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Modification of polyester resins by an oligomeric additive

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ABSTRACT

Blends of unsaturated polyester resin (UP) and polyethylene terephthalate oligomers (PETO) have been prepared with different relative compositions. These materials form a kind of semi-interpenetrating polymer networks (semi-IPN's) in which the microstructure and the tensile properties are shown to depend on composition. Impact strength of the blends is also reported, and the performance of the blends was found to be superior to pure UP.

INTRODUCTION

Interpenetrating polymer networks (IPN's) are a class of materials[1-6], not only because of their unique properties, but also because their chemical and steric structure truly constitute a novel variety of materials. IPN's are formed by two each crosslinked polymers, so they both constitute a network[5]. Semi-IPN's are blends, in which only one of the constituents is crosslinked. The production of IPN's for practical applications has been described but very little work has been reported in the area of producing IPN's with oligomers, and only a handful of papers in this respect have appeared in the literature[5-6]. The industrial fabrication of most polymers involves the formation of oligomer by-products. This is not only a waste of resources but also a source of pollutants in landfills and water deposits. Also, for these IPN-like materials, the microstructure is important, so that characterization[7-9] could lead to a better understanding of the synthesis/properties relationships.

Accordingly, the present work reports the blending of UP with different amounts of a PETO, obtained as a by product of the industrial polymerization of poly(ethylene terephthalate) (PET) by the standard method[6]. The microstructural changes of the resulting polymeric alloy, as observed by scanning electron microscopy (SEM) are reported, along with tensile and impact strength characterization of the final materials.

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EXPERIMENTAL

a) Semi-IPN's preparation. The semi-IPN's were prepared following a method described previously[6]. Different compositions of PETO were used, namely, 0.5, 1, 2.5, 5, 7.5, and, 10 % by weight, in order to know to which extent the flexibility and impact strength are improved.

b) Scanning Electron Microscopy. Samples of the fractured surfaces of semi-IPN's were placed into a vacuum chamber and a thin layer of gold carbon was then deposited onto them to diminish charging effects. The SEM observations were carried out by a JEOL 5200 instrument, at 25 KV.

c) Mechanical characterization. Microtensile specimens were prepared by ASTM D 1708. Five measurements were averaged. Also, some specimens were heat-treated at 120°C for two hours to induce the highest possible degree of crosslinking and to produce materials with improved performance. Impact strength specimens were by ASTM D 256. The samples were evaluated in an impact testing machine, Shimadzu, Charpy type. Four measurements were averaged.

RESULTS AND DISCUSSION

Figure 1 shows a typical view of the fractured surface of pure UP resin. As can be observed, the morphology of the specimen corresponds to a highly homogeneous material. Figure 2 shows the case of UP resin containing 0.5 % of PETO. Even at this low content of oligomer a small phase separation can be observed throughout the sample, seen as rounded domains. As one increases the PETO content, the effect on phase separation becomes clearer, as observed in Figure 3, which corresponds to a concentration of 1 % PETO. Figure 4 now shows the case of a resin with 2.5 % PETO and the morphology shows an increase in the globular features, as compared with the previous cases. The more PETO is added, the bigger and clearer the globular structure, as it shown in Figures 5, 6, and, 7, which correspond to PETO contents of 5 %, 7.5 %, and 10 %, respectively. It is interesting to notice the following : First, the high degree of immiscibility of UP resin and the PETO. Second, the increase in size of the globules as the PETO content is increased. However, after 7.5 % PETO, the size seems to grow slower, as observed when Figures 6 and 7 are compared. Under our experimental conditions, the maximum globule size attained was around 0.3 μ, starting with globules smaller than 0.05 μ, for the 0.5 % PETO case. Thus, it is possible to have some control of the microstructure by the blending. This is relevant since the phases of cured blends play and important role in controlling mechanical properties[3].

This particular globular growth is in good agreement with the tensile properties of the blends reported, in earlier paper[6]. The higher the PETO content the more flexible the blends became, as can be seen in Figure 8. This effect has been already observed in other semi-IPN's based on UP matrix[10,11]. On the contrary, the higher the PETO content the poorer the tensile strength at break, as can be seen in Figure 9 (samples without treatment). At PETO 7.5 % and 10 %, the strength remains relatively constant. It does agree with the globular feature, where, at these concentrations, the globule size remains relatively constant as well.

In order to see the effect of temperature, resins were heat treated at 120°C for 2 h. The elongation at break (Figure 8) and strength at break (Figure 9) indicate that a higher degree of crosslinking has been achieved, because tensile strength increased and elongation at break decreased substantially. The same tendency in properties as the one without treatment of the

blends was found. The higher the PETO concentration in the blend, the poorer the tensile strength and the higher the elongation at break. A more extensive study is currently been done on heat-treated blends, including SEM, FTIR and DSC, to have a better understanding of the reaction involved and to explain what is happening in the blends.

Finally, Figure 10 shows the impact strength of the blends. In all cases, the impact strengths of the blends are higher than that obtained for the pure UP. In some cases an increment of nearly 50 % is achieved by the modified UP's in comparison with the UP without additives. This impact strength modification can be understood by comparing this work with other studies about IPN's already reported[1,11,12], where a brittle matrix is modified with a tougher second component.

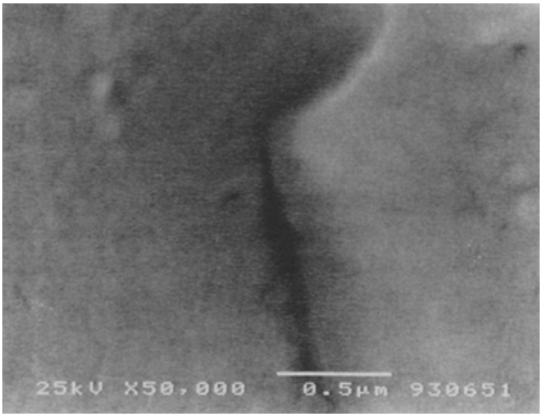

Figure 1. SEM micrograph of pure polyester resin

CONCLUSIONS

Novel semi-IPN's have been produced by mixing UP resin with different amounts of PETO. The results show, first, the possibility of producing materials with controlled phase separation behavior and mechanical properties, through composition. Second, the feasibility of producing novel materials with better impact strength in an ecologically concious way, Since PETO was extracted from the PET polymerization wastes. More extensive characterization of these materials, including physical, thermal, and chemical measurements are currently under way and will be reported.

ACKNOWLEDGEMENT

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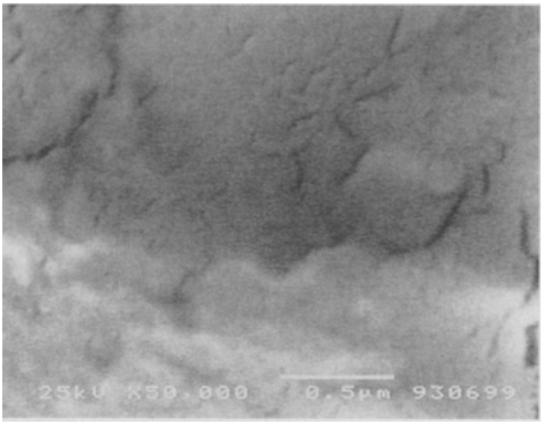

Figure 2. SEM micrograph of a polyester resin containing 0.5 % of PETO

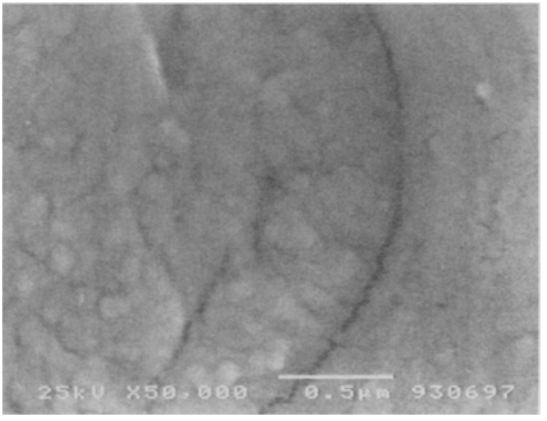

Figure 3. SEM micrograph of a polyester resin containing 1 % of PETO

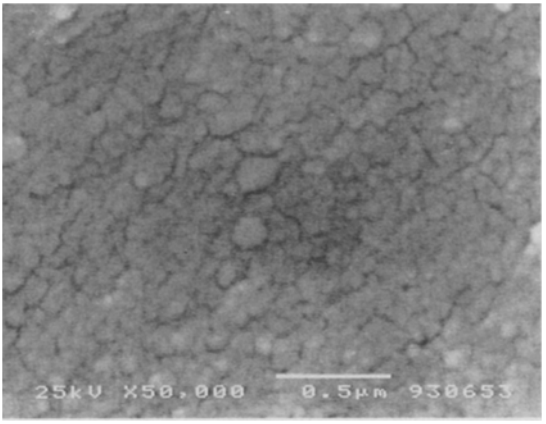

Figure 4. SEM micrograph of a polyester resin containing 2.5 % of PETO

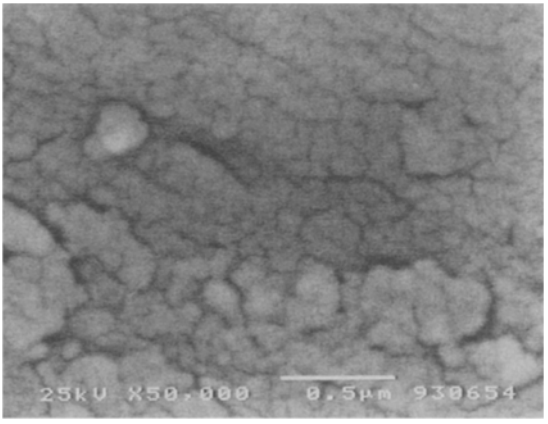

Figure 5. SEM micrograph of a polyester resin containing 5 % of PETO

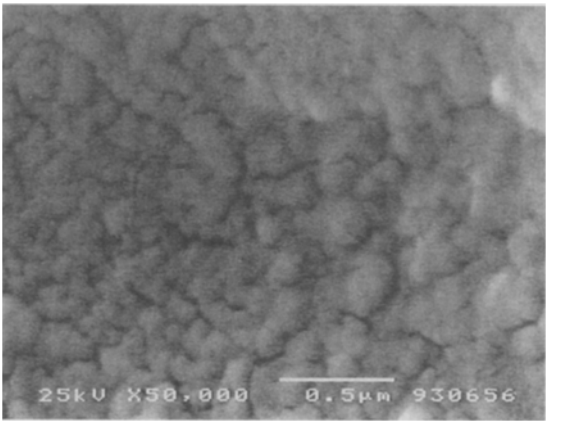

Figure 6. SEM micrograph of a polyester resin containing 7.5 % of PETO

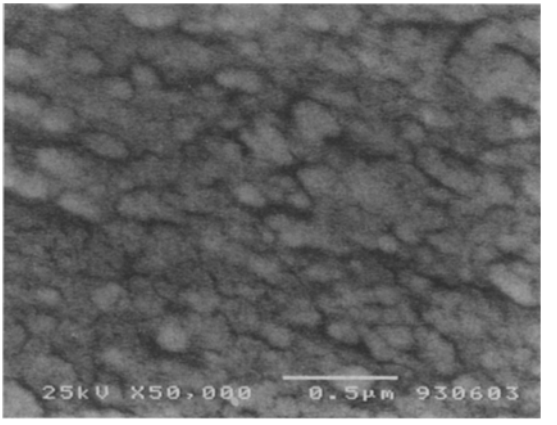

Figure 7. SEM micrograph of a polyester resin containing 10 % of PETO

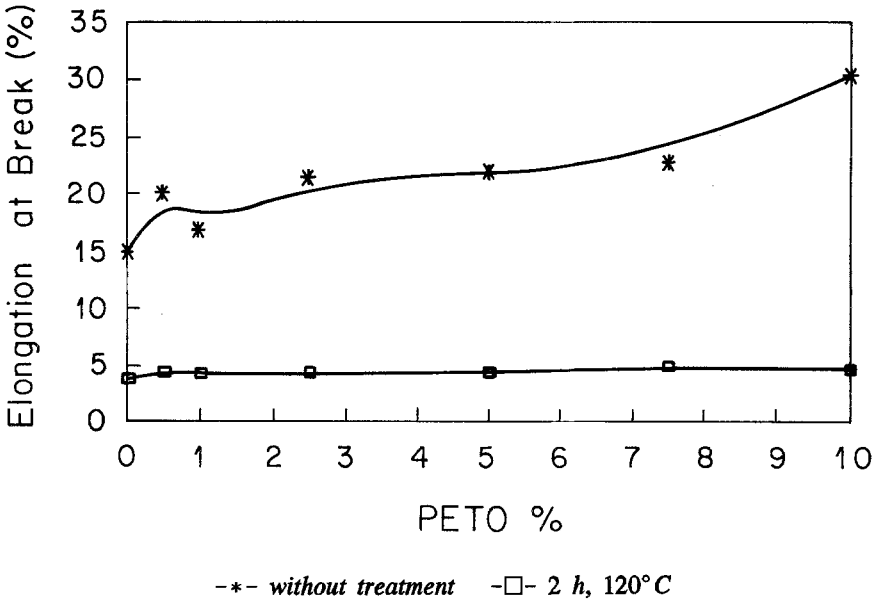

Figure 8. Elongation at break of the blends

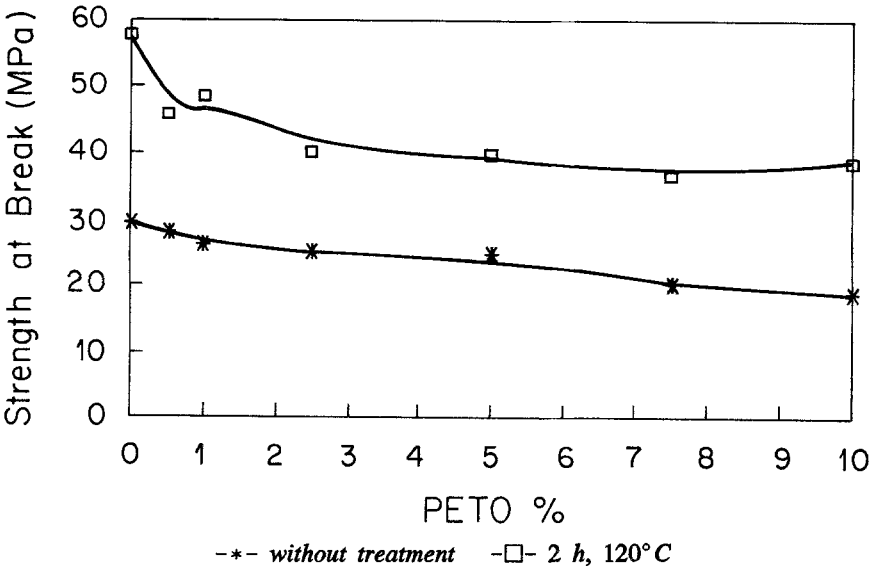

Figure 9. Tensile strength at break of the blends

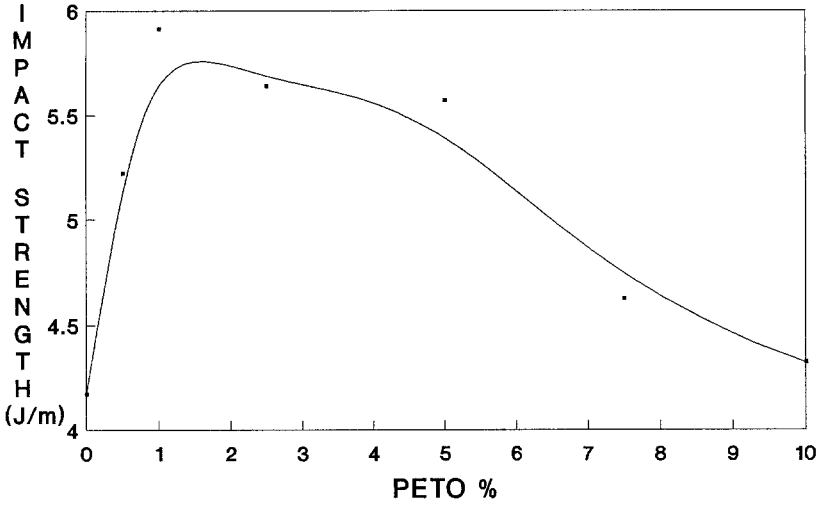

Figure 10. Impact stength modification in the polymeric blends

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