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Chemical Engineering Research Centre

SEMI ANNUAL REPORT

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ELECTRICALLY CONDUCTIVE

STRUCTURED POLYMER BLENDS

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Institution: POLYMAK, Poland

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INTRODUCTION

Carbon black (CB) loaded incompatible polymer blends have currently been the focus of increasing attention (Sumita et al., 1991a, b, 1992; Gubbels et al., 1994), due to fact that their conductivity may be higher than that of their individual constituents at the same CB loading, and that high levels of conductivity may be obtained at very low CB contents (Tchoudakov et al., 1994a, b). This is extremely convenient in practice, due to the understandable desire to reduce the CB content in formulations where CB diminishes the mechanical properties, hinders processing and causes dusting.

Points of interest in these systems are the correlation between the morphology and conductivity of the blends, the CB location within them dependant on the individual polymer properties (Miyasaka et al., 1982; Carmona,1993), and the percolation mechanism within the blend.

In the present research, typical incompatible system of HIPS/LLDPE and HIPS/EVA were examined. The individual polymers were examined in their neat and unloaded state, as were the polymer blends, in attempt to study the effects of polymer properties such as polarity and viscosity on the location of CB and the morphology and electrical resistivity of the polymer blend.

EXPERIMENTAL

The polymers used in this study were the following:

- HIPS - Galirene HT 88-5, of Israel Petrochemical Industries.
- PS - Galirene HH-102-E.
- LLDPE - Dowlex NG 5056, of DOW.
- Low viscosity LLDPE - Dowlex 2552E, referred to in graphs as LL25.
- EVA - Ribolene, of Enimont.

All blend ratios described relate to percentage by weight. Carbon black Ketjenblack EC by 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. The resulting blends were subsequently compression molded at 190°C to obtain 3 mm plaques.

The volume resistivity of disc-shaped samples, 5 cm in diameter, was measured (DIN 53596) using a Keithly 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. Silver or nickel paint was used to ensure contact between sample and electrodes, namely, to eliminate contact resistance.

The blend phase morphology was studied using a Jeol 5400 scanning electron microscope (SEM). Freeze-fractured and microtomed surfaces were investigated.

RESULTS AND DISCUSSION

Neat Polymers

The neat HIPS sample reveals a structure composed of highlighted streaks. These may be crazes typical to polystyrene, in which highly oriented fibrils surround a network of voids. The crazes are observed as crack-like defects, their surfaces bridged by many fine fibrils. As the crazes grow in width the fibrillar structure breaks down leading to large voids (Kramer & Berger,1990). Upon addition of 2 phr CB as observed in Fig. 1, the streaky structure becomes more enhanced and finer. It is difficult to determine the precise CB location and dispersion since many tiny white particles are observed - these could be fibrillar tips of crazes or rubber. The microvoids seen may be attributed either to the crazing phenomenon or to CB detachment from the polymer. Indeed, the appearance of crazes and ductile fracture regions may impede observation of CB particles or chains.

The neat PS sample resembles HIPS greatly, with fibrillar crazes and several fracture planes (Fig.2). Upon addition of CB, it is difficult to obtain a brittle fracture, and ductile nodules appear. The other areas are massively dotted, most of the dots being probably craze tips. Agglomerates of smaller bright points seem to be CB - however, this is difficult to prove through SEM observation only.

LLDPE exhibits a typical ductile fracture, whereupon regions of stretched material produce a particulate-like structure. However, only the smaller white particles seen are the CB. In the 2 phr sample (Fig. 3) CB particles are randomly dispersed in the matrix, too distant for conductive pathways to be formed. The 6 phr CB sample shows that CB is usually located in oval cavities larger than the particles themselves. These gaps are caused either by poor adhesion between the filler and the matrix and also correspond to the non-uniform topography obtained upon the fracture surface due to polymer ductility.

LLDPE of low viscosity was observed as well. The fracture surface differs greatly from the smooth texture of the former sample, appearing much more complicated and ductile (Fig. 4). Upon addition of 2 phr CB, the texture becomes much more smooth, and the CB is very difficult to distinguish. The addition of CB even in small content results in a more brittle behaviour.

In EVA the fracture surface appears smooth, so CB is easily recognized. Particles seem to adhere to the matrix more readily than they did for the LLDPE although not completely - the filler particles are uncoated by EVA, and tiny gaps and microvoids of less than 0.1μm are obtained. As depicted in Fig. 5, the 2 phr CB sample exhibits a uniform dispersion with scattered aggregates; in the 6 phr sample, networks begin to be formed by CB chains; the 8 phr CB sample is clearly conductive, with a chain-like as well as agglomerate structure.

The volume resistivity of the above polymers as a function of CB content is depicted in Fig. 6. The percolation threshold of PS is the lowest of all polymers, at less than 2 phr CB. HIPS percolates at 2 phr CB, slightly higher. This difference is relatively small, and may be attributed to experimental errors stemming from the mixing process or the resistivity measurement device. However, at higher CB loadings beyond the percolation point, PS is more conductive than HIPS by two orders of value. The reason for the low percolation point of PS is obvious from SEM, aggregates being located in the microvoids between craze fibrils. As HIPS contains a polybutadiene phase, the location of CB may be affected by it - however, SEM cannot provide us sufficient information.

The low viscosity LLDPE percolates at approximately 4 phr CB, whereas the high viscosity LLDPE threshold is obtained at 6 phr CB. Taking into consideration the fact that the polarity of the two types of LLDPE is not significantly different, the effects of viscosity may be taken into consideration here. The dispersive mixing process involves several stages, quoted by Manas-Zloczower & Tadmor, 1994: (1) Incorporation of the powder into liquid, whereupon the pellets are wetted by the polymer melt which replaces the entrapped air; (2) deagglomeration by breaking the agglomerates and possibly aggregates; (3) distribution of the agglomerates and aggregates throughout the polymer by random patterns of flow; (4) flocculation, involving diffusion and cohesion of aggregates into a network, reversing some of the effects of the dispersion process. The process of solid agglomerate dispersion within liquid media is highly complex, and must take into consideration forces involved in particle break-up, namely the forces of cohesion within the clusters and the hydrodynamic forces inducing their breakup. All models considering this problem emphasize the importance of the viscosity of the suspending liquid, contributing greatly to agglomerate erosion and eventual rupture. Seemingly, the high viscosity LLDPE disperses CB uniformly, reducing particle size and degrading floccular configurations. The low viscosity LLDPE tends to diminish the agglomerates less, and also has a lower resistance to reagglomeration, enabling the CB aggregates to approach one another and form conductive networks.

EVA exhibits the highest percolation point of all studied polymers. Oxygen containing functional groups on the surface of the aggregates may interact with polymers of appropriate chemical nature. This process is in contrast to the interaction of carbon black aggregates with one another either due to weak van der Waals forces or to stonger interactions of acidic groups on one aggregate with basic groups or graphitic layers on another aggregate, and of course, this may elevate the percolation threshold. This kind of interaction is of course typical to the more polar polymers such

as EVA, in which the vinyl acetate group in these copolymers is polar and thus CB adheres to the matrix and is uniformly dispersed in it (Carmona, 1993).

Polymer Blends

HIPS/LLDPE

The neat blends were studied at proportions of 95/5, 85/15, 70/30, 55/45 with HIPS serving as the matrix and LLDPE as the dispersed phase. All neat blends exhibit behaviour typical of blends of these compositions, the dispersed phase being very small for the 95/5 blend (1 μm order of value), slightly larger for the 85/15 blend and co-continuous for the 70/30 and 55/45 blend of all components, the latter being of coarser structure. When comparing the dispersed phase size and distribution of the blend containing high and low viscosity LLDPE (Fig. 7), it is apparent that the former is of smaller droplet size, while the latter has larger droplets and is of wider distribution. Two different processes taking place here should be considered: mixing versus coalescence. The mixing mechanism involves the deformation of drops promoted by shear stress τ exerted on the drops by the flow field and counteracted by the interfacial stress σ/R (with σ the interfacial tension and R the local radius) minimizing the surface to volume ratio, thus tending to a spherical shape. The ratio between these two stresses is called the capillary number Ca. If the capillary number exceeds a critical value, the viscous shear stress overrules the interfacial stress, no stable equilibrium drop shape exists and the drop is extended and finally breaks up into smaller droplets. The opposite phenomenon taking place is that of coalescence - upon which dispersed particles approach one another and eventually collide, the matrix material between them being removed upon their fusion (Plotchocki, 1990). Coalescence time is shown to be highly dependant on dispersed phase viscosity, which implies rapid coalescence of particles of low viscosity. Apart from the volume fractions of the constituents and the flow field externally applied by the mixer, the viscosities of both phases, the interfacial tension and the mobility of interfaces are the parameters that govern the mechanism of coalescence (Manas-Zloczower & Tadmor, 1994). Coalescence is favoured by small drop radii, low drop viscosity and low capillary number (i.e. low matrix viscosity, low shear rate or high interfacial tension, leading to a smaller flattened area). The final morphology of a blend is a result of the dynamic equilibrium between breakup of large drops and coalescence of the smaller ones during mixing. A morphology once formed may coarsen as a result of of coalescence or colliding drops of the dispersed phase. Apparently, in blends with low viscosity LLDPE both processes of droplet breakup and coalescence occur more rapidly. This may explain the wide distribution of particle size depicted in the 85/15 blends of HIPS with low viscosity LLDPE.

Phase inversion occurs relatively early for the viscous phases as well as the low viscosity polymers - at a 70/30 composition a co-continuous structure is obtained for all the HIPS and PS matrix blends (Fig. 8). This is not in correlation with the simplest model cited by Utracki (1991) for predicting phase inversion and the point of co-continuous network formation, which is the following:

$$\frac{\phi_1}{\phi_2} = \frac{\eta_1}{\eta_2}$$

As stated above, this relationship does not apply in this case. Favis et al. (1990) emphasized the fact 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 our case, the morphology of immiscible blends appears to be controlled by a hierarchy of effects such as interfacial tension, viscosity ratio and shear stress, in this order of significance.

PS/LLDPE blends have been observed elsewhere (Teh & Rudin, 1991). Similiarly to the results obtained here, the PE dispersed phase detaches completely from the PS matrix, exhibiting empty cavities or PE droplets. Another similiar feature is the fact that most of the plastic deformation is seen to be confined to the PS-PE spherical boundary. High viscosity tends to favour rod-like structures of dispersed phase rather than droplets, and this is depicted in the CB-containing composites. A cylinderical structure of the dispersed PE phase in a neat 70/30 PS/LLDPE blend was depicted by Mejias et al. They also described the surprising stability of the original morphology upon post-processing - a feature which could be useful in conductive polymer blends, where it is desired to maintain conductivity by stabilizing the morphology.

Addition of CB to the system results in its preferential location in the LLDPE , as depicted in Fig 9. SEM micrographs reveal that CB is usually positioned upon the surface of the LLDPE dispersed phase, and less incorporated within it. The particles themselves are clearly seen on the surface, and tiny cavities corresponding to them are stationed upon the HIPS surface. The fact that CB favours the LLDPE component in the blend coincides with the higher percolation threshold of the individual LLDPE in comparison to HIPS - LLDPE percolates at a higher CB loading due to their stronger affinity to each other,

CB alters the morphology significantly. The 95/5 blend loaded with 2 phr CB has a dispersed phase of tiny dimesions, 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 inclusions which have no significant effect on the CB location. The 85/15 blend, composed of spherical dispersed phase particles in the neat case (Fig. 7), developes an elongated dispersed phase structure upon CB addition (Fig. 10). The dispersed phase becomes smaller, but as the dimensions are reduced the number of

particles increases, creating numerous CB coated cylinders. The reduction in dispersed phase size has been reported previously and has been said to be caused by dissipation of energy in the system. Friction between coated dispersed particles and the continuous phase causes deformation and elongated structure. The higher viscosity of the CB loaded dispersed droplets has an effect as well. This 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 loaded blends are finer than the unloaded ones, resulting in an enhanced network. The 55/45 composition is of coarser structure than the 70/30 one (Fig. 9).

The percolation curves of the CB loaded blends is depicted in Fig 11. The 95/5 blend percolates at approximately 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 similiarly to the individual HIPS. The dispersed phase creates inclusions and conductivity in this case results from the effective CB content in HIPS. The 85/15 blend demonstrates a percolation threshold at less than 1 phr CB, with lower resistivity values than for the previous composition. This is understandable 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 LLDPE (mainly upon its interface) in high content way above this polymer's percolation point, and the general elongated configuration creates areas of contact between the dispersed domains, leading to conductivity. This demonstrates that co-continuity is not a necessary condition for conductivity, in contrast to the common notion (Gubbels, 1994). The 70/30 composition is slightly less conductive 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. This takes place for the 55/45 blend as well, which has a percolation point similiar to the individual HIPS - at 2 phr CB. For most compositions, the percolation point is not greatly reduced for polymer blends in comparison to the individual HIPS matrix - however, the magnitude of the resistivity is decreased by approximately four orders of value, which is indeed, a significant enhancement. This may be attributed to the unique morphology obtained in the blend systems, in which the CB is placed upon the LLDPE phase surface. The concentration of CB particles upon the interface promotes conductivity a great deal, in comparison to the values obtained when CB is dispersed within a matrix, even above the percolation point.

Blending the ingredients by a different mixing sequence does not produce different resistivity values or morphology, as described elsewhere (Gubbels, 1994; Tchoudakov 1994). 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 exhibit a behaviour similiar to the described above. The lower percolation points exhibited for all blend ratios stems from the lower percolation point of the lower viscosity LLDPE. Contrary to the expected, no unique morphology was obtained due to the extremely low value of polymer viscosity.

HIPS/EVA

The essential behaviour of these neat and loaded blends is very similiar to the above system. It varies in polarity of the EVA dispersed phase. As a result, CB is clearly incorporated within it, and the consequent percolation threshold of the HIPS/EVA blends is higher than in the case of HIPS/LLDPE, especially so in the 55/45 formulation, where the large EVA content diminishes conductivity (Fig. 13)

Vivoni et al. discuss the correlation between conductivity and morphology of PS/EVA blends. As in our case, co-continuity was observed at low EVA contents (beginning at 20%), but was not explained. Another similiar phenomenon exhibited in this work was the reduction in size of dispersed phase domains upon CB addition, and the enhancement of co-continuity.

CONCLUSIONS

The conductive polymer blends examined here continue to exhibit a typical percolative behaviour. The CB is found to locate in the phase to which it has a higher affinity, and the resultant percolation threshold and resistivity value of the blend is lower than values of the individual polymers. The formation of a co-continuous structure is not essential for conductivity of the blend. When the dispersed phase concentration is high enough to form a slightly elongated structure which enables contact between the droplets - conductivity rises. This does not correspond to the double percolation notion widely emphasized in many studies (Sumita et al., 1991a,b).

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FIGURE CAPTIONS

Figure 1 : SEM micrographs of cryo-fractured:

a. Neat HIPS

b. 2 phr CB loaded HIPS.

Figure 2 : SEM micrographs of cryo-fractured:

a. Neat PS

b. 2 phr CB loaded HIPS.

Figure 3 : SEM micrographs of freeze-fractured:

a. LLDPE with 2 phr CB.

b. LLDPE with 6 phr CB.

Figure 4 : SEM micrographs of freeze-fractured:

a. Neat low viscosity LLDPE.

b. Low viscosity LLDPE with 2 phr CB.

Figure 5 : SEM micrographs of freeze-fractured:

a. EVA with 2 phr CB.

b. EVA with 6 phr CB.

c. EVA with 8 phr CB.

Figure 6 : Percolation curves of the individual polymers.

Figure 7 : Cryo-fractured blends of HIPS/LLDPE:

a,b - HIPS with higher viscosity LLDPE at two magnifications.

a,b - HIPS with lower viscosity LLDPE at two magnifications.

Figure 8 : A cryo-fractured 70HIPS/30LLDPE blend, at two magnifications.

Figure 9 : A 55HIPS/45LLDPE blend:

a,b - Freeze-fractured at two magnifications.

c,d - Microtomed at two magnifications.

Figure 10: A 2 phr CB loaded 85HIPS/15LLDPE blend.

Figure 11: Percolation curves of HIPS/LLDPE CB loaded blends.

Figure 12: A freeze-fracture surface of a 70HIPS/30EVA, loaded with 2 phr CB.

Figure 13: Percolation curves of HIPS/EVA CB loaded blends.

a b

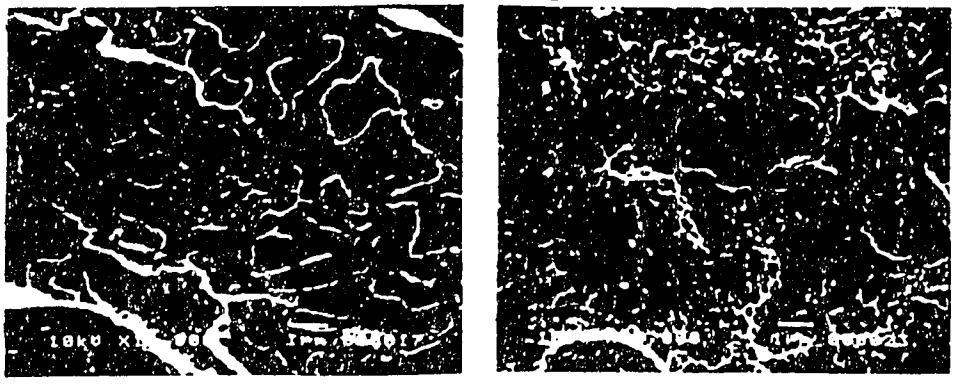


Fig. 1

a b

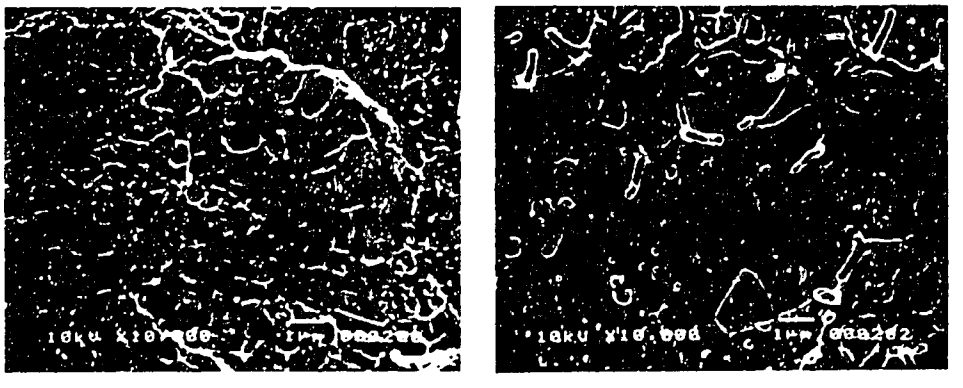


Fig. 2

a b

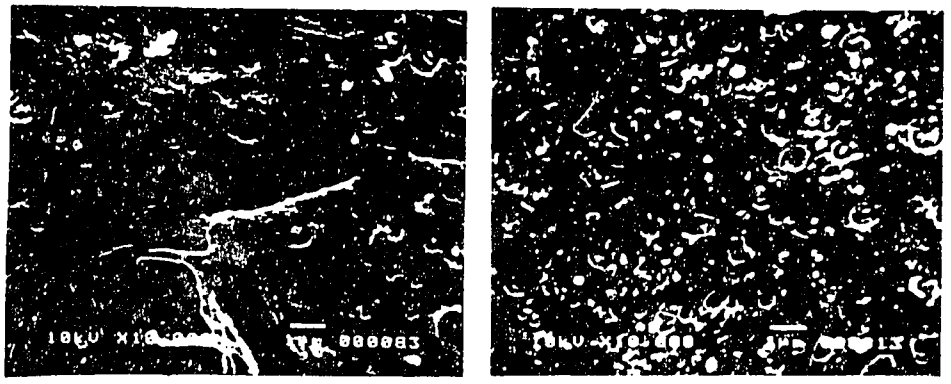


Fig. 3

a b

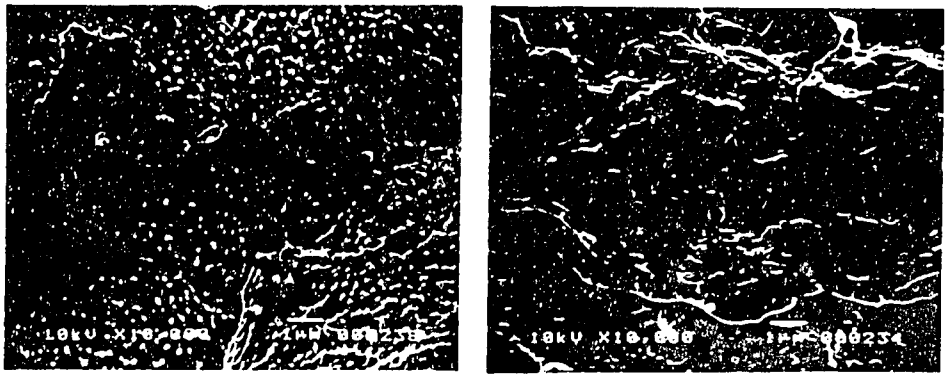


Fig. 4

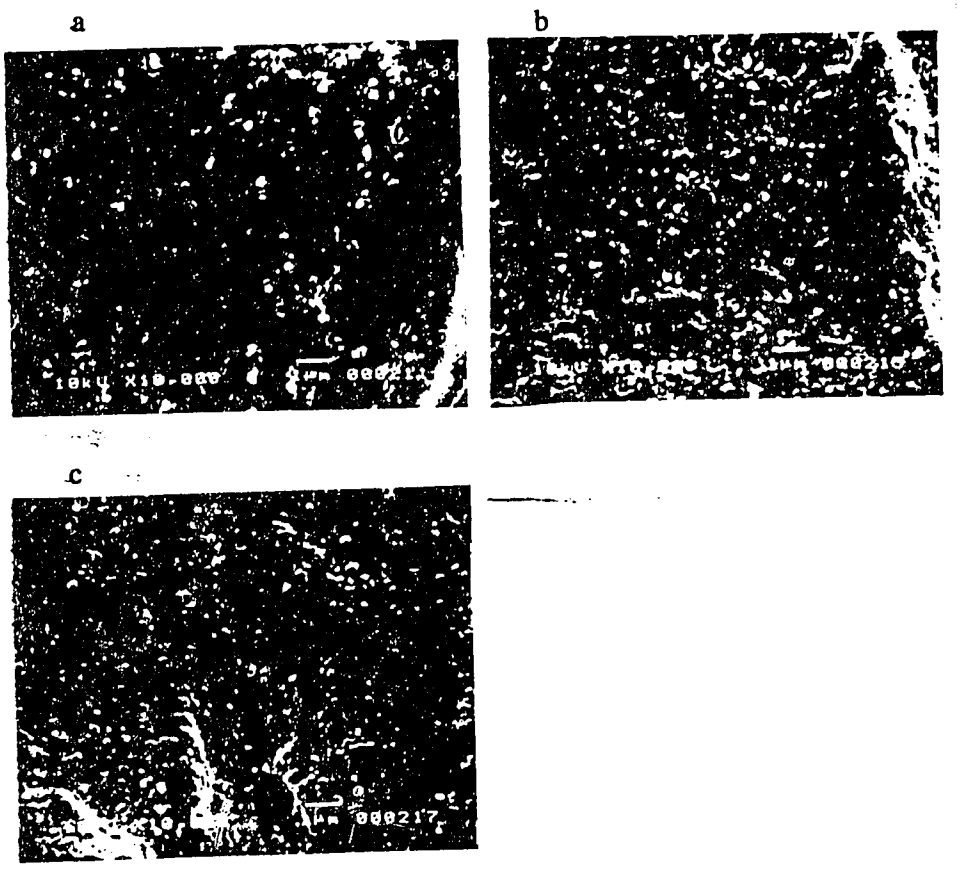


Fig. 5

16

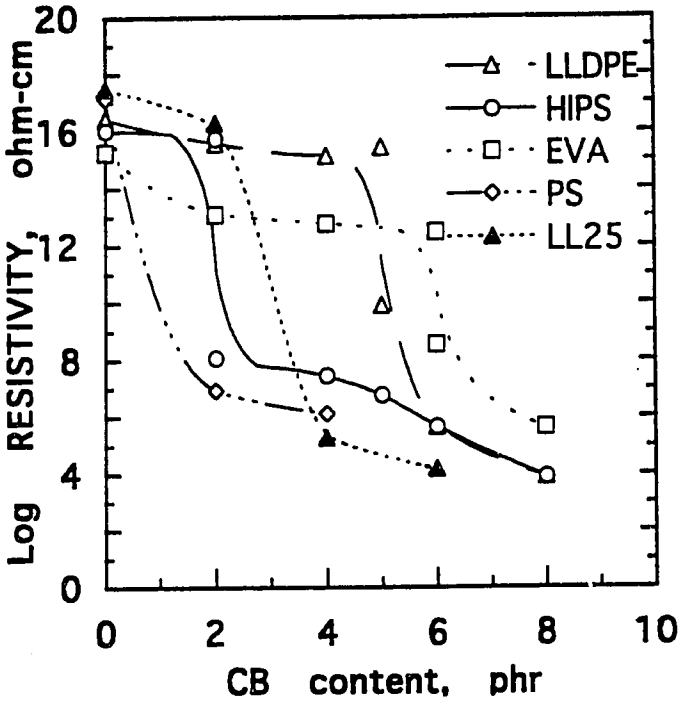

20
16
12
8
4
0
Log RESISTIVITY, ohm-cm
0
2
4
6
8
10
CB content, phr
LLDPE
HIPS
EVA
PS
LL25

Fig 6

17

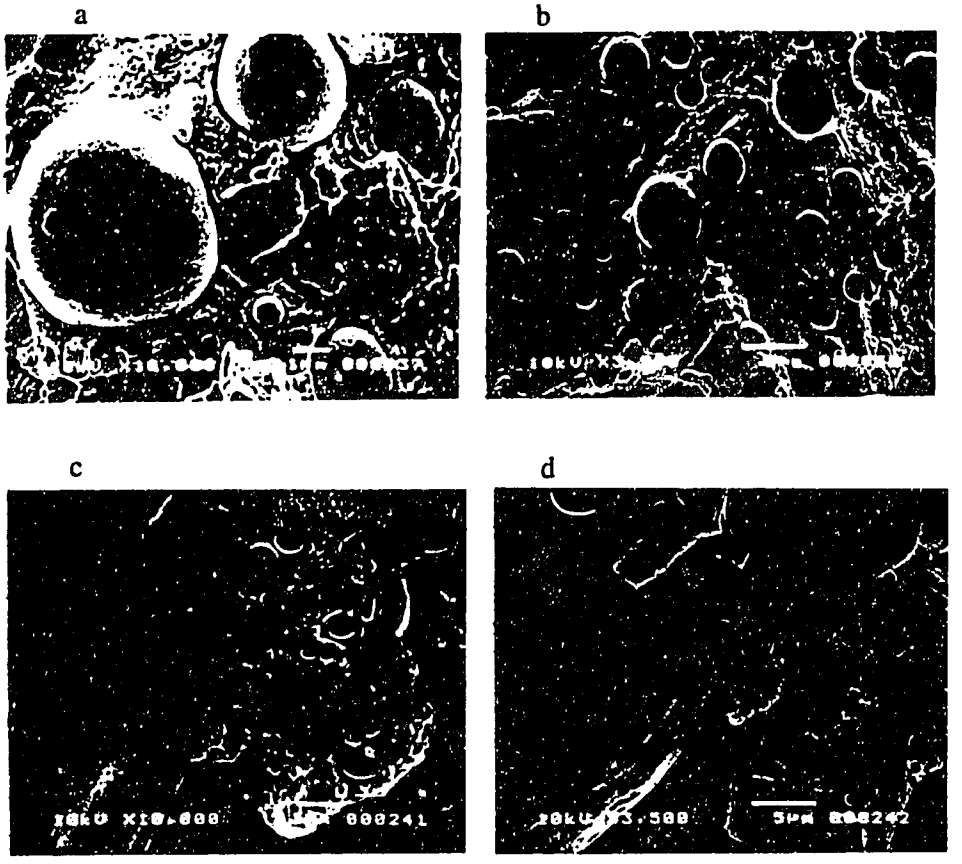


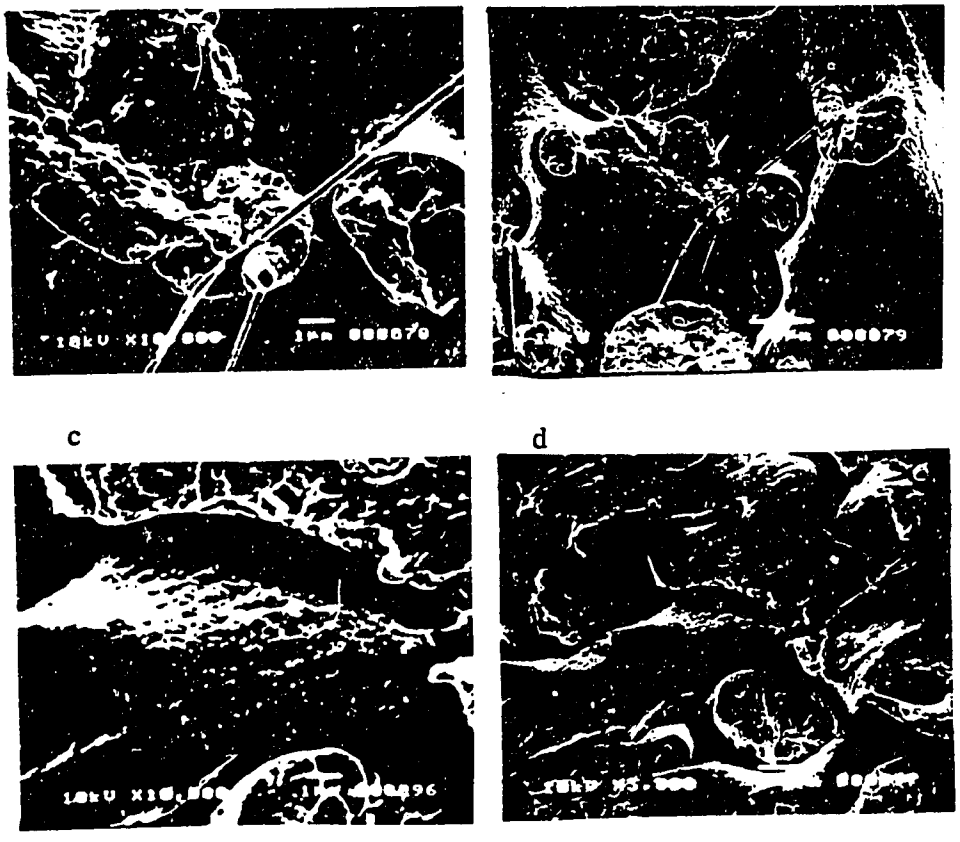
Fig. 7

18

a b

Fig. 8

a b



c d

Fig. 9

19

a b

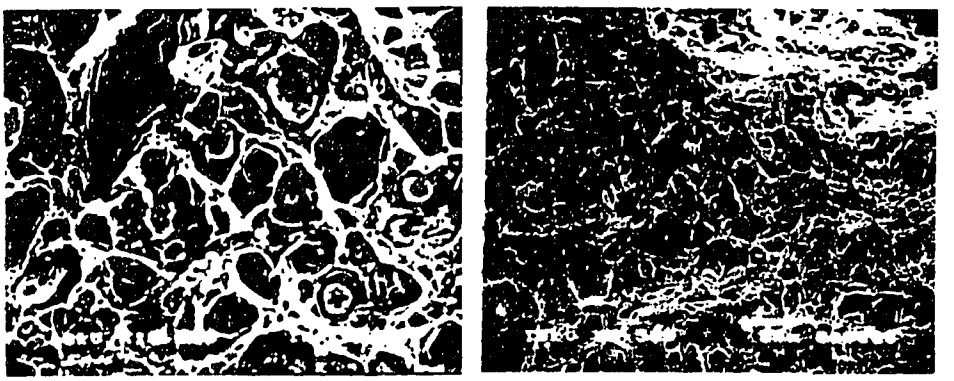


Fig. 10

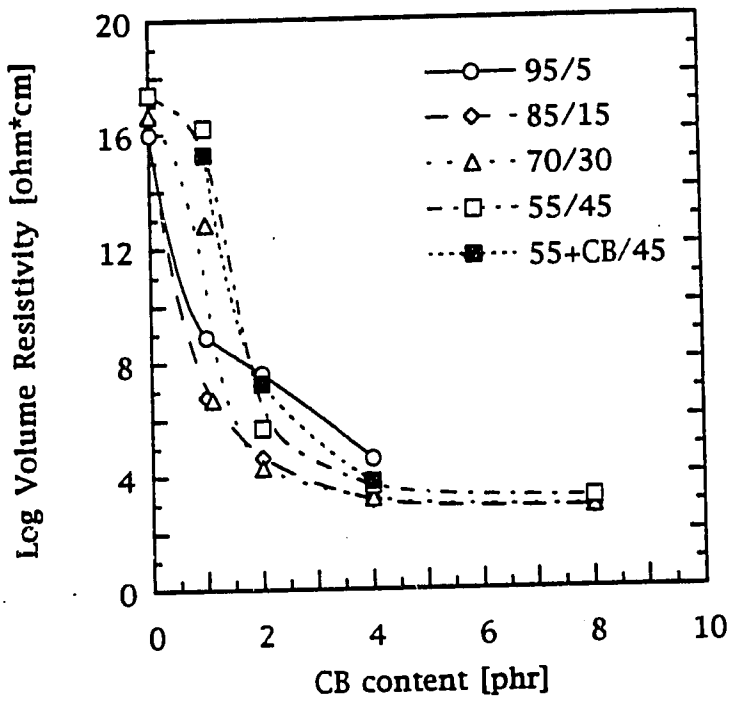

20
16
12
8
4
0
0
2
4
6
8
10
Log Volume Resistivity [ohm*cm]
CB content [phr]
95/5
85/15
70/30
55/45
55+CB/45

Fig. 11

a

b

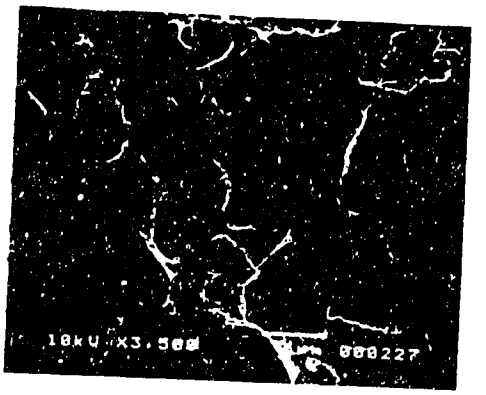


Fig. 12

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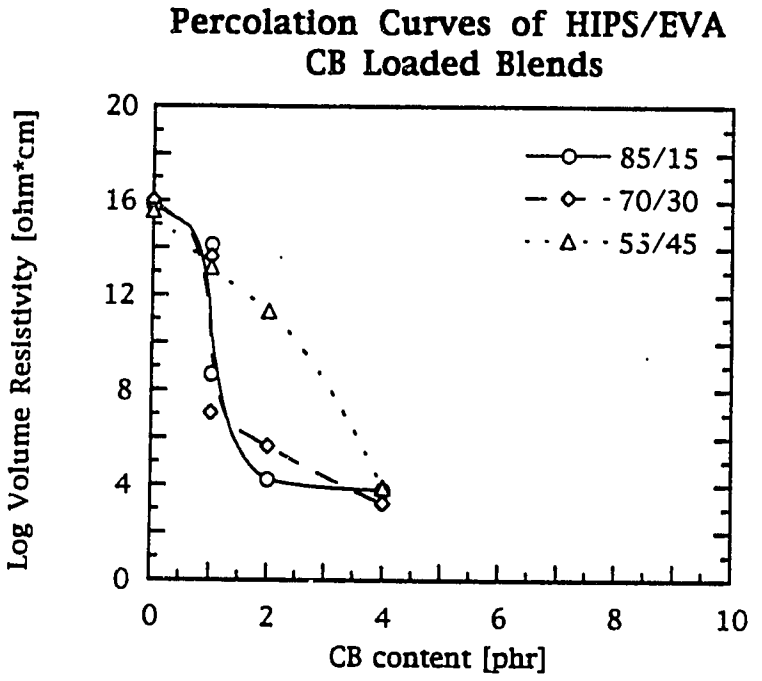
Percolation Curves of HIPS/EVA
CB Loaded Blends
Log Volume Resistivity [ohm*cm]
20
16
12
8
4
0
0
2
4
6
8
10
CB content [phr]
85/15
70/30
55/45

Fig. 13

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Research, Development and Consulting Center POLYMAK

SEMI-ANNUAL REPORT

ELECTRICALLY CONDUCTIVE STRUCTURED POLYMER BLENDS

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THEORY

During the first half of the second year duration of the project an extensive literature review has been continued on following topics:
- carbon black filled polymers and polymer blends,
- intrinsically conductive polymers,
- electrically conductive polymer composites,
- mechanisms for electrical conductivity in heterogeneous systems,
- morphology of polymer blends and alloys.

A comprehensive review on the above subjects is being under preparation. The review has been focused particularly on the conductivity of polymer blends filled with carbon black. Full text should be ready for publication in a second half of this year.

EXPERIMENTAL

The research program has covered experiments with two polymer systems:
- PS/LDPE compatibilized with a partially hydrogenated poly(styrene-b-isoprene) di-block copolymer from Shell Chemicals,
- PS/SBS (styrene-butadiene-styrene) tri-block copolymer from Shell.

Results obtained for the first system are complementary to the results reported by the ANNUAL REPORT of September 1994. 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.

Mechanical properties measured for segregated composites were deteriorate in comparison to that of melt-mixed composites. The tensile properties of LDPE/PS system are determined by the component, which dominates the system. In case of interpenetrating blends a failure occurs by the brittle/ductile - mode, characteristic for a component of the lowest crazing/yielding stress. Simultaneously with the CB-content increase in a composite, the tensile modulus and tensile strength decreased.

Electrical conductivity was of primary interest in our experiments. Influence of particular parameters on its value has been estimated by means of a mathematical planning of experiments. The factorial analysis of 2^4-type has been used, with the following factors:
- PS content in LDPE/PS blend (X_1),
- CB content in a composite (X_2),
- compatibilizer content (X_3),
- temperature of mixing (X_4).

The following regression equations have been obtained for the volume resistivity ρ and surface resistivity ρ_s, respectively:

$$\log \rho = 8.582 - 0.554x_1 - 2.667x_2 + 0.756x_3 + 1.196x_4 + 1.220x_1x_2 +$$

$$+ 0.229x_1x_3 - 0.131x_1x_4 + 1.046x_2x_3 + 0.560x_2x_4 + 0.071x_3x_4$$

$$\log \rho_s = 7.249 - 1.323x_1 - 1.918x_2 - 0.918x_3 - 0.114x_4 + 1.077x_1x_2 +$$

$$+ 0.859x_1x_3 + 0.388x_1x_4 + 1.365x_2x_3 + 0.122x_2x_4 - 0.046x_3x_4$$

Discussion of the above expressions has led us into conclusion, that high PS content in a matrix as well as high CB content in a composite are favorable for the conductivity level (positive regression coefficient). In contrary, compatibilization of LDPE/PS blend and high temperature of mixing are disadvantegous (negative regression coefficient). Significant influence on a conductivity level of composites may be expected from a synergy of x_1x_2, x_2x_3 and x_2x_4.

We have concluded, that very low CB-percolation treshold, which has been evidenced for Ketjenblack EC-600 JD below 1.8 wt.% in a composite, may be reached at following conditions:
- generation of the interpenetrating structure (LDPE/PS 30/70 blends or LDPE/PS 50/50 alloys),
- temperature of mixing should not exceed 190°C.

High mixing temperature and compatibilizer content bring about an increase in a dispersity level of the blends. Compatibilized blends offer easier diffusion of components between the phases. Thus, CB particles may be located not only in the amorphous phase of LDPE (which is our preference), but in PS as well. As a result, the probability of conducting pathways formation is being lower.

Very low percolation treshold, which has been observed at particular conditions, has been interpreted by means of multiple percolation concept. First level of percolation concerns CB particles, which form the continue conductive pathways through a composite. Another interpenetration level has been related to the amorphous phase of polyethylene in LDPE, within which CB-particles have been located (secondary percolation). Eventually LDPE forms a continue network in polystyrene (third level of percolation).

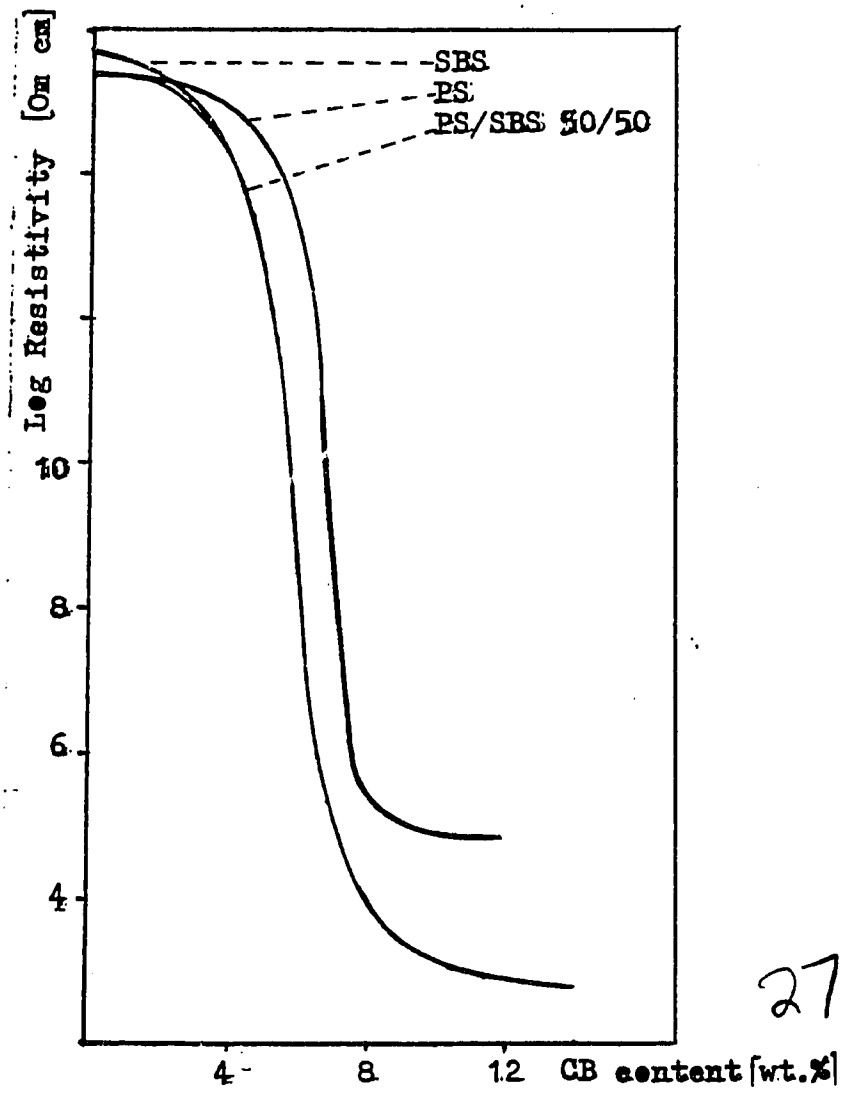
Morphology of the composites has been inspected by the scanning electron microscopy (SEM). The micrographs have evidenced a higher affinity of CB to LDPE than to PS. Interpenetrating structure has been observed in the LDPE/PS 30/70 blend, which has confirmed our supposition on the multiple percolation. 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.
The results of research on LDPE/PS blends and alloys have been reported in the paper "Electrically Conductive Structured Polymer Blends", which has been submitted to the journal "Polymer Networks and Blends" and accepted for publication in volume 5 (1995).

PS/SBS system

First part of a research plan for the second year duration of the project has been focused on determination of influences of following factors on the CB-composite characteristics:
- carbon black content,
- temperature of mixing,
- composition of a matrix.

We have found, that PS/SBS composites are less conductive than that based on a LDPE/PS matrix. The percolation treshold, we have estimated for PS/SBS 50/50 composite with Ketjenblack EC-600 JD was 7 wt.%. Similar values were estimated for the composites based exclusively on SBS or PS (7 wt.% or 7.5 wt.% respectively - Figure 1). The results are distinctly worse in comparison to the percolation level of 1.8 wt.% for the PS/LDPE composite mentioned above.



The components were mixed in a Brabender mixing head within a range of 150°C - 190°C. We did not find any particular influence of temperature on the electrical conductivity of composites.
Melt viscosity decreased with the temperature increase, as expected, similarly like higher CB-content caused an increase in the melt viscosity.
Tensile properties have been dominated by the major component of composites. Negative deviation from the additivity rule has been estimated, as far as the tensile strength and elongation at break (ε) is concerned. In parallel with an increase of the temperature of mixing we observed an decrease in ε, which may be attributed to a thermal destruction of SBS.

ACIVITY PLANNED

- Morphology of PS/SBS composites and blends will be inspected by SEM.

- Mixing program will be performed, which has been designed for blending at temperature ≤ 150°C, using a modified mixing technology.

- Melt rheology will be determined by means of capillary rheometry.

- The next system (PS/EVA) being foreseen in the project will be implemented into a research program. Influence of the CB-content and temperature on the electrical conductivity and mechanical properties will be determined.

- Dissemination of the project results has been planned as follows:
  * submitting a review on electrically conductive plastic materials to the Journal of Polymer Engineering,
  * presentation of lectures, which have been accepted to a program of the IUPAC Congress in Lodz, Poland (July 5-7, 1995) and the EUROFILLERS' 95 in Mulhouse, France (September 11-15, 1995) (enclosed).

CONCLUDING REMARKS

Two papers mentioned in the ANNUAL REPORT' 94 as submitted, have been recently published. There are:

1. M. Kozlowski, "The Formation of Interpenetrating Polymer Blends", J. Polym. Eng., **14**, 15 (1995).
2. M. Kozlowski, "Structure and Mechanical Properties of Heterogeneous Polymer Blends", J. Appl. Polym. Sci., **55**, 1375 (1995).