

Miscibility and Dynamic Mechanical Behavior of Blends with LCP'S

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Abstract. The main advantage of the "in situ" production of blends of thermoplastics with liquid crystalline polymers (LCP's) is viscosity reduction. In this work the phase behavior of blends of poly p-phenylene sulphide (PPS) with two different LCP's is presented. The LCP's are HX1000 (amorphous) and HX4000, crystalline, both from DuPont. The samples were prepared by injection molding and its dynamic mechanical properties were tested after annealing. It was observed that before annealing the blends were slightly miscible at all concentrations. It was also observed a plasticization of the PPS amorphous fraction by the LCP amorphous part. After annealing an increase of the PPS glass transition temperature was observed; the blends were also found to be immiscible. An average β -transition was observed at approximately 76 °C (HX1000) and at 88 °C (HX4000); the glass transition temperatures were 160.48 °C (HX4000) and 171.77 °C (HX1000).

1. INTRODUCTION

Blends of engineering thermoplastics with liquid crystalline polymers (LCP's) have been widely studied due to: i) the synergistic mechanical behavior of these blends compared with the component polymers [1,2]; ii) the surging of new engineering thermoplastics matrixes, highly aromatic, but brittle, that requires reinforcement [3,4]; iii) the viscosity reduction promoted by the LCP's and iii) the advantages relative to the processing of "in-situ" composites, like the lower energy consumption. Poly (p-phenylene) sulphide (PPS) has been used mainly in the automotive and chemical industries due to its high thermal and chemical resistances. It has been reinforced with carbon and glass fibers in order to produce composites of outstanding mechanical properties; lately, however, it has been blended with LCP's in order to obtain the same composite behavior [5].

2. EXPERIMENTAL

2.1 Materials

Two LCP's were employed in order to produce the blends with the PPS; they were HX1000 and HX4000, both from DuPont. These LCP's are random terpolyesters made of terephthalic acid, hydroquinone and phenyl hydroquinone. The HX1000 has $M_w = 35000$ g/mol and an "amorphous" behavior, while the HX4000 has a $M_w = 40000$ g/mol and a "crystalline" behavior. The PPS used was Ryton V6 (Phillips Petroleum. Co) with $M_w = 25300$ g/mol and $M_n = 11000$ g/mol. The blends were made by injection molding in an injection molding machine from Aurburg, with processing temperatures

between : 320- 350 °C and mold temperature between 50-60 °C. The following blends , based on PPS/LCP weight composition were produced: 100/0, 80/20, 60/40, 40/60, 20/80, 0/100. Annealing was also performed on the samples at $T=140$ °C during 48 h.

2.2 Dynamic mechanical analysis

The dynamic mechanical thermal analysis was performed in a DMTA from Polymers Lab. The heat scanning was between 60 and 220 °C, at a heating rate of 2 °C/min , frequency of 10 Hz, and strain of 64 μ m, using a double cantilever geometry, on bending.

3. RESULTS AND DISCUSSION

The criteria for determining miscibility was the glass transition temperature (T_g) change. T_g was assumed to be the temperature where the loss modulus, E'' , has a maximum. Therefore , if the blends presented only one T_g , then miscibility of the amorphous parts occurred. If two peaks were present, then immiscibility of the amorphous parts happened. Figure 1 and Figure 2 show typical DMTA scanings of the PPS/HX1000 (20/80) and PPS/HX4000 (20/80) blends, respectively. The maxima, each corresponding to the T_{g1} of the PPS and to the T_{g2} of the LCP's can be seen. Figure 3 shows the change of the T_{g1} and T_{g2} values as a function of the amount of LCP, after annealing. As it can be seen, the values of T_{g1} (PPS) in the PPS/HX1000 blends remain unchanged at approximately 114 °C, while the T_{g2} of the HX1000 had a slight decrease at high concentrations of PPS. Below PPS 60 wt % , the values of T_g of the HX1000 remain constant. These results suggest partial miscibility. In the case of the PPS/HX4000 blends, it can be seen that the T_{g1} of the PPS also remained unchanged at all concentrations; however, the T_{g2} of the HX4000 showed a slight decrease up to a PPS 20 wt % concentration, being constant after this concentration. This result also can be seen as a consequence of partial miscibility. It can be observed that the analysis of these T_g 's suggest that the LCP has no influence on the PPS. This can be due to the plasticizing effect that the PPS had on the LCP's. Small PPS molecules, rejected during the crystallization process, could diffuse to the low organized (amorphous) regions of the LCP, plasticizing it. Apart from the inherent experimental errors, however, we can conclude that these blends are immiscible or slightly miscible in the solid state. The analysis of the curves also shows the occurrence of the β -transition at 68.99 °C (HX1000) and 89.37 °C (HX4000) . One possible source of this relaxation could be the relaxation of the lateral aromatic rings of the phenyl hydroquinone monomer.

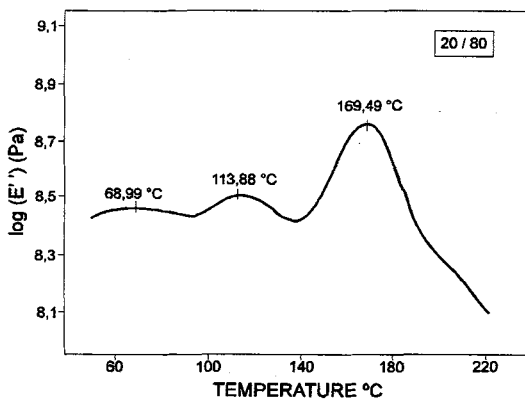


Figure 1. DMTA scanning of PPS/HX1000 blend

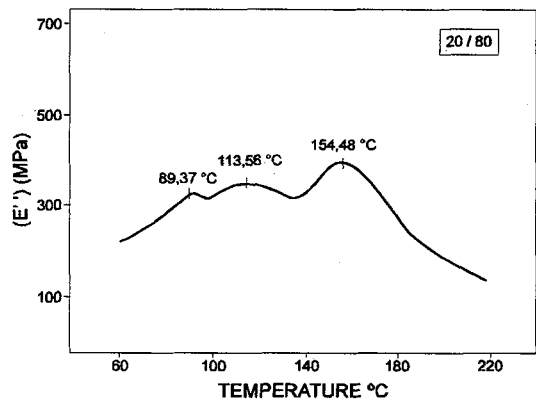


Figure 2. DMTA scanning of PPS/HX4000 blend

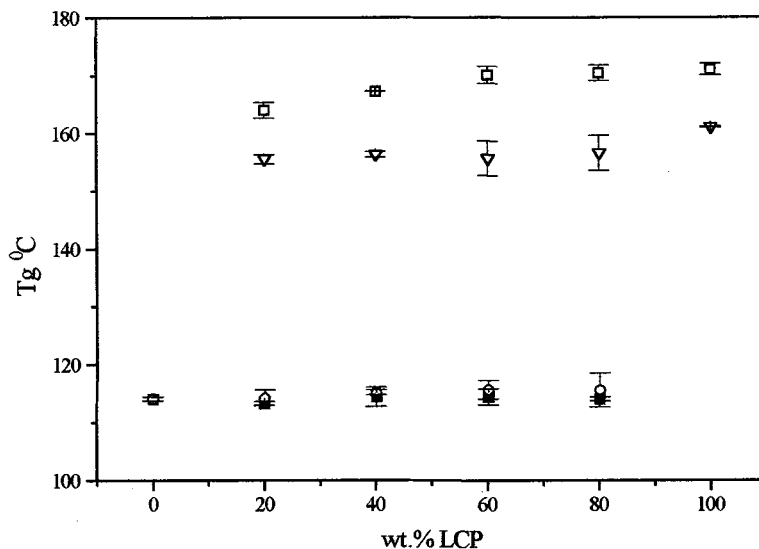


Figure 3. T_{g1} (PPS) and T_{g2} (LCP's) values as function of amount LCP; where T_{g1} of the PPS/HX1000(■), T_{g1} of the PPS/HX4000(O), T_{g2} of the PPS/HX4000(▽) and T_{g2} of the PPS/HX1000(□).

4. CONCLUSIONS

- Blends of PPS and two LCP's, HX1000 and HX4000 were found, by DMTA, to be immiscible (or slightly miscible) in the solid state.
- The PPS has a plasticizing effect on the LCP's.
- A β -transition was found, that can be due to the relaxation of the lateral aromatic ring of the phenyl hydroquinone monomer.

5. ACKNOWLEDGMENTS

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