MULTI-PHASE POLYMER SYSTEMS: UNIQUE STRUCTURING EFFECTS UNDER MELT FLOW PROCESSING CONDITIONS AND RELATED APPLICATIONS

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The morphology of multi-phase blends can be predicted by a spreading coefficient, which is related to the interfacial tension between the various components. The viscosities of a blend's components are important kinetic parameters, whereas the spreading parameters represent important thermodynamic factors. The final morphology obtained in the solid state is a reflection of the blend's structure in the molten state under the melt flow processing conditions. The morphology of ternary systems (polymer/polymer/filler) can range between two extremes: separate dispersion and encapsulation, as in Fig. 1. In the former case, the filler and the minor polymeric phase are independently distributed within the matrix. In the latter case, the minor polymeric phase is preferentially located surrounding the filler, and this "core/shell" structure is distributed within the matrix. Intermediate morphologies, such as distribution of the filler within both polymeric phases, are also possible. The actual blend morphology that is developed during melt mixing is dependent on the surface tensions and the polarity of the three components, and can be predicted by use of spreading coefficients. Thus, in ternary NY6/PP/GF (GF=Glass Fibers) blends with a PA6 matrix, the PP domains and glass fibers are separately dispersed within the matrix. In ternary blends with a PP matrix, most of the PA6 is found surrounding (encapsulating) the fibers [1], as shown in Fig. 2. The spreading coefficient was found to correctly predict the final morphology for most ternary blends studied, except for cases of kinetic hindrance, such as a high viscosity for one component. The spreading coefficient can also be used to predict the structure of four component blends. In such ternary and quaternary component systems, unique structures may be formed, with direct implications for the material properties and performance. Increasing attention is currently being focused on the incorporation of carbon black (CB) into multi-component polymer blends. In such systems, high levels of conductivity can be achieved at extremely low CB loadings. The enhancement of conductivity is owing to the formation of segregated conductive pathways through the structured multi-phase blend and to preferential accumulation of CB in one of the phases and/or at the interphase boundaries. Carbon black may remain in the phase to which it has been initially added, or may migrate under the dynamic mixing conditions from one phase to another.

Most literature reports describe immiscible polymer/polymer/CB ternary systems prepared by hot melt compounding followed by compression molding. Thus, the data and their interpretation refer to compression molded samples, which are of little concern for the industry, where fast extrusion and injection molding are the desired processing methods. Normally, materials classified as conductive, based on studying compression molded samples, become insulating upon extrusion and injection molding. Therefore, a simple method for studying the electrical resistivity as function of shear rate at a given temperature was developed in our laboratories using filaments produced by a capillary rheometer at increasing shear rate levels [2]. This method, which uses small quantities of material, has proven itself as a useful tool for prediction of the potential of conductive polymer systems in industrial processing of conductive thermoplastics. Resistivity-shear rate curves are demonstrated in Fig. 3 for a 70HIPS/30LLDPE/CB blends. It is clearly seen that at 4phr CB, the HIPS/CB blend is insulating throughout the whole shear rate range studied, whereas the 85HIPS/15LLDPE has a low resistivity value maintained up to about 500 1/s.

Recently, these principles have been employed to develop quaternary-component systems, which spontaneously structure in the melt to form electrically conducting materials, with only ~1-2% CB, characterized by a unique triple-percolation morphology [3]. A typical system contains PP/NY/GF/CB four components, which structure into a continuous network of GF, each engulfed by a PA shell with CB located at the NY/PP interfaces, as depicted in Fig. 4. Thus, GF, PA and CB form three continuities in the PP matrix, hence the triple-percolation description. This morphology, developed during the course of hot melt blending/processing, forms as previously described owing to the strong affinity of PA to GF and CB to PA. The new technology has been further developed by Carmel Olefins, Israel into unique electrostatic dissipative (ESD) injection moldable thermoplastic composites [4]. It is important to emphasize that three-component blends, such as PP/NY/CB, conductive as compression molded samples with comparable CB loadings become insulating by extrusion, or injection molding operations. In summary, the quaternary, PP/NY/GF/CB systems, structure upon melt processing and become conductive through the *in-situ* formation of conductive fibers.

Other new systems recently studied in our laboratory comprise PP/UHMWPE/CB, HIPS/UHMWPE/CB, PVDF/UHMWPE/CB and

TPX/UHMWPE/CB. In these systems, UHMWPE, the dispersed phase, is a unique "filler" which preserves its particulate identity due to its extremely high melt viscosity and also attracts the CB particles to its surface (CB particles are unable to penetrate the viscous UHMWPE particles). Therefore, the CB particles locate at the interfaces forming conducting networks at very low CB concentrations. Some of these systems show significant resistivity stability with increasing shear rate levels. In some of the experiments radiation-crosslinked UHMWPE particles were used. These particles preserve their original morphology prior to irradiation and thus exhibit unique structure and performance in some of the polymer/UHMWPE/CB ternary blends [5]. These systems were also characterized for their thermo-electric (PTC) switching behavior, showing interesting results believed to be of commercial potential [6].

Recently, filaments of the structured multi-phase systems were studied as sensors for various liquids [7]. The developed morphologies and the interfaces presence between the immiscible components are the basis for the sensitivity of these systems to contact with liquids. Upon contact the filaments' resistivity increases, thus sensing a given fluid, at levels depending on the specific sensor material and the liquid being sensed.

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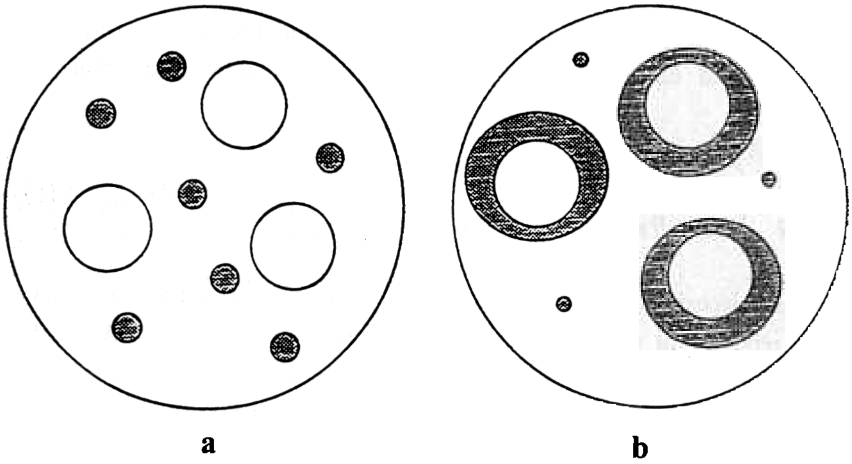

Figure 1: Possible ternary blend morphologies: (a) - separately dispersed, (b) - encapsulated.

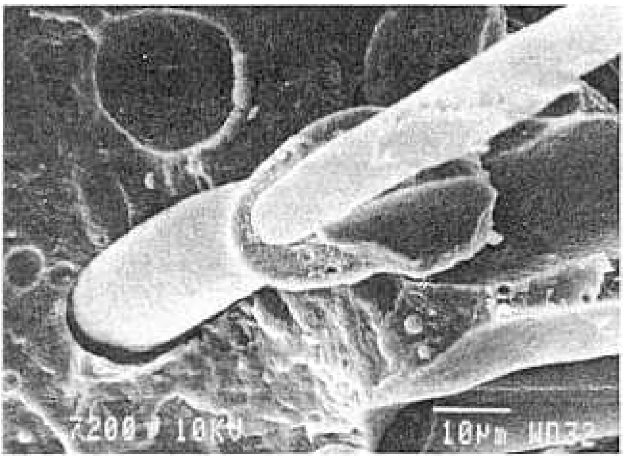

Figure 2: SEM micrograph of glass fiber encapsulated morphology in a PP/PA-6/GF ternary blend.

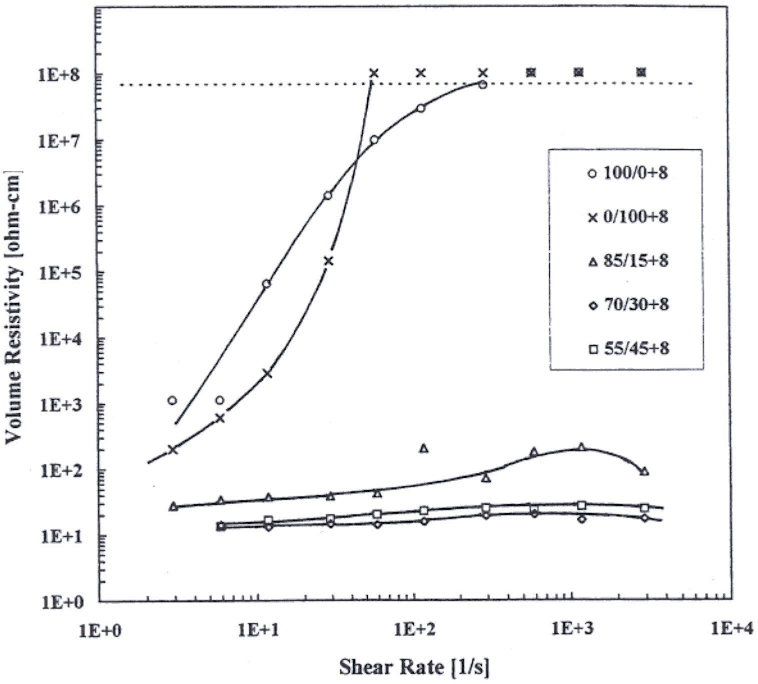

Figure 3: Resistivity vs. extrusion shear rate of 8phr CB containing HIPS/LLDPE filaments. Points of resistivity above 1E+8 ohm-cm, exceed the range of the measuring equipment, and are depicted for illustration purposes only.

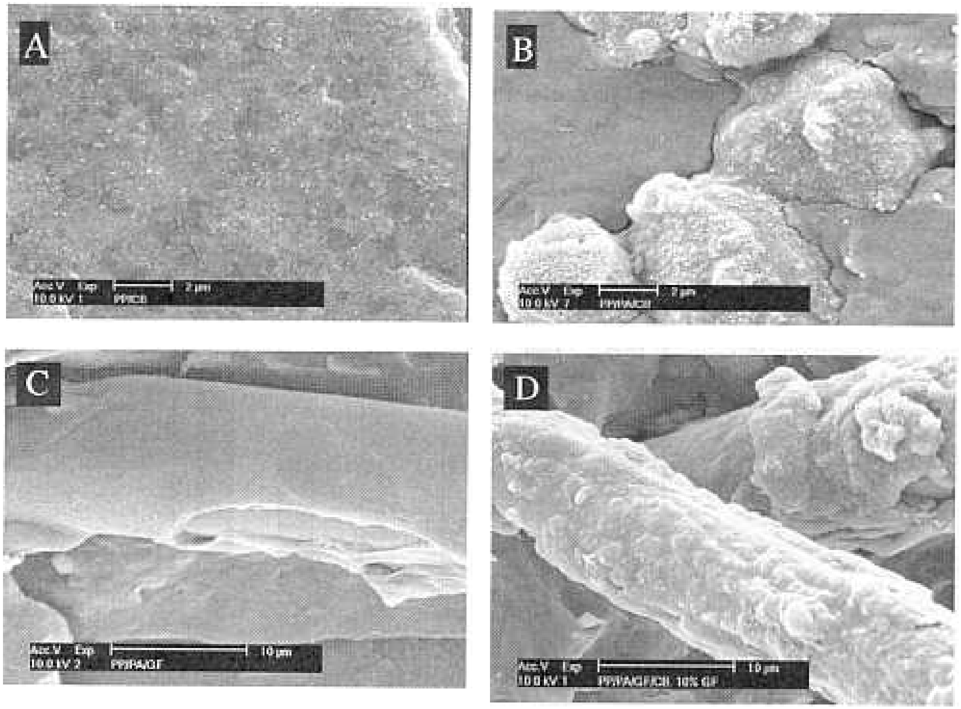

Figure 4: SEM micrographs of freeze fracture surfaces of: (a) - PP, (b) - PP/PA, (c) - PP/PA/GF and (d) - PP/PA/GF/CB.