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MORPHOLOGY OF POLYMER FILMS OF POLYVINYL CHLORIDE/POLYAMIDE-6 BLENDS

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Abstract. *The morphological behaviour of polymer films of polyvinyl chloride (PVC)/polyamide-6 (PA-6) blends was studied by scanning electron microscopy (SEM). The samples were prepared by casting, coprecipitation and phase separation from THF, formic acid and nitrobenzene/phenol solutions. The morphology of the blends prepared by coprecipitation is typical of a binary blend containing one crystallizable polymer. When the PVC is the major constituent of the blend, a crystalline hedritic structure (PA-6) dispersed on a amorphous matrix (PVC) is observed. With a higher PA-6 content, SEM shows spherical PVC particles dispersed on a fibrous PA-6 matrix. Films obtained by phase separation show a better interaction between the polymers, with non distinguishable phases.*

Keywords*: Morphology, Polymer blends, Polyvinyl chloride, Polyamide-6*

1. INTRODUCTION

The blending of polymers is a relatively simple and promising route for developing new and improved materials. Moreover, the necessity for recycling of plastic waste is a reason for the expanding academic and industrial interest in polymer blending.

Polyvinyl chloride is one of the most important thermoplastic materials, with an increasing consumption over the last decades, mainly due to its good compatibility with plasticizers, stabilizers and fillers. This behaviour permits the production of materials varying from rigid to flexible, with a wide range of mechanical properties (Pezzin, 1997). Many PVC blends were studied during the last three decades and some of them are commercialized (Kroeze et al., 1997).

Polyamide-6 is the homopolymer produced from the polymerization of ε-amine-caprolactam, exhibiting high tenacity at low temperatures, good resistance to repeated impacts, resistence to abrasion and to the corrosive attack of many organic solvents.

Blends containing PA-6 are of great industrial importance and were extensively studied (Chuang and Han, 1984; Ellis, 1995; Spadaro et al.,1996), but there are no practical studies on PVC/PA-6 blends reported in the literature, probably due to their incompatible properties for molding at relatively high temperatures. Van Eckenstein et al. (1997) carried out a study of the miscibility of blends of caprolactam/caprolactone copolymers and chlorinated polymers (including PVC) and theoretically deduced, using the binary interaction model based on the Flory-Huggins theory, that the interaction between amide and chloromethylene segments is highly unfavourable for homogeneous mixing.

It is well known that most polymer mixtures are not miscible at a molecular level, leading to an inevitable heterogeneity. Due to the very low entropy for mixing high molecular weight components, miscible blends are obtained only when specific interactions are present, such as hydrogen bonds or strong dipole-dipole interactions. When this phenomenon occurs, the degree of dispersion of the system phases becomes quite important. In a polymer system consisting of two or more phases, the compatibility among them has a critical role over the mechanical-physical behaviour of the final product (Siqueira et al.,1996). Therefore, the miscibility level, the degree of dispersion, and the compatibility among the components are the main factors involved in the development of a polymer blend. The blend compatibility represents states of mixing whose properties are in agreement with those required for a specific application. Thus, a non-miscible polymer system can be a compatible one. Generally, the compatibility depends on the procedure used to obtain it. Chanda et al. (1987) report that the study of polymer solubility in several solvents, and the solubility parameters, are essential to evaluate processing possibilities and blend miscibility.

The main objective of this work is to analyze, by scanning electron microscopy, the morphology of polymer films of some PVC/PA-6 blends obtained by casting and phase separation.

2. EXPERIMENTAL

2.1 Materials

Comercial PVC resin with high molecular weight was supplied by Trikem, S.A. as NORVIC EP 131 (powder). This resin was produced by the emulsion polymerization process. The polyamide-6 (Nylon-6) in pellets, was obtained from DuPont Co. All solvents were analytical grade.

2.2 Procedures

Polymer films of PVC/PA-6 blends were obtained by: (i) coprecipitation, from the mixture of two polymer solutions, and (ii) phase separation, in which the two polymers were dissolved in a common solvent and precipitated by immersion in a non-solvent bath.

Polymer films obtained by casting. Non blended films were prepared by this process. PVC films were prepared by casting from a 1 wt% solution in tetrahydrofuran (THF), and PA-6 films from a 1 wt% solution of the polymer in formic acid. Small amounts (4-5 mL) of a solution of the polymer were magnetically stirred for at least 24 hours and then were slowly evaporated at room temperature to produce thin circular films (*ca.* 0.3 mm thick).

Blending by coprecipitation. Five PVC/PA-6 blends were prepared with the following blend ratios (by weight): 80/20; 60/40; 50/50; 40/60 and 20/80. The blending was carried out by combining different volumes of the two solutions each with pure polymer (PVC/THF and PA-6/formic acid). As the THF/formic acid mixture does not efficiently solubilize either PVC or PA-6, a PVC/PA-6 blend was obtained by coprecipitation. Then, the solvent mixture was slowly evaporated at room temperature and, finally, the blend film was gently air dried.

Search for a common solvent for the PVC/PA-6 system. Many solvent systems were tested in order to achieve a common solvent for the PVC/PA-6 mixture. Binary and ternary solvent systems involving THF, formic acid, acetone, DMSO, ethyl acetate, chlorobenzene and dimethylformamide failed to provide a “solubility window” for the PVC/PA-6 system, even when the mixtures were warmed up to 60^{o}C. The only solvent mixture suitable for use as a common solvent was the nitrobenzene/phenol system. This system shows a solubility window from 20 to 70% nitrobenzene. For the phase separation experiments the 70/30 nitrobenzene/phenol mixture was succesfully used.

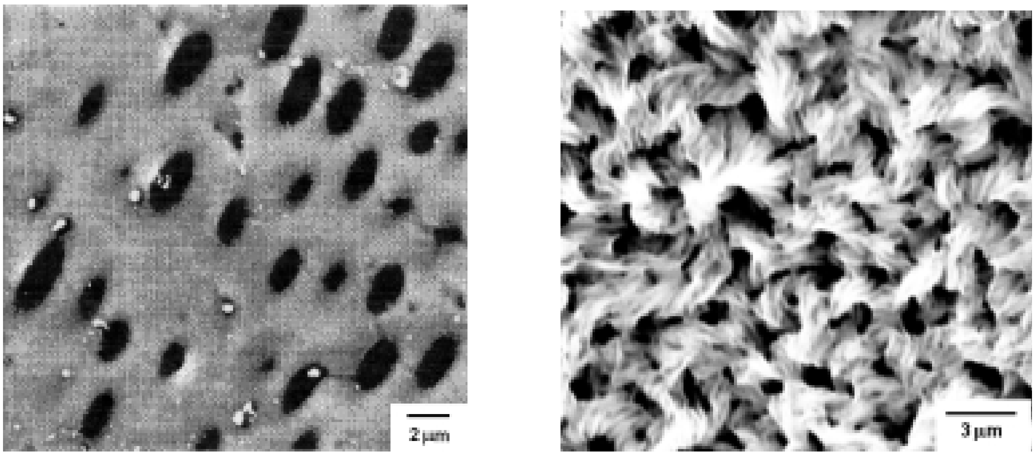
Blending by phase separation. Five polymer films were obtained by phase separation, with the following blend ratios (by weight): 100% PVC, PVC/PA-6 70/30, PVC/PA-6 50/50, PVC/PA-6 30/70, and 100% PA-6. In this method, a solution containing the two polymers (5 wt%) dissolved in a common solvent is spread over a glass microscope slide equipped with graphite spacers of 0.7 mm. This apparatus is immersed in a non-solvent bath, and a polymer film is deposited on the glass support. After film formation, the apparatus is removed from the bath, passed through a second non-solvent bath, and, finally, the film is air dried. In this case, a glass slide (76x26x1mm) was used, the common solvent was a 70/30 nitrobenzene/phenol mixture and methanol was used as the non-solvent bath.

2.3 Characterization by Scanning Electron Microscopy (SEM)

The morphology of the blends was studied by carrying out scanning electron microscopy (SEM) on cryo-fractured specimens, using a Carl Zeiss DSM 940 A SEM. The samples were coated with a thin layer of gold, under vacuum, using a BAL-TEC SCD 050 Sputer Coater.

3. RESULTS AND DISCUSSION

The polymer films produced by casting were visually homogeneous and flexible. The SEM analysis for the pure PVC film showed a porous microstructure (Figure 1a), probably due to a significative sorption of water during the THF evaporation. For pure PA-6 films a fibrous open network structure is observed (Figure 1b).



(a) (b)

Figure 1- SEM micrographs for polymer films obtained by casting: (a) PVC. Magnification: 1000x; (b) PA-6. Magnification: 3000x.

Analyzing the blends obtained by coprecipitation (Figures 2 and 3), a crystalline phase, showing a hedritic morphology, dispersed on an amorphous matrix is observed for a 40/60 PVC/PA-6 blend. This behaviour is typical for binary blends of flexible homopolymers where one of the constituents is crystallizable (Woodward, 1995).

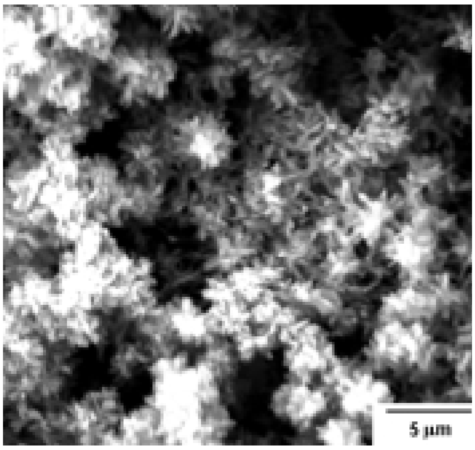


Figure 2 – SEM micrograph for a 40/60 PVC/PA-6 blend obtained by coprecipitation. Magnification: 2000x.

The effects of blending depend on the composition. When the amount of PVC is increased, a more flexible blend is obtained. A 80/20 PVC/PA-6 blend does not show hedrites, but has a porous, non-crystalline aspect, related to non-crystalline PVC behaviour (Figure 3).

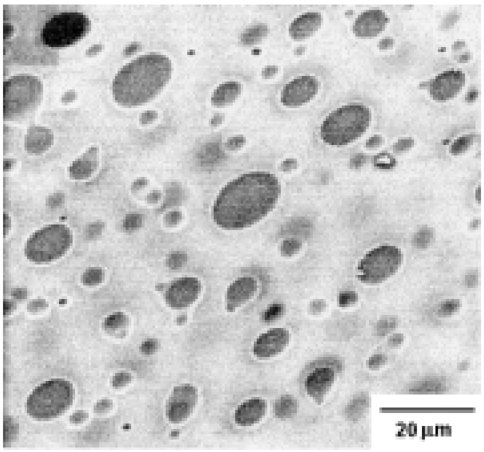


Figure 3: SEM micrograph for a 80/20 PVC/PA-6 blend obtained by coprecipitation. Magnification: 500x

The morphology of a 50/50 blend obtained by coprecipitation can be seen in Figure 4. This micrograph show the formation of PVC particles on a PA-6 matrix. The surface of the particles appears to be very smooth, while there is no indication of any interaction between the PVC particle and the PA-6 matrix.

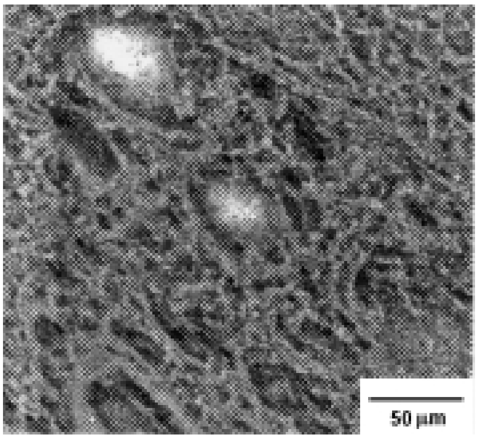
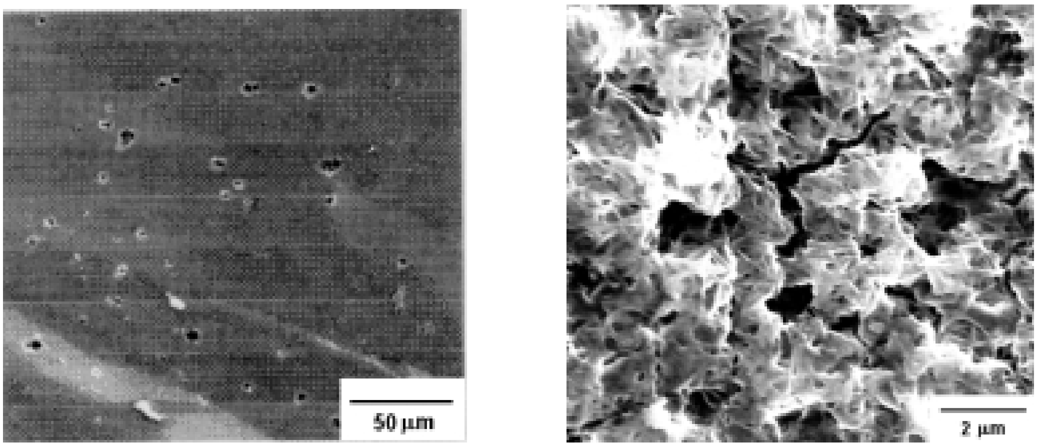


Figure 4 – SEM micrograph of a 50/50 PVC/PA-6 blend obtained by coprecipitation. Magnification: 200x

Figures 5a and 5b shows the morphology of films obtained from the pure polymers by phase separation. These films exhibit lower porosity, as can be seen for the pure PVC film (Figure 5a), than that produced by casting (see Figure 1). For the pure PA-6 film (Figure 5b), a homogeneous hedritic morphology is observed.



(a) (b)

Figure 5- SEM micrographs of polymer films produced by phase separation: (a) pure PVC. Magnification: 200x; (b) pure PA-6. Magnification: 2500x.

Figure 6 shows a 70/30 PVC/PA-6 blend prepared by phase separation. In this micrograph, no separate PA-6 phase can be detected, while the structure of the material shows a rough surface, probably due to the dispersion of small PA-6 particles in the PVC matrix.

A comparison of the morphologies of the blends prepared by coprecipitation and phase separation shows that a much denser microstructure is obtained by phase separation, probably due to the more efective mixing of the polymers prior to the film formation.

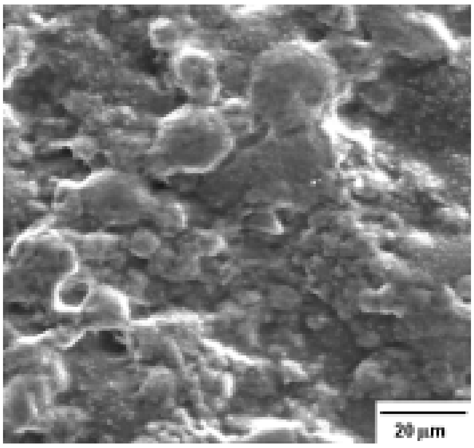


Figure 6 – SEM micrograph of a 70/30 PVC/PA-6 blend produced by phase separation. Magnification: 500x

4. CONCLUSION

The observed morphologies of the films are consistent with a binary blend containing one crystallizable polymer (PA-6). When the PVC is the major constituent of the blend, a crystalline hedritic structure (PA-6) dispersed on a amorphous matrix (PVC) is observed. With a higher PA-6 content, SEM shows spherical PVC particles dispersed on a fibrous PA-6 matrix. Films obtained by phase separation show a better interaction between the polymers, with non distinguishable phases.

It can be also concluded that the compatibility of the polymers may be dependent on the method of blend preparation.

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