

NOTE

Thermomechanical Properties of Unsaturated Polyester Resin Based on Recycled Poly(ethylene terephthalate)

INTRODUCTION

Recycled poly(ethylene terephthalate), PET, mainly recovered from plastic beverage bottles, can be chemically modified to produce unsaturated polyester.¹ Recently, research has shown that proper formulation of unsaturated polyester resins based on recycled PET can also be used for the production of good quality polymer concrete and mortar materials.^{2,3}

Unsaturated polyesters represent a large family of materials with various properties and performance characteristics.^{4,5} Common forms of unsaturated polyesters are isophthalic, orthophthalic, and terephthalic-based types. Phthalic anhydride or isophthalic acid is typically used in the formulation of conventional unsaturated polyester (i.e., isophthalic or orthophthalic-based polyesters). Virgin terephthalic acid is not usually used in the production of unsaturated polyester (i.e., terephthalic-based polyesters) because it is expensive and possesses a high melting point, which presents difficulties in synthesis. Conversely, recycled PET is effective in incorporating terephthalic functionality into the backbone of a polyester resin. Terephthalic-based polyesters exhibit a more uniform and structured cross-linking matrix with a higher degree of strength, stiffness, and toughness than isophthalic or orthophthalic-based polyesters. Another advantage of using recycled PET in making unsaturated polyesters, as compared to using virgin materials, is that it reduces by about 50% the processing time to produce a polyester resin with a certain molecular weight and acid number.⁶

The objective of this paper is to report on the thermomechanical properties of an unsaturated polyester resin based on recycled PET. These properties should provide useful information on the effective utilization of the material in various structural and nonstructural polyesters or their composites' applications.

EXPERIMENTAL

The formulation of the unsaturated, recycled-PET-based polyester that was used in this study is shown in Table I.

This formulation was chosen because it produced good quality polymer composites for construction applications. The production of the resin was done in two steps. The first step consisted of digesting the PET molecules by charging the PET scrap and diethylene glycol into a reactor and heating for several hours in the presence of a transesterification catalyst. The second step consisted of adding dibasic acids (maleic anhydride and phthalic anhydride) to the solution to produce the polyester resin. Maleic anhydride was used to provide the reactive double bonds, while phthalic anhydride was added to reduce the amount of unsaturation present, thus increasing the flexibility of the cured resin. The unsaturated polyester was then diluted with styrene to reduce its viscosity and to allow its further cure to a solid (polymer) upon the addition of suitable free radical initiators and promoters. Curing took place because the styrene combined with the reactive double bonds of the polyester chains, thus linking them together and forming a strong three-dimensional polymer network.

The curing of the polyester was achieved at room temperature by adding 1%, by weight of resin, of methyl ethyl ketone peroxide initiator (9% active oxygen) and 0.1%, by weight of resin, of cobalt naphthenate promoter (12% solution). Curing was done at room temperature.

The weight average molecular weight of the resin was 8000 and its number average molecular weight was 1500. The thermal and mechanical behavior of the polymer is expected to be strongly influenced by the polydispersity index, which is the ratio of the weight average molecular weight to the number average molecular weight. The molecular weights were determined using size exclusion chromatography. The resin viscosity was 1000 cps at 298 K and was measured with a Brookfield viscometer.

Thermal analyses were carried out on a Dupont model 9900 differential scanning calorimeter (DSC). A typical sample size was 25 mg. Samples were heated from 223 K to 823 K at a rate of 10 K/min. All samples were heated under an argon purge stream.

The tensile stress-strain behavior was measured on an Instron Series IX Automated Materials Testing System using a strain rate of 6 mm/min. The tensile test was done according to ASTM specifications. The tensile samples were shaped to conform to the Type I specimens of ASTM D638. The specimens were con-

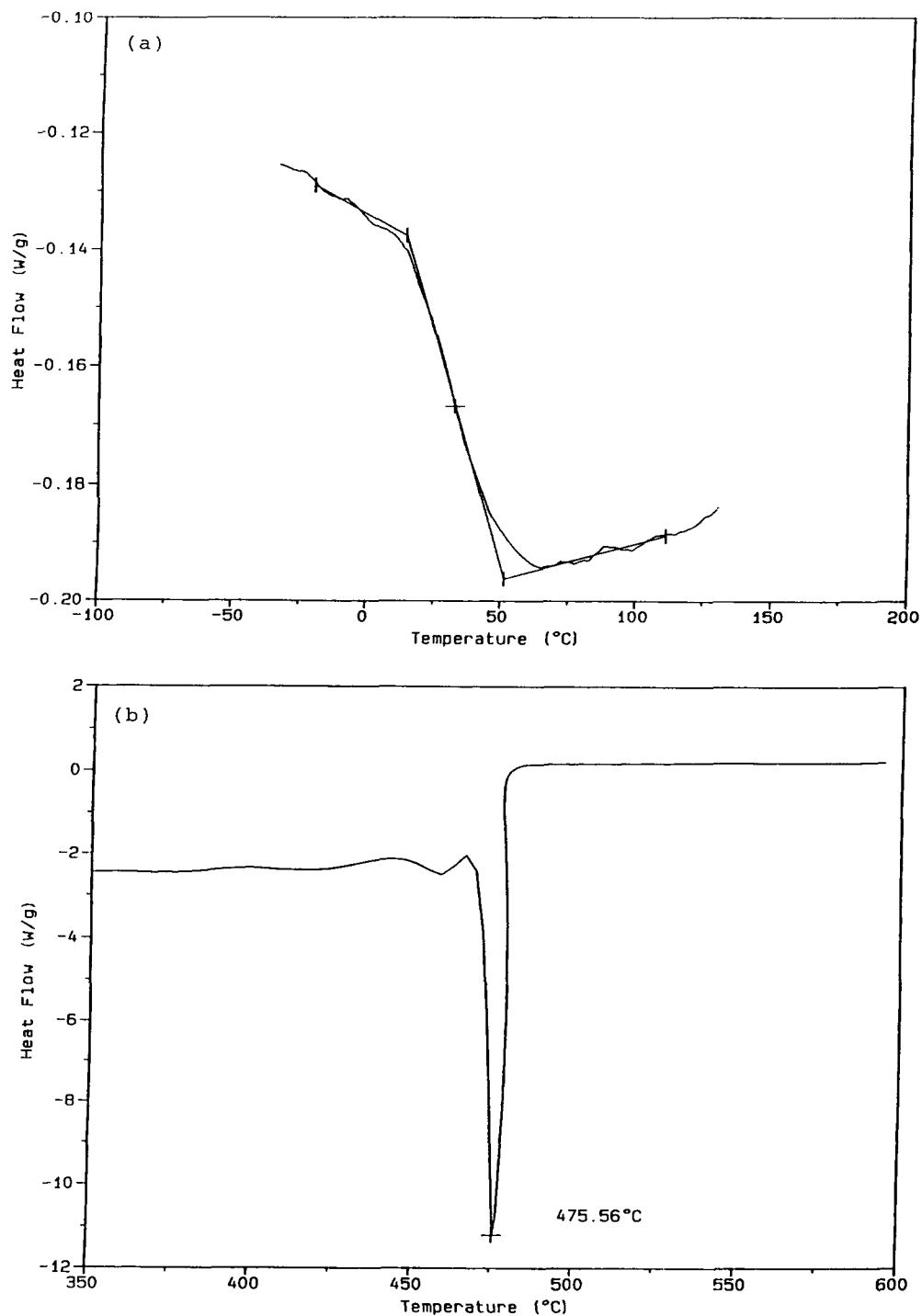


Figure 1 Typical DSC scan showing (a) glass transition and (b) degradation.

ditioned at various constant temperatures using thermostatted water baths several hours before testing occurred. The age at testing was at least 10 days, thus giving ample time for the polyester resin to reach its ultimate strength.

RESULTS AND DISCUSSION

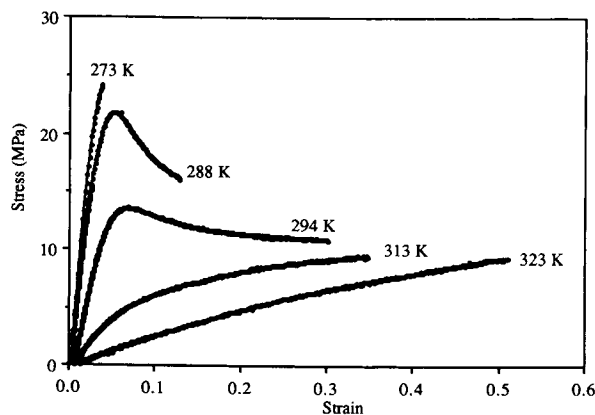
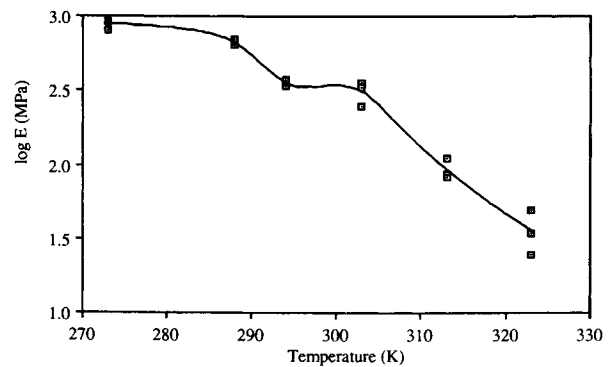
A typical DSC scan of the polyester resin is shown in Figure 1. Two transitions are observed in the figure. The first transition occurs at 303 K, which is the glass tran-

Table I Unsaturated Polyester Resin Formulation

Components	Percent by Weight
Recycled PET	21.0
Diethylene glycol	28.0
Maleic anhydride	10.5
Phthalic anhydride	10.5
Styrene	30.0

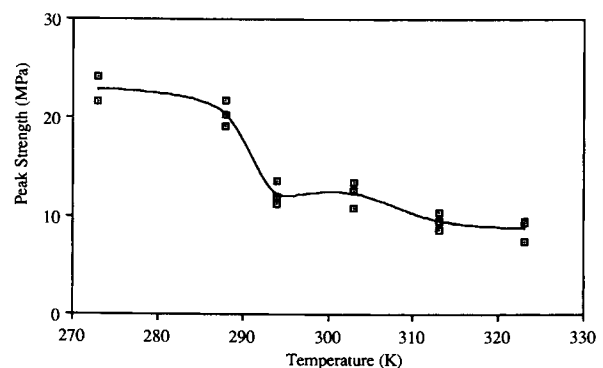
sition temperature of the polyester. This temperature is determined by the half-height method. Half of the vertical distance between the base lines is extrapolated to the temperature axis. This change in behavior at the glass transition temperature is accompanied by a change in heat capacity, which is detected by the DSC. Another thermal change in the polymer occurs at 748 K, which is the degradation temperature of the polyester. A peak is observed in the DSC scan at the degradation temperature. An upward shift can be observed in the heat capacity of the polyester when the degradation temperature is exceeded, since degradation alters the character of the material.

The typical stress-strain curves at different temperatures for the unsaturated polyester are shown in Figure 2. At 273 K, the polyester exhibited relatively high strength and modulus. As the temperature increased, the strength and modulus of the polyester decreased while its ductility and toughness increased. It is interesting to note that at 288 K and 294 K, the polyester exhibited a well-defined yield point, which was not the case for 273 K, 313 K, and 323 K. The exhibition of plastic flow which is manifested in well-defined yield points may be caused by the presence of uncrosslinked material in the cured resin and by secondary relaxation below the glass transition temperature. In many polymer concrete and mortar applications, it is desirable to use unsaturated polyesters that exhibit relatively high elongation before breaking.⁷ The failure mode for the specimens was also very different at various tem-

**Figure 2** Typical stress-strain curves in tension.**Figure 3** Log of the tensile modulus versus temperature.

peratures. At 273 K, the failure mode of the specimens was very fast with virtually no ductility.

The effect of temperature on the log of the tensile modulus ($\log E$) of the polyester is shown in Figure 3. The tensile modulus was obtained using linear regression techniques applied within the proportional limit of the stress-strain curve. A significant decrease in the tensile modulus occurs as the temperature is increased because of the viscoelastic nature of the resin. The modulus decreases by a factor of 64% as the temperature increases from 273 K to 303 K and by a factor of 88% as the temperature increases from 303 K to 323 K. Two relaxations can be observed in Figure 3. One relaxation occurs at 303 K, which is the glass transition temperature of the polyester. This relaxation was already observed in the DSC scan. A secondary relaxation can be observed at 288 K. At that temperature, the polyester undergoes some property changes that are attributed to some specific molecular relaxation mechanisms that cannot be fully explained.⁸ This secondary relaxation occurring below the glass transition temperature may be caused by the presence of uncrosslinked (or much less crosslinked) material in the cured resin. This secondary relaxation was not detected in the DSC scan. It is possible that the energetics of this secondary transition are below the detection limit of the DSC. A low tensile modulus is desirable when the polyester or the polyester mortar or concrete is used in conjunction

**Figure 4** Tensile peak strength versus temperature.

with another material, such as portland cement concrete or steel; the low tensile modulus of the neat polyester resin can relieve relatively high shear and tensile stresses that would occur at the interface of the polyester (or its composite) and the other material due to thermal fatigue.⁹

The effect of temperature on the peak strength of the polyester is shown in Figure 4. As was already observed with the tensile modulus versus temperature, two relaxations were noticed: at 303 K (the glass transition temperature) and 288 K. The peak strength decreases significantly as temperature is increased. The peak strength decreases by about 45% as temperature increases from 273 K to 303 K, while it decreases by about 30% as temperature increases from 303 K to 323 K.

CONCLUSIONS

The thermal characterization of an unsaturated polyester resin based on recycled PET has been evaluated in this paper. Special caution should be used when operating the polyester at very low temperatures because of the resulting low ductility and toughness. At high temperatures, the polyester undergoes a significant decrease in modulus and a significant increase in deformation before breaking, both of which are desirable features in many structural and nonstructural applications. The resulting decrease in strength which occurs with increasing temperature, as well as the occurrence of primary and secondary transitions at specific temperatures, should be taken into account in the design of the material in various engineering applications. Future studies on the material should concentrate on the effect of polymer preparation, composition, and crosslink density on the thermomechanical properties of the material.

REFERENCES

1. U. R. Vaidya and V. M. Nadkarni, *Ind. & Eng. Chem. Res.*, **26**(2), 194 (1987).
2. K. S. Rebeiz, D. W. Fowler, and D. R. Paul, *J. Appl. Polym. Sci.*, **44**(9), 1649 (1992).
3. K. S. Rebeiz, D. W. Fowler, and D. R. Paul, *American Concrete Institute, Materials Journal* to appear.
4. Bjorksten Research Laboratories. *Polyesters and their Applications*, Reinhold Publishing Corp., New York (1956).
5. G. Lubin, *Handbook of Composites*, Van Nostrand Reinhold, New York (1982).
6. K. S. Rebeiz, D. W. Fowler, and D. R. Paul, *Journal of Materials Education*, **13**(5 and 6), 441 (1991).
7. K. S. Rebeiz, D. W. Fowler, and D. R. Paul, *Trends in Polymer Science*, **10**(1), 315 (1993).
8. *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Wiley-Interscience, New York (1988).
9. D. L. Wheat, D. W. Fowler, and A. I. Al-Negheimesh, *Journal of Materials in Civil Engineering*, **5**(4), 460 (1993).

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