real macromolecular systems are of practical value Extensive investigations have led to some empirical expressions and rules

- at the low content of a second polymer ($\phi < 0\ 12$) droplets are expected, whereas at higher ϕ rather fibers or lamella are usually found,
- maximum dispersion level (d_{min}) is achieved when both viscosity and elasticity of the components are of the same values Defining $\delta = N_{11}/N_{12}$

$$\lambda = 1 = \delta \qquad [15]$$

- at $\lambda < 3\ 8$ shearing causes deformation and break of droplets Deformed drops are reported above this value,
- extensional flow is very efficient the droplet deformation is 1 5-2 times higher than that in a simple shear flow with equal gradient,
- at $\lambda < 1$ fibers are expected above $\sigma_{12} = 10$ kPa up to the melt fracture Lower shear stress rarely can surpass the interfacial tension barrier protecting a spherical shape of the dispersed domains,
- co-continuous structures are expected in case

$$\phi_1/\phi_2 \approx \lambda \qquad [16]$$

- extrema on a plot $\eta(\phi)$ may reflect the morphological changes the maximum refers to a change from the spherical to the fibrillar morphology mode, while minimum - *vice versa*

After analysis of the conclusions included in the papers reviewed in this chapter Table 2 was constructed The table summarizes the effects of diverse factors on the polymer blends morphology

CONCLUSIONS

Polymer blending is an exciting possibility of producing new materials with uniquely tailored properties Mechanical performance is determined, to a large extent, by the morphology of heterogeneous polymer systems There exists a great need to develop a knowledge of the factors influencing morphology formation, the effect of processing on the phase structure etc The basic knowledge of these factors should allow modelling of the polymer blends morphology Significant progress made in recent decades this area of science was reviewed and the basic rules were formulated

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LIST OF SYMBOLS AND ABBREVIATIONS

A A_o	final and initial interfacial area respectively
B	minor axis of ellipsoid
d	droplet diameter
D	deformation
f	frequency of particle break up
ΔG_m	free energy of mixing
ΔH_m	heat of mixing
L	major axis of ellipsoid
N	reorientation number
N_1	first normal stress difference
P	pressure
PAB	polymer alloys and blends
q	coefficient of Tomotika s analysis
R	initial droplet radius
R_o	initial filament radius
ΔS_m	entropy of mixing
t_b	time to break
T	temperature
α	distortion amplitude
α	coalescence probability
β	proportionality factor
γ	total shear strain

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γ	shear rate
δ	elasticity ratio
$\dot{\varepsilon}$	rate of elongation
η	melt viscosity
Θ	orientation angle
κ	capillarity number
κ_c	critical capillarity number
λ	viscosity ratio
ν	interfacial tension
σ_{12}	shear stress
ϕ	volume fraction
χ	interaction parameter

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THE FORMATION OF INTERPENETRATING POLYMER BLENDS

M Kozlowski

RDCC POLYMAK Wroclaw Poland

ABSTRACT

Formation of the thermoplastic blends of co-continuous morphology has been discussed, the dynamic character of this process being stressed Interpenetrating polymer blends represent the intermediate stage of a multicomponent polymer system during dispersive mixing The time for reaching such a state of heterogeneity and its stability depend on the viscoelastic characteristics of the component polymers their ratio in a blend interfacial tension and mixing parameters The role of particular factors influencing the formation of interpenetrating polymer blends has been presented for the LDPE/PS system

Because of the dynamic character of the evolution of polymer blend morphology upon mixing, the processing history specifications should accompany every morphology presentation

KEY WORDS

Polymer blend, morphology, interfacial tension, shear stress processing history

INTRODUCTION

Polymer blends (PB) are by and large multiphase systems mainly for thermodynamic reasons They have already been exhaustively discussed /1-4/ Among other factors influencing the final phase state of macromolecular components, the rheological properties and interfacial behaviour of PBs have been mentioned /4-8/

Extensive studies have been carried out on the influence of particular factors on the blend morphology These studies have intensified during recent decades, when the economic advantages of polymer blending over a search for new monomers and (co)polymers has been proved Similarly, the concept which previously prevailed of seeking the miscible polymer pairs of complementary properties failed because of the rarity of such pairs The last twenty years could aptly be called "the age of heterogeneous polymer blends" Owing to the enormous efforts of many researchers, often simply "fans" of polyblend structurization, there already exists the science of polymer blend morphology based mainly on extensive experimental experience, well-proven rules and theoretical considerations It is impossible to mention all the scientists who have contributed to the present "state of the art" but I feel I must mention at least a few leaders in the field (with apologies to all those not mentioned!) Among the papers/books to which I would like to refer are those of L A Utracki /2/ A P Plochocki /6/, J L White /9/, S Wu /10/, B D Favis /11/, E Martuscelli /3/, F P La Mantia /12/ J Lyngaae-Jorgensen /13/, Ph Teyssie /14/ and M Kryszewski /3/

The background knowledge which already exists makes possible to a great extent the design and creation of the morphology required Polymer blends of "tailor made" morphology and properties are already commercially produced and widely used Usually three kinds of morphology are specified

- disperse (droplet- or fiber-type)
- stratified (sandwich- or lamellar-type),
- co-continuous (interlocked)

Disperse type morphology is revealed in rubber-toughened plastics or fiber-reinforced composites /15-17/ Laminar morphology is developed in

systems of controlled barrier properties for diverse permeants /18/ Co continuous morphology transfers the early idea of the coexistence of two polymers with preservation of advantageous characteristics of both of them As examples the conductive blends time-release medicines and ion selective membranes can be mentioned /19 22/

The particular type of morphology will be generated during mixing depending on the nature of the blend components their volume fraction the ratio of the viscoelastic properties and the processing history /23-30/ Adequate relationships have been relatively well known in particular as far as disperse morphology is concerned Numerous papers have reported how to promote the generation of droplets/fibers of recommended shape by the proper choice of a disperse phase content the ratio of its viscosity to that of a matrix (λ), the suitable stress level and flow field It is possible to influence the size of disperse domains either by matching the above parameters or by changing the ratio of the melt elasticity of the disperse to the matrix phase (δ) /5,7 10 31,32/ A number of researchers concluded that the lowest scale size of dispersed domains and the lowest mixing energy input were stated when the melt viscosities were the same Compatibilizers (i e emulsifying agents which decrease the interfacial tension) exert a particular influence on the domain size /15/

Co-continuous structures have only recently begun to receive more attention This term is usually related to interpenetrating polymer networks (IPNs) IPNs are polymer systems obtained in a specific manner by polymerisation/crosslinking of at least one polymer in the presence of the other /33,34/ For the thermoplastic blends of co-continuous morphology the term "interpentrating polymer blends" (IPB) has been proposed The IPB s size scale is two orders of magnitude higher than that of the IPN /35/ Equilibrium thermodynamics allow this kind of structure to be predicted by considering the dynamics of phase separation By controlled (high) depth of quenching co-continuous morphology can be generated by the spinodal decomposition mechanism, even at very low concentrations of a dispersed phase ($\varnothing_1 < 0\ 15$) The structure of the phases that evolve by the superposition of the sine waves of composition fluctuation is characterized

by its periodicity and dual connectivity /36/

Co-continuous structures can be produced within the processing machinery by the mechanical mixing of incompatible polymer systems Avergopoulos *et al* /31/ upon studying the influence of a mixing torque ratio and blend composition on the phase continuity, concluded that when the torque ratio is near unity, the conversion region is characterized by the samples with co continuous phases

Paul and Barlow /37/ have formulated the condition for phase inversion in the form

$$\varnothing_1/\varnothing_2 = \eta_1/\eta_2 \qquad (1)$$

where η_1 η_2 $\varnothing_1$ $\varnothing_2$ are viscosity and volume fraction of the disperse phase (1) and the matrix (2) respectively Jordhamo *et al* /32/ have confirmed the applicability of this relation in blends of polybutadiene with polystyrene

The above condition has been slightly modified with regard to the viscosity dependence on shear rate γ /18/ and on temperature T and pressure p /38/ Because the dependence $\eta_1 = f(\gamma,T,p)$ is usually different from $\eta_2 = f(\gamma\ T,p)$ the value of λ (and consequently the inversion range) will change at different (γ T p)

Metelkhin and Blekht /39/ developed a theory of phase inversion based on the assumption that both polymers deform in the flow field under mixing conditions The domains are oriented and broken-down under the influence of the shear and elongational stresses and by the interfacial tension-driven instability mechanism At critical conditions the disruption time of both components is the same and the interpenetrating structures are being formed Basing their work on a classical filament instability analysis of Tomotika /40/ the authors derived an equation for the critical volume fraction of the co-continuous structure formation

$$\varnothing_2 = 1 / [1 + \lambda F(\lambda)] \qquad (2)$$

Inoue *et al* /41/ have related the phenomenon of phase inversion to the dissymetry of the interface not only to λ

Utracki /42/ has similarly pointed out the influence of the melt viscosity ratio and the intrinsic viscosity of the dispersed phase value [η] on the concentration range within which the co continuous structure is formed The concept presented by the author was based on the presumption that the dependence η vs $\varnothing$ is determined by two mechanisms the interlayer slip and viscosity maximum at the inversion concentration The system of immiscible polymer melts was treated as the emulsion of one liquid dispersed in another As a result of the addition of one polymer melt into another the viscosity increase is observed in such systems The same goes for both polymer components (i e from one side polymer 1 is a matrix and from the opposite polymer 2 is a continuous phase) – the phase inversion occurs at the isoviscous state At this point

$$\lambda = [(\varnothing_m - \varnothing_2)/(\varnothing_m - \varnothing_1)\ [\eta]\varnothing_m] \qquad (3)$$

where $\varnothing_m$ is the maximum packing volume fraction

After the transformation and simplification of the equation one obtains an expression which allows prediction of a phase inversion region

$$\varnothing_2 = \{1 - (\log \lambda)/[\eta]\} / 2 \qquad (4)$$

According to the percolation theory /43/, the infinite spatial structures of monodisperse droplets can be formed in a matrix after the percolation threshold has been exceeded The critical volume fraction $\varnothing_{cr}$ is 0 156

Lyngaae-Jorgensen and Utracki /13/ investigated the influence of the flow field on co-continuous structure formation They found that the elongated domains of different size oriented in the flow field can yield dual phase continuity at even lower volume fraction ($\varnothing_{cr}$ = 0 113)

Lyngaae-Jorgensen *et al* /20/ after their study on the structure and properties of polymer blends with interpenetrating phases concluded that complex precursors decrease the percolation threshold value

Numerous authors argue with the currently postulated rules of phase structure evolution in polymer blends based on rheological data and the volume fraction of the component polymers They stress that additional degrees of complexity are added by the non-Newtonian character of polymer

melts and by the crystallinity of polymers In general one can formulate a statement that critical conditions for the formation of co-continuous structures in polymer blends have not yet been definitively established and therefore they require further discussion

The main goal of this investigation is to study the role of mixing history on the formation of interpenetrating polymer blends Another goal is to estimate the influence of compatibilizer on development of this particular structure

EXPERIMENTAL

The materials used throughout the study were low density polyethylene (LDPE) grade BP33 and polystyrene (PS) grade HH101 – both from BP Chemicals The compatibilizer was partially hydrogenated poly(styrene-b-isoprene) di block copolymer (SEBS) Kraton G1701 from Shell Chemicals These polymers have been characterized satisfactorily in one of the recent IUPAC research projects /44/

Blends were prepared using Brabender Plasti-Corder at 200°C and 30 rpm rotor speed for 15 minutes For the purposes of the blending dynamics study a dispersion tester described elsewhere /45/ was used The tests were performed at 200°C 12 rpm disc speed and at controlled gap clearance between the disc and the spreader

A scanning electron microscope (SEM), Jeol JSM 840 was used for evaluation of the blend morphology Prior to observation the polymer samples were freeze fractured or cryomicrotomed at -150°C using the Reichert Ultramicrotome and then etched with toluene Finally the samples were gold-palladium coated and observed in the secondary electron imaging mode

A semiautomatic image analysis system was used in order to quantify the dimensions and orientation of the minor phase domains The system consists of a video camera coupled with a computer About 100 to 500 particles were scanned with the image analyser to obtain the size distribution and average diameter of the dispersed particles

RESULTS AND DISCUSSION

Preparation of the interpenetrating polymer blend was preceded by calculation of the LDPE/PS phase-inversion region using different equations The first was the most popular Paul-Barlow Eq (1) in the form /37/

$$\varnothing_2 = 1 / (1 + \lambda) \qquad (5)$$

The next was that of Metelkin-Blekht /39/

$$\varnothing_2 = 1 / [1 + \lambda F(\lambda)] \qquad (6)$$

with empirically determined

$$F(\lambda) = 1 + 2.25 \log \lambda + 1.81 (\log \lambda)^2 \qquad (6)$$

The third was the equation proposed by Utracki /42/ in its final form

$$\varnothing_2 = \{1 - (\log \lambda) / [\eta]\} / 2 \qquad (4)$$

The values of melt viscosity were taken from /46/ corresponding to $\gamma = 90\ s^{-1}$ (the approximate shear rate in a Brabender mixing chamber) These values were $\eta_{LDPE} = 1.30$ Pas $\eta_{PS} = 0.85$ Pas $[\eta] = 1.9$ Pas The solution of the above equations gives LDPE volume fraction at which phase inversion occurs namely $\varnothing_2^{PB} = 0.60$

$\varnothing_2^{MB} = 0.70$

$\varnothing_2^{U} = 0.55$

The practical value of these predictions was examined by the preparation of LDPE/PS systems and by the blend morphology inspection Mixing was performed in the Brabender Plasti Corder this technique has frequently been applied by researchers who deal with polymer blending

The blend with a ratio of 60/40 was found to have the co continuous morphology (Figure 1) Irregularly shaped domains of different components were found The morphology of mutually interlocking polymers was revealed and is shown in more detail in Figure 1b which visualises the fracture surface along the flow direction The thickness of the intertwined threads differs in a range 5-10 μm depending on the coalescence proceeding

a

b

Fig 1 Morphology of Brabender-mixed blend LDPE/PS 60/40 Fracture surface perpendicular (a) and along the flow direction (b)

In order to check the morphological difference influenced by the volume ratio of particular components other blends were also prepared LDPE/PS 75/25 manifests more uniform morphology of a lamellar type (Figure 2) In addition the thickness of sandwich-ordered sheets is also more regular (2 μm) The different mode of morphology can be related to a higher elasticity of LDPE matrix than that of the PS-minor phase /46/ According to the rheothermodynamic theory of van Oene the extra interfacial tension appearing in case $\delta > 1$ stratifies the dispersed phase /5/

Fig 2 Morphology of LDPE/PS 75/25 blend (Brabender mixer)

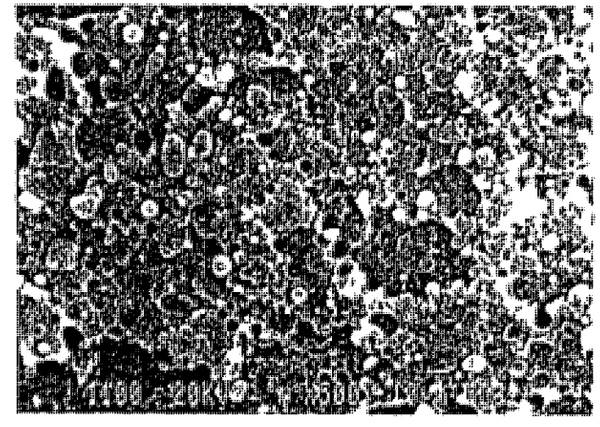


Fig 3 Phase structure of LDPE/PS 40/60 Brabender mixed blend

The LDPE/PS 40/60 blend is neither co continuous nor lamellar Disperse morphology with regularly distributed droplets/fibers (Figure 3) shows the possibility of qualitative changes in morphology (i e its type) within the composition range of 35 vol % In order to differentiate between the blends a characteristic number κ was introduced

$$\kappa = (\eta_1/\eta_2)\,(\varnothing_2/\varnothing_1) \qquad (7)$$

The values corresponding to LDPE/PS systems 75/25 (κ = 0 5), 60/40 (κ = 1 0) and 40/60 (κ = 2 25) suggest the existence of the tendency of the κ -value to increase with increasing dispersity

For interpenetrating blends κ = 1 However, more experimental evidence would be needed to confirm this tendency and to define possible characteristic limits (criteria) of the particular morphological type

A comparison of the resulting morphology for different LDPE/PS blends with analytical predictions of $\varnothing_2$ suggests that the equations of Paul-Barlow and Utracki fit the reality best The one restriction which must be mentioned is that the conclusion deals with the specific conditions of mixing (temperature, rpm, time) and with the flow field generated within the Brabender mixing chamber

The practical meaning of the above findings is that in different points of mixing machinery, diverse kinds of dispersed domains arrangement can be found, if distributive mixing is not effective enough (i e , location-dependent differences in composition are possible)

The dependence of polymer blend morphology on the parameters essential for dispersive mixing was determined using the dispersion tester The apparatus captures key elements of internal mixers high shear zone preceded by the wedge-shaped entrance region Polymer components are forced by a moving disc to pass repeatedly through such regions while the dispersed phase is reduced in size A possible mechanism of flow in such a spreader disc unit has recently been proposed /47/

By using the system LDPE/PS 60/40 (κ = 1), the dynamics of the process of interpenetrating polymer blend formation was investigated PS-domains were diminished step-wise after consecutive passages under the spreader at 1 mm gap clearance (Figure 4) During the first steps of mixing, the large spherical domains of polystyrene suspended in LDPE-melt were flattened in a flow field generated in an entrance convergent to the mixing unit The initial size of ca 1 mm was reduced to approx 10-50 µm after 5 passages During consecutive mixing steps, further disruption of the stratified sheets into long strips was followed by their splitting into narrow threads and fibers After 20 passages of a blend under the spreader IPB was developed

a

b

c

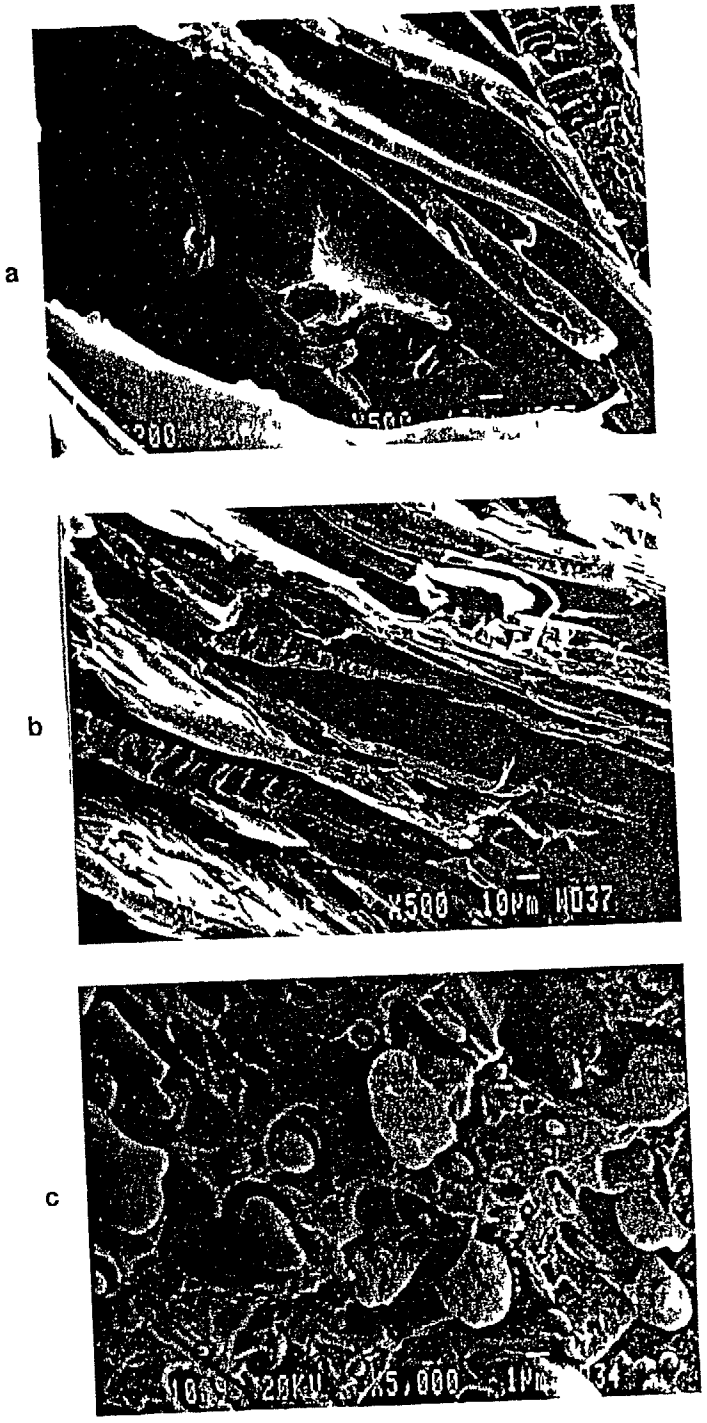


Fig 4

d

Fig 4 Morphology of LDPE/PS 60/40 blend mixed in a dispersion tester (1 mm gap clearance)
a 5 b 10 c 20 d 50 passages

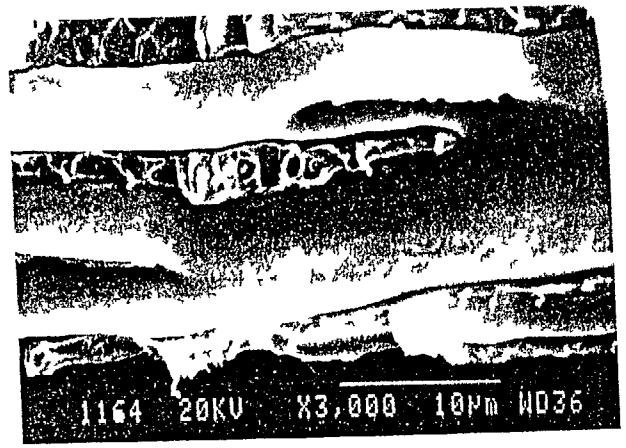


Fig 5 Co continuous morphology after 20 passages under the spreader (LDPE/PS 60/40 blend)

Details of the co-continuous morphology are presented in Figure 5 The scale of the structure is approx 5 μm The non-equilibrium character of the IPB morphology was discovered if the blend was subjected to prolonged stress PS fibers of broad distribution of their diameter observed after 50

passages become more uniform as mixing proceeds After 100 passages droplet-like morphology of ca 1 μm scale size was revealed Etching enhanced phase morphology both in the parallel and perpendicular cross section with regard to the flow direction is presented in Figure 6 Bar histograms of the minor phase average diameters after 100 passages are shown in Figure 7a and b respectively Comparable mean values in both directions (1 1 and 0 9 μm) suggest that these domains represent droplets slightly elongated along the flow direction

The dynamic character of the phase structure evolution is evidence of the strong influence of the stress level on polymer blend morphology The shear stress σ_{12} calculated according to the procedure developed in /47/ is 110 kPa per revolution The stress level is adjusted by means of gap clearance control Changes up to 2 mm and 0 5 mm in gap clearance resulted in 51 kPa and 232 kPa per revolution respectively The corresponding phase state of LDPE/PS 60/40 blend is illustrated in Figures 8 and 9 respectively The lower stress level brings about the coarsening of morphology under the initial steps of its evolution After 20 passages the blend is still of a stratified type – only the subsequent passages cause the development of fibers

The opposite effect was observed when polymer components were dragged through a high shear-generating gap of 0 5 mm clearance size PS fibers were formed after 20 passages To compare the characteristic size d (average domain thickness) of the dispersed phase under different processing conditions the plot of its dependence on overall work expended in the mixing process is presented in Figure 10

Among other factors influencing IPB formation an interfacial tension effect has been revealed The compatibilizing function of SEB was definitely confirmed After the addition of 5 phr of the compatibilizer considerable acceleration of the morphology evolution process was observed After just eight passages of the blend LDPE/PS 60/40 under the spreader at 1 mm gap clearance a co-continuous morphology was manifested For the alloy (i e the compatibilized blend) succeeding steps of morphology evolution according to a recently developed model /47/ were reached in a shorter time (see dotted line in Figure 10) The blend morphology after 50 passages is

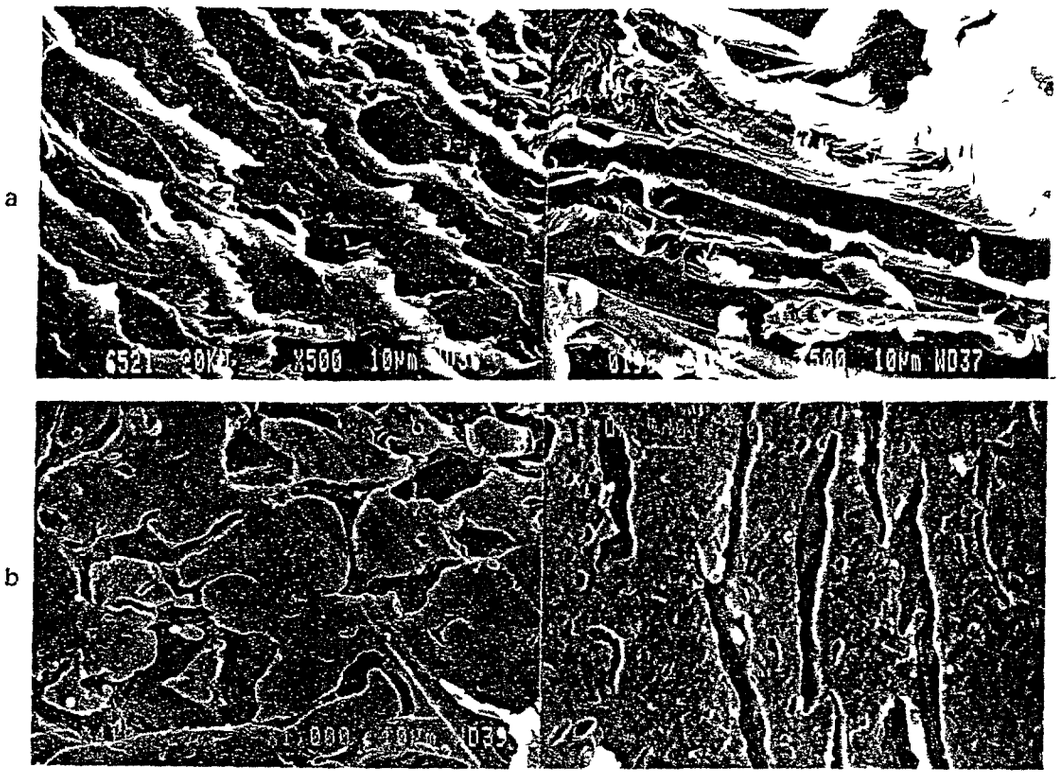
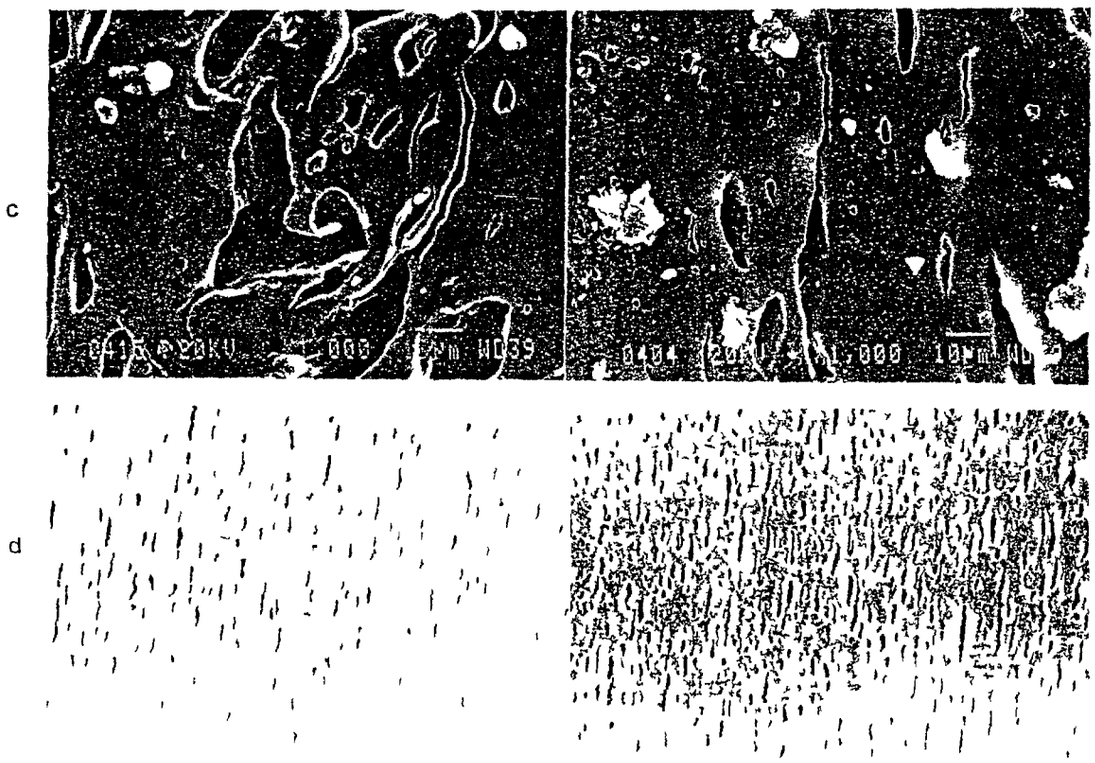


Fig 6 SEM-micrographs of etched microtomed surface for LDPE/PS 60/40 system mixed in a dispersion tester Perpendicular (left row) and longitudinal to flow axis a - 10 b - 20 c - 50 d - 100 passages



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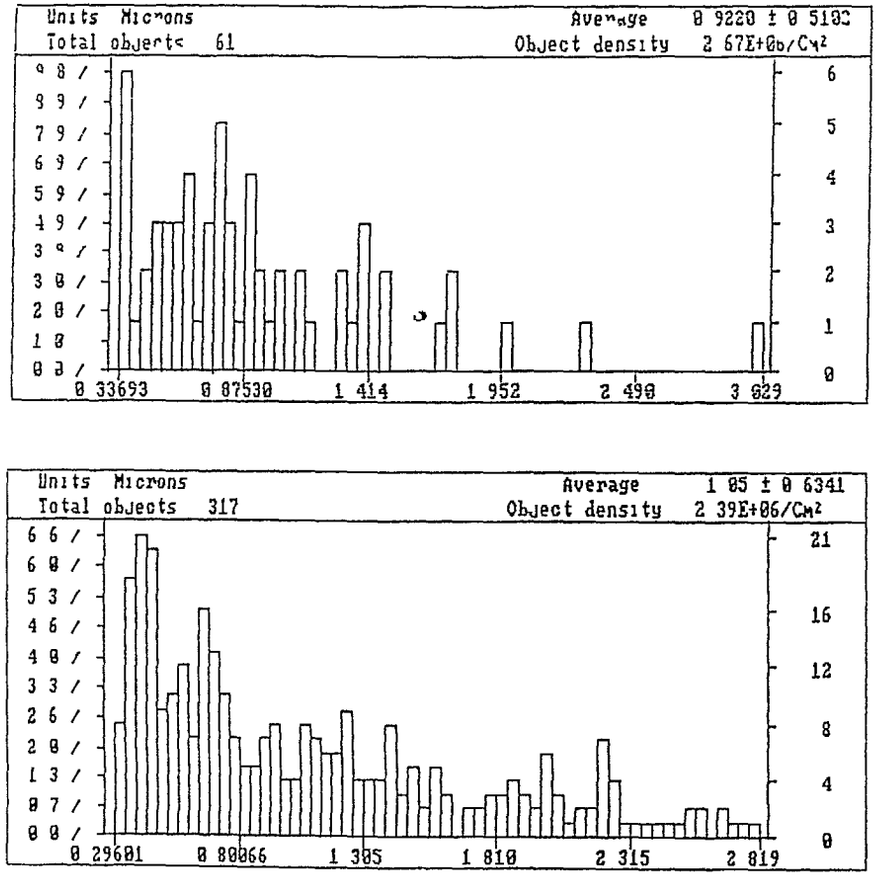

Fig 7 Bar histograms of the dispersed phase average diameter in the cross-section perpendicular and parallel to the flow aixs LDPE/PS 60/40 blend after 100 passages under the spreader

pictured in Fig 11, which gives evidence of a decrease in the interfacial tension barrier, i e, SEB is of the desired efficiency

As far as the speed of the disc which drags a polymer melt into the high shear region is concerned it is of less importance for the blend morphology This is because, in parallel with the increasing disc velocity, the residence time under high stress is shortened Exemplary data, corresponding to

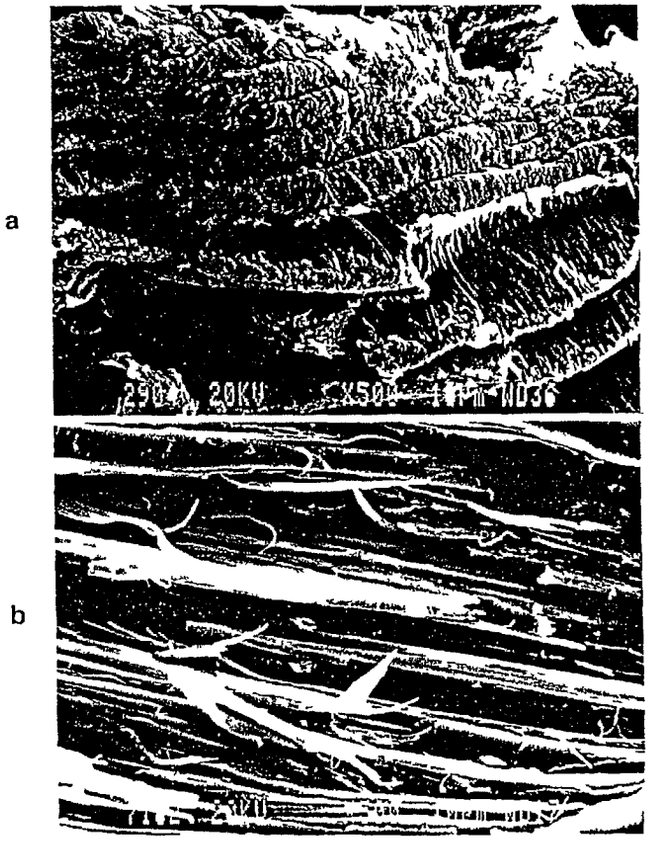

Fig 8 Morphology of LDPE/PS 60/40 blend (2 mm gap clearance) a - 5, b - 20 passages

different disc speeds calculated according to /47/ are presented in Table 1

The mean shear rate γ has been obtained from

$$\gamma = V_0^2/Q \tag{8}$$

where V_0 - speed of the disc, Q - flow rate

The mean shear stress σ_{12} is given by

$$\sigma_{12} = \eta\,\gamma \tag{9}$$

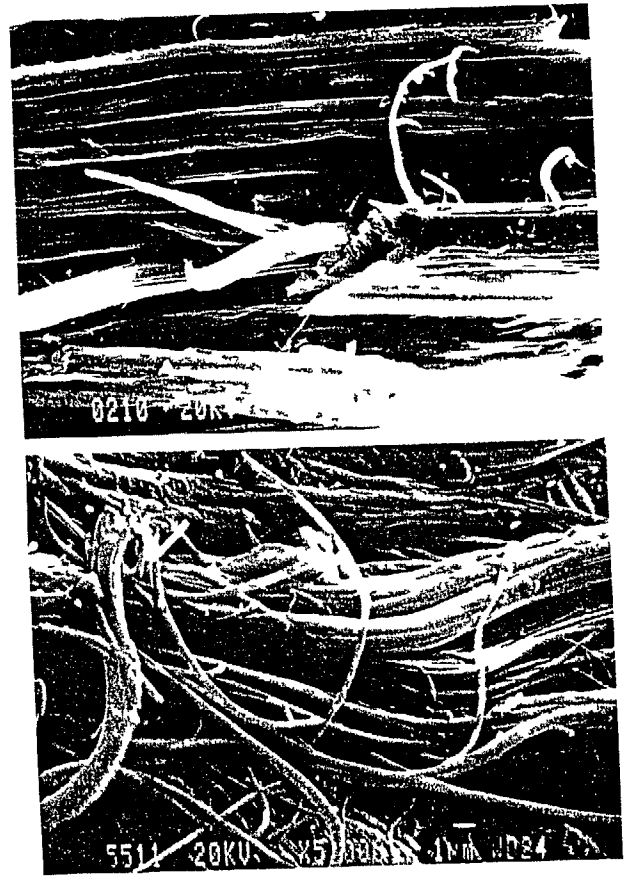

Fig 9 Morphology of LDPE/PS 60/40 blend (0 5 mm gap clearance) a b 20 passages

whereas the mean residence time t has been calculated from

$$t = V/Q \tag{10}$$

where V flow volume under the spreader

According to the data presented in Table 1 one can conclude that neither the shear rate nor the shear stress are sufficient characteristics for the mixing history description They must be accompanied by the residence time of a material under the specified shear/stress conditions

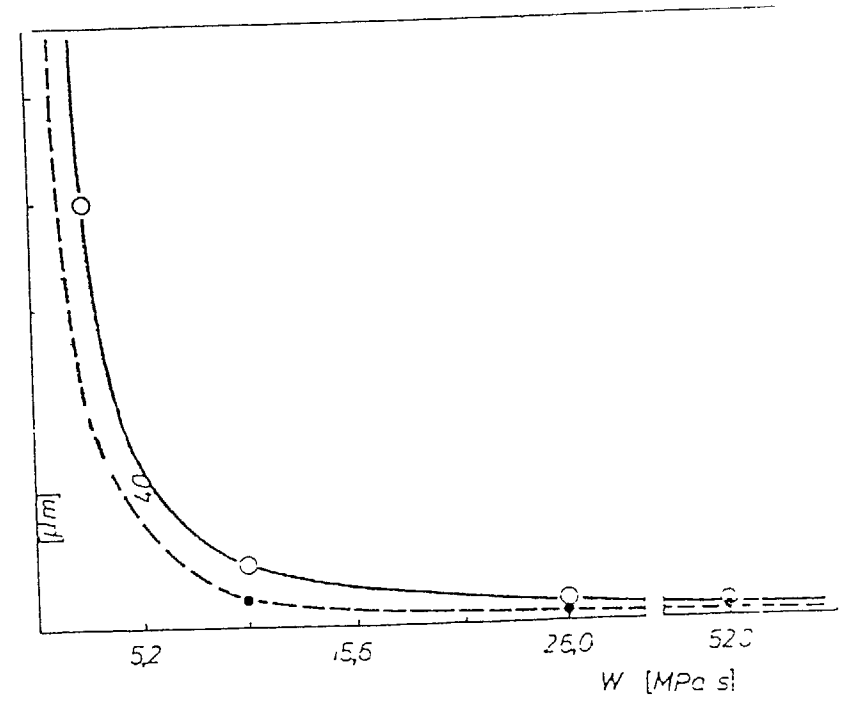

Fig 10 Average size of the dispersed phase domains versus the work expended upon mixing for LDPE/PS 60/40 system

Therefore similar blending observed in Figures 2 4b 8b and 7b obtained in spite of different mixing conditions – must be attributed to the equal total shear S ($S = \gamma t$) or total work W ($W = \sigma_{12} t$) expended on the system The concept dealt with from various points of view by Stirna et Tokita /15/ Manas-Zloczower Nir and Tadmor /49/ and Schreiber and Olguin /24/, suggests the existence of a critical value of the total strain stress required for the breaking-up of the dispersed phase domains This is related to the time scale of a mixing process Numerous papers have reported the plot of a mean disperse phase diameter d versus the mixing time shear stress or energy input /6 15 16 21 24 35 49/ The plots are of an exponential nature describing a fast reduction in size during the initial steps of mixing followed by a much slower process leading asymptotically to the equilibrium

Fig 11 Morphology of LDPE/PS/SEBS alloy (1 mm gap clearance) after 50 passages under the spreader

Table 1

Parameters of the mixing history for LDPE/PS blend

Disc speed, rpm	12	24	36
Mean shear rate γ, s^{-1}	220	438	657
Mean shear stress σ_{12}, kPa	120	150	170
Mean residence time t, s	4.3	2.1	1.4

domain size Figure 10 is a kind of master curve – its initial drop would be governed by the stress-induced breakdown of the large domains of a dispersed phase into smaller droplets The limit of the straight line of the plot would be relevant to "the macroscopic bulk breaking energy E_{OK}'

according to Tokita /15/ or to the rigidity of the dispersed phase referred to by Utracki /42/ In our treatment (see Figure 10 units kPa s) it should exceed the viscosity of a dispersed phase The progressive breakdown (intermediate part of the plot) would be related mainly to the rheological characteristics posing hydrodynamic barriers to the dispersion process (differences of the melt viscosities and elasticities of component polymers)

Additionally one must take into account the coalescence phenomenon and the interfacial tension γ which resists the deformational stress The first contribution is small until the dispersed domain size is small enough The asymptote to the equilibrium size value is related to the interfacial tension driven disruption of relatively small domains (d < 10 μm) Again the competition between the breaking down and the coalescence has to be taken into account /6 15 47/ Interfacial driven processes are slow in their nature additionally in the shear field the capillary instabilities are disturbed causing the prolongation of the time to break up The interfacial tension barrier prevents us from ever reaching in immiscible polymer systems the region governed by diffusivity (scale 10 nm /35/) essential to mixing on the molecular level

When considering the final domain size for the LDPE/PS system various results of individual scientists must be mentioned For example Min et al /26/ concluded that the minor phase diameter diminished inversely to the stress level The equilibrium size was almost unaffected when the mixing time was prolonged Lyngaae-Jorgensen *et al* /26/ stated that at a sufficiently high shear stress level the transition from a two phase system to a homogeneous one takes place Trochimczuk *et al* /29/ concluded that depending on the composition and molecular weight of PS a blends morphology changed from spherical domains dispersed in a matrix to highly elongated fibers or cabbage-like structures close to phase inversion Plochocki *et al* /6/ reported a minimum on the plot of the domain size versus the mixing energy After critical energy input domain size rose surprisingly This can be attributed to the progressive domain coalescence and thermomechanical degradation of a matrix polymer

A possible reason for the ambiguity of these and other ambiguous statements published within the last few decades could be the different processing history of particular samples From Figure 10 it is obvious that, depending on the mixing parameters (σ_{12}, residence time) applied by individual researchers, the morphology details can be significantly different, even if the blending preparation was performed carefully and according to the best state-of-the-art in every case

Therefore, arbitrary statements like "Polymers A and B form interpenetrating (or any other) structures at the range of composition x/y" should be avoided It is essential that particular conditions of mixing should accompany every such statement

Summarizing the above discussion the necessity for a detailed description of the mode and conditions of polymer blending preparation must be stressed since this is crucial for the blend morphology and therefore for the end use properties of the blends

CONCLUSIONS

- Quite different morphologies can be produced for LDPE/PS systems within the composition range of 35 wt %, if strictly defined mixing conditions are used
- Use of the compatibilizer causes the interpenetrating structure to be produced faster and to be more stable
- The characteristic number κ has been introduced in order to differentiate/predict the dispersity level
- Fine dispersions of one component in the other can be produced even at the composition range for which the interpenetrating polymer blends are expected
- The key factor for the morphology generated during the mixing process is the processing history comprising the stress level and the residence time, i e the work expended while mixing
- A detailed description of the mixing history is essential for polymer blends/alloys preparation, and is just as important as the type and composition of the components

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Structure and Mechanical Properties of Heterogeneous Polymer Blends

M KOZLOWSKI

RDCC 'POLYMAK' Trentowskiego 21 PL 52-430 Wroclaw Poland

SYNOPSIS

Material response under uniaxial stress has been reported for heterogeneous systems low density poly(ethylene)–poly(styrene) The ystems differed in a component ratio and in a content of the macromolecular modifier type compatibilizer Tensile properties have been determined for the systems in a molten state (473 K) and below T_g as a function of elongation rate The modifier which diminishes the interfacial tension is advantageous for mechanical properties of the system—both in the melt and the solid state The differences in mechanical characteristics have been related to a specific phase structure of polymer systems © 1995 John Wiley & Sons Inc

INTRODUCTION

Polymer blends have recently comprised ca 20% of the overall plastics production The high dynamics of 10% annual increase lasting already over 10 years allows the prediction that in the near future most products made of plastics will be manufactured from multicomponent polymer systems [1-3] Among the reasons for such high interest in polymer blends at least the most important should be mentioned

- properties adjustment is the needs by a proper choice of the particular kind of components and their ratio in the blends,
- modelling of the phase structure of heterogeneous systems has recently become accessible,
- better economy (lower costs and shorter time scale) of the new polymeric material designed through blending rather than searching of new monomers for the new (co)polymers synthesis,
- reduction of the price of the blends based on "engineering polymers", and
- ecological aspects (utilization of the plastic wastes by blending)

The above-mentioned advantages can be of practical worth only in the case of thorough knowledge of the polymer mixing process theory and of the proper application of empirical rules which determine the interrelations of melt rheology, the phase structure formation, and the end use properties of the finished products [3-13]

Most polymer blends are heterogeneous because of the thermodynamically substantiated immiscibility of the components These systems are usually of poor mechanical strength resulting from weak interfacial adhesion For example, the relationships between the empirical Young modulus or tensile strength and the component ratio represent a negative deviation (NDB) from the theoretically predicted values Significant differences in the mechanical properties of polymer blends of identical component ratios suggest an important role of the phase structure mode, size of the morphology elements, and interfacial characteristics

Among the factors influencing the morphology of polymer systems, the most significant are[3 7-20]

- composition,
- viscosity ratio of the molten components,
- melt elasticity ratio,
- interfacial tension, and
- processing history

The usually designed morphology comprises micro dispersions of the minor phase component in the matrix polymer, because of favorable properties of

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such systems By increasing the dispersed phase content in the system, one can enlarge the size of the domains until the phase inversion occurs Under specific conditions, the characteristic interpenetrating structure is formed [15 16 21 22] The domain size is dependent also on the interfacial tension, i e , the size usually decreases as the interfacial tension diminishes Such effects can be attained by the addition of macromolecular modifiers of compatibilizer type [23-31] Usually these are block or grafted copolymers which contain blocks of a high affinity to the blended polymers Such units commonly form an interfacial layer which enhances the adhesion between components Such structural modification involves differences in mechanical properties Throughout this paper the correlation of the compatibilizer influence on the tensile strength of polymer systems, both in the molten and solid state, was studied

EXPERIMENTAL

Materials

The polymers used were low density poly(ethylene) (LDPE) and poly(styrene) (PS) from BP Chemicals and partially hydrogenated di-block copolymer (styrene-*b*-isoprene) Kraton G1701 (SEBS) from Shell Chemicals These polymers were used within the IUPAC Working Party IV 2 1 by participants in the research project "Melt Rheology and Comi tant Morphology of Polyblends," performed during 1985–1992 under the coordination of A P Plochocki [32]

Samples Preparation

Multicomponent polymer systems composed of various volume content (ϕ) of particular polymers with compatibilizer (alloys are coded A in the Tables) or without it (blends) were prepared within the framework of the IUPAC research project, using the two screw compounder type ZSK 30 from Werner Pfleiderer

The granules were used for rheological measure ments and for studying the melt elongational strength Tensile strength at room temperature was examined using the dog-bone-shaped tensile bars produced by injection molding

Melt Rheology

Rheological characteristics were obtained by using the capillary rheometer type MCR 3210 mounted into the Instron 1122 machine The measurements were performed at a temperature of 473 K using a capillary $L/D = 40$ Results were computed in a rou tine manner receiving the relationship of viscosity (η) versus shear stress (σ_{12}), the exponent n of the Ostwald deWaele equation, and the exponent m of the elasticity equation [33] The viscoelastic characteristics of the polymers, polymer blends, and alloys are presented in Table I

Rheotensometry

Mechanical strength in the molten state[34-36] was examined using the Gottfert Rheotens at 473 K The elongation was performed by the cogged wheels rotated with an acceleration of 1 5 cm s^{-2} Representative diagram force versus extension has been presented in Figure 1 Table II includes the torque values (M_d) of the extrusiometer upon the extrusion of particular compositions, as well as the breaking force (F) and elongation (Δl) at the break of extrudate

Mechanical Strength at the Solid State

The uniaxial tension of normalized samples was ex amined using the FU 100eZ testing machine at room temperature Cross head speed was changed within a range 1–100 mm min^{-1} The tensile modulus of elasticity (E), yield stress (σ_y), tensile strength (σ_r) and the elongation at break (ε) were calculated Results are presented in Table III

Microscopy

The damage region of the samples was inspected both in parallel and in perpendicular direction to the elongation axis For in-axis observations the

Table I Viscoelastic Characteristics of Polymers, Polymer Blends (Sample Code Expressed with PS Content, Wt (%) and Polymer Alloys (Additionally Code A)

Sample Code	$n \times 1000$	η, Pa s	$m \times 1000$
LDPE	453	1,780	625
15	472	1 320	555
15A	498	1 390	726
33	367	970	476
33A	457	1 340	543
67	356	780	476
67A	302	790	—
PS	307	590	636
SEBS	370	2 270	194

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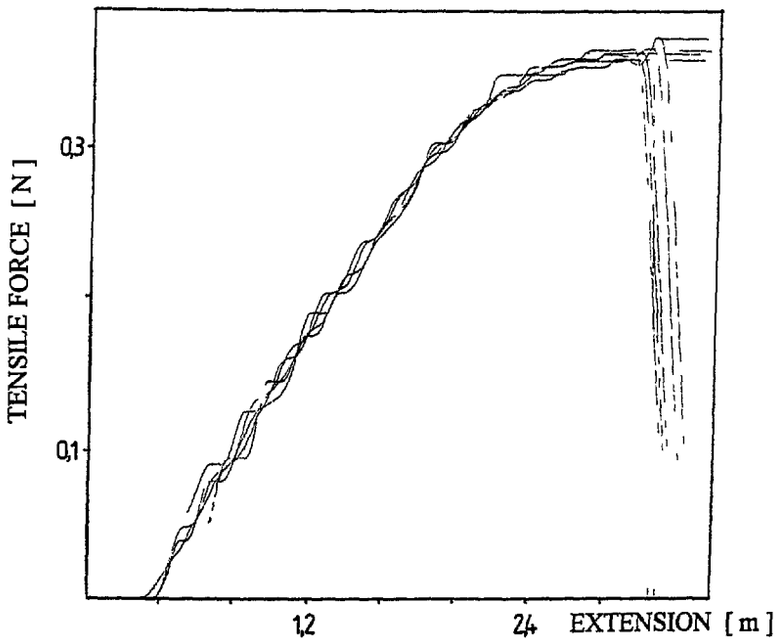

Figure 1 Diagram of uniaxial stretching of LDPE melt

cold-fractured (liquid N_2) samples were used The surfaces were vacuum coated with the Au–Pd layer and then observed using the JEOL JSM840 scan ning electron microscope (SEM) The SEM-micrographs are presented in Figures 2–7

RESULTS AND DISCUSSION

Melt Flow

The rheological characteristics of the polymer systems in the molten state are presented in Table I Viscosity versus shear rate dependence, both for blends and alloys, was non-Newtonian, and similarly for the homopolymers LDPE and PS The melt viscosity of multicomponent systems has been comprised between the values measured for poly(ethylene) and poly(styrene) The highest melt viscosity has been found for the block copolymer SEBS, whereas PS showed the lowest viscosity

Flow instabilities of the "melt fracture" type were observed at high shear rates As a rule, this feature revealed for blends and for a virgin PS at the shear rates of one order of magnitude higher than for the alloys and for LDPE

Table I comprises the viscoelastic characteristics at the shear stress $\sigma_{12} = 10^2$ kPa Melt viscosity increase has been noted as a result of the block copolymer addition—the most distinct for the systems LDPE–PS of the weight fraction ratio of 2 1 The elastic behavior of alloys has been more pronounced in comparison to blends of the same ratio of the component polymers The viscoelastic characteris tics suggest enhanced interactions between the components, resulting from the block copolymer addition Simultaneously, the microheterogeneity level was increased in this system composed of two high viscosity fluids (LDPE and PS at temperature 473 K) SEBS behaves like emulsifier, indeed

Melt Stretching

The results of rheotensometry (Figure 1, Table II) show only small differences between the tensile

Table II Rheotensometry Results

Sample Code	Torque M_d, J	Melt Strength F, mN	Melt Elongation at Break Δl, m
LDPE	40 2	361	2 78
15	36 8	371	2 47
15A	40 2	417	6 22
33	36 5	386	2 22
33A	38 3	352	3 64
67	35 3	276	2 80
67A	34 3	362	6 01
PS	38 2	323	7 28
SEBS	14 7	352	1 30

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strength of particular systems Addition of SEBS is favorable for a tensile strength of the melts, excluding the system LDPE/PS 2/1 Much higher differences have been found for the elongation at break, both between the neat polymers and between blends and alloys The PS strand was extended 2 6 times more than PE under the same conditions This can be attributed to a different viscosity of the polymer melts (viscosity of PS melt is 3 times higher than that of PE) There exists an interesting relationship between the results of the uniaxial melt elongation and the previously reported "melt fracture' appearance, which can explain the above findings Melt defects that deteriorate the material strength arise at lower stress in LDPE, therefore poly(ethylene) dominated systems break at a lower extension ratio

The melt elongation at break for all blends was similar to that of the LDPE melt This allows for a supposition that this polymer forms an intermeshed (network) phase structure, according to the percolation model This tendency was diminished with the addition of the component which decreases the interfacial tension (compatibilizer), resulting in distinctly higher extensibility of the alloys

Solid State Tensile

Diverse relationships were found as far as the results of tensile tests performed at 293 K and reported in Table III are concerned Poly(ethylene) exhibits much higher elongation at break and distinctly lower tensile modulus than poly(styrene) This can be related to the semicrystallinity of LDPE and to the much higher brittleness of PS Essential differences of the neat polymers influence the fracture mode and therefore the tensile results for LDPE/PS blends and alloys

In the discussion below, we consider the heterogeneous polymer systems as the matrix fiber composites In the course of stretching, the following phenomena may take place[37-48]

- detachment of the fiber/matrix connection,
- slippage in this interfacial area,
- pulling-out of fibers and the stress relaxation in a matrix,
- fracture of a brittle phase, and/or
- fracture of a ductile phase

The total fracture energy W consists of three components

$$W = W_f + W_m + \sum W_{fm}^{\alpha} \quad (1)$$

where W_f and W_m are the fracture energy of the fibers and matrix, respectively, and $\sum W_{fm}^{\alpha}$ is the whole spectrum of interactions on the fibers/matrix interface

After Wu[13], we correlated the molecular parameters to the fracture modes of LDPE and PS Semicrystalline LDPE was considered as a composite of crystallites distributed in an amorphous matrix The matrix behavior is more particularly dominant as the growth of crystallites is disturbed by the second polymer According to Wu classification, polymers are brittle (tending to craze under stress) or pseudoductile (tending to yield) Crazing starts with the chain breaking, which is related to the entanglement density ν_e The entanglement density is defined by

$$\nu_e = \rho_a / M_e \quad (2)$$

where ρ_a is the amorphous phase density and M_e the molecular weight of an entanglement

On the other hand, yielding is a function of the intrinsic chain flexibility measured by the characteristic ratio of chain C_∞

Table III Tensile Properties Versus Tensile Rate

Sample Code	Crosshead Rate mm/min	Tensile Modulus MPa	Yield Stress MPa	Tensile Stress MPa	Elongation at Break %
LDPE	1	201	14 4	13 8	73
	10	226	15 0	14 2	73
	100	—	16 5	16 0	65
15	1	348	14 8	13 8	38
	10	404	15 7	14 5	38
	100	—	16 8	16 1	34
15A	1	266	15 5	14 7	61
	10	346	15 6	14 9	58
	100	—	16 7	16 1	55
33	1	720	15 5	15 3	3
	10	690	18 7	18 7	3
	100	—	20 3	20 3	4
33A	1	488	15 0	14 1	38
	10	567	15 8	14 8	36
	100	—	15 5	15 3	31
67	1	1137	28 7	28 7	2
	10	1214	29 5	29 5	2
	100	—	27 6	27 6	3
67A	1	1424	29 1	29 1	2
	10	1186	31 1	31 1	2
	100	—	28 2	28 2	3
PS	1	2695	46 5	46 5	3
	10	2205	50 5	50 5	4
	100	—	47 2	47 2	3
SEBS	1	88	1 8	1 4	2

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$$C_\infty = \lim(R_o^2/nl^2) \quad (3)$$

where R_o^2 is the mean square end to-end distance of an unperturbed chain, n is the number of the statistical skeletal units, and l^2 is the mean square length of a statistical unit

Wu criteria predict crazing for the polymers having $\nu_e < 0\ 15$ mmole/cc and $C_\infty > 7\ 5$ Polymers characterized by $\nu_e > 0\ 15$ mmole/cc and $C_\infty < 7\ 5$ should yield Respective values for poly(ethylene) are $\nu_e = 0\ 613$ mmole/cc and $C_\infty = 6\ 8$, whereas for poly(styrene), $\nu_e = 0\ 056$ mmole/cc and $C_\infty = 10\ 8$ Therefore, we expected crazing as the predominant fracture mechanism of PS and yielding as typical for LDPE Our anticipation was strengthened by the comparison of the test temperature with relaxation temperatures Following Wu[37] we used thereafter the notations $\{\alpha\}$ and $\{T_\alpha\}$ for the primary (glass) transition as well as $\{\beta\}$ and $\{T_\beta\}$ for the secondary transition (subglass relaxation related to localized skeletal motions) The $\{\beta\}$ relaxation corresponds to the brittle/ductile transition related to the crazing/yielding behavior under the stress

The primary relaxation $\{\alpha\}$ which is for amorphous polymers the glass transition, occurs for poly(styrene) at $\{T_\alpha\} = T_g = 373$ K, whereas the brittle/ductile relaxation $\{\beta\}$ at $\{T_\beta\} = T_b = 363$ K In poly(ethylene) the glass transition is at 275 K and $\{\beta\}$ relaxation at 165 K According to Wu,[13 37] for chains with tetrahedral skeletal bonds, the highest intrinsic flexibility or the "maximum" ductility is attained when $C_\infty = 2$ and $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 0\ 3$

For the chains having $C_\infty > 10\ 5$ there is $\{T_\beta\}/\{T_\alpha\} = T_b/T_g = 1$ This ratio for poly(ethylene) is 0 60 and for poly(styrene), 0 97 In other words, in LDPE, yielding which arises from the onset of conformational rotation of skeletal bonds under the stress can occur at much lower temperature than that at which the tensile test was performed More over, because the test temperature was above $\{T_\alpha\}$, segmental motions (C_{10}–C_{100}), alignments, and mutual sliding of chains, as well as motions in the crystalline domains or at domain boundaries, should be taken into account To the contrary, in PS the brittle/ductile transition occurs only near the glass transition, therefore brittle behavior (crazing) must be expected at the tensile test temperature

The analysis of the data presented in Table III shows that the tensile modulus of LDPE rich systems is dominated by the E value for poly(ethylene), especially as far as the alloys are concerned PS-rich systems are characterized by a high tensile modulus, close to that predicted by a linear mixing rule In the elastic region of deformation, the chain coils and van der Waals distances are reversibly strained In poly(ethylene), which is of high entanglement density, the stretching of polymer chains occurs under low stress value, whereas the corresponding strain value is pretty high Therefore LDPE and LDPE-dominated systems are of low elasticity modulus To the contrary, the poly(styrene), having one order of magnitude lower ν_e-value is being stretched to the yield point at low strain but with considerable stress Interestingly, the elasticity modulus of PS is one order of magnitude higher than that of LDPE

The tensile strength of LDPE/PS systems represents similar correlations, the values are determinated by the component dominating the system Therefore, the predominant mode of fracture (crazing/yielding) should be the same as that of the matrix

The analysis of the elongation at break versus the content of specific polymers led to interesting

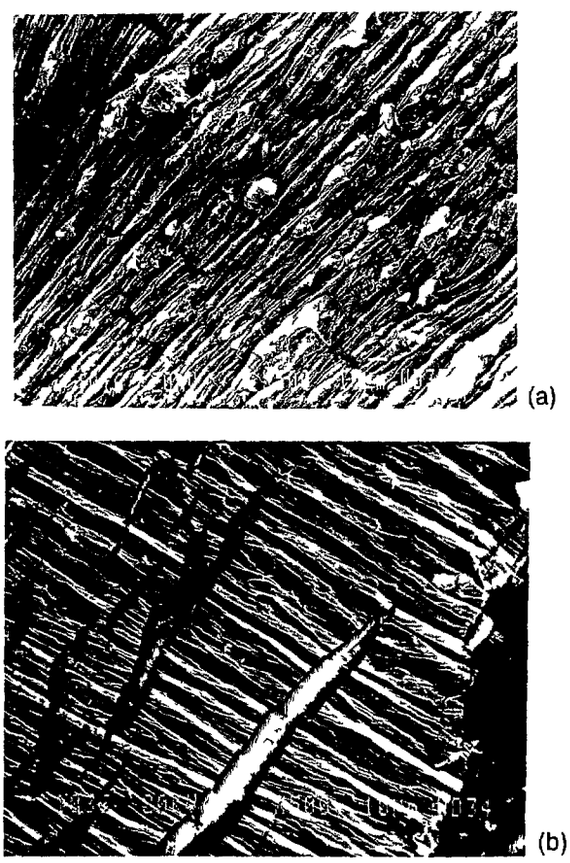

Figure 2 SEM micrographs of LDPE/PS 85/15 blend failure surface (a) and in axis cold fracture in a damage region (b)

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findings The blend containing 15 wt % of PS shows elongation equal to approximately 50% that of LDPE itself The corresponding ϵ-value for the alloy is equal to that theoretically predicted according to

$$\varepsilon = \varnothing_1\varepsilon_1 + \varnothing_2\varepsilon_2 \quad (4)$$

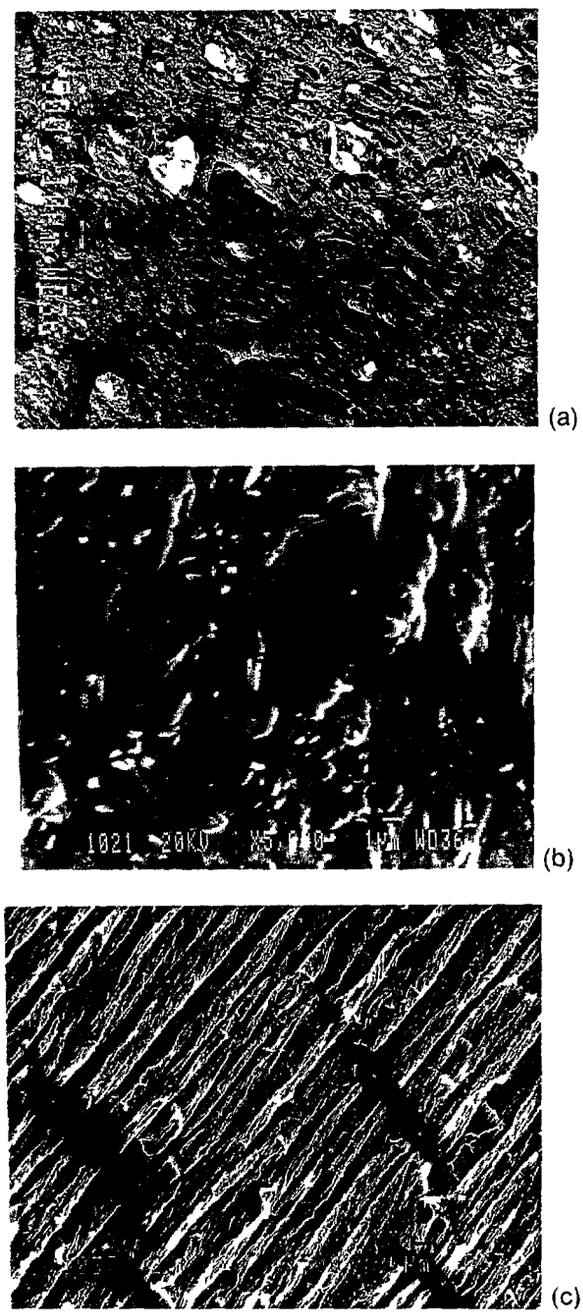

Figure 3 Morphology of LDPE/PS 85/15 alloy failure surface (a) and (b)—higher magnification In axis cold fracture (c)

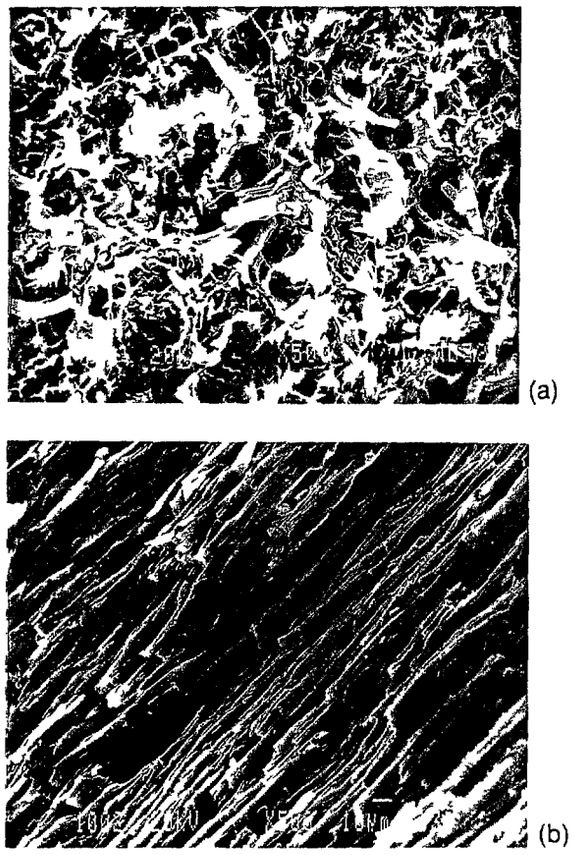

Figure 4 SEM micrographs of LDPE/PS 2 1 blend failure surface (a) and longitudinal cold fracture (b)

where indexes 1 and 2 refer, respectively, to the component polymers

In turn, the elongation of the blend LDPE/PS 2 1 is like that of poly(styrene), whereas the elon gation of the system containing an additional 5% of SEBS copolymer is one order of magnitude higher It has been found that both the blend and alloy dominated by PS exhibit the elongation at break typical of this polymer

Such characteristic changes of the parameters describing the tensile tests course suggest specific phase structure differences for individual systems Considering micromechanics and the microstruc tural and molecular analysis, one can expect an in terpenetrating type of the blend and allov LDPE/ PS 1 2 and of the blend LDPE/PS 2 1 Moreover, similar characteristics of the blend containing 85 wt % of LDPE and the alloy of 67 wt % of LDPE allow us to expect similarities in their morphology The above expectations have been confronted with the actual phase structure of LDPE/PS systems, observed by means of scanning electron microscopy

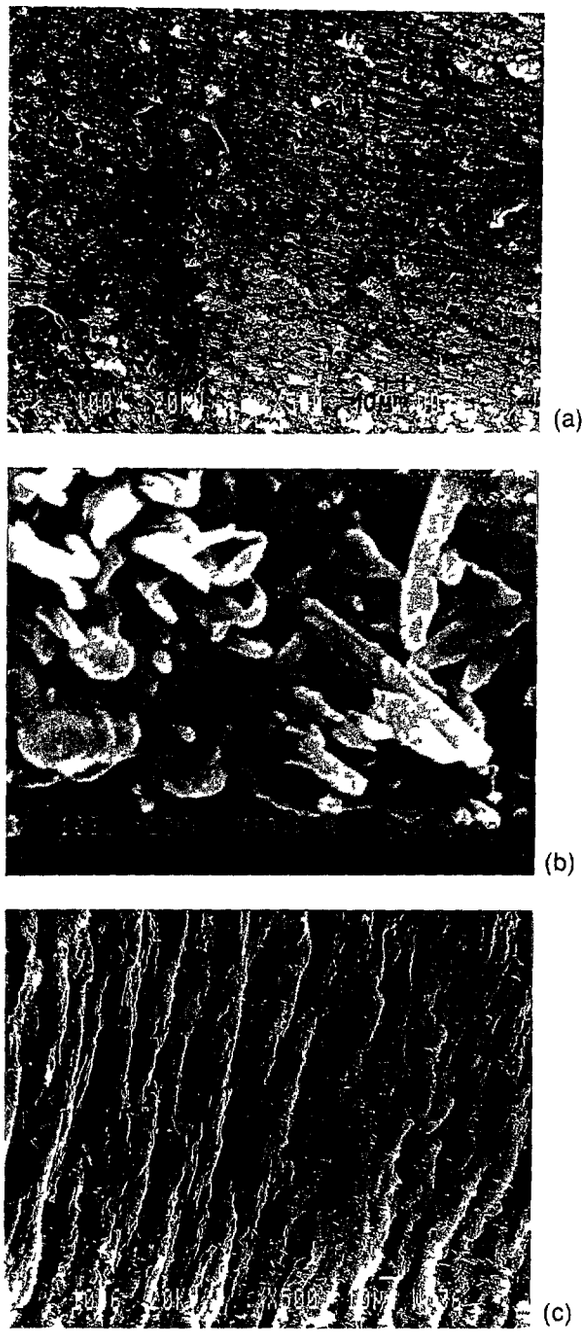

Figure 5 Morphology of LDPE/PS 2 1 alloy failure surface (a) and (b)—higher magnification In axis cold fracture (c)

Morphology

The systems containing 15 wt % of poly(styrene) (Figs 2 and 3) represent heterogeneous morphology within which characteristic regions of high orientation have been recognized (Figs 2[b] and 3[c]) We ascribe these regions to poly(ethylene) the flexible phase of which flows under tensile stress The blend is of stratified morphology, composed with sheets of few μm thickness (Fig 2[a]) In a failured specimen (Fig 2[b]), fractures can be observed perpendicular to the stretching axis ("crazes") The crazes are typical of brittle polymers such as PS Therefore we suppose that the PS domains are big

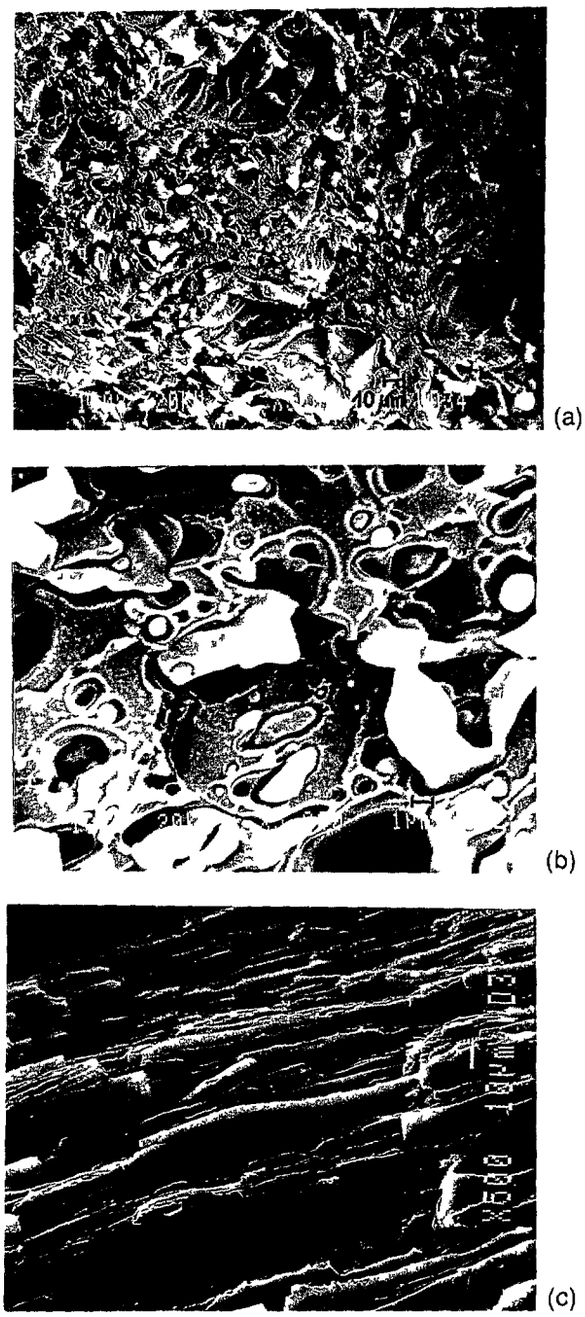

Figure 6 SEM micrographs of LDPE/PS 1 2 blend failure surface (a) and (b)—higher magnification Longitudinal cold fracture (c)

enough to initiate microcracks in the system A part of the overall fracture energy W is consumed for the crack development, including the debonding of the interface LDPE/PS and the yielding of poly(ethylene) bridges The microfilaments observed in a crack zone have resulted from the plastic de formation of the ductile polymer

Higher microheterogeneity of the alloy (Figs 3[2] and 3[b]) and lack of "crazes" (Fig 3[c]) evidences considerably smaller domains of PS (ca 0 5 μm) and diminishing of the interfacial tension In a macro scale this has been observed as a much higher elongation at break for the alloy in comparison to the blend

Increasing the PS content to 33 wt % resulted in a significant change of the blend phase structure (Fig 4) Instead of stratification, the interconnecting structure revealed threads of 2–10 μm width This finding supposed that the percolation threshold had been surpassed The failure took place in the poly(styrene) phase with the elongation being characteristic of this polymer Successive morphology change was observed after the addition of the block copolymer (Fig 5) The alloy LDPE/PS 2 1 represents a dispersive structure of fibrillar type, with fibers of 0 4–0 8 diameter (Fig 5[b]) A similar mode of the phase structure was observed for the alloy containing 15 wt % of PS The change of interactions between the phases and breaking of the continuity within the PS phase resulted in the increase of the elongation at break of one decade This suggests that a significant part of the fracture energy W was transmitted by the poly(ethylene) fibrils, being clearly seen at magnification 10,000×

The system LDPE/PS 1 2 is again of an inter penetrating type as far as the blend is concerned (Fig 6) and microdispersive in the case of the alloy (Fig 7) Width of the threads in polyblend is 1–10 μm (Figs 6[a] and 6[b]), whereas the fibers in poly alloy are of 0 4–0 8 μm diameter (Fig 7[b]) The dominating character of the poly(styrene) matrix is decisive for tensile properties The continuity of the PS phase caused the samples to fail at a low elon gation and under stress twice as high as that ob served for other systems

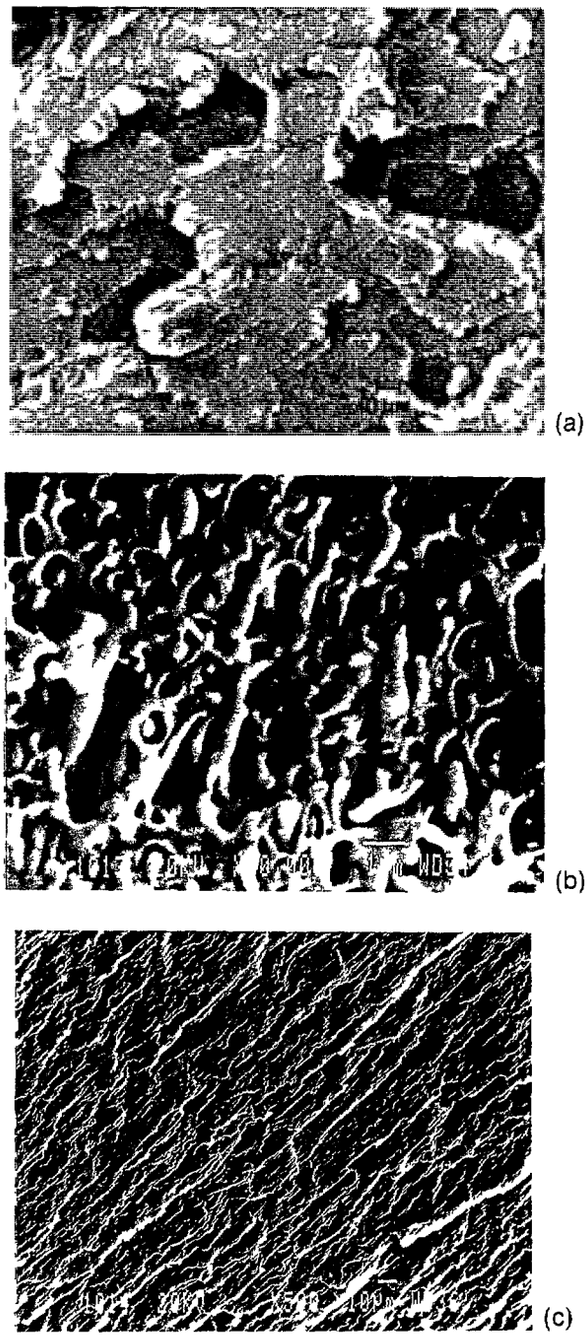

Figure 7 Morphhology of LDPE/PS 1 2 alloy failure surface (a) and (b)—higher magnification In axis cold fracture (c)

CONCLUSIONS

1 Properties of heterogeneous LDPE/PS systems depend on the component ratio and on the compatibilizer content
2 Block copolymer of compatibilizing activity enhanced melt viscosity and elasticity of LDPE/PS systems Addition of the SEBS copolymer caused decreasing of the dispersed-phase domains
3 Tensile strength and deformability for the systems of the disperse morphology are determined by the type of the matrix (brittle/ductile) and by the domain size of the dis

persed phase In case of interpenetrating type morphology, the polymer systems fail by the brittle/ductile mode depending on the component of the lowest crazing/yielding stress

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Electrically Conductive Structured Polymer Blends

M Kozlowski
Research Development and Consulting Center POLYMAK Trentowskiego 21 PL 52 430 Wroclaw Poland

The efficiency of eight carbon black grades as electrically conductive fillers was evaluated for plastic composites The polymer matrix components were polystyrene PS polyethylene LDPE their blends and alloys The volume and surface resistivity melt rheology morphology and tensile properties were studied Significant improvement in conductivity was found for the composites containing Ketjenblack EC 600 JD from Akzo Nobel Chemicals Multicomponent matrices were more suitable for preparation of electrically conductive plastics of a low CB content compared to plastics based on a single polymer matrix Because carbon black was located preferentially in LDPE phase the conducting filler content required to increase electrical conductivity of composite markedly decreased Interpretation of the results in terms of a multiple percolation concept allowed an explanation of such low percolation threshold as 0 01 of carbon black in LDPE/PS blends

Keywords Carbon Black Conductivity Morphology Percolation Polymer Composites Resistivity

INTRODUCTION

Polymers are, as a rule, electrical insulators Their conductivity is in the range of 10^{13} - 10^{-16} S/cm In order to make organic polymers intrinsically conductive, one has to introduce into macromolecules specific functional groups or atoms containing free electrons Polyaniline (PANI)[1] is a typical example of intrinsically conductive polymer Also, polyacetylene, polyphenylene, and polypyrolle are included in a group of intrinsically conductive polymers [2-4] These polymers have been reported in technological applications of the new plastic materials The conductivity level for this class of polymers is around 10^2 S/cm, whereas conductivity of copper is 5 9 x 10^5 S/cm and 6 3 x 10^5 S/cm of silver

Mixing polymers with electrically conductive fillers is a common practice for increasing their conductivity Such fillers are usually metals, carbon black, or intrinsically conducting polymers As a rule, fillers are in a form of fine powder, however by using fibers or flakes one can enhance their performance and reduce their concentration Carbon black, CB, is widely used because it is less expensive and lighter than metallic particles Depending on a filler content, one may obtain insulating antistatic, or electrically conductive material

Increasing the conductive filler content in a composite one observes a familiar insulator-to-conductor transition Classical percolation estimates the critical volume fraction at 0 156 [5] According to the percolation theory, above the critical content of a filler, conductive pathways are formed throughout a matrix material, making filled polymer conductive At the critical filler content, the quantum mechanical tunneling between the conducting particles and the interfacial phenomena at the CB-polymer matrix surface are prevailing Below the percolation threshold the hopping charge carrier transport has the highest contribution to the conductivity mechanism

As the distribution of a filler is crucial for the electrical conductivity level, blending different polymers opens unlimited horizons for possible structures in polymer blends, such as filler location within one polymer phase, its distribution between both phases or location at the interface All these parameters influence the conductivity level at a given amount of filler content Recently, the amount of papers on the conductivity of polymer blends filled with carbon black has increased rapidly A comprehensive review on this subject is currently being prepared [6] Numerous authors refer to a widely known observation from the rubber industry that CB used as a reinforcing filler in rubber blends is often unevenly distributed between the phases Hetero-distribution of the conductive filler may give an additional advantage, such as decrease of concentration required to obtain electrically conductive composite

In some cases, the addition of filler may deteriorate the mechanical properties of polymer, using the lowest possible filler content offers advantage Searching for an appropriate compromise of conductivity level and mechanical strength, many researchers investigate highly sophisticated structures in heterogeneous polymer blends, aiming at development of a network of the conductive paths through the material and providing a high interfacial adhesion - as equally important for the end-use properties Sumita *et al* [7] revealed uneven CB distribution in components of HDPE/PMMA and PMMA/PS blends They detected the blend ratio, at which the structural connectivity of a filler-rich phase is formed The filler content is another main factor determining the electrical conductivity of polymer composites Because both factors affect the conductivity simultaneously, the double percolation approach has been introduced

Levon *et al* [8] gave an explanation for a very low percolation threshold, $\varnothing_c$, in conductive polymer blends, which is due to their phase separation Referring to the system of ethylene-co-vinyl acetate and poly(3-octylthiophene) as a conducting polymer the authors concluded that the phase separation and crystallization are the main

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processes, which influence generation of an interconnecting structure, giving the desirable conductivity to the system

Gubbels *et al* [9] reported a selective localization of carbon black in multiphase system PE/PS as a very efficient method for decreasing the percolation threshold The authors indicated the percolation level of 0 002, being reached at a very specific localization of CB at the interface of the blend

Modelling of the polymer blends morphology made recently significant progress - basic rules have been defined according to the theoretical considerations and empirical evidences [10 14] Properties of heterogeneous systems, as closely related to their phase structure, may be a priori predicted with a high probability, provided that the viscoelastic properties of components, interfacial tension, and the processing history are known

Recently, we have studied the morphology formation in the model LDPE/PS blends and alloys [15] We concluded that a detailed description of the mixing history (shear stress, residence time) is required for polymer blending as equally important for the resultant morphology as the type and concentration of components Generation of a disperse, stratified, or co-continuous morphology has been performed within a composition range of 35 wt% in a controlled manner The interpenetrating-type LDPE/PS blends and alloys are of the highest interest as far as the electrically conductive plastic materials are concerned Significant reduction of filler content can be achieved, if a selective distribution in only one phase is possible Our goal in this study was to define preparation conditions of highly conductive polymer composites with a low carbon black content Different polymer grades and blends of virgin polymers in diversity of ratios, different CB-grades and CB-content, as well as mixing technology were among the factors studied regarding their influence on the conductivity and morphology

EXPERIMENTAL

MATERIALS

Commercial grade polystyrene, PS, from ZCh Oswiecim, Poland and low density polyethylene, LDPE, from ZCh Blachownia, Poland have been used in the study Three grades of LDPE have been in the form of pellets, whereas three others in a powder form Particular grades differed in a flowability in the MFI range of 0 86 - 20 0 g/10 min Characteristics of LDPE grades are presented in Table 1

Partially hydrogenated poly(styrene-b-isoprene) diblock copolymer, Kraton G1701 from Shell Chemicals has been added as a compatibilizer

Eight different grades of electrically conductive carbon black have been supplied by Akzo Nobel Chemicals, Netherlands, Cabot Co , USA, and Degussa AG, Germany All the grades have been declared as highly conductive The most important parameters which influence the CB-electroconductivity have been included in Table 2 The surface area, measured by iodine or nitrogen adsorption is a total sum of external and internal surface areas of the basic carbon particles in the primary aggregates The tendency to aggregation is characterized by the structure of carbon black, measured by di-butylphthalate, DBP, absorption The oxygen-containing organic groups formed on the CB surface, so called "volatiles", act as a barrier for the electron-tunneling effect, hence decreasing conductivity

Table 1 Characteristics of LDPE grades

LDPE code	LDPE grade	MFI g/10 min	Sample form
1	GGNX D006	0 86	pellets
2	HGNX D090	6 2	pellets
3	MGNX D200	20 0	pellets
4	P10C	8 3	powder
5	P11	17 3	powder
6	P11	20 0	powder

Table 2 Characteristics of carbon black grades

CB code	CB grade	DBP ml/100 mg	IOD mg/g	Density g/l	Volatiles %	Janzen s $Ø_c$
			AKZO Nobel - Ketjenblack			
1	EC 600JD	490	1077	107	0 6	2.5
2	EC 300J	327	752	134	0 7	3 7
			Cabot			
3	Vulcan P	115	175	322	1 0	9 8
4	Elftex 160	89	37	436		12.3
5	Vulcan XC72	171	284	278	1 5	6 8
			Degussa			
6	Printex XE2	367	1107	150	0 1	3 3
7	Printex L6	123		120	1 2	9 2
8	Printex L	118		200	0 8	9 6

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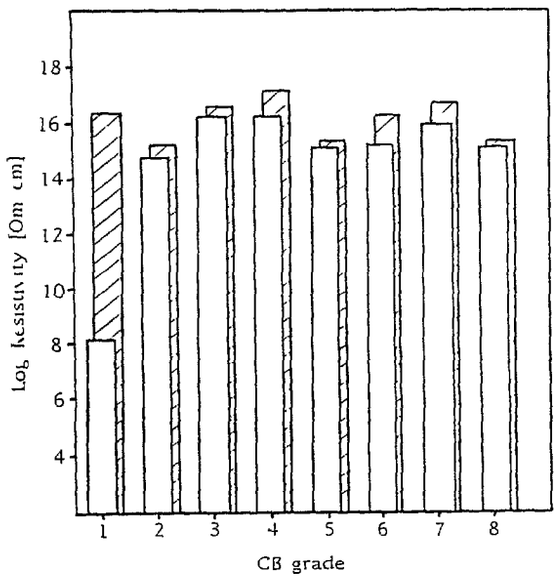

Figure 1 Resistivity of PS composites with different CB grades (2 wt% (hatched) and 6 wt% (white))

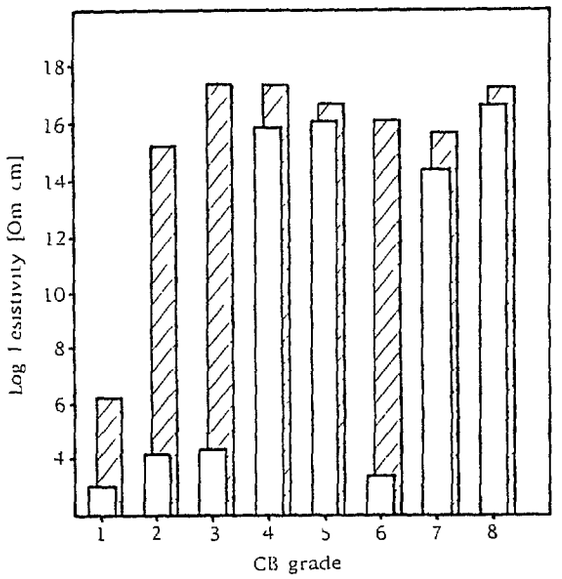

Figure 2 Resistivity of LDPE 1/PS 50/50 composites with different CB grades (2 wt% (hatched) and 6 wt% (white))

BLEND PREPARATION

Polymer components were mixed with carbon black using the Brabender Plasticorder mixing unit Composite plaques, approximately 1 mm thick, were compression molded at 170°C under pressure of 12 MPa for 5 minutes

Segregated blends were prepared by thorough mixing of the powdery components and subsequent compression molding under the same conditions as used for the melt-mixed blends

Samples for the electrical resistivity and mechanical strength measurements were cut out from the plaques

MEASUREMENTS

Volume resistivity, ρ, and surface resistivity, ρ_s, were estimated according to ASTM D257 We used the three-electrode electrometer arrangement for the DC-measurements of insulation resistance The apparatus used was Keithley 617 or Meratronic V 641, depending on the resistivity range Similarly, the voltage level was 100 V or 1 1 V The samples were Al-coated by evaporation prior to the measurements

Rheological measurements were performed with the capillary rheometer type MCR 32 10 at 190°C The capillary used had diameter, d = 1 27 mm, and length to diameter ratio, L/d = 40 The Rabinowitch correction was applied, whereas the Bagley correction was neglected because of the high L/d ratio

Tensile tests were performed at room temperature using the FU 1000 eZ machine The crosshead speed was 50 mm/min The tensile modulus of elasticity, E tensile strength, σ_r and the elongation at break ε were registered

Morphology inspections were performed by means of scanning electron microscopy, SEM Freeze-fractured and microtomed surfaces were vacuum-coated with the Au/Pd layer and then observed using the scanning electron microscope JEOL JSM-5400, operating at 15 kV

RESULTS AND DISCUSSION

COMPARISON OF CB GRADES

The efficiency of particular CB grades, as electrically conductive fillers for PS and LDPE/PS systems, was compared for the melt-mixed composites with 2 wt% and 6 wt% of carbon black

Volume resistivity of PS-CB composites has been presented on Figure 1 Resistivity of all composites with 2 wt% of a filler exceeded 10^{15} Ohm cm Increasing the carbon black content up to 6 wt%, we have found a significant conductivity improvement in the case of EC-600 JD (10^8 Ohm cm)

Similarly, the resistivity of composites based on LDPE/PS 50/50 matrix (Figure 2) was above 10^{15} Ohm cm at 2 wt% of CB, with the only exception of the above mentioned CB-grade (10^6 Ohm cm) Increasing the filler content up to 6 wt%, we evidenced higher conductivity for four carbon black grades (below 10^4 Ohm cm) The lowest resistivity value (10^3 Ohm cm) was found again for the composite with the carbon black Ketjenblack EC-600 JD This grade has been chosen for further experiments because it provided the highest electrical conductivity

Our results are in a good agreement with Janzen s predictions based on a particle contact percolation [16] Janzen proposed the following equation to relate the perco-

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Figure 3 Structure of Ketjenblack EC 600 JD carbon black

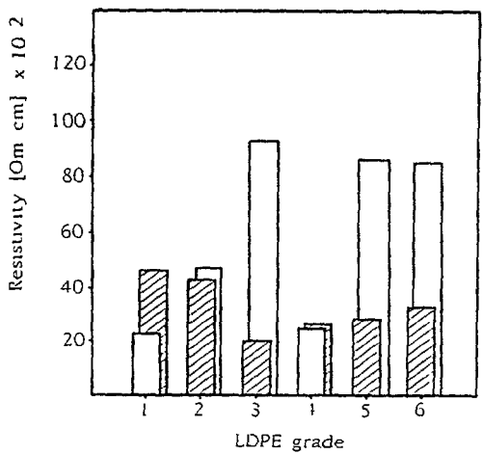

Figure 4 Resistivity of LDPE/PS 50/50 blends (white) and alloys with 6 wt% of EC 600 JD (hatched) for different LDPE grades

lation threshold, $\varnothing_c$, to the structure of carbon black in the CB-composites

$$\varnothing_c = (1 + 4\varphi v)^{-1} \quad [1]$$

where φ = density of the filler, v = dibutylphthalate (DBP) value in cm^3/g as a measure of the specific void space of random dense packed filler

Theoretically predicted $\varnothing_c$ for CB-grades used through this study are shown in Table 2 The percolation threshold calculated for Ketjenblack EC-600 JD is 0 025 - the lowest among all carbon blacks investigated Only two other grades may be compared to EC-600 JD Ketjenblack EC-300 J and Printex XE2 - next five are less efficient In fact Ketjenblack EC-600 JD is reported as an ultra-high efficiency black determined by the amount needed to reach a certain level of conductivity in polymer composites which is several times lower than that of other high-conductive blacks [17]

High DBP-value, observed for this CB-grade, indicates a high pore volume and thus a high structure (aggregation of basic carbonic particles into highly branched species) This method measures both intra- and inter-aggregate pore volume Maximum packing fraction of Ketjenblack is 0 11, whereas its value for other CB-grades is in a range of 0 22-0 33 High porosity and branching mean better contact between aggregates, resulting in better electroconductivity The well developed structure of Ketjenblack EC-600 JD is illustrated in Figure 3

SIGNIFICANCE OF LDPE GRADE AND COMPATIBILIZER

Composites LDPE/PS 50/50 with 6 wt% of carbon black were prepared with different polyethylene grades, then the volume and surface resistivity were measured The volume resistivity is shown in Figure 4 Composites with LDPE-grades of higher melt viscosity provided higher conductivity (2×10^3 Ohm cm) in comparison to that based on the lower-viscous grades (9×10^3 Ohm cm)

The influence of a compatibilizer on the electrical conductivity of LDPE/PS 50/50 system containing 6 wt% of CB is also shown on Figure 4 Significant decrease in resistivity of the alloys in comparison to that of blends, observed in case of polyethylene grades of higher MFI-value may be attributed to the viscosity increase caused by the compatibilizer and, in turn, to a better dispersion of carbon black particles in the alloy Higher stress level in the melt is favorable for disaggregation of large CB-domains into smaller aggregates and primary particles, which eventually form the conducting paths

The influence of the carbon black content on the conductivity level for different LDPE-grades has been presented in Figure 5 Composites containing 4 and 6 wt% of the filler are fairly well conductive (10^3-10^4 Ohm cm), contrary to that with 1 wt% of CB (10^{13}-10^{16} Ohm cm) which is clearly below the percolation threshold Among all composites the lowest resistivity values have been observed for the composites based on the LDPE-grade of the lowest MFI-value

The estimation of the LDPE/PS ratio (2/1, 1/1, 1/2) effect on resistivity of the composites containing 6 wt% of carbon black evidenced that for all polymer blends the resistivity is in the range of the neat polyethylene-based composites (10^2-10^4 Ohm cm Figure 6) Taking into account a markedly higher resistivity of the neat polystyrene composites (10^8 Ohm cm), one observes a negative deviation from the additivity rule in case of the matrices composed of polymer blends The lowest resistivity level observed for composites based on LDPE/PS 1/2 matrix allows a suggestion that carbon black has been located preferentially in polyethylene Relative increase of CB-

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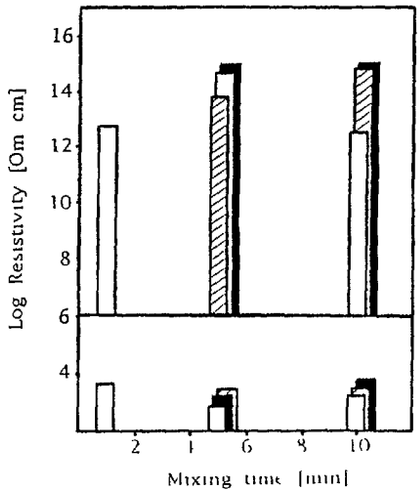

Figure 8 Resistivity of LDPE/PS 50/50 composites with 6 wt % (bottom) and 2 wt % CB versus mixing time ((white) LDPE 1 (hatched) LDPE 2 (black) LDPE 3)

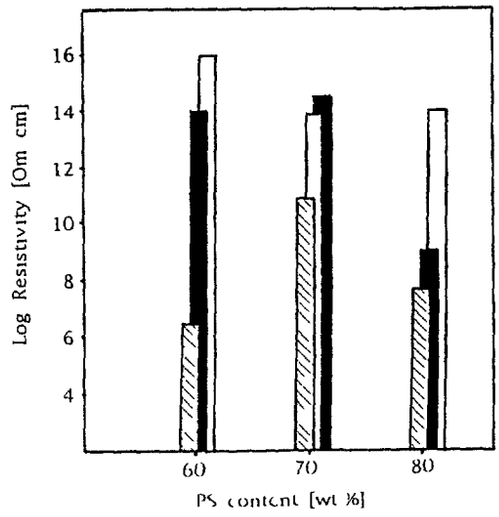

Figure 10 Resistivity of LDPE/PS composites mixed at 210°C ((white) 1 wt% of CB (black) 2 wt% (hatched) 3 wt%)

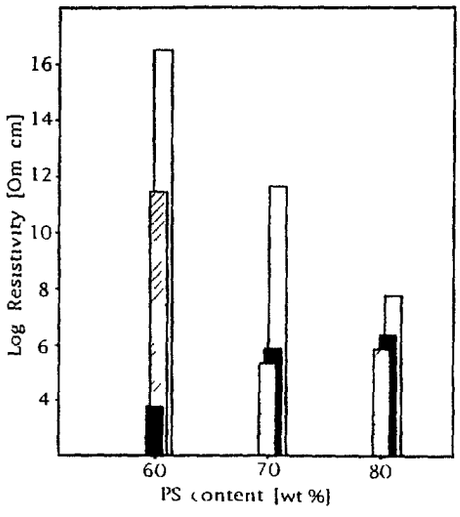

Figure 9 Resistivity of LDPE/PS composites mixed at 190°C ((white) 1 wt% of CB (hatched) 2 wt% (black) 3 wt%)

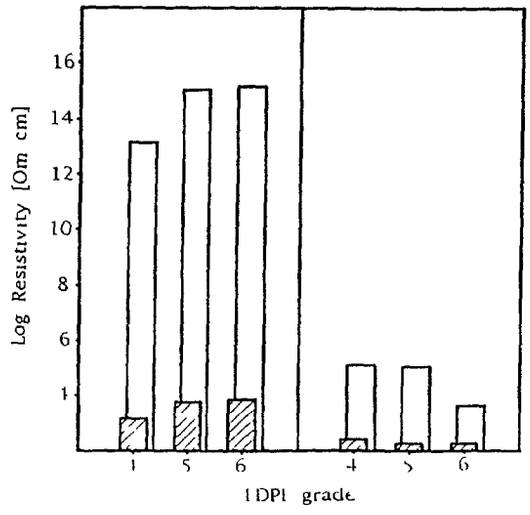

Figure 11 Resistivity of LDPS/PS 50/50 composites with 6 wt% (hatched) and 2 wt% (white) of CB for different LDPE grades Melt mixed (on left) and segregated

disadvantageous to the desirable heterogeneous blends with carbon black located in only one component (preferably at the interface)

Segregated blends LDPE/PS 50/50 were prepared using LDPE grades 4-6 The volume resistivity of the melt-mixed and segregated composites has been compared in Figure 11 The segregated blends exhibit much higher electrical conductivity, especially if we compare the composites containing 2 wt% CB This implies that a percolation threshold in the segregated blends lies at much lower CB content than in the melt-mixed blends High anisotropy of the segregated structures is suggested, based on comparison of the surface resistivity of the melt-mixed versus segregated composites (Figure 12) The honeycomb structures with conducting CB-pathways, expected in such systems, are probably better developed across the sample than in the planar direction Results obtained for the segregated-type composites suggest that easily flowing components should be used for their preparation

Summarizing the results of the volume versus surface resistivity for the composites based on LDPE/PS blends and alloys of various compositions in Figure 13, we expect entirely different conductivity character for the two kinds of composites prepared with different technologies

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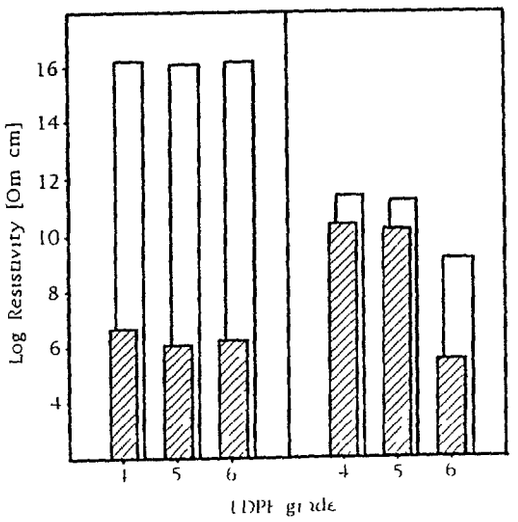

Figure 12 Surface resistivity of LDPE/PS 50/50 composites with 6 wt % (hatched) and 2 wt % (white) of CB for different LDPE grades Melt mixed (on left) and segregated blends

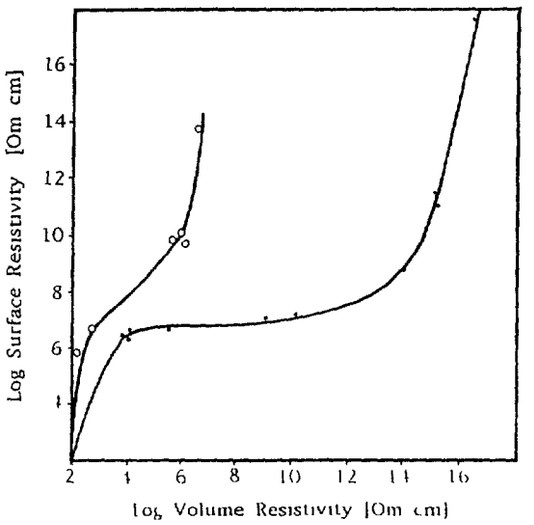

Figure 13 Surface versus volume resistivity for LDPE/PS composites Segregated (O) and melt mixed (●) blends

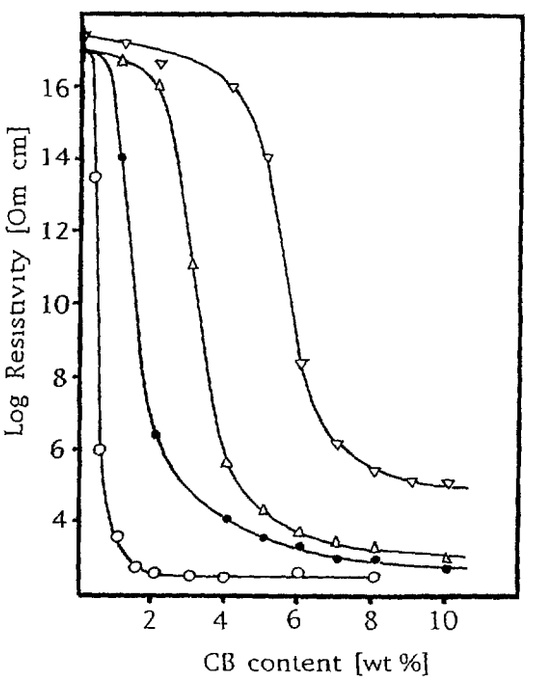

Figure 14 Resistivity of composites with different CB content (▽ PS matrix △ LDPE 1 matrix ● LDPE/PS 50/50 melt mixed O LDPE/PS 50/50 segregated)

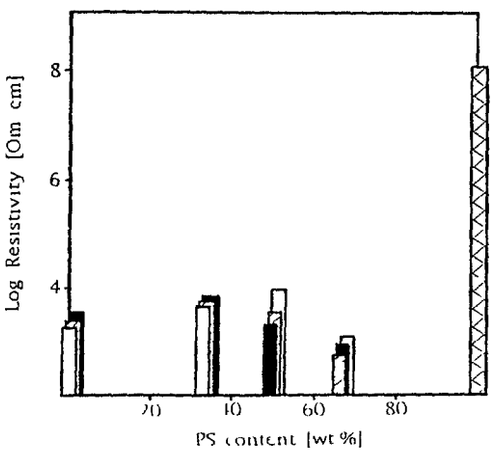

Figure 15 Resistivity of LDPE/PS composites with 6 wt% of CB versus composition ((black) LDPE 1 (hatched) LDPE 2 (white) LDPE 3)

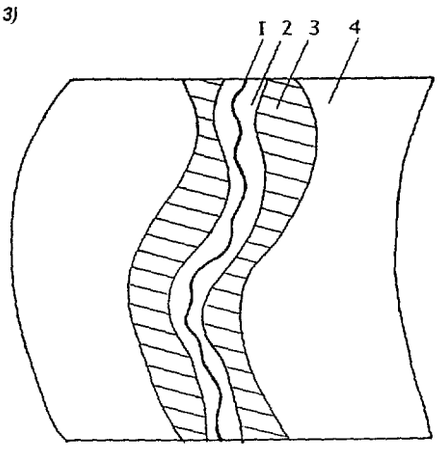

Figure 16 Scheme of multiple percolation in electrically conductive composites (1 CB 2 amorphous phase of LDPE 3 crystalline LDPE 4-PS)

CARBON BLACK CONTENT

The results presented above have shown that polymer composites with the carbon black EC-600 JD are conductive at a much lower content of the filler than expected theoretically The primary reason is a specific structure of the filler itself The conductivity threshold depends also on the polymer-matrix composition and on the processing technique

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The volume resistivity versus CB-content for the segregated and melt-mixed blends LDPE/PS 50/50, as well as for LDPE and PS, have been summarized in Figure 14 The dependence has familiar Z-shape for LDPE and PS It is similar for blends, but the percolation threshold $Ø_c$ is located at a significantly lower CB content Segregated-type composites exhibit the dependence of a more asymptotic character (L-shaped)

In the figures, one can distinguish two critical regions We relate the upper (drop in resistivity) to the formation of the first conducting path through a composite, with an electron tunneling effect between CB particles At this loading, which we define as a primary percolation, $Ø_p$, the material loses its insulating properties The lower critical region, at a slightly higher filler content, in our interpretation, corresponds to a well developed conducting network of carbon black particles, contacting directly each other Higher CB loadings do not influence markedly the overall conductivity of the material The majority of researchers estimate this critical region as the percolation threshold, $Ø_c$ The resistivity - filler content dependence at critical regions can be fairly well described analytically by the scaling relation

$$\rho = C(Ø - Ø_{p/c})^t \qquad [3]$$

where C, $Ø_p$, $Ø_c$, and t are fitting parameters

Table 4 contains values of the parameters which have been deduced from fits of the scaling law to the experimental data, for particular composites The t-value in the upper critical region is unusually high and constant (6 6), which can be related to a unique character of the single conductive path The t-values in the lower critical region are typical of the 2-dimensional percolation model (1 3) in case of the single-polymer matrices For the segregated LDPE/PS composites we found the power law exponent corresponding to the 3-dimensional percolation model (1 9)

Table 4 Critical parameters of Eq 3 for CB composites

Polymer Matrix	Primary percolation region		Conductive network region	
	$Ø_p$	t	$Ø_c$	t
PS	0 049	6 6	0 065	1 33
LDPE	0 028	6 6	0 042	1 35
melt mixed*	0 010	6 6	0 018	3 0
segregated*	0 002	6 6	0 005	2 0

*LDPE/PS 50/50

According to the existing theories, one can expect a multiple percolation in LDPE/PS melt-mixed composites At a particular ratio of the components we expect the formation of interpenetrating blends with a conducting filler located mainly in LDPE The results presented in Figures 6 and 15 allow one to define the mutual connectivity of polymer components in a range of 50-80 wt% of PS (depending on viscosity ratio) Our choice for LDPE 1/PS system is 70 wt% PS We expect that the conducting filler is located in an amorphous phase of LDPE, which amounts only 30 wt%

High conductivity may be reached, when the carbon black particles are located so close to each other that they form continuous conductive pathways (first level percolation CB percolation) Another interpenetration level is related to the amorphous phase of polyethylene in LDPE within which carbon black particles are located (second level percolation) Eventually, LDPE forms a network in PS (third level percolation) Schematic view of such self-similar fractal structure has been presented in Figure 16

A generalization of a scaling law for n-level percolation gives a following equation

$$\rho = C(Ø_1 - Ø_{c1})^{t_1}(Ø_2 - Ø_{c2})^{t_2} \quad (Ø_n - Ø_{cn})^t \qquad [4]$$

The effective exponent, t, estimated from a slop of the (log ρ) - log (Ø - $Ø_c$) graph may be compared to the theoretical one, expressed as follows

$$t = t_1 + t_2 + \quad + t_{n\ 1} \qquad [5]$$

In the case of LDPE/PS composites we found t = 3 0, which may result from a combination of the three- and two-dimensional percolation on particular levels of percolation (t = 1 9 + 1 3 = 3 1)

The effective percolation threshold, $Ø_c$, in turn, can be expressed by a relation

$$Ø_c = Ø_{c1} Ø_2 \quad Ø_{n\ 1} \qquad [6]$$

The multiple percolation concept can be effectively applied for explanation of such a low percolation threshold as 1 8 wt% (ca 0 01 in volume parts), observed in the case of composites based on LDPE/PS blends ($Ø_c$=0 16 x 0 4 x 0 25 = 0 016) Respective polynomial components denote the classical percolation threshold, the amorphous phase fraction in LDPE, and polyethylene content in a blend

The critical CB content of 0 5 wt% which has been found for segregated blends has its origins also in percolation, but one of different evolution PS spheres are suspended in LDPE, first melted while being compression molded Carbon black particles can be located at the interface of such blend, heterogeneous for physical reasons This specific percolation mode (interfacial percolation) is characterized by very low critical concentration

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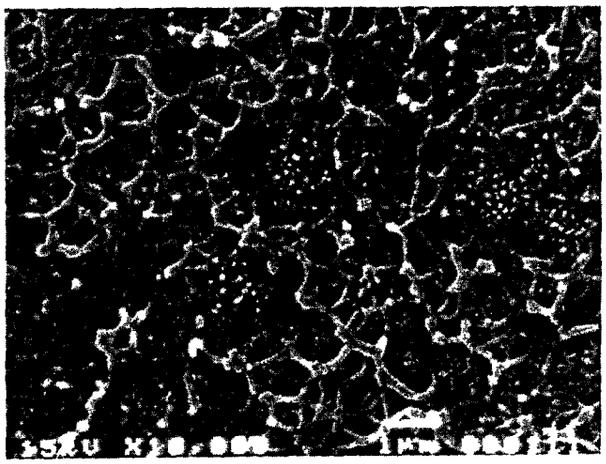

Figure 17 SEM micrograph of PS carbon black composite with 6 wt% of CB

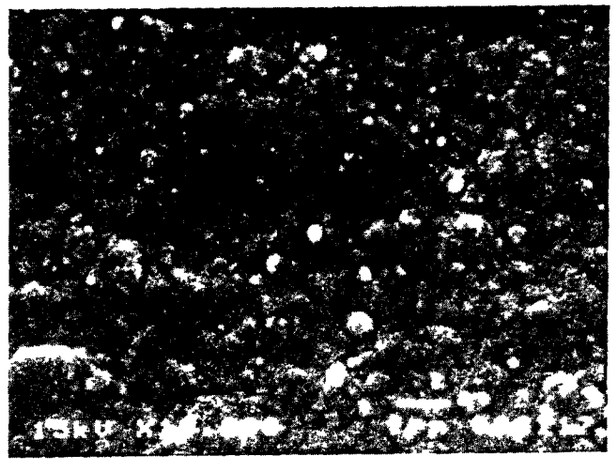

Figure 18 SEM micrograph of LDPE carbon black composite with 6 wt% CB

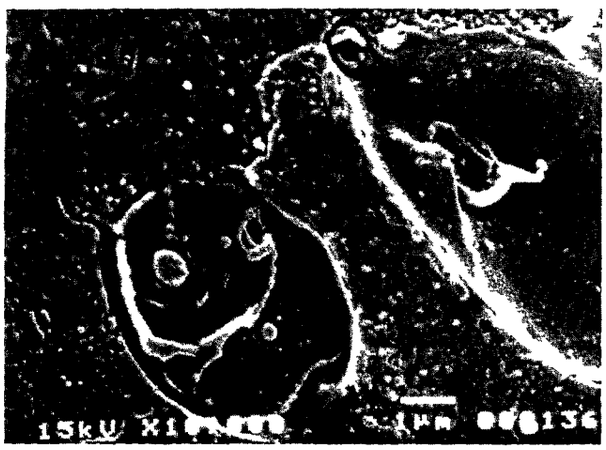

Figure 19 SEM micrograph of LDPE/PS 50/50 composite with 6 wt% of CB

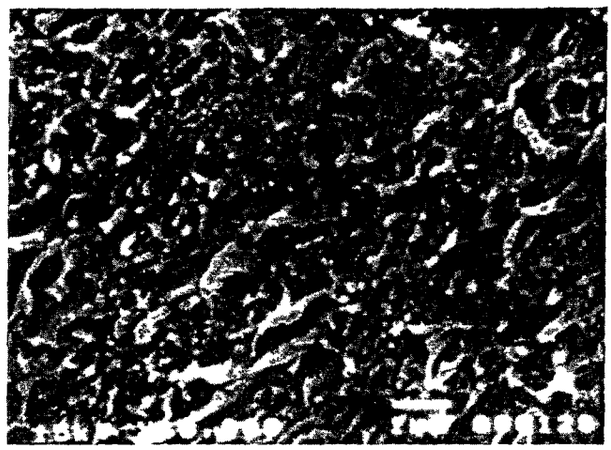

Figure 20 Morphology of compatibilized LDPE/PS 50/50 compos ite with 6 wt% of CB

of filler, because of microdimensions of the interface layer Our result is comparable to that of Klason *et al* [20] (0 5 vol %) and Gubbels *et al* [9] (0 4 wt %) Kryszewski *et al* [21] reported a percolation threshold of 0 2% whereas Chapoy[22] even 0 02% Such extraordinary low percolation threshold in comparison to the theoretically predicted value, one may obtain in highly oriented heterogeneous systems with molecular dimensions of the conductive phase (metallic' crystals, nematic thermotropic liquid crystals, interfaces)

MORPHOLOGY OF THE COMPOSITES

SEM inspections allowed us for the straight evidences of morphology The PS-CB composite (Figure 17) contains clearly visible carbon black aggregates, whereas in LDPE-CB composites fairly well distributed carbon black particles have been evidenced (Figure 18) Higher affinity of CB to LDPE than to PS can be seen in Figure 19 - the majority of carbon black has been located in LDPE phase Large domains of PS in LDPE/PS 50/50 blend are unfavourable to the volume conductivity of the material After the addition of a compatibilizer the phase structure changed from a disperse into interpenetrating one (Figure 20)

The well developed interconnecting morphology in LDPE/PS 30/70 blend (Figure 21) confirmed our supposition on multiple percolation, discussed above

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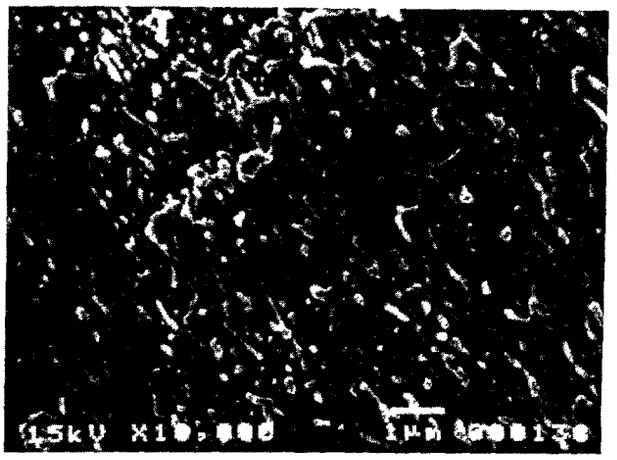

Figure 21 SEM micrograph of LDPE/PS 30/70 composite with 6 wt% of CB

Table 5 Mechanical properties

Polymer matrix	CB content	Tensile modulus	Tensile strength	Elongation at break
	%	MPa	MPa	%
PS	0	2600	54 1	4 6
LDPE	0	230	16 0	70 0
LDPE	6	238	9 8	35 1
melt mixed*	1	710	10 0	2 8
melt mixed*	6	496	4 0	2 3
segregated*	1	306	5 6	4 8
segregated*	6	448	1 1	2 9

*LDPE/PS 50/50

MECHANICAL PROPERTIES

Results of the tensile tests have been presented in Table 5 The results are in a good agreement with the earlier conclusion[23] that mechanical properties of LDPE/PS system are determined by the component dominating the system In case of interpenetrating blends, a failure occurs by the brittle/ductile-mode depending on the component of the lowest crazing/yielding stress

Increasing a filler content we observed a further drop in mechanical strength of the systems Comparison of the melt-mixed and segregated composites confirmed our observations that the last are out of the scope of practical applications because of their poor mechanical properties

CONCLUSIONS

Highly conductive materials were developed using LDPE and PS as the blended polymer matrix for carbon black composites Composite based on LDPE/PS 30/70 blend is of interpenetrating structure with the CB percolation threshold below 1 8 wt% Such low percolation level has been explained in terms of the multiple percolation concept

Structured blends offer the percolation threshold as low as 0 5 wt% of CB, but poor mechanical strength of such blends is a significant drawback

Carbon black Ketjenblack EC-600 JD has been shown as a grade of ultra-high conductivity

ACKNOWLEDGMENTS

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COMPARISON OF ELECTRICALLY CONDUCTIVE FILLERS IN POLYMER SYSTEMS

Marek Kozlowski and Anna Kozlowska

Research, Development and Consulting Center POLYMAK
Trentowskiego 21 PL 52 430 Wroclaw Poland

Abstract A comparative evaluation of different carbon black grades was performed for polymer composites whose matrices were composed of a single polymer or polymer blend. The electrical resistivity rheological properties tensile strength and morphology were evaluated The highest conductivity level was measured for the composites with Ketjenblack EC 600 JD from Akzo Nobel

INTRODUCTION

It has been known that polymers are as a rule electrical insulators A common practice for increasing the conductivity of plastics is blending of the organic polymers with electrically conductive fillers Widely used filler is carbon black (CB) as much cheaper and lighter than metallic particles (Refs 1-4) Carbon black itself is a semi conductive material having an intrinsic resistivity of 0 01 0 1 [Ω cm] CB is available in a powder or pellets form ranging in size from 100 μm to a few milimeters The pellets are of hierarchical structure being composed of the agglomerates (typically 10 - 100 μm in size) which in turn contain the primary aggregates of a few micrometers diameter The aggregates consist of carbonic particles (30 100 nanometer in size) which are composed of a few thousand carbon crystallites (Refs 5 6)

Depending on a filler content in a composite one obtains the insulating antistatic or electrically conductive materials At particular CB level the familiar insulator to conductor transition occurs A conductive network is being formed from the primary aggregates The classical percolation estimates a critical volume fraction at 0 156 (Ref 7) However the producers of electrically conductive CB grades declare much lower percolation level above which the conductive pathways are formed through a matrix polymer The improved grades offer twice as much efficiency This is of great importance because a high degree of loading brings about deterioration of the mechanical properties and increase in the melt viscosity

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There exist numerous grades of carbon black which differ in their size structure porosity surface area and surface chemistry Obviously the conductivity of particular grades may be also different The goal of our study was a comparative evaluation of electrically conductive CB grades in polymer composites with the matrices composed of a single polymer or polymer blends The choice of a polymer is of importance to the final electroconductive properties In general the electroconductivity of a compound increases with increasing crystallinity and decreasing polarity or surface tension of a matrix polymer (Refs 5 6 8 9) The volume resistivity of polymer composites melt rheology tensile tests and morphology inspections have been included in the research program The estimated characteristics have been related to the physical properties of respective carbon blacks

EXPERIMENTAL PART

Materials

Eight grades of electrically conductive carbon blacks were evaluated The most important parameters which may influence the CB electroconductivity have been presented in Tab 1

Tab 1 Characteristics of the carbon black grades

CB code	CB grade	DBP ml/100g	IOD mg/g	Density g/l	Volatiles %	Janzen s $Ø_C$
	AKZO Nobel Ketjenblack					
1	EC 600JD	490	1 077	107	0 6	2 5
2	EC 300J	327	752	134	0 7	3 7
	Cabot					
3	Vulcan P	115	175	322	1 0	9 8
4	Elftex 160	89	37	436		12 3
5	Vulcan XC72	171	284	278	1 5	6 8
	Degussa					
6	Printex XE2	367	1 107	150	0 1	3 3
7	Printex L6	123		120	1 2	9 2
8	Printex L	118		200	0 8	9 6

The polymer components were polystyrene (PS) and low density polyethylene (LDPE) - an amorphous and semi crystalline polymer respectively In a multicomponent type matrix the polymers were blended in a weight ratio 1 1

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e tests and morphology
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n presented in Tab 1

Volatiles %	Janzen s $\varnothing_c$
0 6	2 5
0 7	3 7
1 0	9 8
	12 3
1 5	6 8
0 1	3 3
1 2	9 2
0 8	9 6

olyethylene (LDPE) an
mponent type matrix the

Sample Preparation

Polymer components were mixed with carbon black at 190 C using [illegible] Plasticorder mixing head Samples for measurements were cut out from [illegible] molded plaques The mixing parameters and molding conditions were kept identical to all composites in order to avoid a possible influence of other factors on the conductivity [illegible]

Measurements

Electrical measurements were performed with the three electrode electrometer [illegible] for DC measurements The samples were Al coated by evaporation prior to the measurements The direct current measurements were carried out using the Keithley 617 or Metrohm [illegible] electrometers

Melt viscosity was measured using the capillary rheometer type Instron MCR 3210 at 190 C Rheological measurements were performed with a capillary diameter of 1 27 mm and L d ratio of 40 The Rabinowitch correction was applied, whereas the Bagley correction was neglected because of the high L/d ratio

Mechanical strength was evaluated with tensile tests at room temperature and the crosshead speed of 50 mm/min The tensile modulus of elasticity E tensile strength σ_r and elongation at break ε were registered

Morphology inspections were performed by means of scanning electron microscopy (SEM) The surface of freeze fractured samples was vacuum coated with the Au Pd [illegible] and observed using the scanning electron microscope JEOL JSM 5100

RESULTS AND DISCUSSION

The efficiency of particular CB grades as electrically conductive fillers was estimated for PS and LDPE/PS systems loaded with 2 wt % and 6 wt % of CB Results of the volume resistivity are shown on Figures 1 and 2 Significant improvement in conductivity was found for the composites with Ketjenblack EC 600 JD from Akzo Nobel

PS composites with 2 wt % of a filler are of poor conductivity for all CB grades Raising amount of carbon black up to 6 wt % one obtains only slight decrease in resistivity with the only exclusion for the composite with EC 600 JD whose resistivity was reduced to eight decades

Multicomponent matrices were shown to be better suitable for preparation of the conductive plastics with a low CB content in comparison to the PS matrix alone Although the resistivity of composites based on LDPE/PS 50/50 matrix is still high (above 10^{15} [Ω cm]) for [illegible] of 2 wt % of every CB grade excluding Ketjenblack EC 600 JD (10^{9} [Ω cm]) [illegible] carbon black up to 6 wt % brings about the markedly improved conductivity for [illegible]

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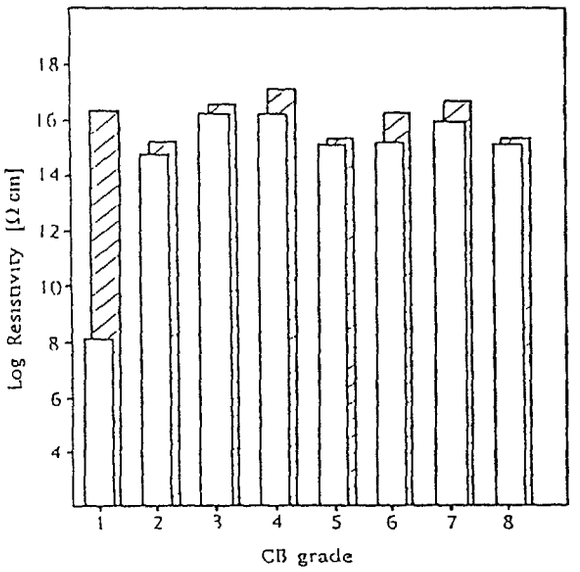

Fig 1 Resistivity of PS composites with different CB grades - 2 wt.% (hatched) and 6 wt.%

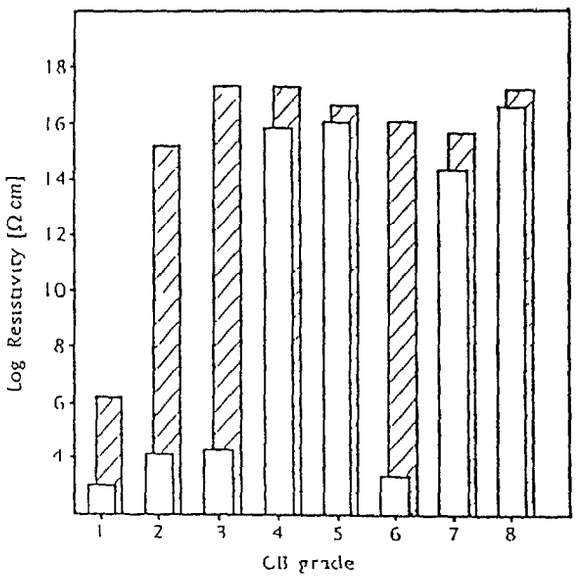

Fig 2 Resistivity of LDPE/PS 50/50 composites with 2 wt.% (hatched) and 6 wt.% of CB

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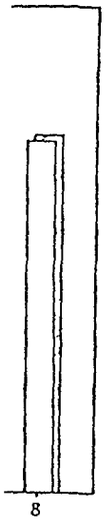

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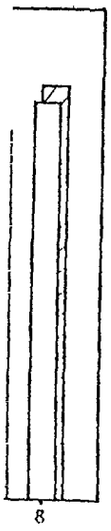
6 (hatched) and 6 wt.%



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d) and 6 wt.% of CB

with four CB-grades Both Akzo Nobel products and two blacks from Cabot and D [illegible] respectively gave a resistivity level below 10^4 [Ω cm]

Significant increase in electrical conductivity of the composites based on a two component matrix may be assigned to the particular morphology of a system LDPE/PS 50/50 blend [illegible] of interpenetrating type (Ref 10) with carbon black being located preferentially in polyethylene These observations may explain the lower percolation treshold for multicomponent systems Our results are in a good agreement with Janzen s predictions based on a particle contact percolation (Table 1) Janzen (Ref 11) proposed the following equation to relate the percolation treshold $\varnothing_c$ to the structure of carbon black in the CB composites

$$\varnothing_c = (1 + 4\varphi\nu)^{-1} \qquad (1)$$

where φ density of the filler and ν dibutylphthalate (DBP) value cm^3/g as a measure of the specific void space of random dense packed filler

Melt viscosity of composites is higher than that of polymers without filler (Fig 3) The flow curves exhibit non Newtonian behavior with negligible differences between particular CB grades

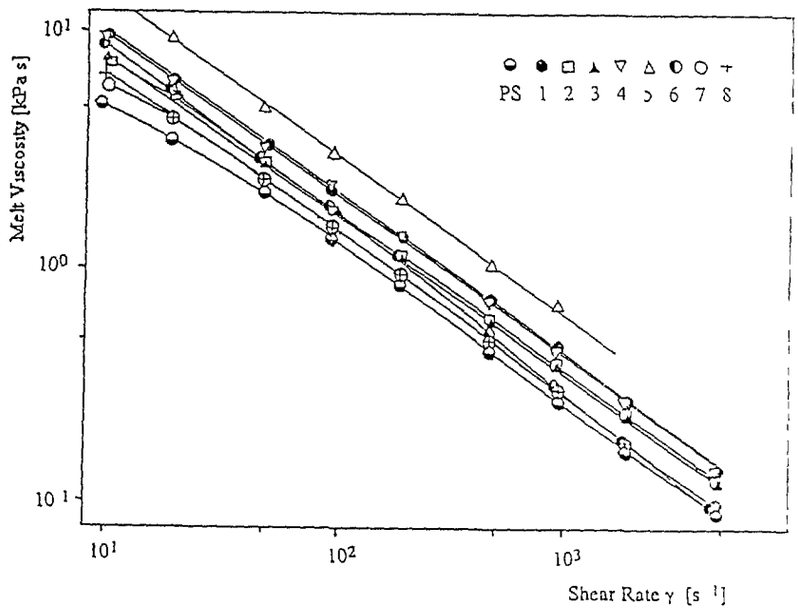

Fig 3 Melt viscosity for polystyrene filled with different carbon black grades (T = 190 C)

Tensile strength of the systems depend on the filler content and type of a matrix (Tab 2) In general an increase in filler content brings about deterioration of mechanical properties of polymer composites

Tab 2 Mechanical properties of PS composites with 6 wt% of CB

Tensile value	PS	CB code							
		1	2	3	4	5	6	7	8
E [MPa]	2600	504	445	480	705	521	680	594	645
σ_r [MPa]	54 1	5 6	2 2	3 8	10 1	6 0	8 9	7 1	8 9
ε [%]	4 6	2 0	1 3	1 6	2 3	1 8	2 2	2 0	2 3

Using Ketjenblack EC 600 JD we performed a study on influence of the preparation technology on the conductivity level for LDPE/PS composites with CB The segregated blends exhibit distinctly lower percolation treshold than the melt mixed ones Significant decrease in the tensile strength is an important drawback of such composites which does not exist in the case of melt mixed blends (Tab 3)

Tab 3 Mechanical properties of polymer composites with Ketjenblack EC 600 JD

Polymer matrix	CB content %	Tensile modulus MPa	Tensile strength MPa	Elongation at break %
PS	0	2 600	54 1	4 6
LDPE	0	230	16 0	70 0
PS	6	504	5 6	2 0
LDPE	6	238	9 8	35 1
LDPE/PS 50/50 melt mixed	6	496	4 0	2 3
LDPE/PS 50/50 segregated	6	448	1 1	2 9

The above observations have been related to the system morphology which was inspected by scanning electron microscopy (Fig 4) In a range of 50 80 wt % of PS a mutual connectivity of the matrix components was evidenced Because the carbon black was located preferentially in LDPE phase the conducting filler content required for making the composite electrically conductive decreased markedly

We have reached fairly high conductivity level after taking advantage from the technology of mixing which comprises the specific ratio of components and the polymer pair composed of the amorphous and semi crystalline polymer Since the blend is interpenetrating and carbon black is located in an amorphous phase of LDPE CB forms a conductive path at low loading

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705	521	680	594	645
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Fig 4 Interpenetrating structure of LDPE/PS composite with 6 wt% of Ketjenblack E
600JD (SEM micrograph)

Interpretation of the obtained results in terms of a multiple percolation conce, al
explanation of such a low percolation treshold as 0 009 of carbon black in LDPE PS bl
(Ref 2) Schematic representation of the dependency of electrical conductivity on
polymer and taking advantage from the difference in order to minimize the Cb con
electrically conductive materials has been shown on Fig 5

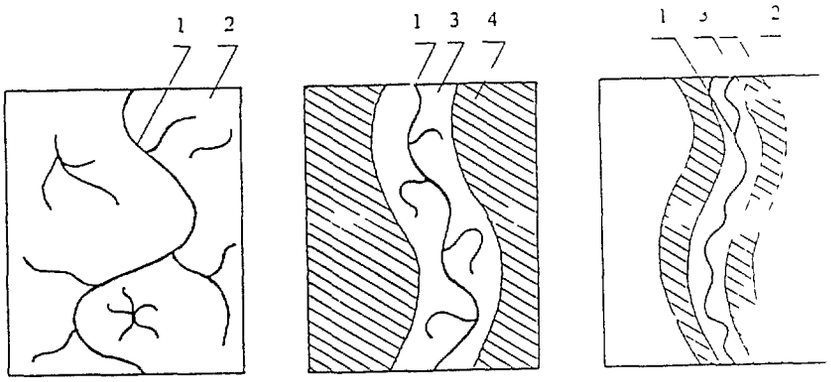

Fig 5 Scheme of carbon black location in the amorphous polymer semi crystalline poly
and the blend of both (from left to right)
1 CB 2 PS 3 amorphous phase of LDPE 4 crystalline phase of LDPE

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CONCLUSIONS

Ketjenblack EC 600 JD is a carbon black extremely suitable for electroconductive applications in polymer systems

Electrical behavior of electroconductive carbon blacks is directly related to their physical properties e g surface area structure and to the surface chemistry

Multicomponent heterogeneous polymer matrices may form particular morphology being highly suitable for conductive composites

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