

Semi-interpenetrating polymer networks produced with polyethylene terephthalate oligomer and unsaturated polyester resin

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Abstract

A series of semi-interpenetrating polymer networks (semi - IPN's) based on different compositions of an acyclic polyethylene terephthalate oligomer and unsaturated polyester resin (UP) were prepared. The oligomer was dissolved in the resin containing styrene crosslinker. Later this mixture was crosslinked at room temperature using methyl ethyl ketone peroxide catalyst and cobalt naphthanate as promoter. The tensile strength of the IPN's decreases as the concentration of oligomer increases, whereas, elongation to break increases. A characterization of the oligomer used is also presented.

Introduction

The use of polymer blends to produce new materials for specialty applications is becoming widely employed for various applications. Interpenetrating polymer networks (IPN's) belong to the category of polymer blends with special characteristics, such as, impact strength modification^{1,2} and pH sensitive hydrogels³. In a semi - interpenetrating polymer network (semi-IPN's) only one of the constituents is crosslinked⁴. Polyurethane-polyester IPN's has been synthesized to improve the flexibility of the resulting polymer network⁵. Only one literature⁶ has been found related to the modification of a polymer with oligomer. In this earlier work an unexpected increase of tensile strength and T_g was found.

There does not seem to be any literature on the modification of unsaturated polyester resins (UP) with oligomer. Accordingly, the aim of this work is the generation of a novel oligomer-polyester semi-IPN's and the corresponding relationship of compounding conditions with mechanical properties, such as tensile strength and elongation to break. A characterization of the polyethylene terephthalate oligomer used in this work is also presented.

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Experimental

a) Materials

(i) The polyethylene terephthalate oligomer (PETO) used was extracted from the residues of industrial polyethylene terephthalates (PET). The structure was determined using proton nuclear magnetic resonance ($^1\text{H NMR}$), FTIR spectroscopy, and thermal analysis. The structure of this oligomer is presented in Figure 1.

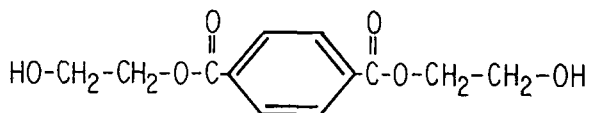


Figure 1. Bis(2-hydroxyethyl) terephthalate. PET oligomer used in the production of semi-IPN's with unsaturated polyester resin.

(ii) Unsaturated polyester resin. A commercially available UP was used (Mexicana de Resinas, type M-70). This resin is based on orthophthalic and maleic acid containing approximately 35 % by weight of styrene as crosslinking agent.

b) Compounding and crosslinking.

The PETO is added to the UP as finely milled particles to improve the rate of dissolution. Then the mixture is heated gently until all the PETO particles are dissolved. Crosslinking is initiated by adding methyl ethyl ketone peroxide as catalyst and cobalt naphthanate as promoter. With these components the reaction occurs at room temperature. This procedure was done for different compositions of PETO, namely, 0.5, 1, 2.5, 5, 7.5, and, 10 % by weight, to elucidate the flexibility improvement.

c) Mechanical measurements

Tensile properties were measured using an apparatus for mechanical properties by Adamel Lhomargy Cia., type E630, model DY 22, with a capacity of 500 daN. The conditions were $23 \pm 2^\circ\text{C}$, room temperature, $50 \pm 5\%$ RH, and, a crosshead speed of 5 mm/min. The casting molded specimens were prepared by ASTM standard D 1708 for microtensile probes. Five measurements were averaged.

Results and Discussion

a) Oligomer characterization

Figure 2a shows the thermogram obtained using a Dupont DSC 2100 apparatus from ambient temperature to 250 °C, for a PETO sample extracted from the PET residues. The conditions used were, heating rate 10 °C/min and H₂ atmosphere. The fusion temperature obtained, 106 °C, agrees with that reported in references 7 and 8 for the PETO shown in Figure 1. It is well known that the preparation of PET is usually carried out by polycondensation of bis (2-hydroxyethyl) terephthalate (BHET) or its oligomer⁹, hence, is not too surprising to find this oligomer in the residues of PET polymerization. On the other hand, the continuous heating of BHET leads to an increase of Mw by polycondensation^{8,9}. It can be seen in Figure 2b, which shows the second heating DSC of BHET at the same conditions of the first heating, Figure 2a. The melting temperature of the oligomer has increased to 227 °C. This temperature corresponds to the fusion point of PET cyclic dimer⁷ or a PET alicyclic trimer¹⁰

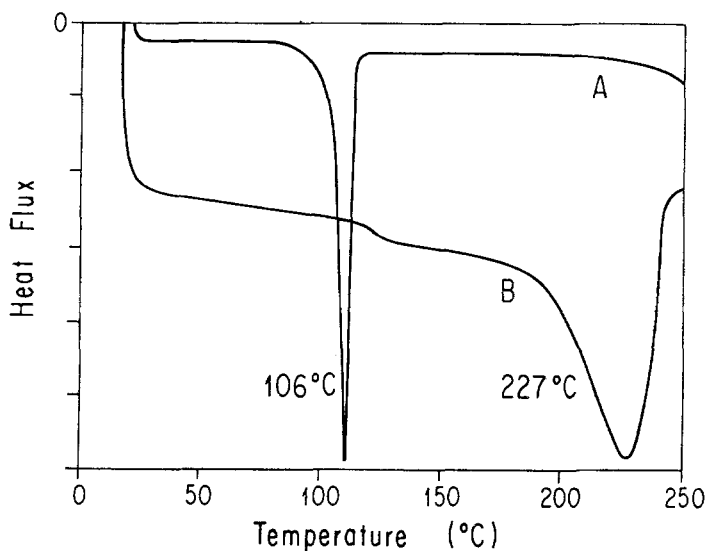


Figure 2. DSC thermogram of the extracted PETO oligomer (A) First heating; (B) second heating

Additional characterization of this oligomer was made in order to be sure that the PETO extracted corresponds to the compound shown in Figure 1. Figure 3 shows the FTIR spectrum of the extracted oligomer which agrees perfectly with the expected BHET peaks and with the one reported previously (α crystallographic form)¹¹. Figure 4 shows the ¹HNMR spectrum, peaks, concentration, and their chemical shift correspond

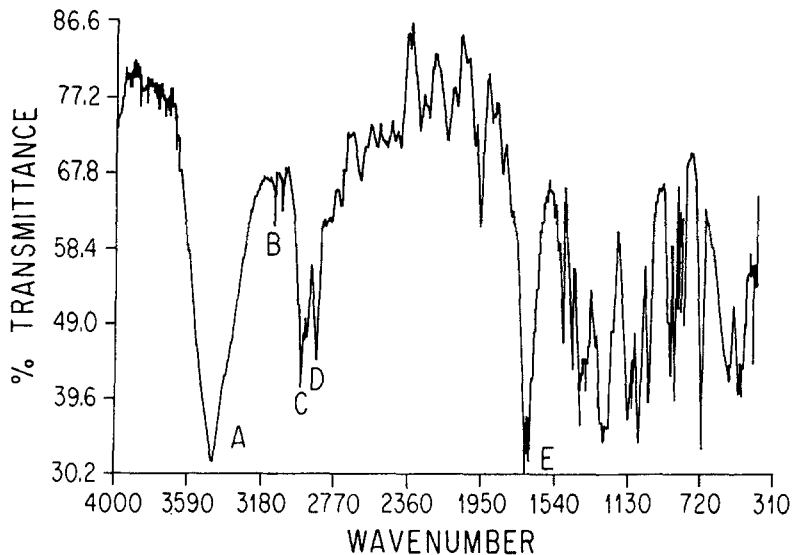


Figure 3. FTIR spectrum of the Extracted PET oligomer. A = OH stretching intermolecular hydrogen bonded; B = Aromatic CH stretching; C = Assymetrical CH_2 stretching; D = Symmetrical CH_2 stretching; E = Carbonyl group stretching.

clearly to the chemical formula of BHET. All the characteristics related to the BHET are indicated in the figures.

b) Mechanical properties

The curves related to the change in mechanical properties under tension versus the amount of PETO, for the semi-IPN's are shown in Figures 5 and 6. The tensile strength decreases as the amount of PETO increases (Figure 5). In contrast, the elongation to break increases (Figure 6). Therefore the flexibility of the semi-IPN's has improved substantially. This effect has already been seen in the production of semi-IPN's based on polyurethane - unsaturated polyester⁵.

Conclusions

The results in this first report open several and exiting areas for research and development. Indeed, the feasibility of producing novel materials with tailored properties by such a simple compounding procedure as described above, represents an interesting field. Second, and perhaps more relevant, the feasibility of reutilizing waste materials

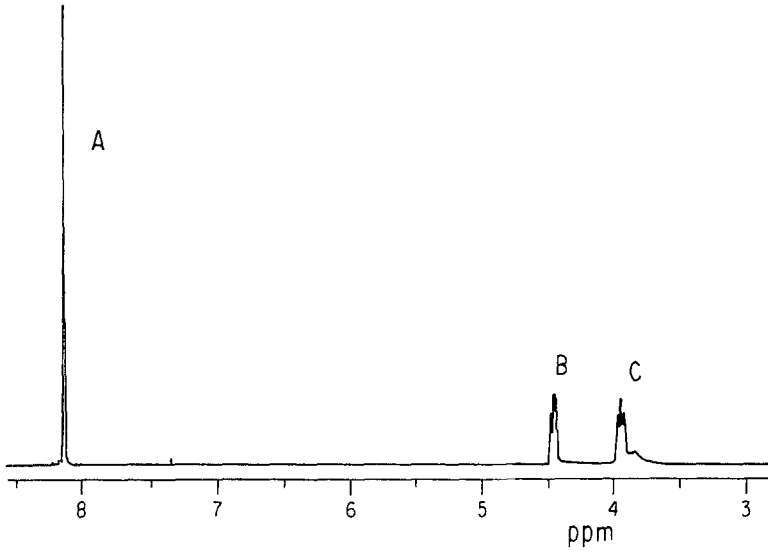


Figure 4. ^1H NMR spectrum of the extracted PET oligomer. A = Aromatic hydrogens; B = Hydrogens bonded to oxygen; C = Hydrogens bonded to OH.

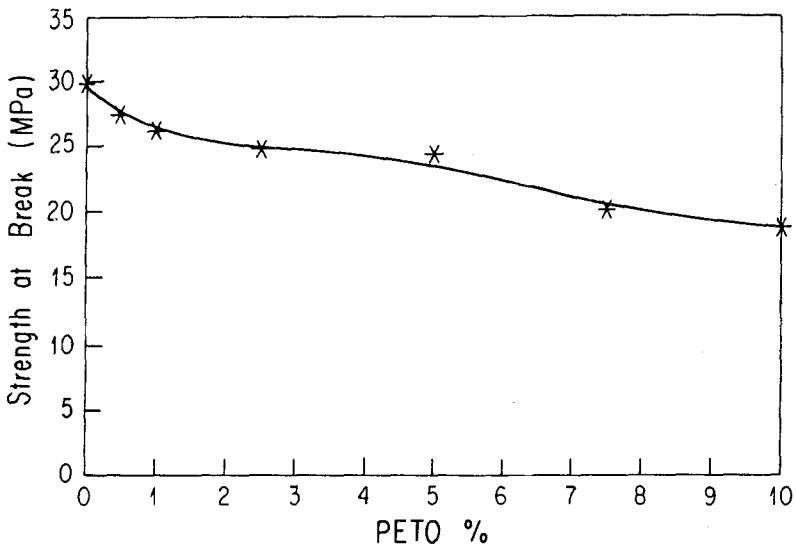


Figure 5. Strength at break of the semi-IPN's versus the concentration of PET oligomer

(remember that PETO was obtained from industrial residues) for producing engineering

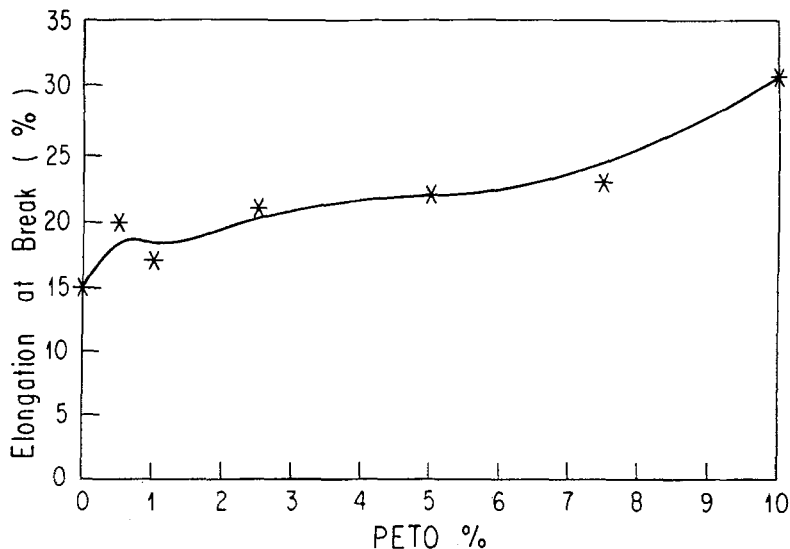


Figure 6. Elongation at break of the semi-IPN's versus the concentration of PET oligomer

materials is certainly a deserving area of research. Further applications and studies in this field are currently under way in our group.

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