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Electrically Conductive Structured Polymer Blends

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ELECTRICALLY CONDUCTIVE STRUCTURED POLYMER BLENDS

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Electrically Conductive Structured Polymer Blends

This annual report reflects the research efforts during the first project's year, both in Poland and in Israel. The two teams have maintained a close collaboration aiming at complementary efforts. The Polish's team visits to Israel have greatly contributed to both analyzing the data produced, and to the outlining and updating of the future objectives.

The overall objective of the project is to develop model compounds of electrically conductive incompatible polymer blends, combining electric/dielectric properties and stable structures suitable for thermoplastic melt processing operations.

The annual reports, prepared separately by each group, follow.

Technion Contribution

Departments of Chemical and Materials Engineering

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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].

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 component is an amorphous matrix and the latter serves as a semi-crystalline 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 (Chapters 1, 2.2) with regard to former results obtained for polypropylene/polyamide [9] and polypropylene/polycarbonate[10] blends.

Addition of a low content of liquid crystalline polymer (LCP) to a thermplastic polymer is known to enhance the mechanical properties and processibility of the latter by creating a fibrillar structure which tends to reinforce the polymer and reduce its melt viscosity [28-31]. Blended with HIPS and incorporated with CB, interesting electrical [32], rheological and morphological properties are obtained.

1. SEGREGATED STRUCTURES IN CARBON BLACK-CONTAINING IMMISCIBLE POLYMER BLENDS: HIPS/LLDPE SYSTEMS

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 approximately 15 minutes. 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 discs, 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 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 for investigation, due to presence of excessive crazing in the brittle fractured surface, the craze tips hindering recognition of CB particles. A microtomed sample, such as in Fig. 1, produces a more coherent picture. HIPS reveals circular regions unoccupied by CB. These areas probably correspond to the crosslinked polybutadiene phase dispersed within polystyrene due to their size (approximately 1 μm) and the fact that CB does not penetrate them. CB particles seem very small within the HIPS matrix, detached from it and non-uniformly 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. 2a) CB particles are randomly dispersed in the matrix, too distant for conductive pathways to be formed. The 6 phr CB sample (Fig. 2b) 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 non-uniform topography obtained upon the fracture surface due to polymer ductility.

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 behaviour.

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

The LL25 percolates at approximately 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 carbon black filled thermoplastics has been well established [5,15]. An increase in surface tension increases the percolation threshold, favoring CB uniform 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 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 less than 10 wt% dispersed crosslinked rubber particles, was found not to have a direct effect on the percolation threshold, as a similiar 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, 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. 5a) and co-continuous for the 70/30 (Fig. 6a,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 et al. [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 vs. 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 sub-inclusions 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. 7a,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 is highly dependant 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, 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 Figs. 5b, 6c,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. 5b). 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 Figs. 5,7. The reduction in dispersed 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 et al. [24], deformation should be less pronounced. In practice, since CB tends to locate more on the dispersed particle surface rather 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 described 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 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 Figs. 8-9. The 95/5 blend (Fig. 9) 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 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 less than 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 which 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 percolation point similiar 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 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 similiar 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 which were of low resistivity by the former compression molding processing method.

SEM micrographs of HIPS/LLDPE+CB blends depict, as expected, significant differences between the directions parallel and transverse to flow. Within the CB loaded 85/15 HIPS/LLDPE blend (Fig. 12a,b), the dispersed PE phase becomes highly extended, obtaining cylindrical structures of relatively low diameter (~ 1μm) 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 similiar (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 towards 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 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, vs. 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 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 non-continuous highly deformed dispersed phase structures in which CB agglomerates disintegrate and only partially reagglomerate.

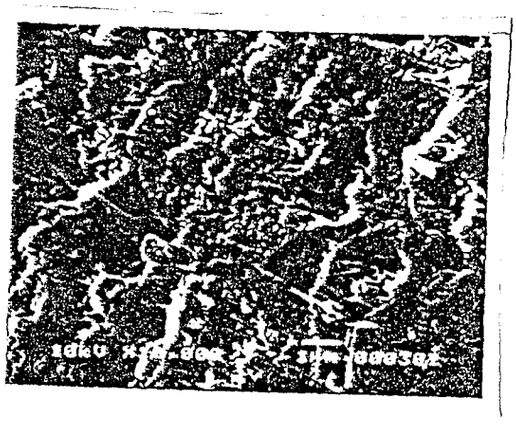

Figure 1: SEM micrograph of microtomed HIPS+2 phr CB.

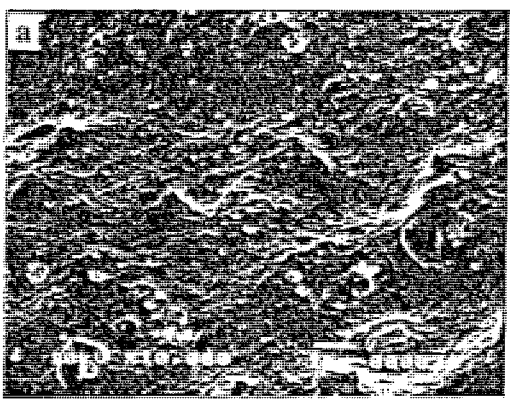

Figure 2: SEM micrographs of freeze-fractured:

a. LLDPE+2 phr CB.

b. LLDPE+6 phr CB.

Figure 3: SEM micrograph of freeze-fractured LL25+2 phr.

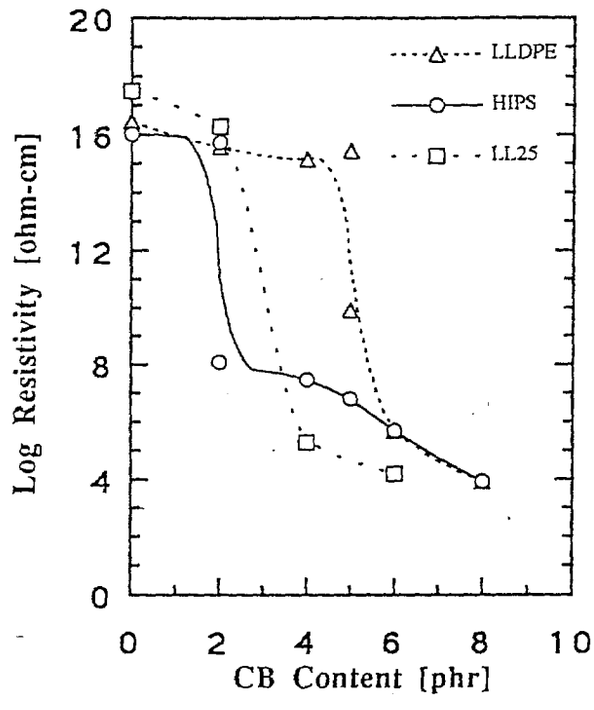

Figure 4: Resistivity of individual polymers vs. CB content.

Figure 5: SEM micrographs of freeze-fractured 85HIPS/15LLDPE:

a. Neat blend

b. 2 phr CB-loaded blend.

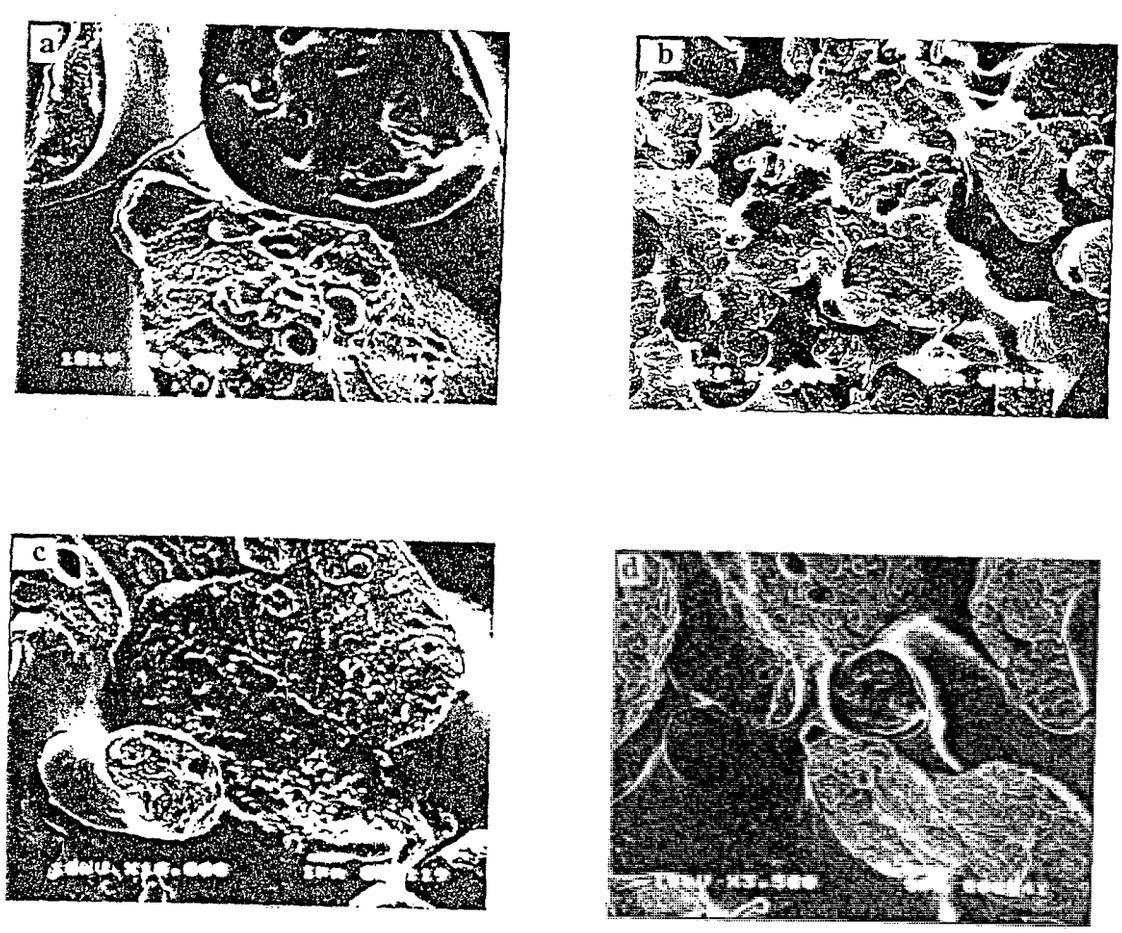

Figure 6: SEM micrographs of freeze-fractured 70HIPS/30LLDPE blend:

a,b. Neat blend at two magnifications.

c,d. 2 phr CB-loaded blend at two magnifications.

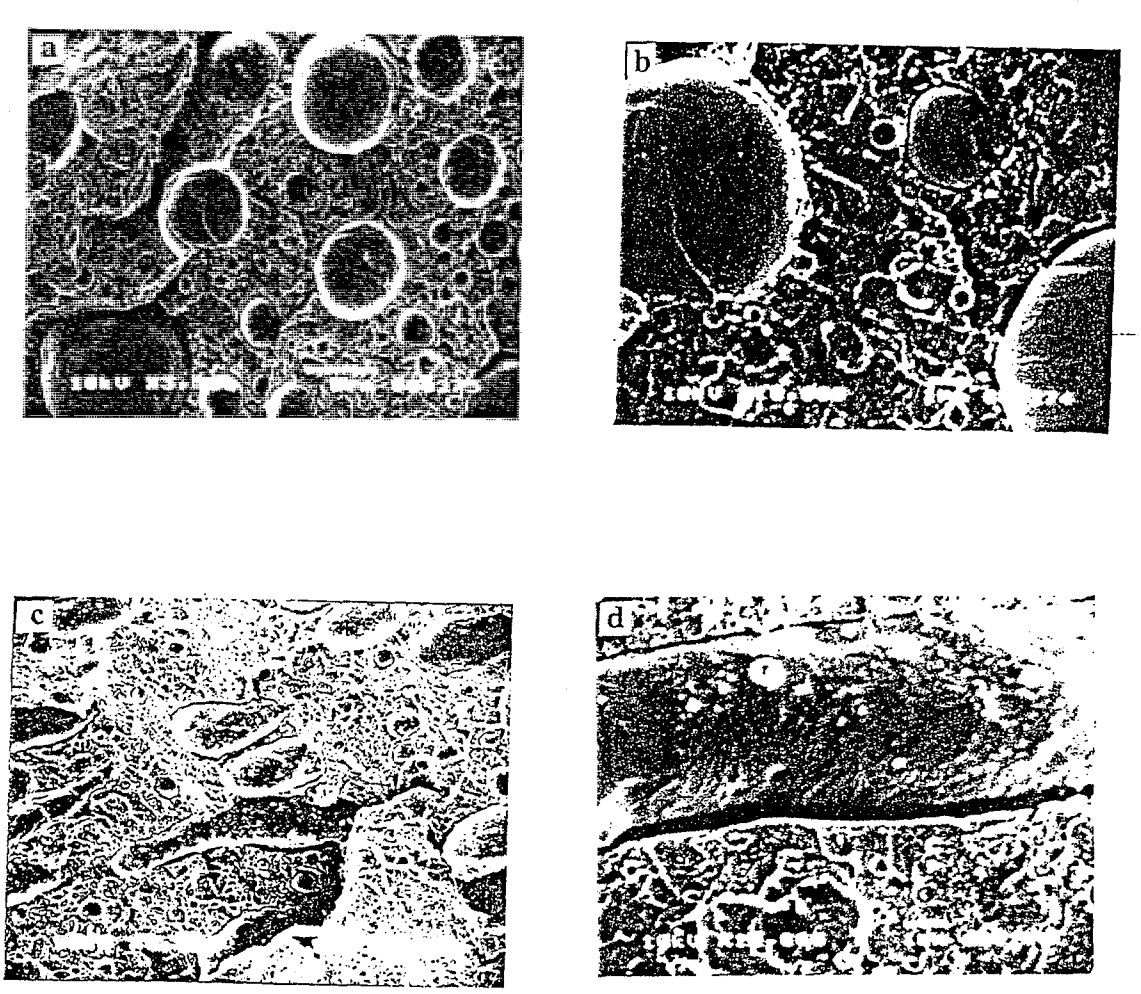

Figure 7: SEM micrographs of freeze-fractured 85HIPS/15LL25:

a,b. Neat blends at two magnifications.

c,d. 1 phr CB-loaded blend, at two magnifications.

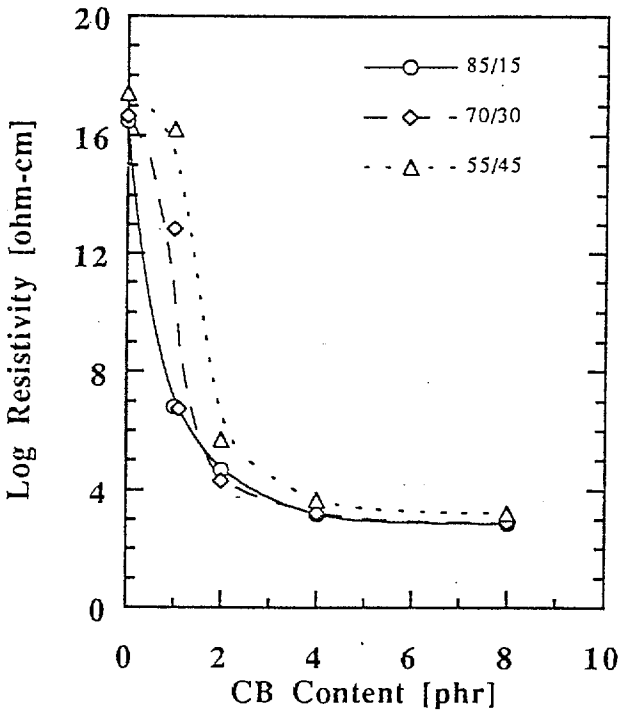

Figure 8: Resistivity vs. CB content of various HIPS/LLDPE blends.

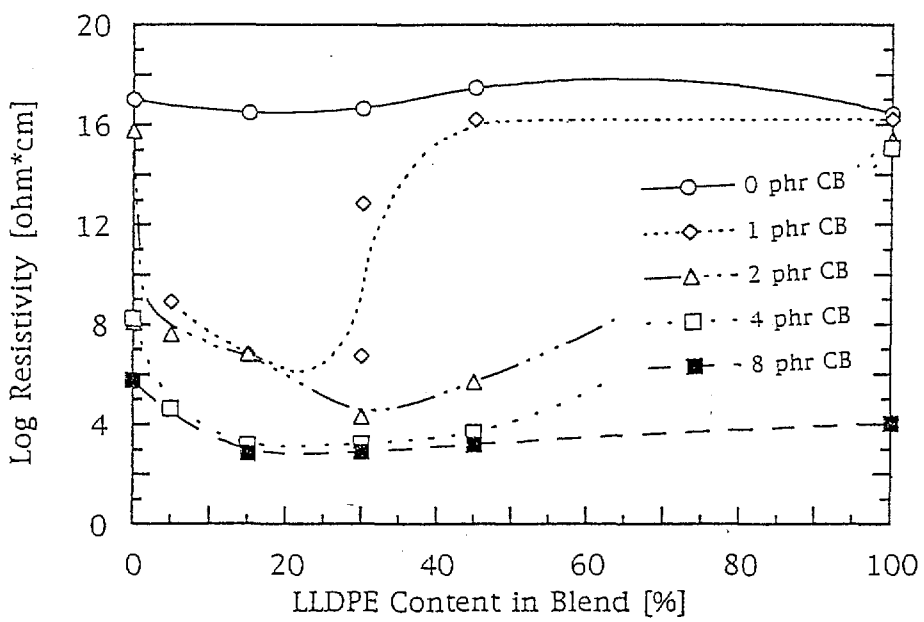

Figure 9: Resistivity as a function of LLDPE content in HIPS/LLDPE blends, for various CB loadings.

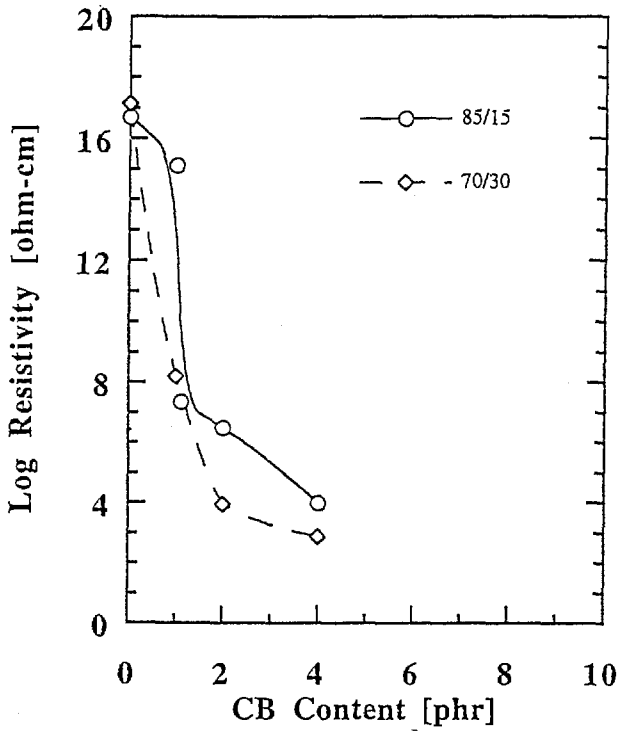

Figure 10: Resistivity vs. CB content of various HIPS/LL25 blends.

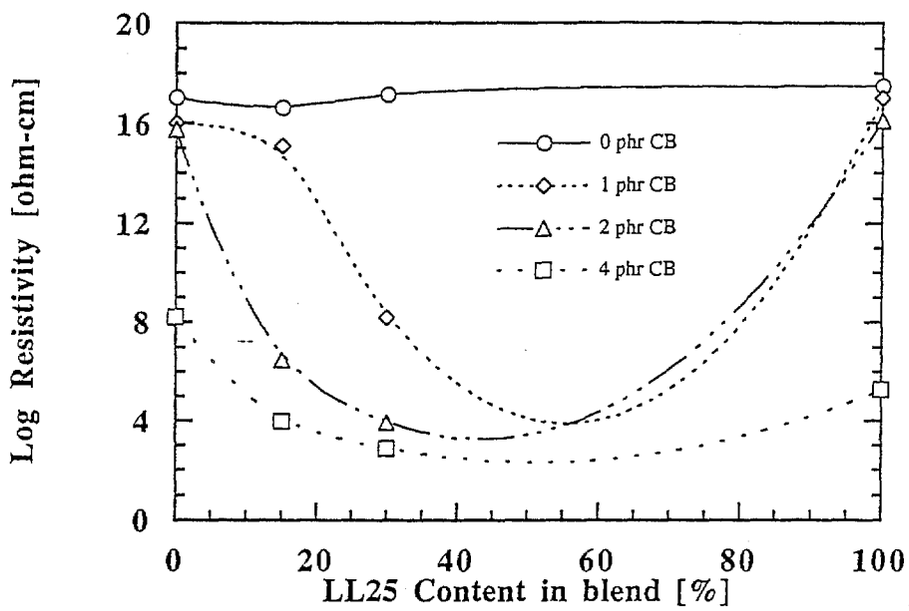

Figure 11: Resistivity as a function of LL25 content in HIPS/LL25 blends, for various CB loadings.

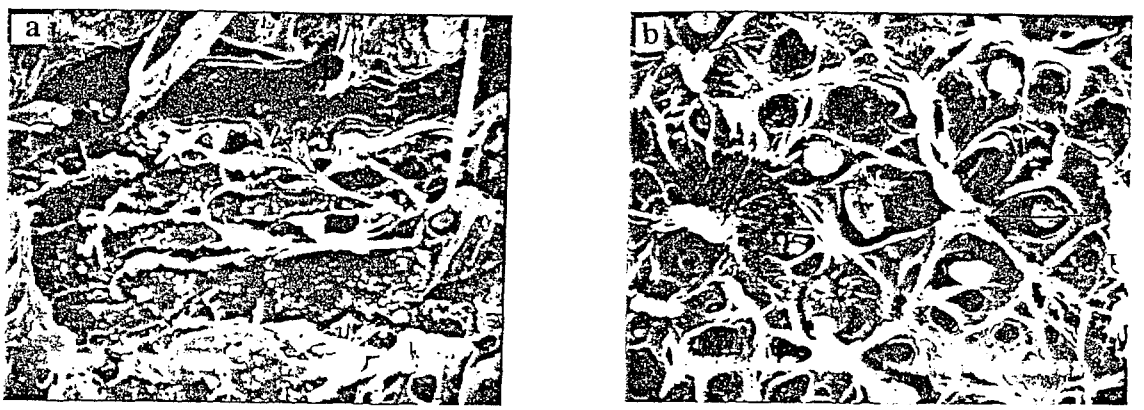

Figure 12: SEM micrographs of microtomed samples of injection molded 85HIPS/15LLDPE+ 4 phr CB:

a. parallel to flow

b. transverse to flow

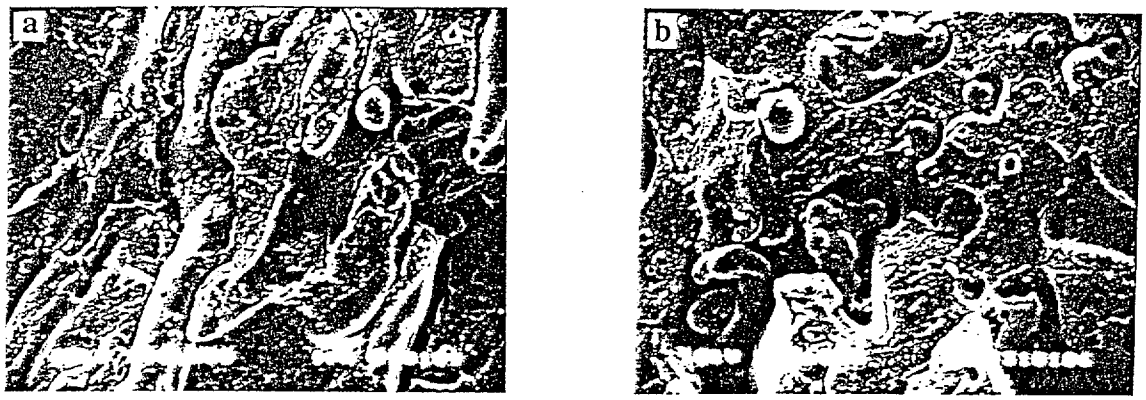

Figure 13: SEM micrographs of freeze fractured samples of injection molded 70HIPS/30LLDPE+ 4 phr CB:

a. parallel to flow

b. transverse to flow

2. RHEOLOGICAL PROPERTIES OF HIPS BLENDS

2.1 HIPS/LCP - Rheology and extrudate morphology

The rheological and morphological propertes of Brabender-mixed HIPS/LCP/CB blends are presented in this chapter. Rheological measurements were carried out in Instron machine at 210 °C and 270 °C with a capillary of 2" length and 0.05" diameter. Some extrudates were freeze-fractured for SEM observation. The influence of LCP content on the HIPS/LCP blend viscosity is presented in Fig. 2.1.1. It is clearly seen that the initial viscosity of neat HIPS decreases upon LCP addition at all the shear rates. It is important to notice that this viscosity reduction becomes less significant as the shear rate increases. At 270 ° C the viscosity of the HIPS/LCP=80/20 composition is almost one order smaller in comparison to that at 210 ° C. Conversely, CB addition to HIPS leads to an increase in the initial HIPS viscosity (Fig. 2.1.2), in a similar manner for all shear rates. The influence of temperature on viscosity was studied only for the (HIPS+2 phr CB) composite, and a drastic reduction in viscosity was observed at the low shear rates region.

The viscosity-composition relationship changes in a complex manner for three-component blends (HIPS/LCP/CB). For blends containing 2 phr CB (Fig. 2.1.3), a decrease in viscosity is observed for all HIPS/LCP ratios compared to the viscosity of neat

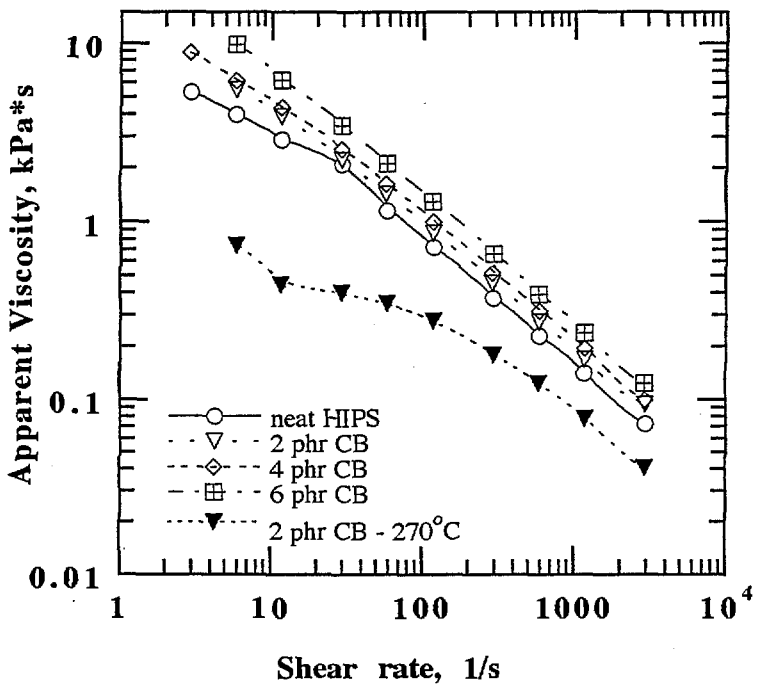

Figure 2.1.1: Apparent viscosity vs shear rate for HIPS with various CB content.

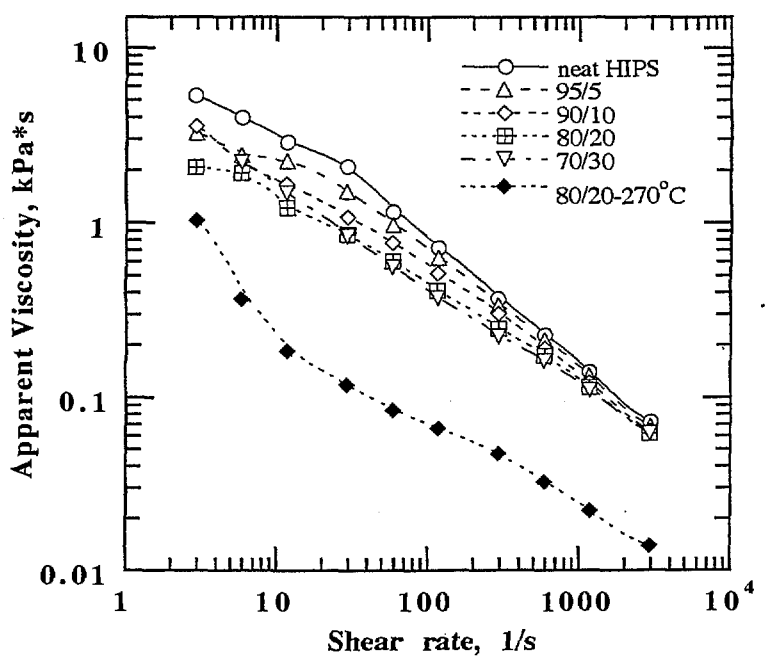

Figure 2.1.2: Apparent viscosity vs shear rate for HIPS with various LCP content.

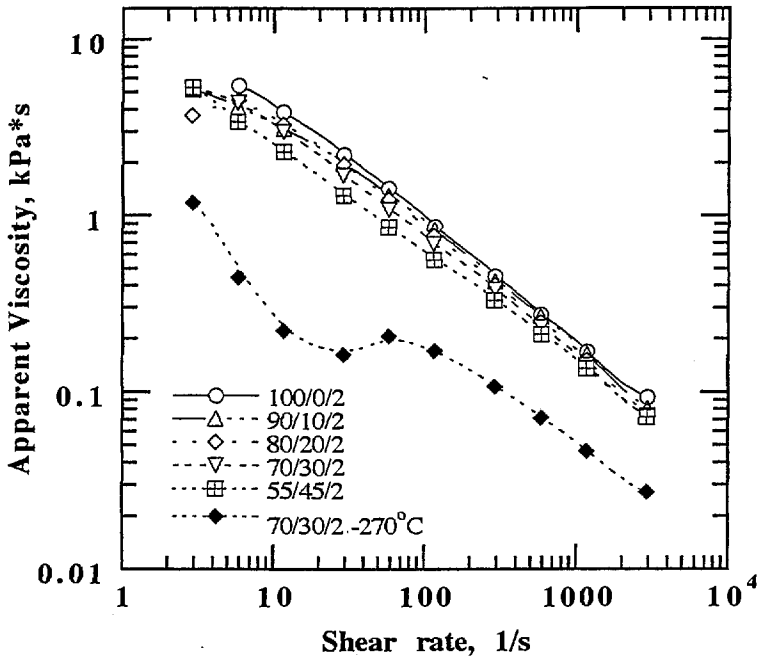

Figure 2.1.3: Apparent viscosity vs shear rate for HIPS with various LCP content at 2 phr CB content.

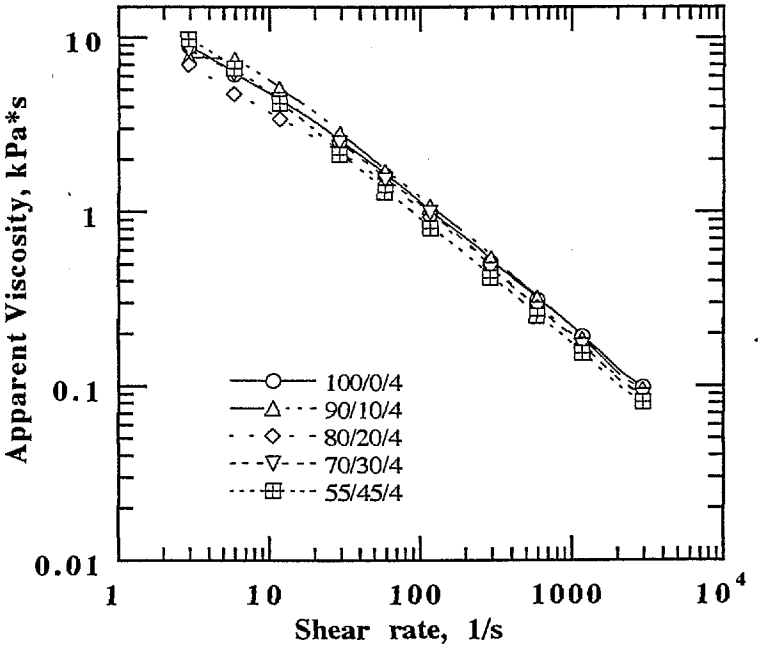

Figure 2.1.4: Apparent viscosity vs shear rate for HIPS with various LCP content at 4 phr CB content.

HIPS. For the blends containing 4 phr CB (Fig. 2.1.4), intersection points are detected for viscosity-shear rate curves. It is rational to assume that for the HIPS/LCP/2phrCB blends the influence of LCP presence on the blends' viscosity is more crucial than that of CB; however, when 4 phr CB are incorporated, a competition arises between CB and LCP, resulting in a more complicated behaviour of blend viscosity. This is reflected in Fig. 2.1.5, depicting viscosity changes with LCP content for different shear rates. Apparently, blends with 4 phr CB demonstrate the strongest variation. These results are indeed understandable in correlation with structure of blend extrudates, obtained at various shear rates rate and temperatures. Morphology was studied using SEM Jeol 5400. Extrudates were fractured in liquid nitrogen in two directions: parallel and transverse to the flow direction.

Figure 2.1.6 depicts micrographs of HIPS/CB composites. As mentioned earlier, it is very difficult to identify CB paticles within the fractured HIPS matrix. The butadiene rubber phase within HIPS is clearly seen. These regions are especially noticable for samples with 6 phr CB in comparison to those with 2 or 4 phr CB. There is no difference in the appearance of 2 phr CB samples, prepared at 210 ° C and 270 ° C. The direction of flow does not affect the morphology either.

Figures 2.1.7 - 2.1.9 show freeze-fractured surfaces of HIPS/LCP extrudates in the absence of CB. It is clearly seen that the both parameters of rheological meagurements - shear rate and temperature - are essential for the structural transformation of the extrudate

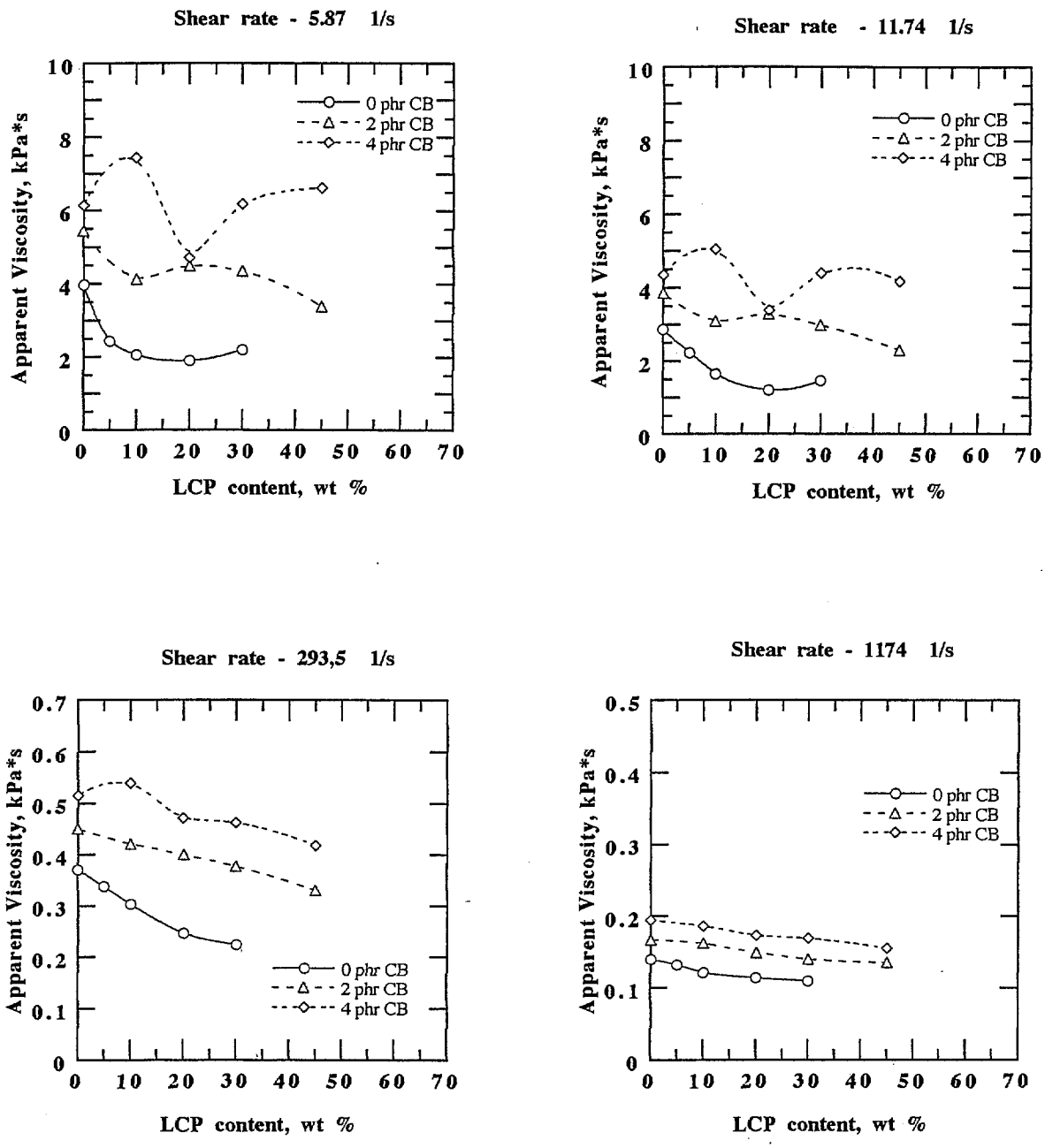

Figure 2.1.5: Apparent viscosity vs LCP content at constant shear rate for HIPS with various CB content: a - 5.87 1/s; b - 11.74 1/s; c - 293.5 1/s; d - 1174 1/s.

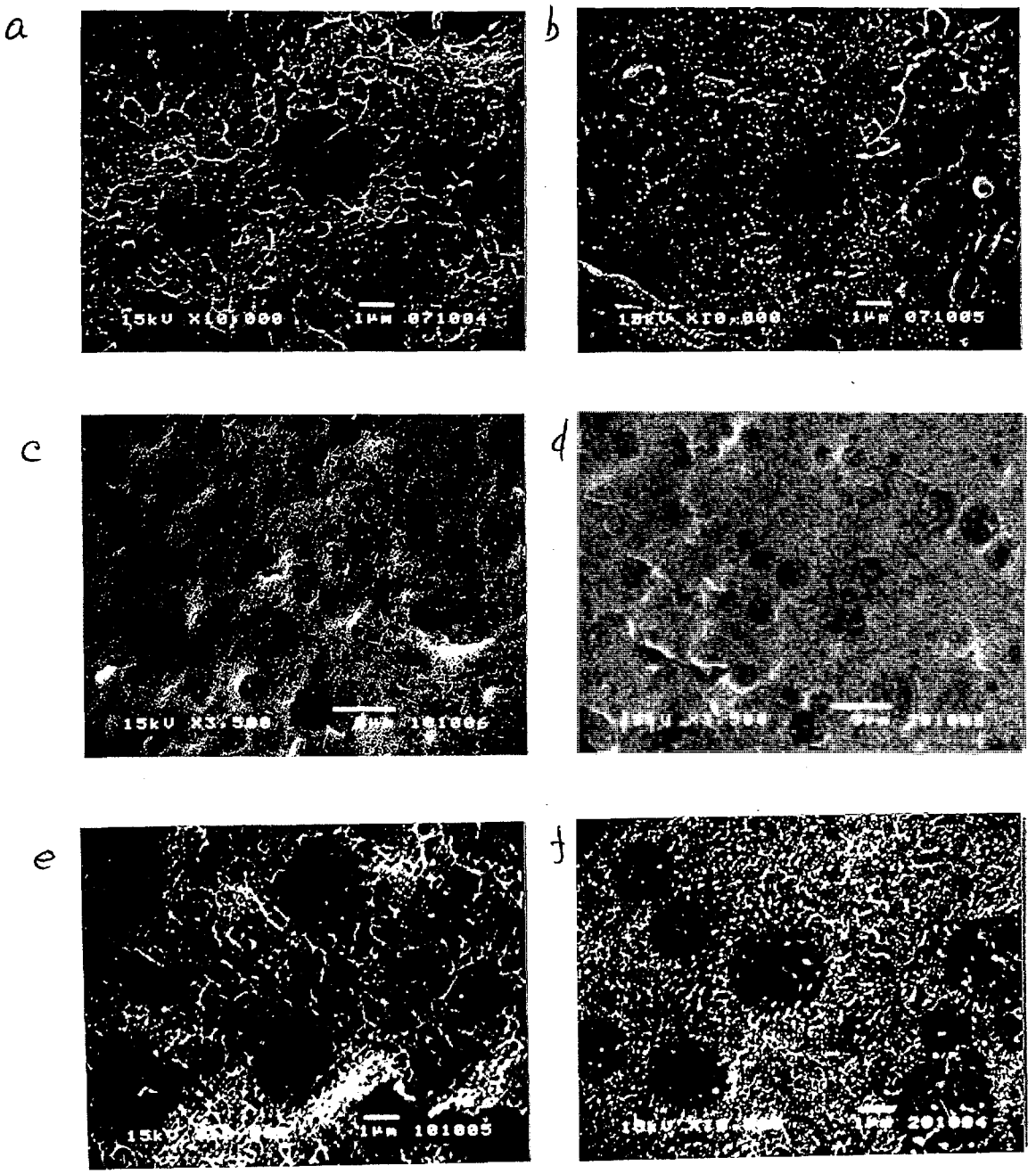

Figure 2.1.6: SEM micrographs of HIPS/CB extrudates: a, b - 2 phr CB, 5.87 1/s, transverse to flow direction; c, e - 4 phr CB; d, f - 6 phr CB; c, d, e, f - 1174 1/s, parallel to flow direction; a, c, d, e, f - 210 °C; b - 270 °C.

at a given composition ratio. As shown in Fig. 2.1.7, at 210 °C for HIPS/LCP=80/20 blend the increase of shear rate from 11.74 1/s to 1174 1/s is accompanied by a significant decrease of the cross section of the LCP dispersed phase with a simultaneous decrease of its length. Rupture of the LCP dispersed particles under high shear stress during flow may cause the observed change in morphology. A different morphology is found for the same composition and shear rates at 270 °C (Fig. 2.1.8). At low rates LCP is dispersed as spherical particles of widely distributed diameters, transforming into an elongated structures at high rates. This transformation may arise from coalescence of the LCP particles within the melt flow. Both rupture and coalescence tendencies together with deformation of the dispersed phase occur during melt mixing and flow. Change in viscosity of polymer components due to temperature coincidentally with the above-mentioned factors determine the observed alternation in structure.

It is evident that the polymer ratio in the blend is also an important factor, responsible for size and shape of the dispersed phase. Figure 2.1.9 depicts micrographs of the HIPS/LCP=70/30 blends at 210 °C. An additional content of LCP in the blend does not lead to a principal modification of the morphology as shear rate varies. Although the LCP particle diameter is reduced as the shear rate increases, the particle shape remains elongated, contrary to the former blend.

As already well-established [9,10], incorporation of CB in the blend affects its morphology radically. This presence of CB influences the rheological properties, thus

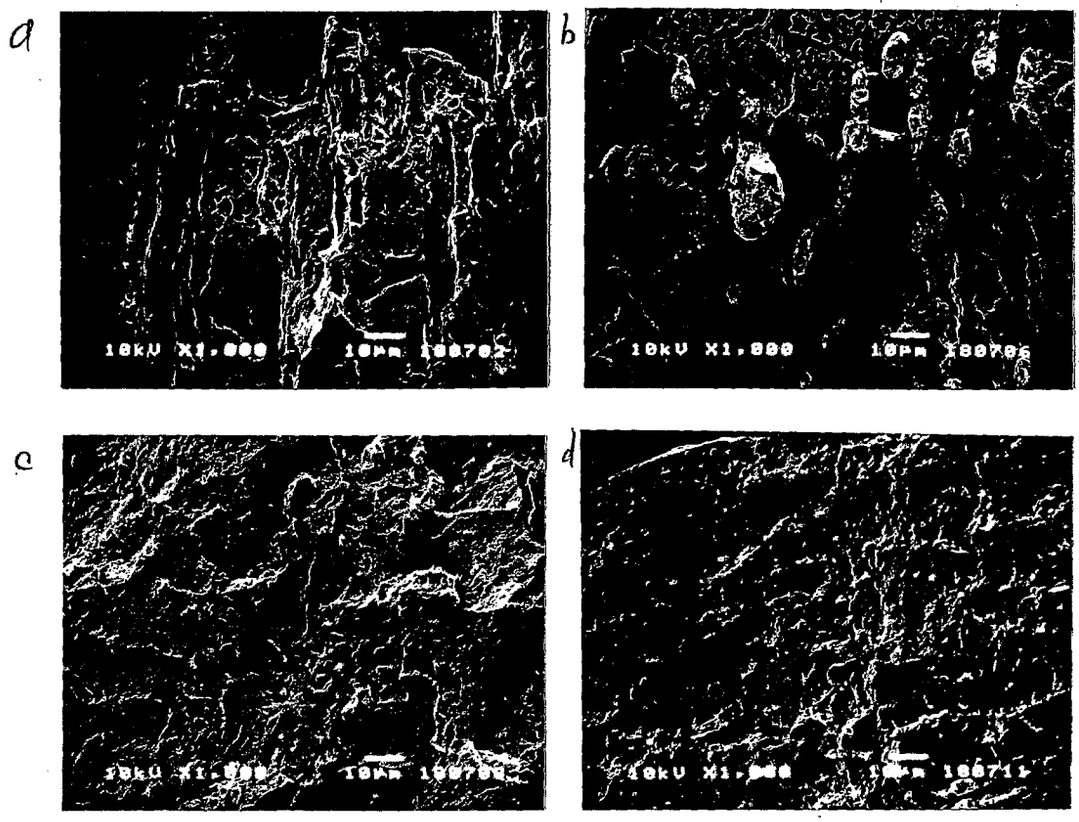

Figure 2.1.7: SEM micrographs of HIPS/LCP=80/20 extrudates, 210 °C; a, b - 11.74 1/s; c, d - 1174 1/s; a, c - parallel to flow direction; b, d - transverse to flow direction.

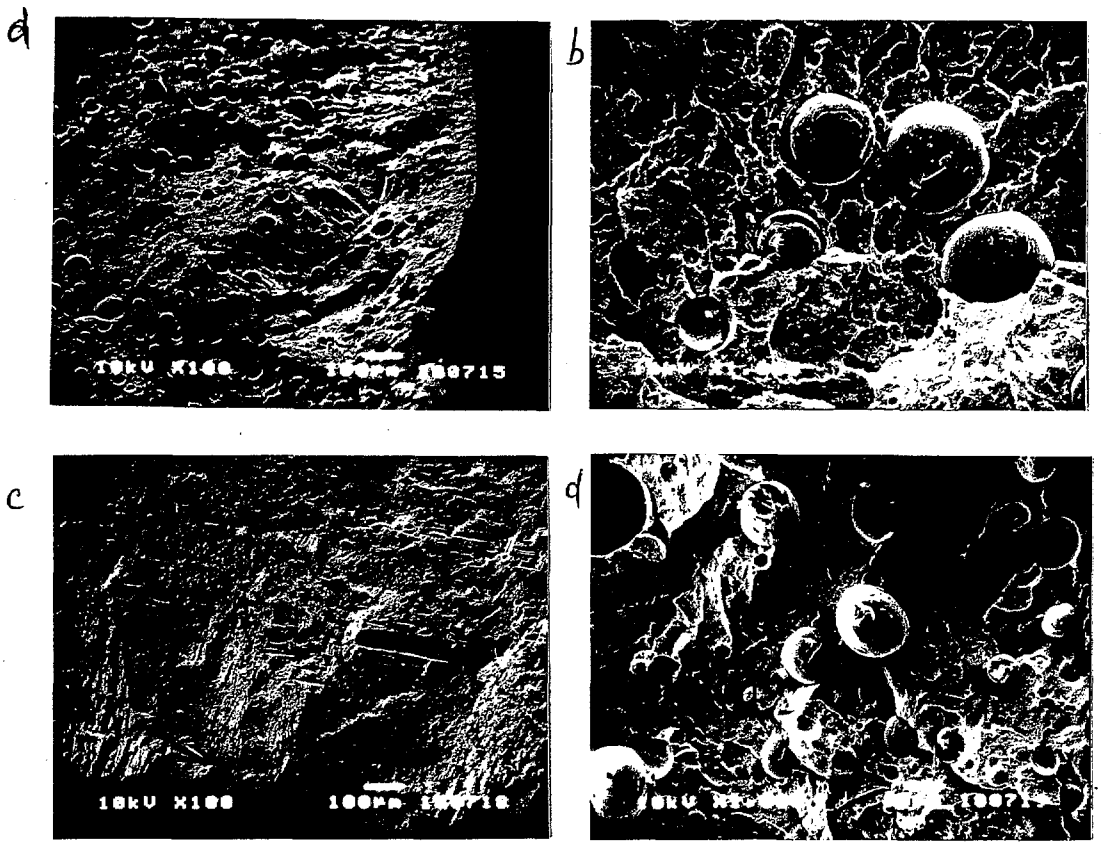

Figure 2.1.8: SEM micrographs of HIPS/LCP=80/20 extrudates, 270 ° C; a, b -11.74 1/s; c, d - 1174 1/s; a, c - parallel to flow direction; b, d - transverse to flow direction.

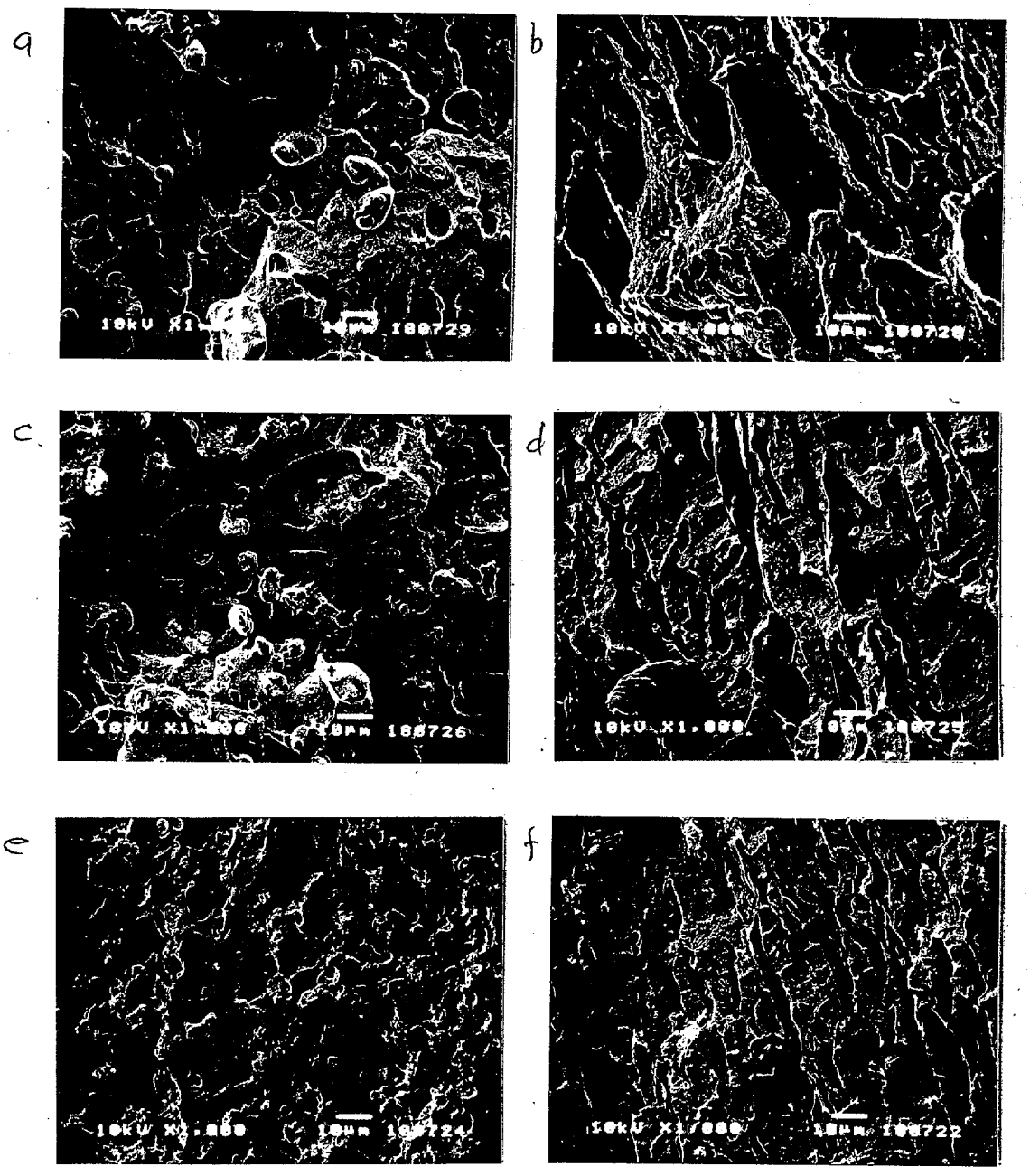

Figure 2.1.9: SEM micrographs of HIPS/LCP=70/30 extrudates, 210 ° C; a, b - 11.74 1/s; c, d - 293.5 1/s; e, f - 1174 1/s; a, c, e - transverse to flow direction; b, d, f - parallel to flow direction.

governing the structure of the extrudates. As was reported previously [32], in the HIPS/LCP/CB blends CB is located in the LCP phase, decreasing markedly its dimenson compared to that of the neat blend. Figure 2.1.10 depicts the distribution of the CB-filled LCP paricles in the HIPS/LCP/CB=80/20/2 blend. As expected, LCP is distributed as very fine particles in this blend in comparison to the neat blend, its particles smaller in diameter than 1 μm. Analysis of blend strucrure - with and without of CB (Fig. 2.1.7 and Fig. 2.1.10) detects an additional difference, namely, for CB-containing blends of 80/20 component ratio the LCP phase is more elongated at the high shear rate than the blend free of CB, which appears more elongated at low shear rates.

More detailed SEM observation was carried out for the CB-filled blends of 70/30 component ratio. These micrographs are shown in Fig. 2.1.11- 2.1.14. Again, the LCP phase is dispersed more finely as the CB content and the shear rate increase (Fig. 2.1.11 and 2.1.12). At 210 °C, elongation of the CB-containing LCP phase seems less sigificant than for the neat blend, practically disappearing for the 70/30/4 blend (Fig. 2.1.12 d). At 270 °C the LCP phase is dispersed more coarsely, and is more elongated for the 2 and 4 phr CB filled blends (Fig. 2.1.13 and 2.1.14). It should be emphasized that the influence of high temperature on the shape of the LCP phase is similar for the both blends with and without CB: at 210 °C LCP is more elongated at a low shear rate and at 270 °C - at a high shear rate. This may be explained again in terms of a competition of rupture and

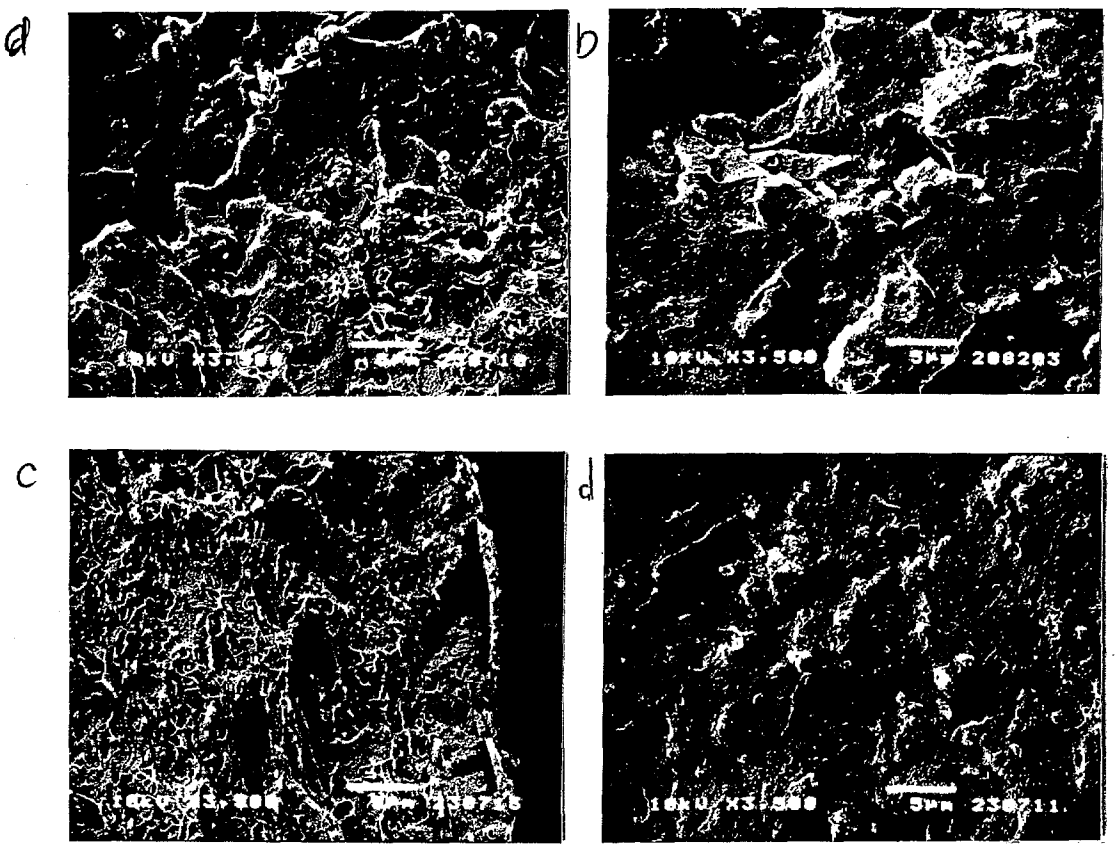

Figure 2.1.10: SEM micrographs of HIPS/LCP/CB=80/20/2 extrudates; 210 ° C; a, b - 11.74 1/s; c, d -1174 1/s; a, c - parallel to flow direction; b, d - transverse to flow direction.

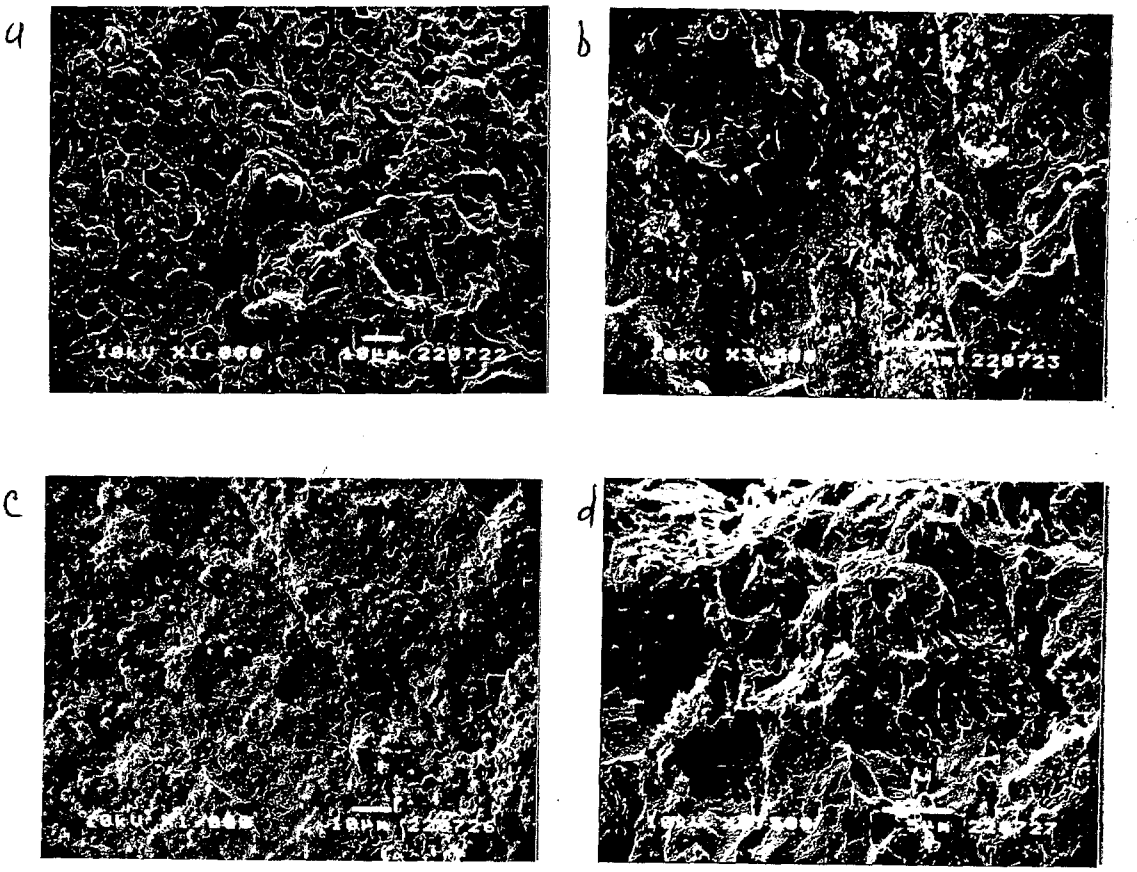

Figure 2.1.11: SEM micrographs of HIPS/LCP/CB=70/30/2 extrudates; 210 °C; a, b - 11.74 1/s; c, d- 1174 1/s; a, c - parallel to flow direction; b, d - transverse to flow direction.

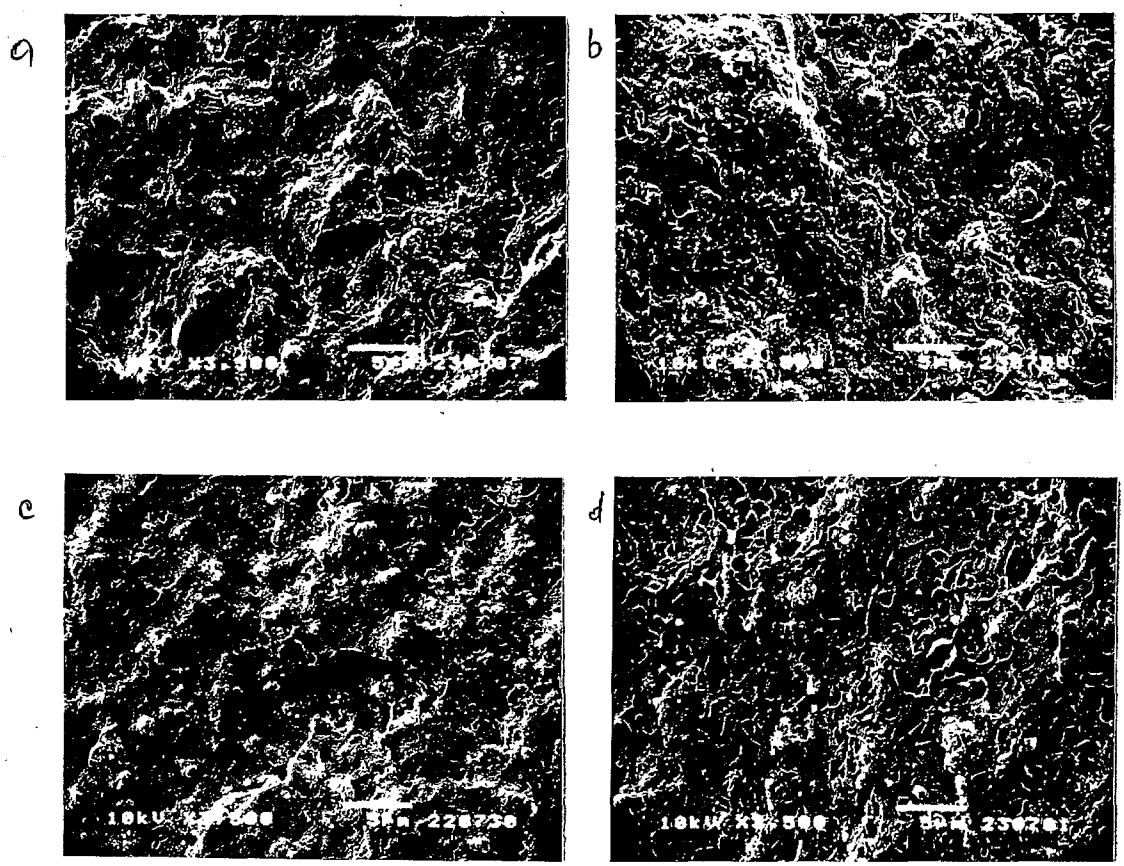

Figure 2.1.12: SEM micrographs of HIPS/LCP/CB=70/30/4 extrudates; 210 ° C; a, b - 11.74 1/s; c, d- 1174 1/s; a, c - parallel to flow direction; b, d - transverse to flow direction.

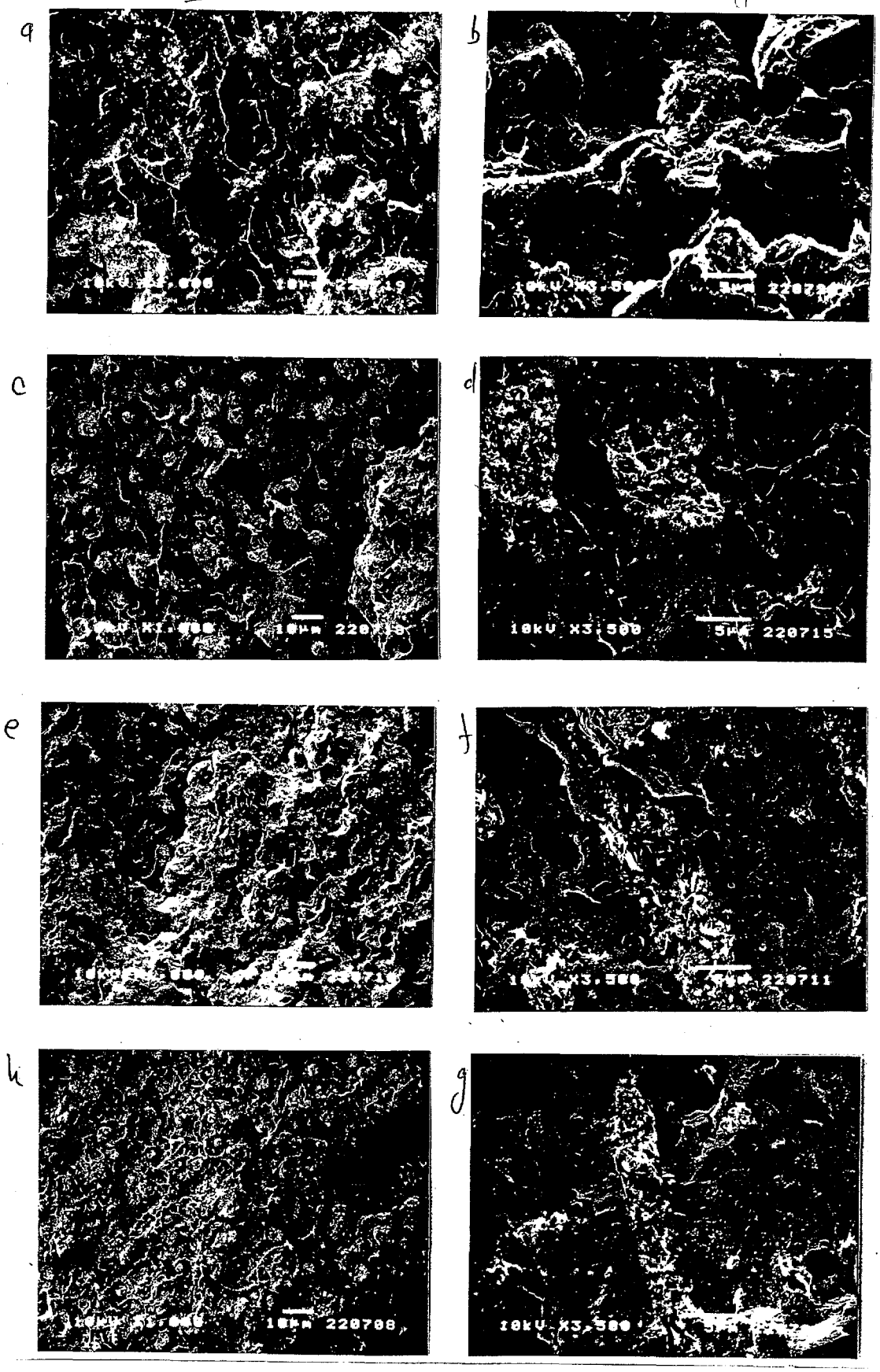

Figure 2.1.13: SEM micrographs of HIPS/LCP/CB=70/30/2 extrudates; 270 ° C; a, b - 11.74 1/s; c, d - 293.5 1/s; e, f - 1174 1/s; h, g - 2945 1/s; a, c, e, h - transverse to flow direction; b, d, f, g - parallel to flow direction.

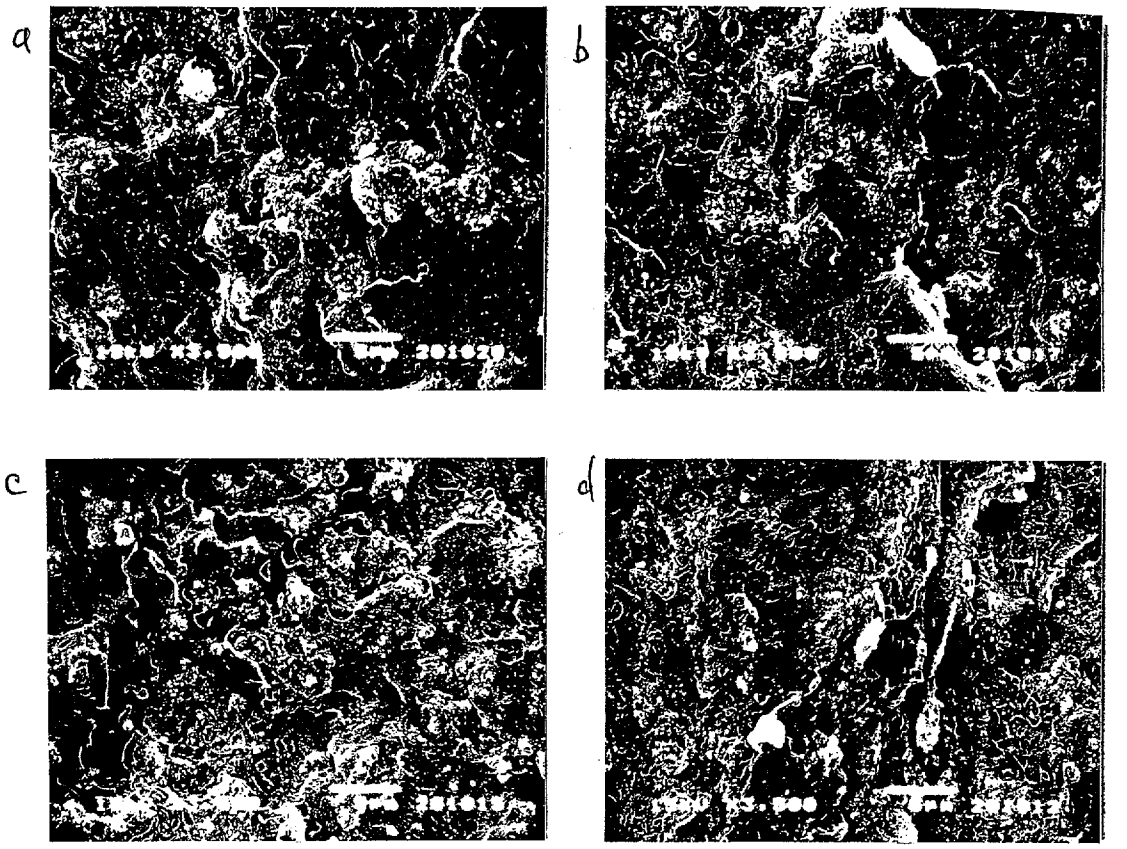

Figure 2.1.14: SEM micrographs of HIPS/LCP/CB=70/30/4 extrudates; 270 ° C; a, b - 5.87 1/s; c, d- 1174 1/s; a, c -transverse to flow direction; b, d - parallel to flow direction.

coalescence tendencies in the melt during flow, resulting from the viscosity change of each component with temperature.

The above-mentioned tendencies are retained for the CB-filled HIPS/LCP=55/45 blends as well (Fig. 2.1.15 and 2.1.16). It addition to this, a noticeable distinction is seen in the LCP dispersion in the center of the extrudate cross section and close to it skin, where the LCP phase is very elongated and strongly flattened in its cross section.

And finally, it is nessesary to point out that the well-known fibrillar structure of the LCP phase, which is observed for the neat samples, maintains its form in the same compositions with CB. CB seems located upon the LCP surface and between its separate fibrils.

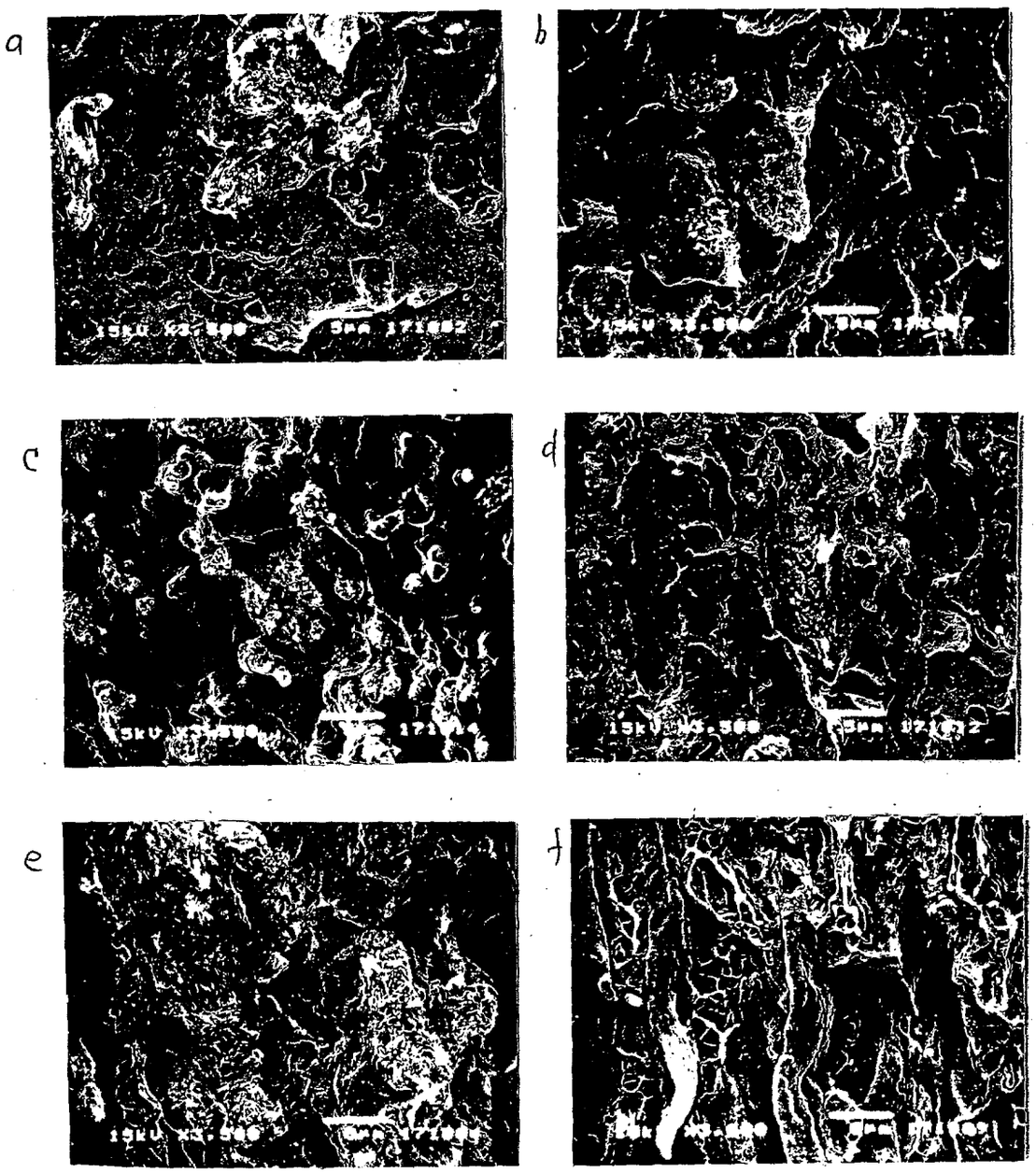

Figure 2.1.15: SEM micrographs of HIPS/LCP/CB=55/45/2 extrudates; 210 °C; a, b, e - 5.87 1/s; c, d, f - 1174 1/s; a, c - transverse to flow direction; b, d, e, f - parallel to flow direction, a, b, c, d - core, e, f - skin.

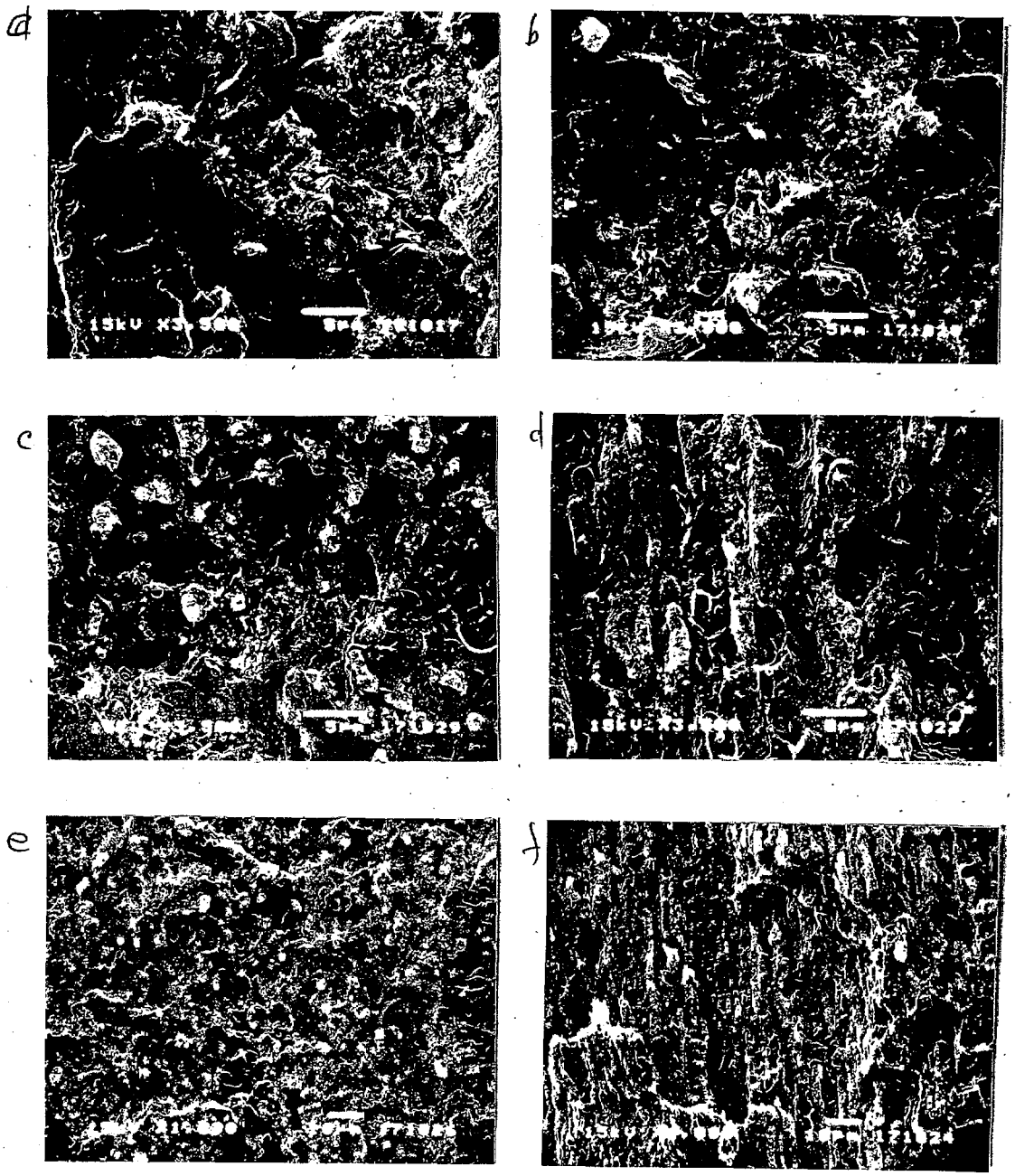

Figure2.1.16: SEM micrographs of HIPS/LCP/CB=55/45/4 extrudates; 270 ° C; a, b - 5.87 1/s; c, d, e, f - 1174 1/s; a, c - transverse to flow direction; b, d, e, f - parallel to flow direction, a, c, e - core; b, d, f - skin.

2.2 HIPS/LLDPE/CB - Rheological Data

CB-loaded LLDPE and HIPS, as well as Brabender mixed HIPS/LLDPE blends (previously analyzed for electrical properties and morphology [32]), were studied for electrical properties in a capillary rheometer situated upon an Instron.

For all samples of LLDPE (neat and CB-filled), the curves depict a similar trend (Fig. 2.2.1). Rheological behavior of samples containing 0, 2 and 4 phr CB is indistinguishable, the curves overlapping each other. LL+8 phr CB has a slightly higher apparent viscosity at low shear rates, but combines with the other samples at high values of shear rates at approximately 1000 1/sec.

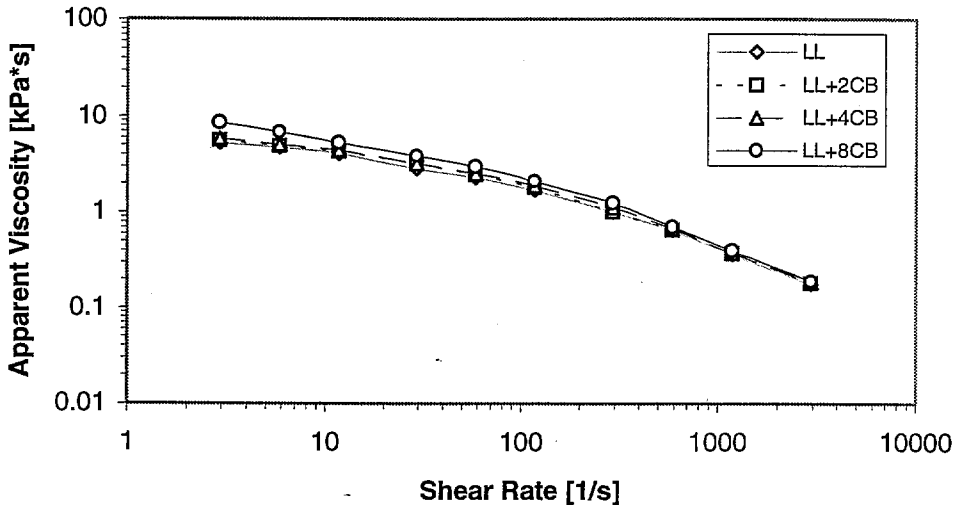

Figure 2.2.1: Apparent viscosity vs. shear rate for LLDPE with various CB loadings.

HIPS reveals a higher apparent viscosity than LLDPE compounds (Fig. 2). Differences in the apparent viscosity of the various samples are maintained throughout the entire shear rate range. Even at CB loadings as low as 2 phr, the apparent viscosity is affected, further increasing when 4 and 8 phr CB are incorporated.

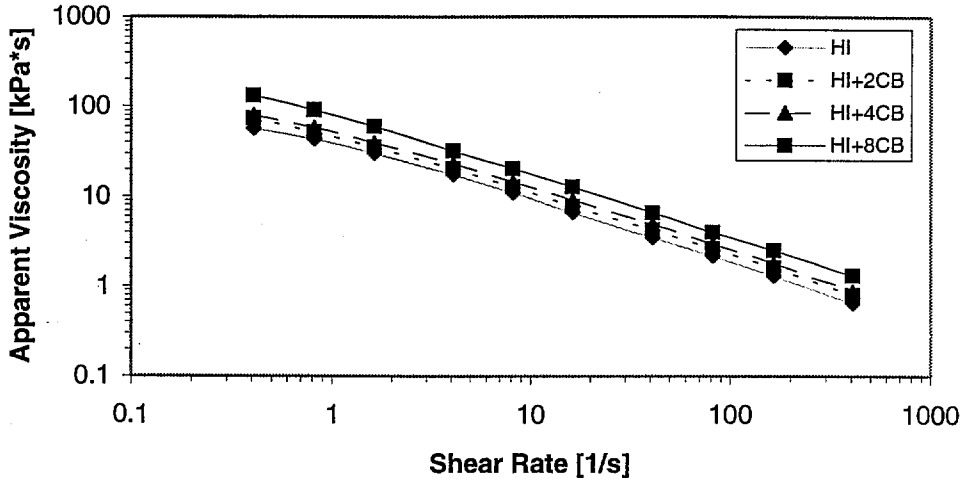

Figure 2.2.2: Apparent viscosity vs. shear rate for HIPS with various CB loadings.

The effect of CB content on the apparent viscosity may be interpreted in terms of the interaction between CB and polymer. LLDPE is relatively unaffected by low CB contents, possibly indicating weak interaction between filler and matrix. Even when the CB content is higher, as is the case for LL+8 phr, interactions which increase viscosity at low shear rates are broken at high shear rates, reducing the viscosity to values typical of the neat polymer. SEM micrographs of these samples (Chapter 1) depict the poor bonding between CB and the LLDPE matrix. CB appears to detach easily from the matrix, the slippage between them preventing an increase in apparent viscosity.

The higher extent to which HIPS is affected by CB presence may indicate stronger interactions between them in comparison to the former matrix/filler system. Both the tendency of HIPS` viscosity to rise significantly at low CB loadings and the increase of viscosity with CB content at high shear rates suggest that bonding between HIPS and CB is more significant. This is affirmed by SEM observations.

It appears to be more relevant to attribute the viscosity rise to CB/matrix interactions than to CB network formation, due to the low CB contents involved. However, it should be emphasized that percolation of HIPS occurs at 2 phr CB loading rather than at 6 phr CB, the value for LLDPE (Chapter 1). Thus, a well established filler network is formed at low CB contents in HIPS, providing some

resistance to flow, resulting in higher viscosity. In LLDPE this comes into effect only above percolation at 8 phr CB loading.

Apparent viscosity vs. shear rate curves of HIPS/LLDPE blends vary according to polymer and CB content, the 85HI/15LL blend relatively similar to HIPS and the 55HI/45LL similar to LLDPE in rheological behavior (Fig. 2.2.3-5). Curves depicting apparent viscosity vs. dispersed phase (LLDPE) content reveal large viscosity differences between the blends at various CB loadings, more so for the low shear rate region (Fig. 2.2.6) than for the high shear rate values (Fig. 2.2.7). These differences become less significant when the LLDPE content in the blend increases. At 15% LLDPE, the apparent viscosity of both neat and loaded blends is drastically reduced, for all shear rates. At low shear rates the apparent viscosity decreases very gradually with increasing LLDPE content especially for the 4 and 8 phr contents. At high shear rates, changes in apparent viscosity for 15, 30, 45 and 100% are very mild, remaining practically constant. The variation of viscosity with LLDPE content is non-monotonic, but depicts a negative deviation behavior.

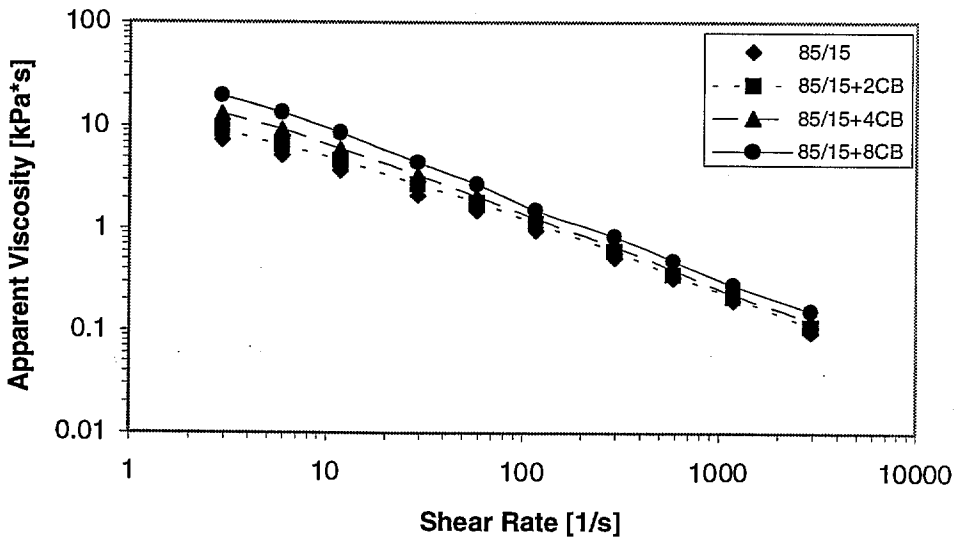

Figure 2.2.3: Apparent viscosity vs. shear rate of various CB-loaded 85HIPS/15LLDPE blends.

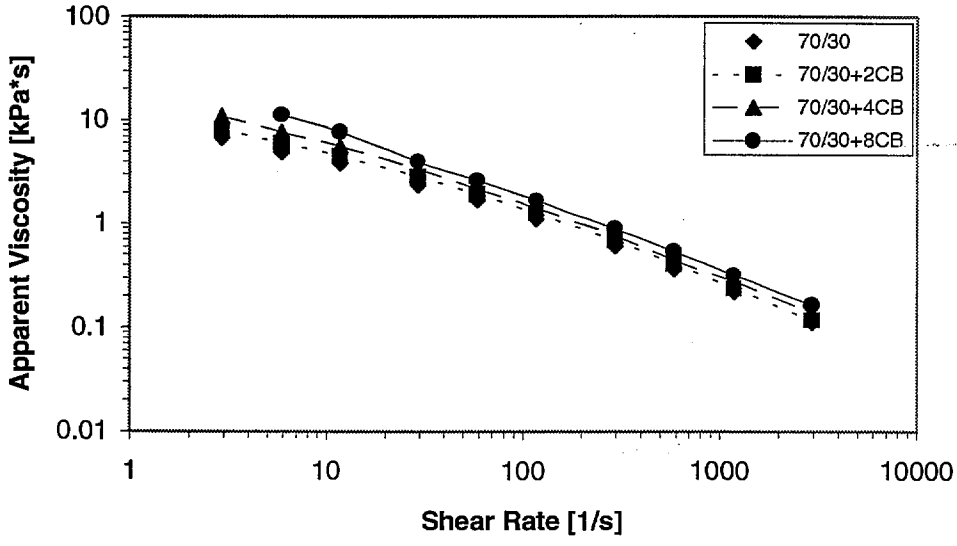

Figure 2.2.4: Apparent viscosity vs. shear rate of various CB-loaded 70HIPS/30LLDPE blends.

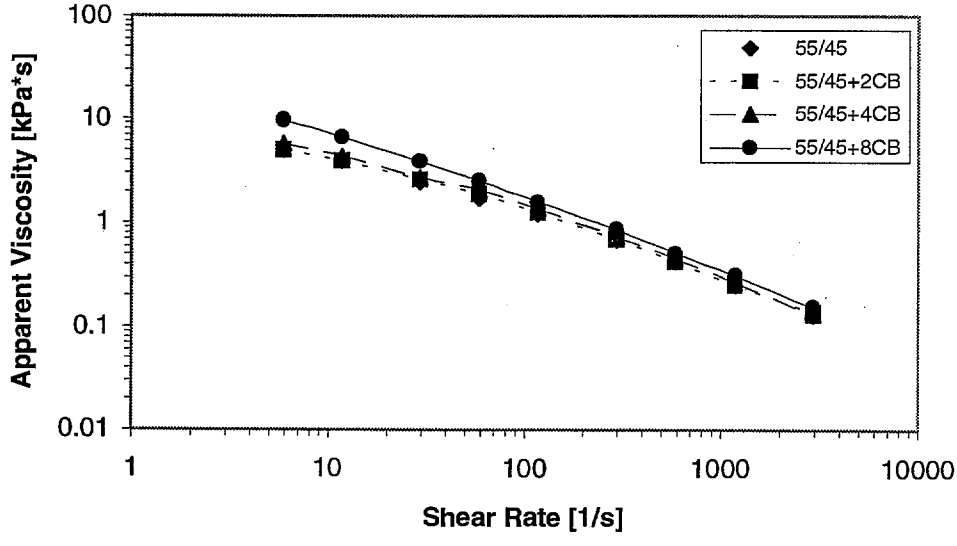

Figure 2.2.5: Apparent viscosity vs. shear rate of various CB-loaded 55HIPS/45LLDPE blends.

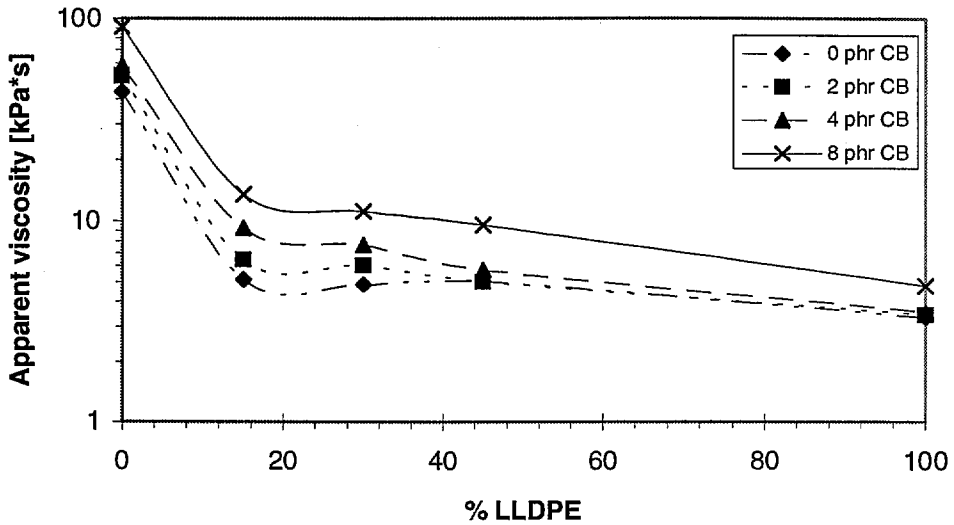

Figure 2.2.6: Apparent viscosity vs. LLDPE content for various CB-filled HIPS/LLDPE blends (low shear rate).

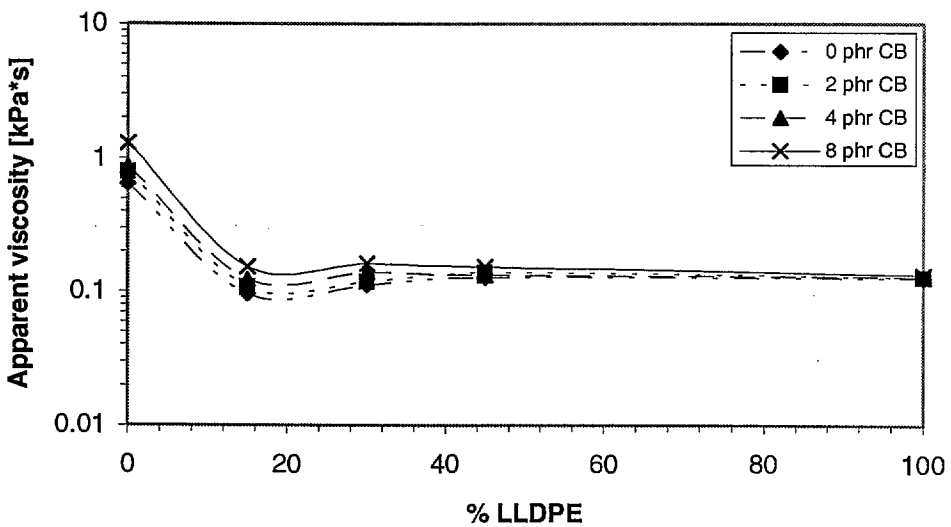

Figure 2.2.7: Apparent viscosity vs. LLDPE content for various CB-filled HIPS/LLDPE blends (high shear rate).

The changes in viscosity of HIPS/LLDPE/CB systems, may be attributed to a combination of effects: the addition of a lower viscosity dispersed phase to a matrix of higher viscosity, as expected even by a simplified rule of mixtures; the incompatibility between the phases, causing slippage between them; the inclination of the dispersed phase to elongate and orient under shear induced flow; and finally, the effect of CB on matrix viscosity, pertaining to the extent of interaction between filler and matrix. The radical reduction in apparent viscosity observed upon addition of 15% LLDPE may be attributed mainly to the low LLDPE viscosity, the interphase slippage as well as orientation effects. When LLDPE content is increased to 30% and 45%, the values of apparent viscosity do not change dramatically. At these compositions, phase inversion occurs and the low viscosity element becomes co-continuous, providing a structure of interlocking phases less mobile, the LLDPE dominant in determining the viscosity value. The CB, located upon the LLDPE surface, has a more significant effect at low shear rates, friction between CB-coated LLDPE and HIPS being more important than for high shear rates. As the dispersed phase content in the system increases, the effective CB content within it decreases as well, diminishing the effect of increased viscosity due to CB presence. It is therefore apparent that a combination of factors determine the overall behavior of CB-filled polymer blends.

Due to the fact that CB locates in LLDPE rather than in HIPS, but does not affect its viscosity significantly, the point of phase inversion remains unchanged for the CB loaded blend in comparison to the neat blend. Although the HIPS/LLDPE does not correspond exactly to the viscosity ratio law for phase inversion [33], the lower viscosity LLDPE does tend to envelope the higher viscosity phase by becoming co-continuous at a relatively low dispersed phase content. Due to the fact that some of the HIPS is sub-included within the dispersed LLDPE phase, the apparent LLDPE volume fraction is actually higher than the nominal content incorporated [34]. Again, because interfaces between both polymers are mobile viscosity does not increase.

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Research, Development and Consulting Center POLYMAK

ANNUAL REPORT

ELECTRICALLY CONDUCTIVE STRUCTURED POLYMER BLENDS

M. Kozlowski and A. Kozlowska

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September 1996

INTRODUCTION

Polymers are predominantly electrical insulators, which is unfavourable for several applications. A common practice for increasing their low conductivity is mixing polymers with electrically conductive fillers, like carbon black, metal powder or flakes, carbon fibers. Recently significant attention has been paid to modification by means of intrinsically conductive polymers. Above a critical content of electrically conductive polymer or filler, it forms conductive pathways thoroughout the matrix polymer. Percolation concept has been widely used for a treatment of electrical conductivity in polymer materials.
Our previous results on composites filled with carbon black (CB) have evidenced that matrices composed of polymer blends are especially suitable for manufacturing materials with a low filler content. In the research program performed during previous two years four kind of polymers have been taken into consideration: PS, LDPE, EVA and SBS. We have concluded, that advantegous matrices are composed of heterogeneous blends with one component being partially crystalline. The electroconductivity of polymer-CB compounds increases with the increasing crystallinity. Interpretation of our results in terms of a multiple percolation concept allows an explanation of such low pecolation treshold as 0.01 of CB in LDPE/PS blends.
During the third year duration of the project a research has been continued on carbon black filled liquid crystalline polymer (LCP) as well as PS/LCP blends.
The research has been focused particularly on the conductivity and melt rheology of polymer blends filled with carbon black. Morphology of polymer blends was inspected, which is of crucial importance for conductivity of multicomponent materials. Tensile tests complement the characteristics of investigated systems.

Additional set of experiments deals with the mixing technology modification:
- CB composites obtained by delayed addition of one component;
- CB composites with a three-component polymer matrix.

EXPERIMENTAL

Materials

The research program has covered experiments with the following polymers:
- PS from ZCh Oswiecim, Poland;
- LCP Rodrun LC 3000 from Unitika Ltd.;
- EVA(ethylene-vinyl acetate) copolymer Ribolene from Enimont;
- SBS (styrene-butadiene-styrene) tri-block copolymer from Shell.

All blend ratios described relate to percentage by weight.
Carbon black EC-600 JD from Akzo Nobel was used as a filler in this study.

Liquid crystalline polymer blends and composites were prepared by melt mixing of the components in a Brabender Plasticorder mixing unit at 210°C. We used 60 rpm rotor velocity, at 5 minutes of a mixing time. The plaques of approximately 1 mm thick were compression molded at 210°C.
Other blends were compounded at a mixing head temperature of 160°C.

Test methods

The volume and surface resistivity were measured using a Keithley 6512 Programmable Electrometer. We used the three-electrode arrangement for the DC-measurements of insulation resistance. The samples were Al-coated by evaporation prior to the measurements.

Morphology inspections were performed with a scanning electron microscope Jeol T300, on specimens fractured in liquid nitrogen and vacuum-coated with the Au/Pd layer.

The rheological properties of polymers and CB-composites were evaluated both by the steady state and dynamic mode. Steady state flow was characterised by the measurements 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.

Dynamic measurements were performed using Rheometrics RDSII dynamic spectrometer. 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 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_r and the elongation at break ε were registered.

RESULTS AND DISCUSSION

1. Liquid crystalline polymer - based matrices.

Electrical conductivity was of primary interest in our experiments. Influence of CB-content on the volume resistivity level of PS, LCP and their blends has been presented in Figure 1. The results presented below have shown that LCP and LCP based blends are conductive at much lower loading of carbon black than the PS composites, proportionally to the liquid crystalline polymer content in a system.

Although at higher CB content, polystyrene based composites give rise to higher level of electrical conductivity in comparison to the matrices containing liquid crystalline polymer. This finding may be of importance for particular applications (the difference is approximately two decades).

The percolation treshold for respective composites filled with carbon black has been estimated and presented in Table 1. Critical CB content in LCP (1.9 wt.%) is of similar value to that observed for PS/LDPE blends. Although crystallinity of both polymers is of primary importance, the mechanisms of conductivity in the liquid crystalline polymer and in partially crystalline polymer depend on different parameters (e.g. flow field and cooling dynamics, respectively).

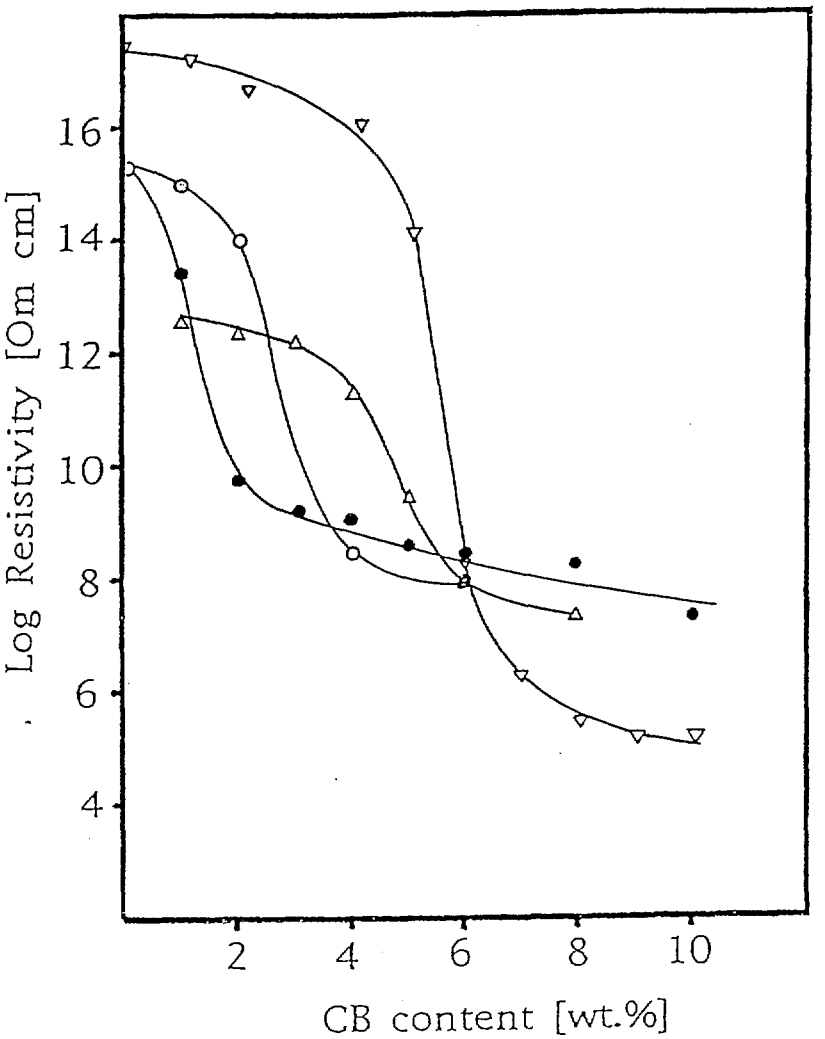


Figure 1. Volume resistivity of composites with different CB content and polymer matrices (▽ - PS; ● - LCP; Δ - PS/LCP 90/10; o - PS/LCP 50/50).

Table 1. Percolation treshold of CB-composites.

Polymer matrix	Percolation treshold, wt.%
PS	6.5
LCP	1.9
PS/LCP 90/10	5.5
PS/LCP 50/50	3.5

Very low percolation treshold, which has been observed for LCP-composite, may be attributed to self-organisation of the thermotropic polymer macromolecules. Such structurization may favour a particular CB particles distribution, thus leading to formation of conductive pathways through the composite.

Significantly lower critical carbon black content in case of PS/LCP blends in comparison to that of PS, has been interpreted by means of multiple percolation concept. At particular conditions CB-particles may be located preferentialy in only one phase, which percolating a matrix performs electrical conductivity. Seeking the optimum PS/LCP composition we prepared blends with 10-20-50 wt.% of liquid crystalline polymer. Electrical conductivity of such composites has been presented in Figure 2.

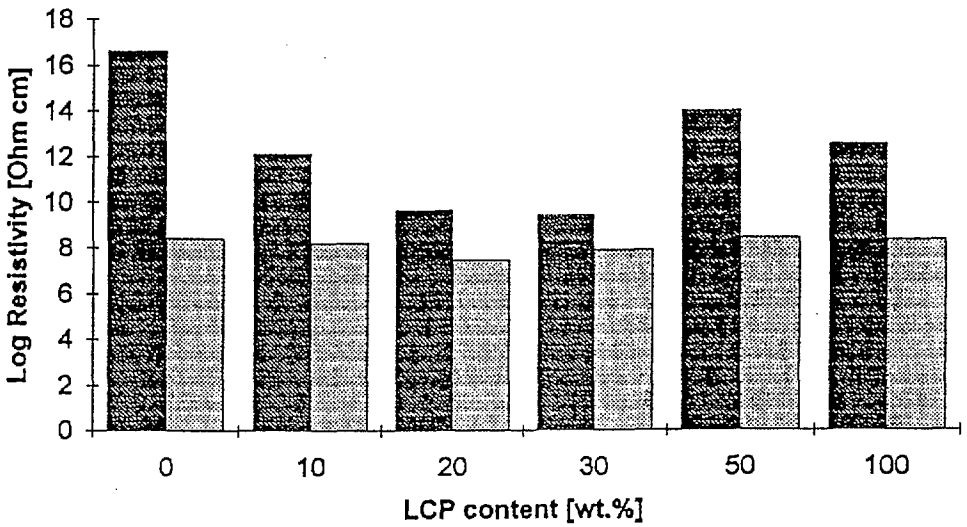
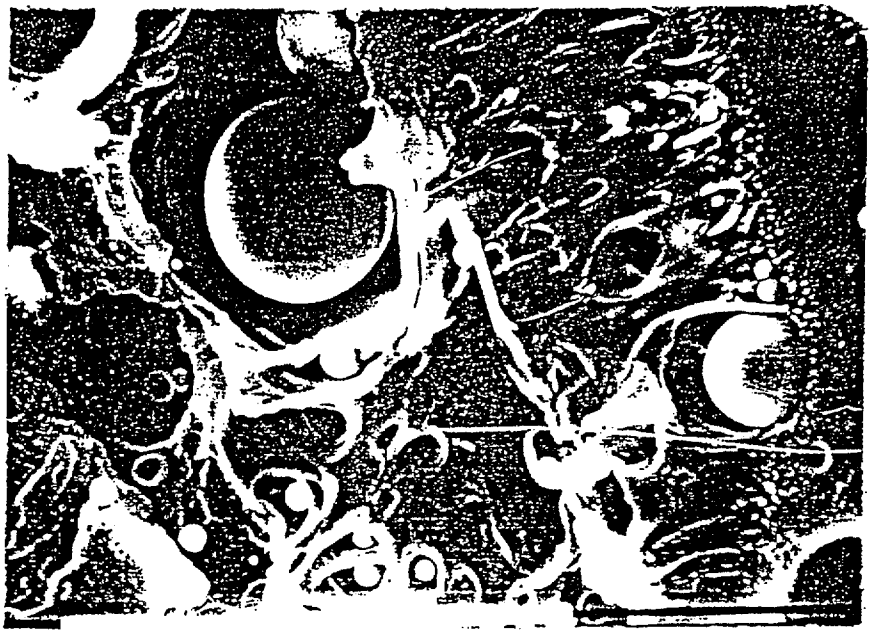


Fig. 2. Resistivity of PS/LCP composites with 2 wt.% (hatched) and 6 wt.% of carbon black.

All composites with 6 wt.% of CB exhibit similar level of conductivity, which shows that a percolation treshold has been surpassed for every composite. Slightly lower level of conductivity has been found for composites with 2 wt.% of CB, composed of matrices with 20 or 30 wt.% of LCP. Therefore one may expect particular properties of such materials.

However, our expectations concerning self-organization of LCP blends resulting from a characteristic performance of this polymer under processing, and subsequent significant decrease in a percolation treshold were not satisfied. After inspection of morphology we found, that for composites with 10 wt.% of LCP the orientation of liquid crystalline polymer domains does not occur (Figure 3 and 4). We assume that the stress level upon mixing in a Brabender mixing unit was not sufficient, and particularly, that the elongational forces partition was to low.

One may expect that with increasing LCP-amount a coalescence probabilty will increase up to the formation of larger domains, which should deform in a matrix into interpenetrating network of fiber-like bodies. Similar effect should have an intensive flow with increased shear rate and high fraction of elongation. This has been verified by SEM observations of extruded strands after the capillary rheometry measurements.



0.1 mm

Figure 3. Phase structure of PS/LCP 90/10 blend after 5 min. mixing in a Brabender mixing unit at 40 rpm.

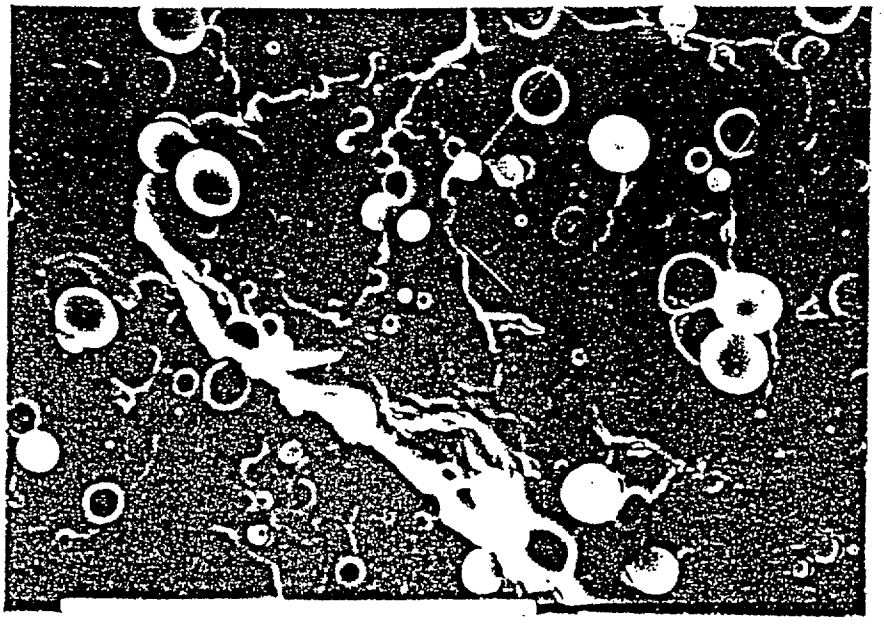


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Figure 4. SEM-micrograph of PS/LCP 90/10 blend after 5 minutes of mixing at 60 rpm.

Surface resistivity of LCP-based composites exhibit similar dependence on a carbon black content (Figure 5). The percolation treshold estimated for LCP, PS/LCP 90/10 and PS/LCP 50/50 amounts 4.5, 4.0 and 3.5, respectively. In contrary to the volume resistivity results, critical concentration of carbon black is the highest for LCP. This confirms a supposition of self-organisation of LCP domains across the sample. Other composites seem to be not very much oriented. Therefore interesting should be results of a surface/volume resistivity for compression molded extruded strands after the capillary rheometry measurements

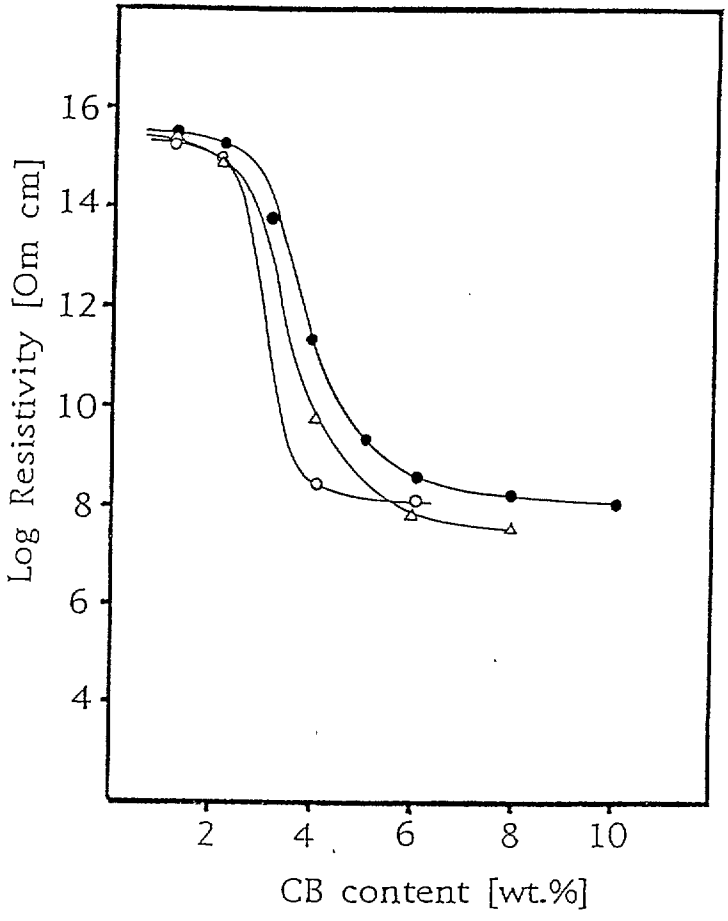

Figure 5. Surface resistivity of composites with different CB content and polymer matrices (• - LCP; △ - PS/LCP 90/10; o - PS/LCP 50/50').

The rheological measurements were performed according to specific rules, which allowed application of general rheological relations even if the basic principles of continuum mechanics (isotropicity, homogeneity and continuity) are not valid for heterogeneous materials. In order to avoid significant errors the characteristic dimension of a measuring device (capillary radius or plate-to-plate distance) should be possibly low.

Flow characteristics obtained for PS and LCP-melts at dynamic shearing exhibit remarkable differences. Polystyrene shows viscoelastic response typical for thermoplastic melts with G" dominating at low angular frequency and G' dominating at high frequencies. Liquid crystalline polymer at 210° behavior is different, with elastic modulus dominating within full scale of frequencies. Additionally melt viscosity of PS is higher than that of LCP (Figures 6 and 7).

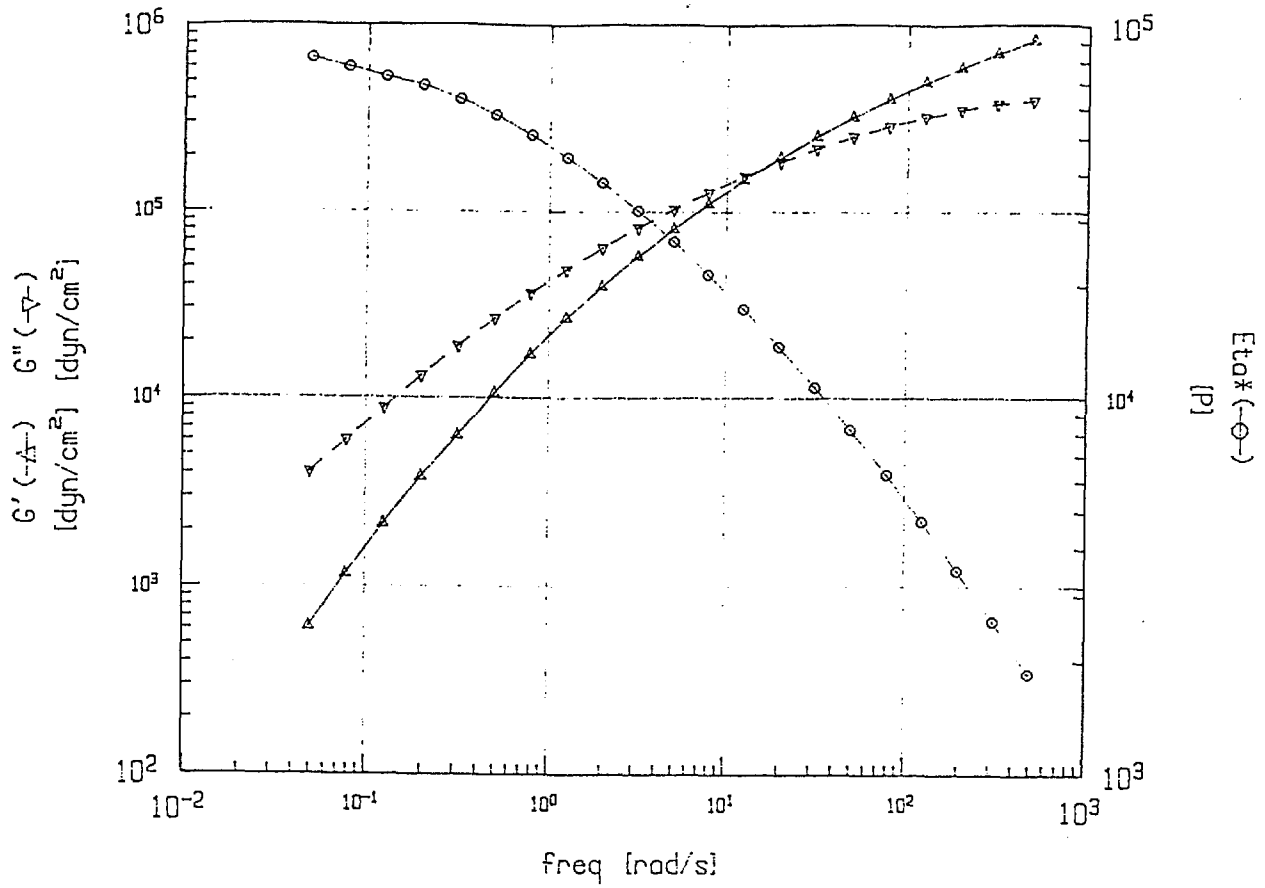

Figure 6. Melt rheology of polystyrene at 210°C - frequency sweep.

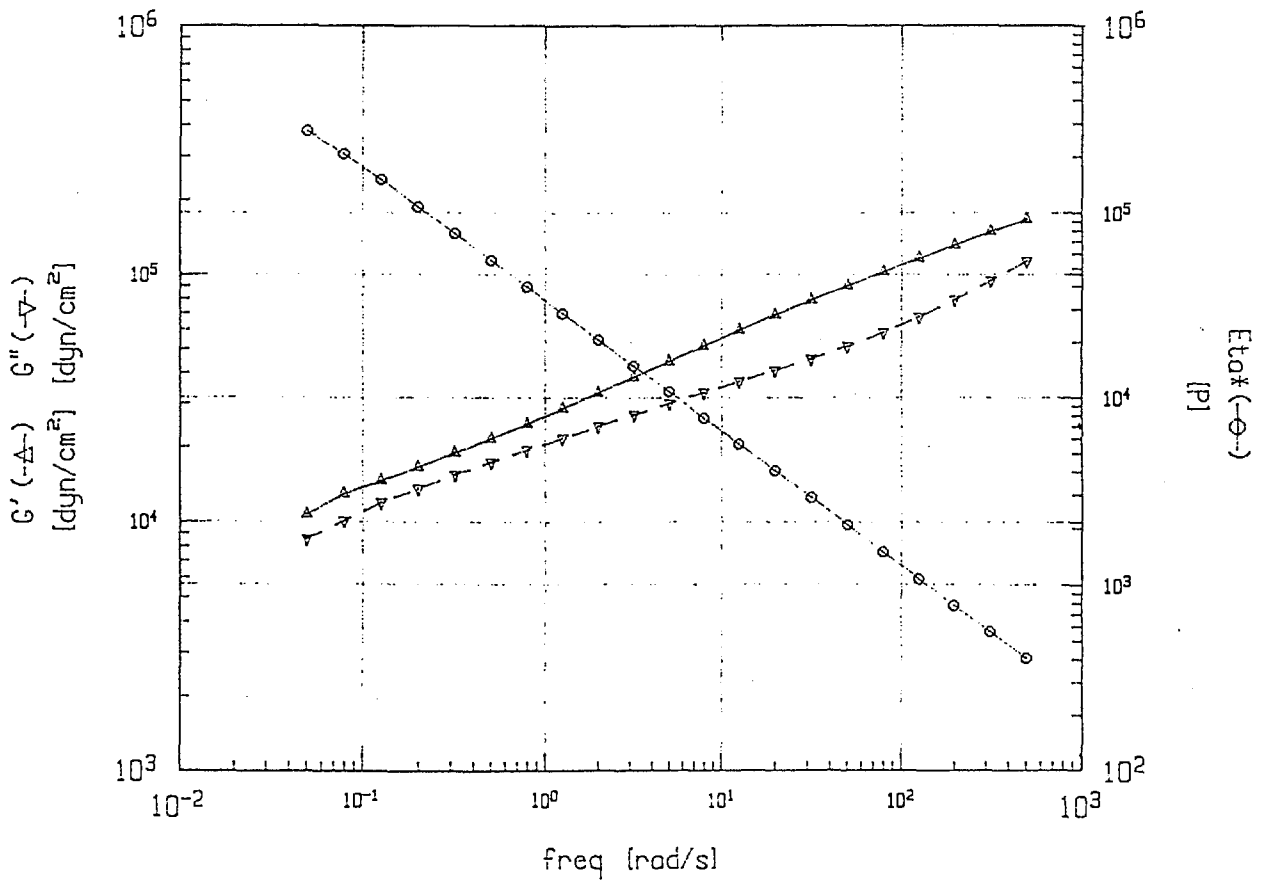

Figure 7. Melt rheology of liquid crystalline polymer at 210°C.

Blending of both polymers in a ratio of 50/50 give rise to highly elastic response, similar in nature to PS, but with G' domination over the measured frequency range (Figure 8). Slight tendency to the plateau formation has been observed at very low shear (below 10^{-1} rad/s). After addition of 6 wt.% of carbon black to such blend the elastic response becomes more pronounced. Linear shear thinning has been evidenced in a manner typical for filled polymer melts (Figure 9).

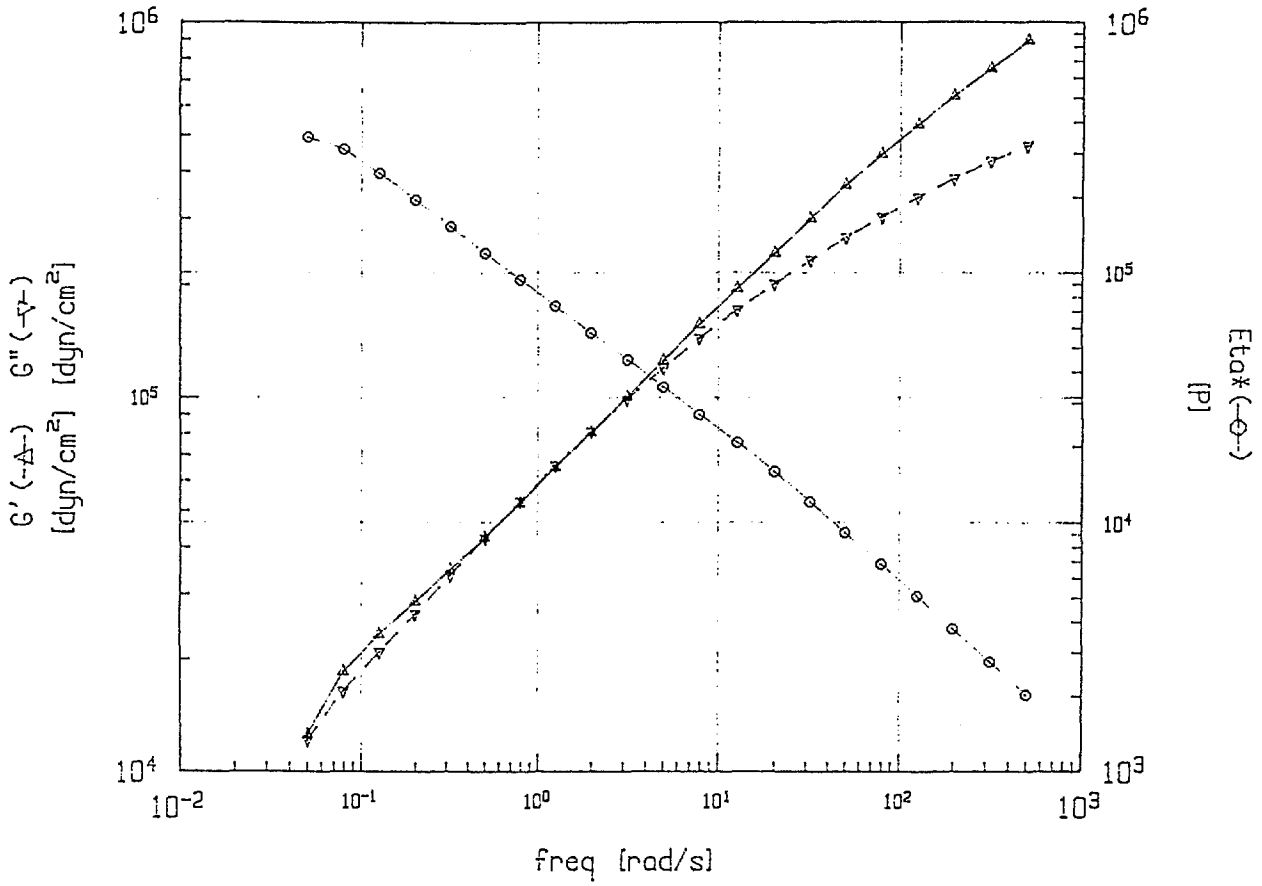

Fig. 8. Rheology of PS/LCP 50/50 blend at 210°C - frequency sweep.

Viscosity of particular LCP systems has been presented on Figure 10 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 improves with increasing CB loading.

Viscosity of composites with 2 wt.% of carbon black, but of different PS/LCP ratio has been presented on Figure 11. Respective systems may be differentiated as far as low frequency viscosity is concerned. In a range of 10^{-2} - 10^{-1} rad/s one may observe decrease in the melt viscosity with increasing PS content. This finding may suggest specific interactions between components, which can be detected only at low external forces. At higher shear the flow curves form asymptotically one set of closely packed parallel lines. Again one may expect the liguid crystalline polymer has been oriented and forms a low viscous outer layer.

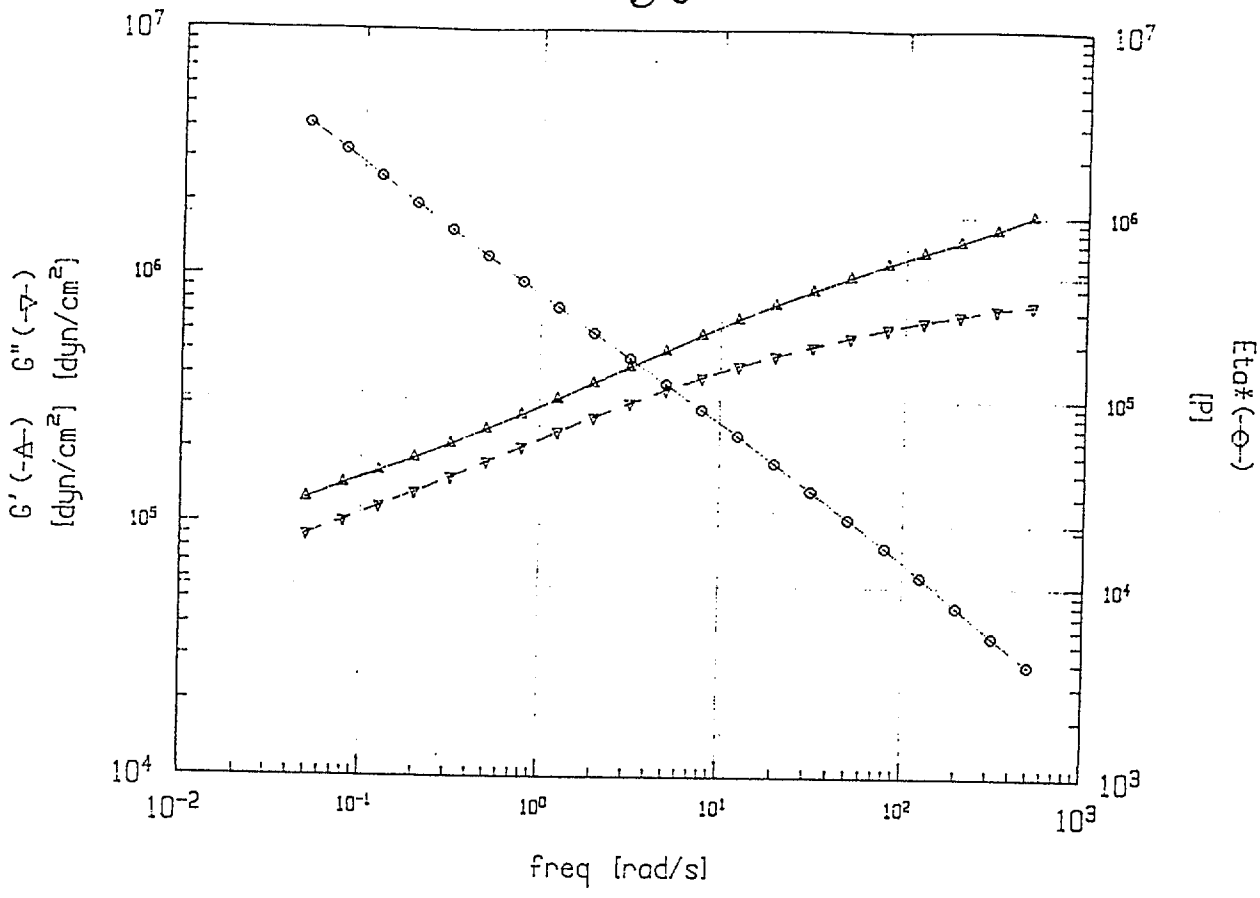

Figure 9. Melt rheology of PC/LCP 50/50 composite with 6 wt.% of CB.

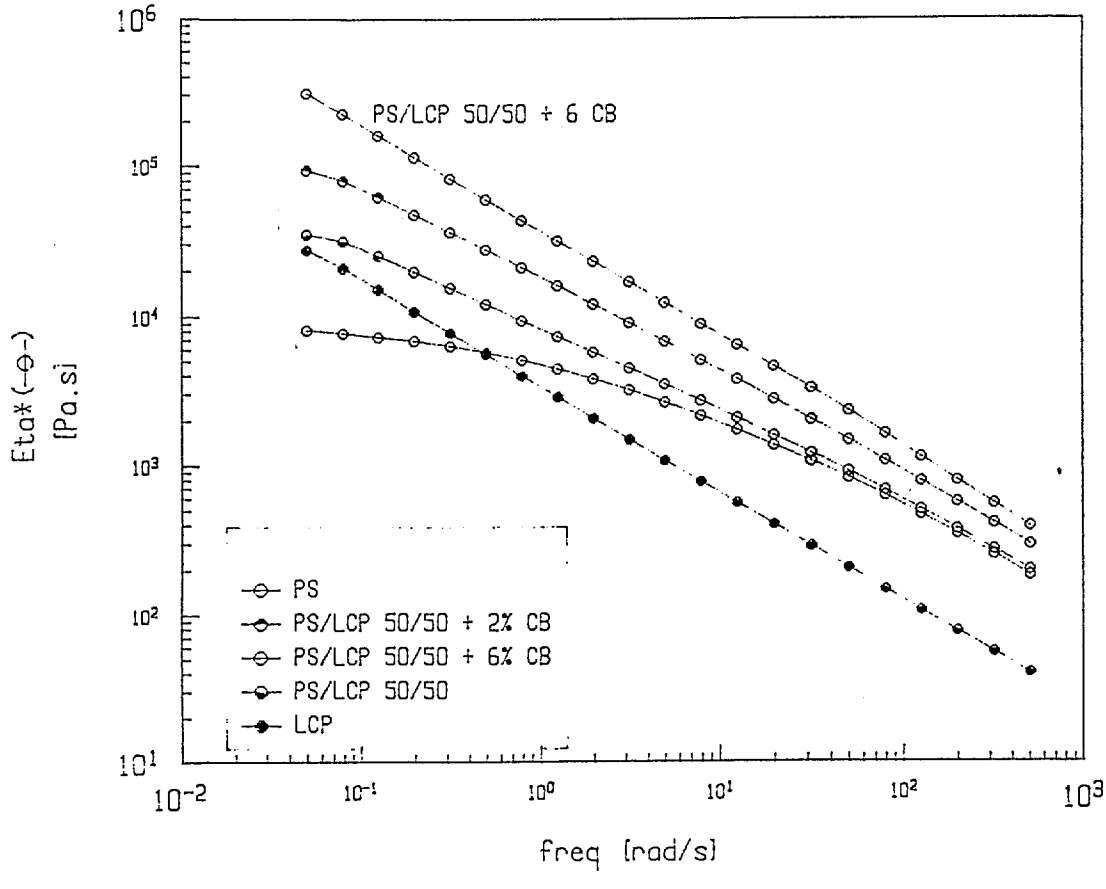

Figure 10. Melt viscosity of polymers and composites at 210°C - frequency sweep

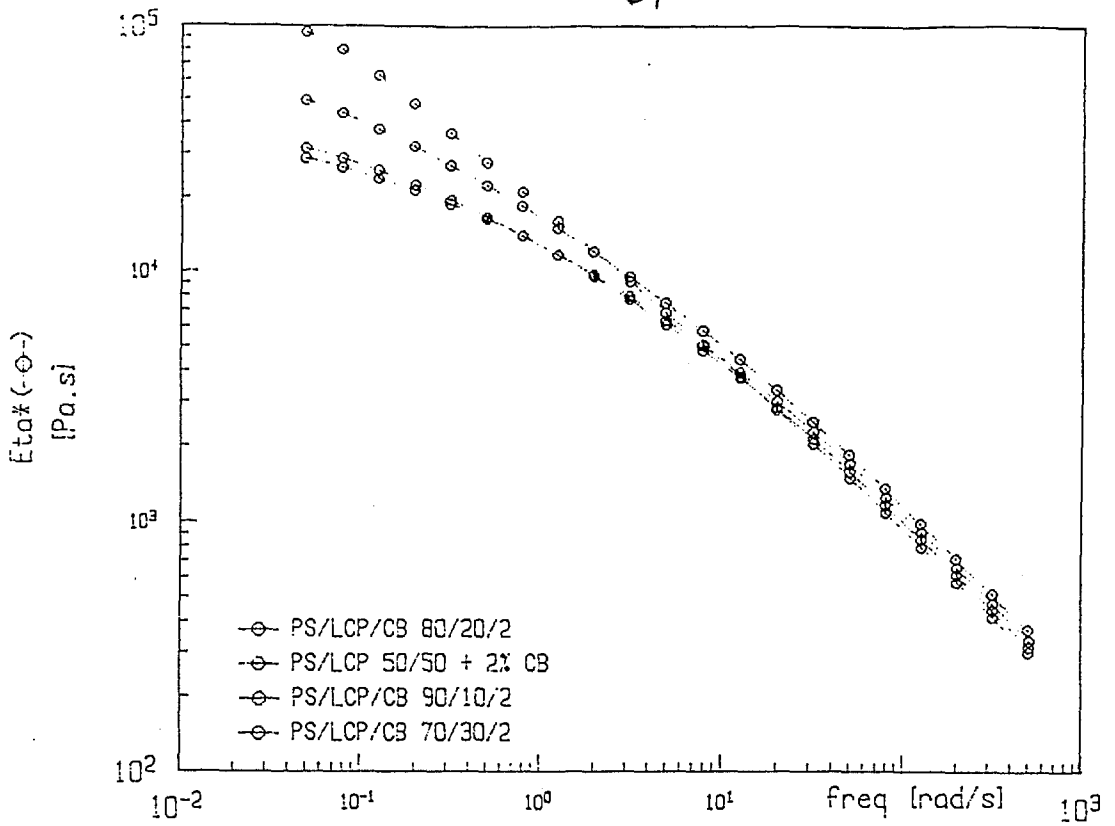

Figure 11. Melt viscosity of PS/LCP composites with 2 wt.% of CB.

Similarly sensitive for a matrix composition is elastic modulus, measured at low frequency. High G' values for LCP melt increase only moderately with frequency, whereas PS/LCP composites exhibit low G' at low shear, increasing significantly with frequency. Above 10 rad/s the elastic moduli of LCP and PS/LCP blends are of similar values (Figure 12).

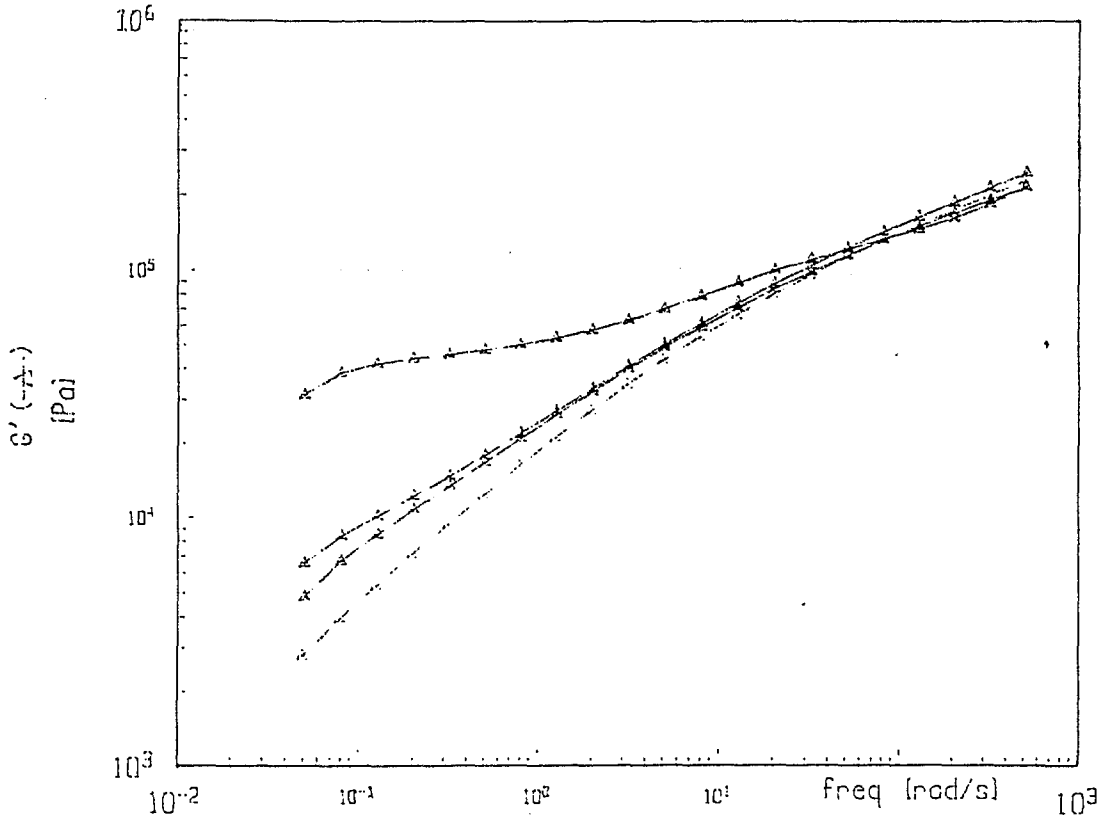

Figure 12. Storage modulus of LCP composites with 6 wt.% of CB.

Rheological properties at capillary flow are slightly different than that measured at dynamic shearing. General observation concerns higher differences between melt viscosity of LCP and all other systems. Since apparent viscosities have been measured at much higher shear (up to thousands of reciprocal second), the orientation of liquid crystalline polymer which makes flow much easier is more pronounced. Melt viscosity of LCP and LCP blends and composites have been presented on Figure 13.

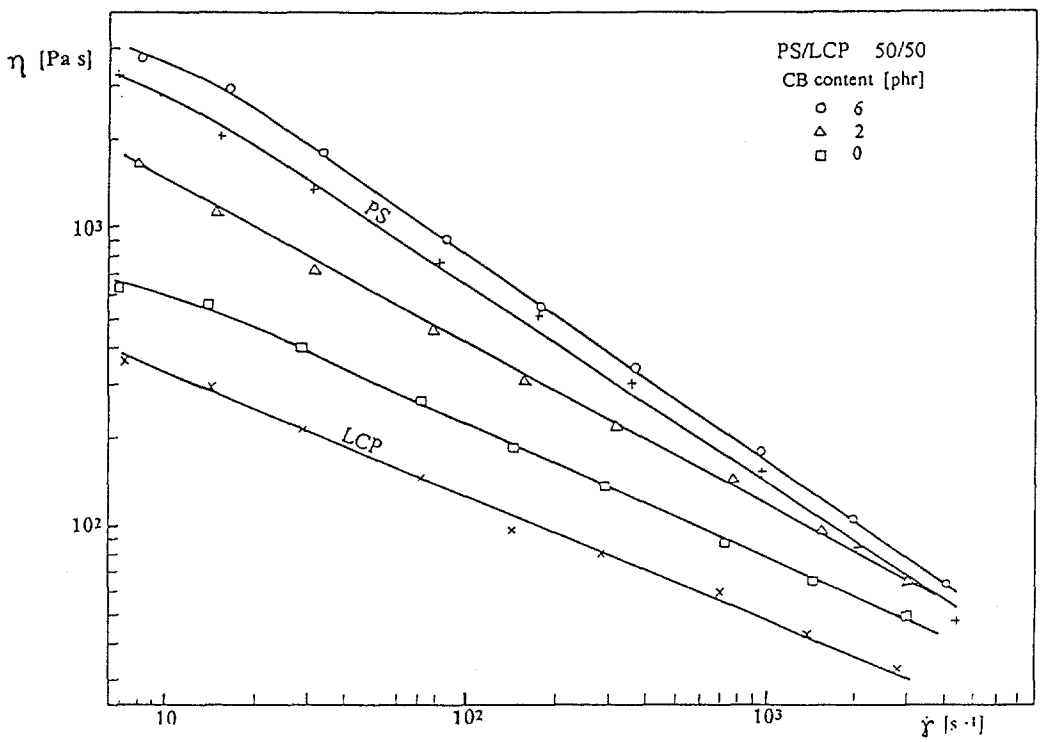

Figure 13. Capillary flow of LCP systems at 210°C.

Liquid crystalline polymer is obviously less viscous than PS, but also its influence on flow of PS/LCP blends is dominating. Viscosity of 50/50 blend is lower than that predicted by additivity rule and tends to follow LCP mode of flow (shear thinning of the same character). This finding suggest that liquid crystalline polymer forms an outer layer of lower viscosity, thus lubricating the blend. The same causes that even PS/LCP composite with 2 wt.% of carbon black is less viscous than neat polystyrene and 6 wt.% loading give rise to only slightly higher melt viscosity of the composite than PS.

Influence of carbon black loading on the melt viscosity of liquid crystalline polymer has been presented on Figure 14. Viscosity increase with CB content is observed, but up to 8 wt.% of the filler other composites are less viscous than neat polystyrene. Comparison of the melt viscosity at different shear rates for the filled liquid crystalline polymer gives interesting picture (Figure 15). At 10 s^{-1} shear rate an exponential dependence has been observed, interpreted in terms of aggregation of the filler. The structure is destroyed while flow under higher shear - at 10^3 s^{-1} only slight increase in viscosity with CB loading has been observed, which suggests LCP-domination at flow with high velocity.

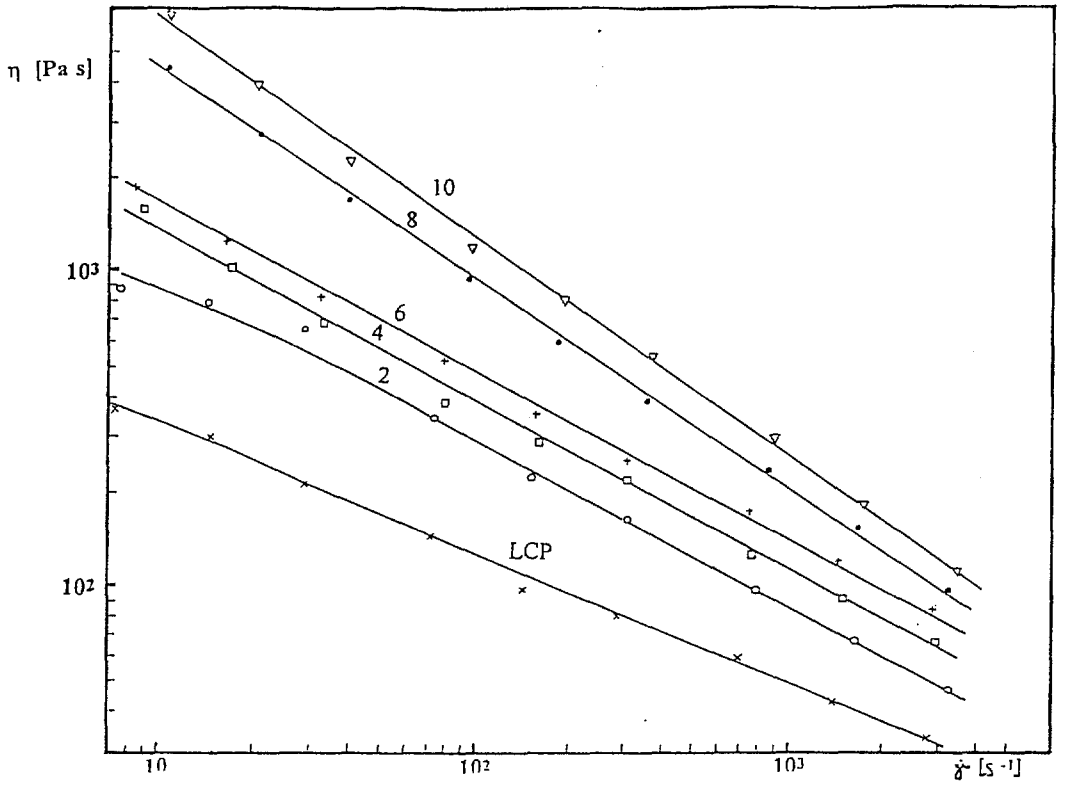

Figure 14. Melt rheology of LCP/CB composites at 210°C - capillary flow.

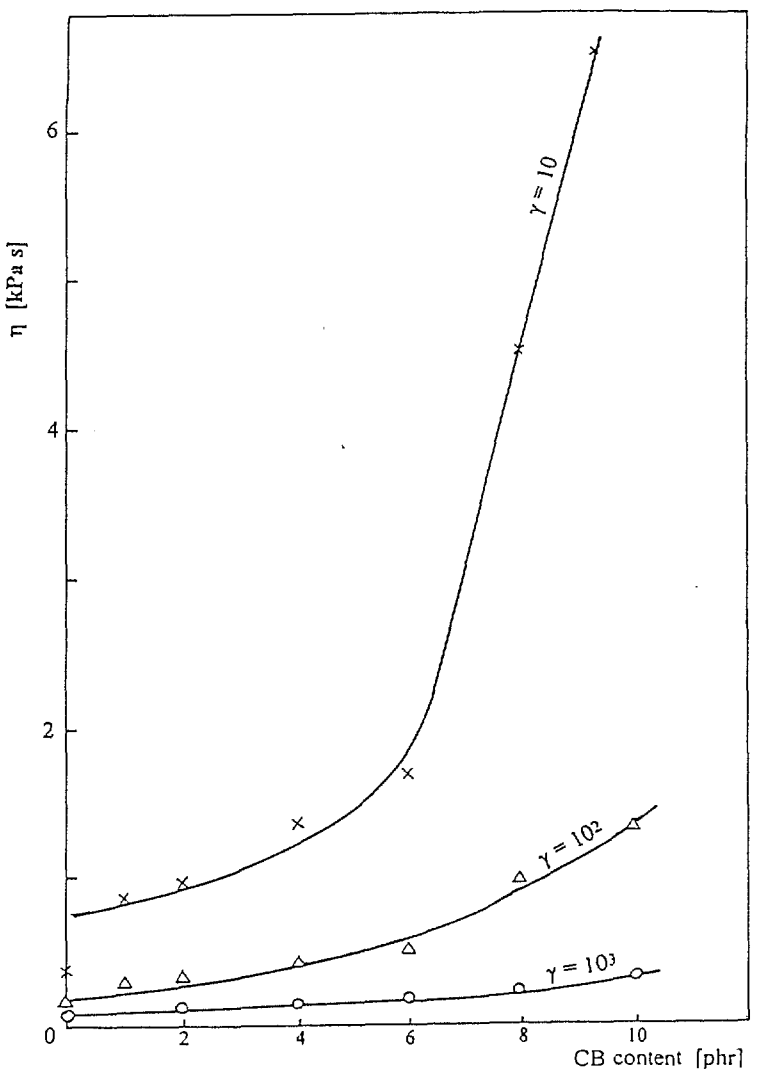

Figure 15. Melt viscosity of LCP composites at different shear rate.

Composites containing 2 wt.% of carbon black with matrices composed of PS/LCP blends have comparable melt viscosity up to PS/LCP 70/30 ratio. All values are in a range of unfilled polystyrene. Further increase of liquid crystalline polymer up to 50/50 brings about to distinct decrease in the composite melt viscosity (Figure 16).

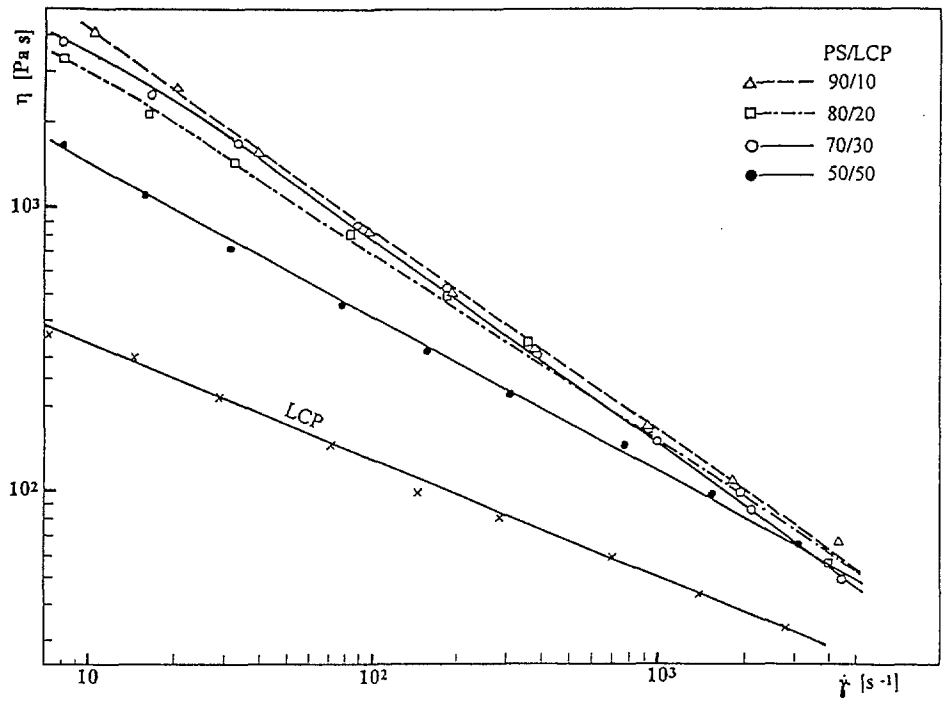

Figure 16. Melt viscosity of PS/LCP composites with 2 wt.% of CB.

Flow of the composites with 6 wt.% of carbon black has been dominated by the filler. Viscosity of all composites, even that based on PS/LCP 50/50 matrix is higher than that of neat polystyrene (Figure17).

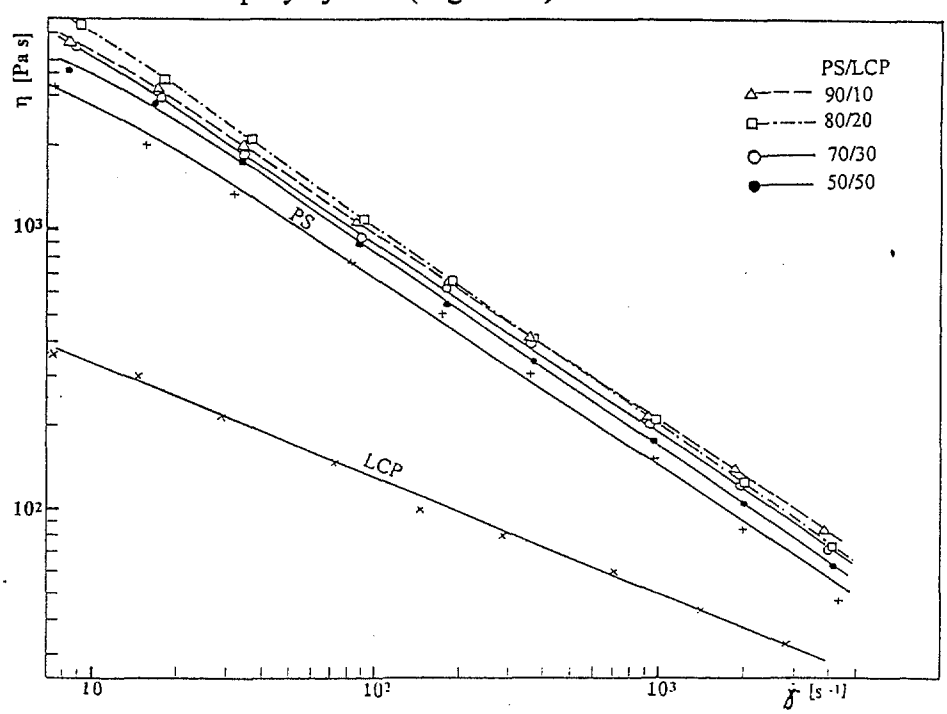

Figure 17. Melt viscosity of PS/LCP composites with 6 wt.% of CB.

The mechanical properties of PS, LCP as well as their blends and composites with carbon black were evaluated by means of tensile tests. Results have been presented in Table 2. Liquid crystalline polymer exhibit markedly higher tensile modulus and tensile strength than polystyrene, resulting from the characteristic orientation of LCP macromolecules.

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.

Moreover, the addition of carbon black is of negative influence on tensile properties - both the tensile modulus and tensile strength of composites decreased in comparison to blends. Increasing a filler content give rise to a further drop in mechanical strength.

Ultimate elongation is low for all tested samples, which is related to a brittle character of failure under the tensile conditions both for polystyrene and liquid crystalline polymer.

Table 2. 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

2. Delayed addition of one component.

Preliminary results on modification of the mixing technology, reported in 1995 suggested that a delayed addition of one component upon mixing is favourable for a higher conductivity of the resulting material. The supposition has been proved in a set of experiments performed recently with PS, LDPE, EVA, SBS, LCP and carbon black.

The components were mixed in the Brabender Plasticorder at 60 rpm rotor velocity for 5 minutes. Under delayed mixing mode the initial blend was compounded for 3 minutes, followed by addition of remaining components and mixing for 2 minutes. If different mixing time was applied, it has been assigned with asterisk.

Resistivity of PS/LDPE composites with 1 wt.% of CB has been presented in Table 3. Polymer components were mixed in a ratio PS/LDPE 70/30 for blends, or alloys - in case the compatibilizer Kraton (hydrogenated styrene-butadiene-styrene block copolymer) was used (5 phr). Delayed addition of CB or LDPE and LDPE-CB dry blend was also performed.

The best results have been observed for the composite obtained by mixing of PS with LDPE for 3 minutes and addition of carbon black afterwards, followed by mixing of all components for another 2 minutes. The different affinity of CB to particular components and short mixing time of carbon black with the molten polymers give rise to a relatively low electrical resistivity. Possible explanation is that CB was located on interface upon its way towards the polyethylene phase, which tendency has been revealed elsewhere.

Reducing the interfacial bareer by addition of a compatibilizer makes the CB distribution within both polymer components easier - therefore alloying is unfavourable for the electrical conductivity. Particular technology of two-stage mixing with PS/compatibilizer preblend, to which LDPE-CB dryblend was admixed within 2 minutes, resulted in a lower resistivity of the material. In this case we take advantage of decreasing the interfacial tension, since interconnected structure may be developed even after short mixing time. Additionally, carbon black starts travelling towards PS phase in order to equilibrate its chemical potential within the whole mixture. Short mixing time is thus advantageous for keeping CB at interface, therefore making the material electrically conductive.

High temperature of mixing is worse for the selective distribution of such a low amount of carbon black as 1 wt.%, therefore it should be avoided. In further experiments a possibly low temperature of mixing was applied and carbon black was introduced as a concentrate within one of the blend components. The concentrates were prepared by mixing the particular polymer with CB, which content (wt.%) has been marked after the polymer abbreviation (e.g. PS 12 means a concentrate of polystyrene, which contains 12 wt.% of carbon black).

Table 3. Influence of mixing technology on resistivity of PS/LDPE 70/30 systems with 1 wt.% of Ketjenblack 600-JD.

System classification Mixing temperature	Mode of mixing			Resistivity, Ohm cm
	Simultaneous	Delayed		
		Initial mixture	Component added	
Blend	+	PS/LDPE/CB	-	4.9e+11
	-	PS/LDPE	CB	8.9e+10
190° C	-	PS/CB	LDPE	1.7e+14
	-	PS	LDPE/CB	1.7e+12
Alloy 190° C	+	PS/LDPE/comp/ CB	-	5.3e+10
	-	PS/LDPE/comp	CB	4.2e+14
	-	PS/comp	LDPE/CB	2.2e+10
Blend 210° C	+	PS/LDPE/CB	-	6.5e+13
	-	PS/LDPE	CB	3.1e+15
	-	PS	LDPE/CB	1.6e+15
Alloy 210° C	+	PS/LDPE/comp/ CB	-	3.5e+14
	-	PS/LDPE/comp	CB	2.9e+14
	-	PS/comp	LDPE/CB	1.9e+09

In case of PS/SBS composites (Table 4) it has been found that carbon black should be admixed rather to SBS polymer than to PS. Delayed addition of CB concentrate brings about better results in comparison to simultaneous introduction of all components. Extended mixing time at the second stage seems to be favourable for the electrical conductivity. Snce there was no special preference observed as far as CB location in a particular polymer of the pair is concerned, but only a transfer between the CB-richer and CB-poorer phase, therefore one may expect gathering of carbon black at interface, thus making the polymer blend conductive.

Table 4. Resistivity of PS/SBS composites with 1 wt.% of Ketjenblack 600-JD prepared with CB concentrates at 150° C.

Polymer component ratio	Mode of mixing			Resistivity, Ohm cm
	Simultaneous	Delayed		
		Initial mixture	Component added	
PS/SBS 50/50	+	PS/SBS/CB	-	4.2e+11
	+	PS 12/SBS	-	3.7e+12
	-	PS 12	SBS	3.9e+10
PS/SBS 50/50	+	PS/SBS 12	-	5.9e+10
	-	PS	SBS 12	2.5e+11
	-	PS	SBS 12*	3.9e+10
	-	SBS 12	PS	5.7e+07
PS/SBS 88/12	+	PS/SBS 50	-	7.4e+10
	-	PS	SBS	1.2e+15
	-	PS	SBS 50*	5.8e+10

* 5 minutes of mixing

The experiments performed for PS/EVA blends have hardly delivered any suggestions for higher conductivity level by means of the mixing technology modification (Table 5). In case of the system, which is highly suitable for multilevel percolation (high heterogeneity of the system, partial crystallinity of EVA and possibility of CB location in the amorphous phase)and therefore it CB composites are highly conductive, the technology itself seems to influence the mechanism of conductivity only in a limited extent. Anyway the delayed addition of CB concentrate and short mixing afterwards should be advantageous. Taking into account the electrical conductivity level of EVA 12 concentrate, which is of 1.6e+04 Ohm cm (n.b. higher than that of the composites based on heterogeneous PS/EVA blends), one may assume the CB transport to interface, which enhances conductivity.

Table 5. Resistivity of PS/EVA composites with 6 wt.% of Ketjenblack 600-JD prepared with EVA concentrates at 150° C.

Polymer component ratio	Mode of mixing			Resistivity, Ohm cm
	Simultaneous	Delayed		
		Initial mixture	Component added	
PS/EVA 50/50	+	PS/EVA/CB	-	5.0e+03
	+	PS /EVA 12	-	6.4e+03
	-	PS	EVA 12	1.1e+03
	-	PS	EVA 12*	4.9e+03
PS/EVA 75/25	+	PS/EVA 24	-	2.9e+04
	-	PS	EVA 24	1.0e+03
	-	PS	EVA 24*	3.0e+03

* 5 minutes of mixing

Similarly the effect of CB preferential location at interface is believed to play a substantial role for the electrical conductivity of PS/LCP blends. All blends prepared from LCP/CB concentrates have been of higher conductivity than that manufactured by mixing all components at single stage. Delayed addition of LCP-CB dry blend gives rise to a further increase in conductivity. Again, location of carbon black at interface is assumed, especially because the orientation of a liquid crystalline polymer may give preference for such CB location. The supposition has been confirmed by a relatively high electrical conductivity of the LCP concentrate with 10 wt.% of carbon black (3.4e+07 Ohm cm). Since the liquid crystalline orientation increases with the LCP content in a blend, it should be high in LCP/CB concentrate either.

Summarising the mixing technology modification, 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.
Technological advantage for using CB concentrates is additionally attractive, since it avoids dust and therefore is more safe and operator-friendly.

Table 6. Resistivity of PS/LCP composites with 2 wt.% of Ketjenblack 600-JD prepared with LCP concentrates at 210° C.

Polymer component ratio	Mode of mixing			Resistivity, Ohm cm
	Simultaneous	Delayed		
		Initial mixture	Component added	
PS/LCP 50/50	+	PS/LCP/CB	-	1.2e+14
PS/LCP 80/20	+	PS /LCP 10	-	9.2e+12
PS/LCP 67/33	+	PS/LCP 6	-	5.7e+11
PS/LCP 50/50	+	PS/LCP 4	-	4.7e+11
PS/LCP 90/10	-	PS	LCP/CB	2.8e+10

3. Multicomponent polymer matrices.

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 different thermoplastic polymers, which exhibit specific interpenetrating structure Such two-component matrices have been studied in our project. In this section the first results on three-component polymer matrices filled with carbon black have been presented.

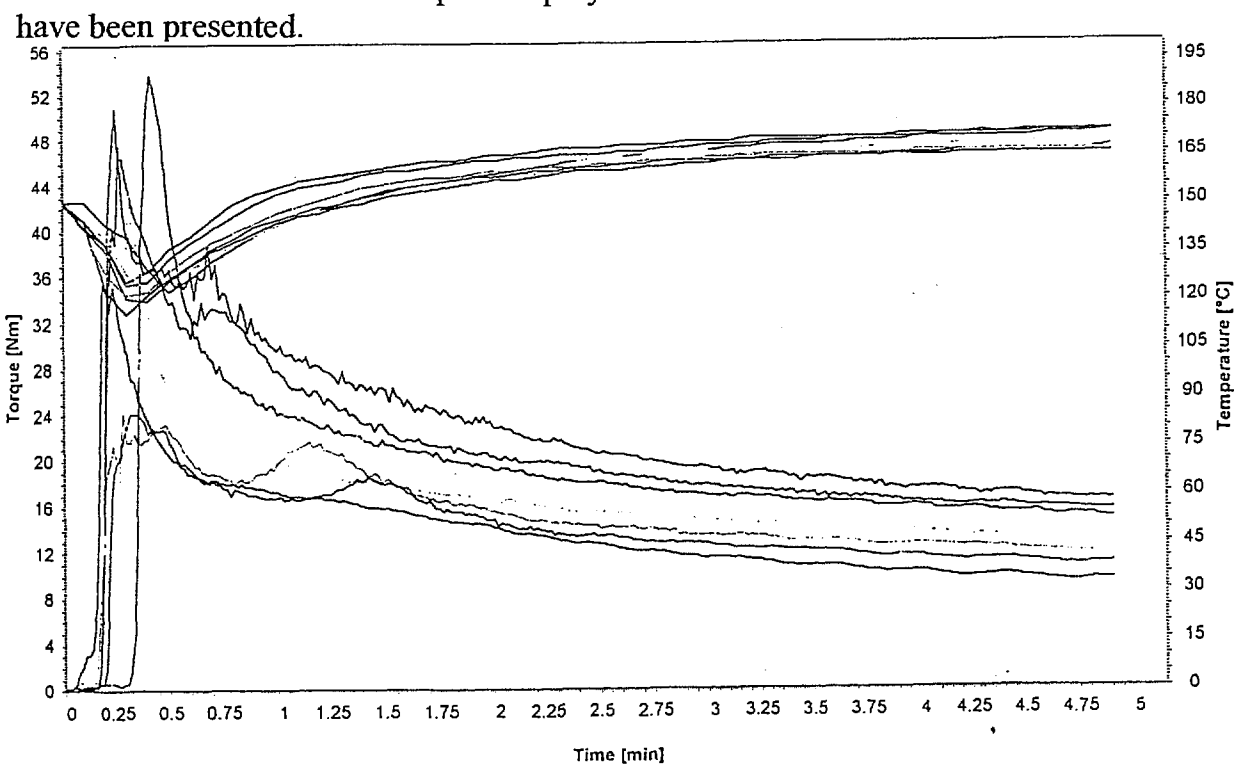

Figure 18. Torque while mixing of multicomponent systems at 160° C.

Three polymers used in the project have been applied for the blends preparation: PS, SBS and EVA. The polymers were mixed in different proportions at 160° C for 5 min. Torque while blending has been registered (Figure 18) and its value for respective systems after 5 minutes of mixing has been presented in Table 7. One may observe increase in the melt viscosity of the blends with PS content. Similar influence on the viscosity has been observed after addition of carbon black.

Electrical conductivity of the blends and composites loaded with 2 wt.% and 6 wt.% of carbon black EC-600 JD has been also included in Table 7. According to expectations the conductivity increases with CB loading. Composites based on the three-component matrix PS/SBS/EVA 2/1/1 offer the lowest resistivity level. An interesting finding is higher surface conductivity of the composites with 2 wt.% of CB than with 6 wt.% of the conductive filler. Morphology inspections of the material may deliver an explanation of such unusual behavior. Possible reason is the phase structure is neither interpenetrating nor dispersive, but of sandwich type. Preferential location of carbon black in specific regions would give rise to the results we have observed.

Table 7. Equilibium torque and electrical properties of multicomponent polymer blend and composites.

Polymer matrix composition PS / SBS / EVA	CB content, wt.%	Equilibrium torque, Nm	Volume resistivity, Ohm cm	Surface resistivity, Ohm cm
0 / 1 / 1	0	9.6	5.0e+15	1.5e+16
1 / 1 / 1	0	10.9	4.4e+15	1.1e+16
2 / 1 / 1	0	11.7	8.4e+15	2.5e+16
0 / 1 / 1	2	13.0	2.6e+13	3.8e+07
1 / 1 / 1	2	13.0	1.5e+13	3.1e+07
2 / 1 / 1	2	13.9	2.6e+11	5.2e+05
0 / 1 / 1	6	14.8	8.1e+09	8.5e+09
1 / 1 / 1	6	15.6	4.5e+09	7.6e+09
2 / 1 / 1	6	16.5	7.3e+08	1.7e+09

The results of mechanical tests exhibit significant differences between respective materials. Tensile modulus and ultimate elongation have been dominated by polystyrene at its content of 50 wt.%. Increase in the modulus and elongation at break with CB loading suggest again a specific structure of the composites.

Table 8. Tensile properties of multicomponent polymer blends and composites.

Polymer matrix composition PS / SBS / EVA	CB content, wt.%	Tensile modulus, MPa	Tensile strength, MPa	Elongation at break, %
0 / 1 / 1	0	8.3	3.2	405.9
1 / 1 / 1	0	20.4	2.1	63.6
2 / 1 / 1	0	150.1	3.1	7.5
0 / 1 / 1	2	11.1	4.9	558.4
1 / 1 / 1	2	28.4	4.6	203.1
2 / 1 / 1	2	171.6	5.4	49.7
0 / 1 / 1	6	17.5	5.9	591.8
1 / 1 / 1	6	99.2	5.0	110.6
2 / 1 / 1	6	497.2	9.1	31.5

4. Conclusions

- Application of the liquid crystalline polymer as a component for electrically conductive composites offers an opportunity of reduction in the percolation treshold, additionally decreasing the melt viscosity of a composite and improving mechanical strength of the material.

- Modification of the mixing technology into a two-stage process, operating with carbon black concentrates has been found advantageous as far as the electrical conductivity and environmental effects is concerned.

- Thermoplastic composites based on the three component matrices offer a combination of the relatively high electrical conductivity and mechanical properties.