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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Avendaño, R. G. , Alvarez-castillo, A. , Vázquez, C. , Real, A. Del and Castaño, V. M.(1997) 'Unsaturated Polyester Resin Modified With Nylon 66 Oligomers', *International Journal of Polymeric Materials*, 35: 1, 21 – 27

To link to this Article: DOI: 10.1080/00914039708039750

URL: <http://dx.doi.org/10.1080/00914039708039750>

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Unsaturated Polyester Resin Modified With Nylon 66 Oligomers

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(Received 25 January 1996)

Nylon 6,6 oligomers, obtained from industrial wastes, were used for modifying an unsaturated polyester resin, creating a series of semi-interpenetrating polymer networks (semi-IPN's) with different compositions. The oligomer was dissolved in the resin by heating. Then, the modified polyester was crosslinked at room temperature. The tensile strength, impact strength and thermal properties of the prepared semi-IPN's are reported. A relationship between the mechanical properties and thermal characterization with the developed morphology of the semi-IPN's was established.

Keywords: Unsaturated polyesters; Semi-IPN's; Nylon 66 Oligomers; Mechanical properties

INTRODUCTION

The industrial fabrication of most plastics, resins and engineering polymers involves the production of oligomers as by-products of the polymerization. This represents not only a waste of resources but also a source of pollutants that, in many cases, taint landfills and water deposits. Therefore, this is an extremely relevant and practical reason

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for finding novel and profitable uses for oligomers, in addition to the basic science behind the study of polymeric materials based on oligomers.

Besides, oligomeric materials obtained from the polymerization wastes are mechanically poor due to their low molecular weights, which make them not suitable to be used in most commercial applications. Therefore, a new way of recycling these materials by means of blending with a suitable polymer has been reported in the literature (1–4). The result of this blending is the generation of novel semi-interpenetrating polymer networks (semi-IPN's) with an improvement of some of the mechanical properties in relation with the original polymer. Also, since in these IPN-like materials, the morphology plays a key role, it is important to perform characterization which, as in other polymer blends already reported (2, 5–10), could lead to a better understanding on the synthesis-microstructure-properties relationships.

In the present work the procedure of blending unsaturated polyester resin (UP) with different amounts of Nylon 66 oligomers, obtained as a by product of the industrial polymerization of Nylon 66, is reported. An unusual microstructure developed by the polymeric alloys (homogeneous material), which forms a semi-IPN, is also reported, along with some mechanical characterization of the final materials.

EXPERIMENTAL

a) Materials

- (i) The Nylon 66 oligomers (NYL660's) used were obtained from the residues of industrial Nylon 66 polymerization. It was characterized by using FTIR spectroscopy and thermal analysis. The experimental results showed that the residues correspond to a mixture of two NYL660's: linear dimer and Nylon salt. The characterization and separation process of the NYL660's were reported elsewhere (11).
- (ii) Unsaturated polyester resin (UP). A commercially-available UP (type M-70) was bought to Mexicana de Resinas. This resin is based on orthophthalic and maleic acid containing approximately 35% by weight of styrene as crosslinking agent.

b) Compounding and Crosslinking

The NYL660's is added to the UP as finely-milled particles to improve its dissolution. Then, the mixture is heated gently until all the NYL660's particles are dissolved. The crosslinking reaction is initiated by adding methyl ethyl ketone peroxide as catalyst and cobalt naphthanate as initiator. Once the mixture had hardened (3 days), it was heated for 2 hours at 100°C to allow a complete crosslinking reaction. This procedure was followed for different compositions of NYL660's, namely, 0.5, 1, 2, 3, 4 and 5% by weight, in order to know to what extent the flexibility and impact strength is improved.

c) Mechanical Measurements

i) Tensile Properties

The samples were evaluated by using an apparatus for mechanical properties from 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 in accordance with ASTM D 1708 standard for microtensile probes. Five measurement data were averaged in each case.

ii) Impact strength

The specimens dimensions of the specimens fit the requirements described in ASTM D 256 standard. The samples were evaluated in an impact testing machine Shimadzu, Charpy type, at room temperature ($23 \pm 2^\circ\text{C}$). Four measurements were averaged in each sample.

RESULTS AND DISCUSSION

Figure 1 shows the change in mechanical properties under mechanical tension versus the amount of NYL660's added to the polymeric blends. The tensile strength remains relatively constant until the amount of NYL660's reaches the value of 2%. After that value this

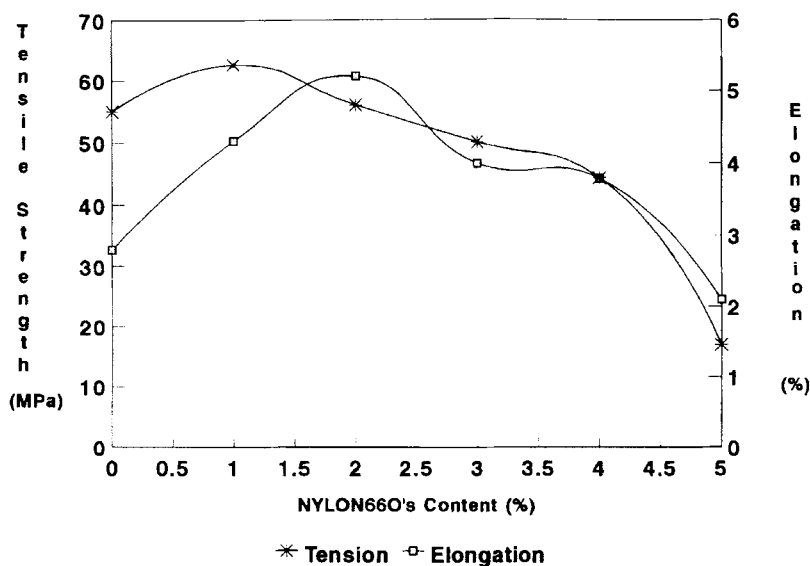


FIGURE 1 Tensile Mechanical Properties of the NYL660's Polyester resin semi-interpenetrating polymer networks.

property starts to decrease drastically. The elongation at break increases until a maximum (2% of NYL660's) and then starts to decrease. Therefore in the first stage (higher elongation), the flexibility of the semi-IPN's obtained is improved. This effect has been already seen in the production of semi-IPN's based on polyurethane (12) and polyethylene terephthalate oligomer (1) both blended with unsaturated polyester resin.

On the other hand, Figure 2 shows the increment obtained in the impact strength at each NYL660's concentration. In all cases, an increment in impact strength is observed as in others IPN's studied before (2,12). The bigger increment obtained corresponds to the case where the NYL660 content is 1% (experimental value 5.96 J/m). It is what we do really expected because of the addition of a second tougher component (NYL660's) to a brittle resin.

The typical morphology reported for the semi-IPN's obtained in the present work (3) corresponds to a highly-homogeneous material but this is not the case of a usual morphology of IPN's already (2, 12–14). Therefore, the question arises on whether or not the two components

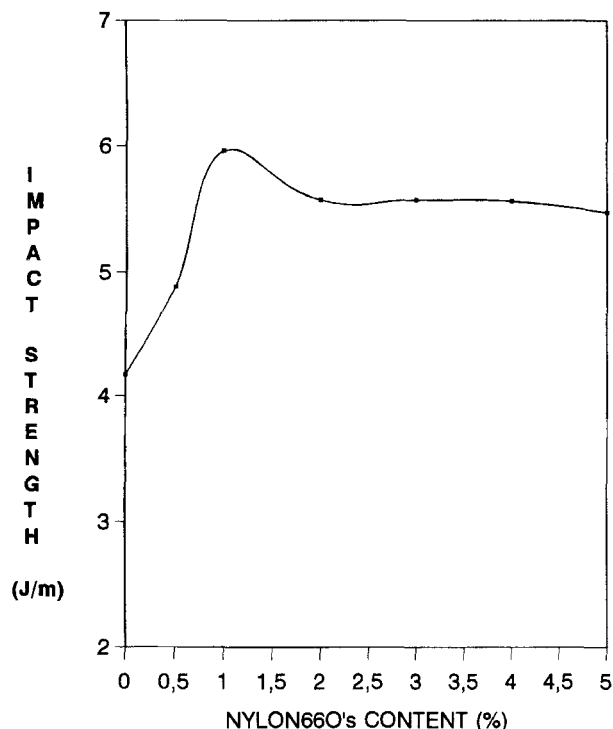


FIGURE 2 Impact Strength of the NYL660's/Polyester resin semi-interpenetrating polymer networks.

(UP and NYL660's) has crosslinked. For this reason we conducted DSC experiments in order to determine if the NYL660's melt with temperature. The experiments were performed in a Du Pont 2100 DSC apparatus in N_2 atmosphere with a heating rate of $20^\circ C/min$. A typical DSC thermogram of the blends is shown in the Figure 3. As can be observed, no fusion point is presented during the experiment but only the T_g of the UP resin ($55.71^\circ C$). It does indicate that NYL660's in the blends has been affected with a some kind of crosslinking reaction. Besides, the T_g of the UP does not change at all with NYL660's content. According to polymer blend theory, the T_g of the blend components must change if chemical compatibility has been achieved (13). This is the case of complete miscibility of the two components but the question arise why it does not happen in our case.

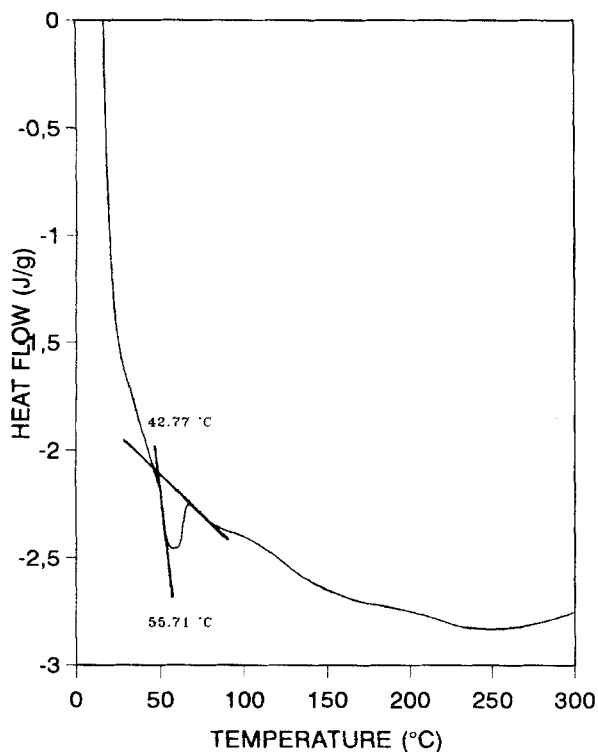


FIGURE 3 Typical DSC thermogram of the NYL660's Polyester resin semi-interpenetrating polymer networks with a 5% of NYL660's content.

Additional experiments are currently being done in our group to clarify the reaction involved in the crosslinking process of NYL660's, and why the T_g of the UP did not change in the semi-IPN's and develop a homogeneous phase.

CONCLUSIONS

Novel semi-IPN's have been produced by mixing UP resin with different amounts of Nylon 66 Oligomers (residues of industrial Nylon 66 polymerization). The results show, first, the possibility of producing new materials with improved impact strength; second, the plastifying

effect of Nylon 66 oligomers on the UP resin; and third, and ecologically more important, the feasibility of reutilizing waste materials for producing engineering materials with tailored properties, certainly an area deserving more research. Further applications and studies in this field are currently under way in our group.

Acknowledgement

The authors are indebted to Mrs. Jackeline Cañetas, Mrs. Elena Oliva and Mr. Alfredo Maciel for their technical support.

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