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Recycling of unsaturated polyester resin using propylene glycol

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Cured unsaturated polyester resin was degraded with propylene glycol, and the degraded material was used to make recycled resin by reaction with maleic anhydride. The curing reaction for the recycled resin was faster than that of the neat resin. The mechanical properties of mixtures of neat and recycled resins were measured and, among them the (90 wt% neat/10 wt% recycled) mixture showed the highest impact strength. The addition of 15 wt% of glass fibre to the recycle mixtures further increased the impact strength, with the (90 wt% neat/10 wt% recycle) mixture again exhibiting the highest value. © 1997 Elsevier Science Ltd.

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Introduction

The chemical recycling of waste polymers has received a great deal of attention in recent years[1]. Unsaturated polyester (UP) resin is of interest as a candidate for recycling because it is one of the most widely used thermoset resins as a matrix for polymeric composites. One of the large-volume applications of unsaturated polyesters is in sheet moulding compounds (SMCs) used for body panels and other automotive parts.

At present, SMCs are recycled by incorporating ground waste into virgin SMCs (up to 30 wt%) and using the mixture in the production of automotive parts and other consumer products. Some automobile companies are working on pyrolysis of SMCs, but no commercial process has yet been developed. In a recent study, Kinstle *et al.*[2] hydrolysed cured unsaturated polyester resin under neutral conditions at 225°C for 2–12 h. Filtration of the solids remaining after hydrolysis yielded isophthalic acid, styrene–fumaric acid copolymer, and unhydrolysed starting material. The copolymer was recovered by acetone extraction in high yield. Propylene glycol recovery was below 50%. Tesoro *et al.*[3,4] have described hydrolysis of a cured UP in a mixed-solvent system (butanone/water) in an autoclave at 220–275°C for 2–6 h. After hydrolysis, the products separated into two layers. The upper layer (butanone) contained primary oligomer; the lower layer (water) contained phthalic acid. In another study, Pater *et al.*[5] have described hydrolysis of ground SMCs using 30% methanolic KOH in dioxane under reflux conditions.

The objective of this work is to report on chemical recycling of cured unsaturated polyester by glycolysis. Cured UP resin was degraded by propylene glycol (PG) at different temperatures, and then reconstituted (i.e. recycled) with maleic anhydride and styrene monomer. The cure kinetics and the mechanical properties of the neat, recycled resins and their mixtures are reported.

Experimental

UP resin containing 29 wt% of styrene was supplied by the Ashland Chemical Co. (MR 11090). PG and maleic anhydride were obtained from the Aldrich Chemical Co. Inc. Benzoyl peroxide was used as the initiator.

D.s.c. (TA instrument, 2920) was used to investigate the kinetics of curing of the UP resin. Dynamic experiments were carried out at a heating rate of 10°C min^{-1} from 25 to 250°C. Isothermal experiments were carried out at 70, 80 and 90°C, after an initial ramp of 200°C min^{-1} to reach the desired cure temperatures. The amount of heat evolved during the curing reaction was measured.

After curing, the neat resin was ground to 0.5 mm mesh size using a Thomas-Wiley Laboratory Mill (model 4). The ground material was reacted with PG at 170°C for 3 h, followed by 225°C for specified periods of time. Infrared spectra of samples at different reaction times were obtained with a Micro IR (Spectra Tech. Inc., model 004-904) in order to measure the extent of reaction. Upon completion of this first step, the temperature of the reactor was decreased to 150°C, maleic anhydride was introduced, and the reaction was continued for 24 h at constant temperature. Upon completion of the reaction, the temperature was decreased to 60°C, and 29 wt% of styrene was introduced.

Tensile tests were carried out on an Instron Universal Test Instrument (model 1011) at 25°C. Samples were made in accordance with ASTM D638M. The cross-head speed of the tensile tester was set at 40 mm min^{-1}. Tensile properties were determined from the average of five specimens. Charpy impact tests were conducted on a CEAST USA Inc. model 513. Unnotched samples were

Table 1 Kinetic parameters for the second-order ($m + n = 2$) reaction of the unsaturated polyester resin

Temperature (°C)	$k_1 \times 10^4$ (s^{-1})	$k_2 \times 10^3$ (s^{-1})	m	n
70	0.192	1.974	0.94	1.06
80	2.964	4.515	1.02	0.98
90				

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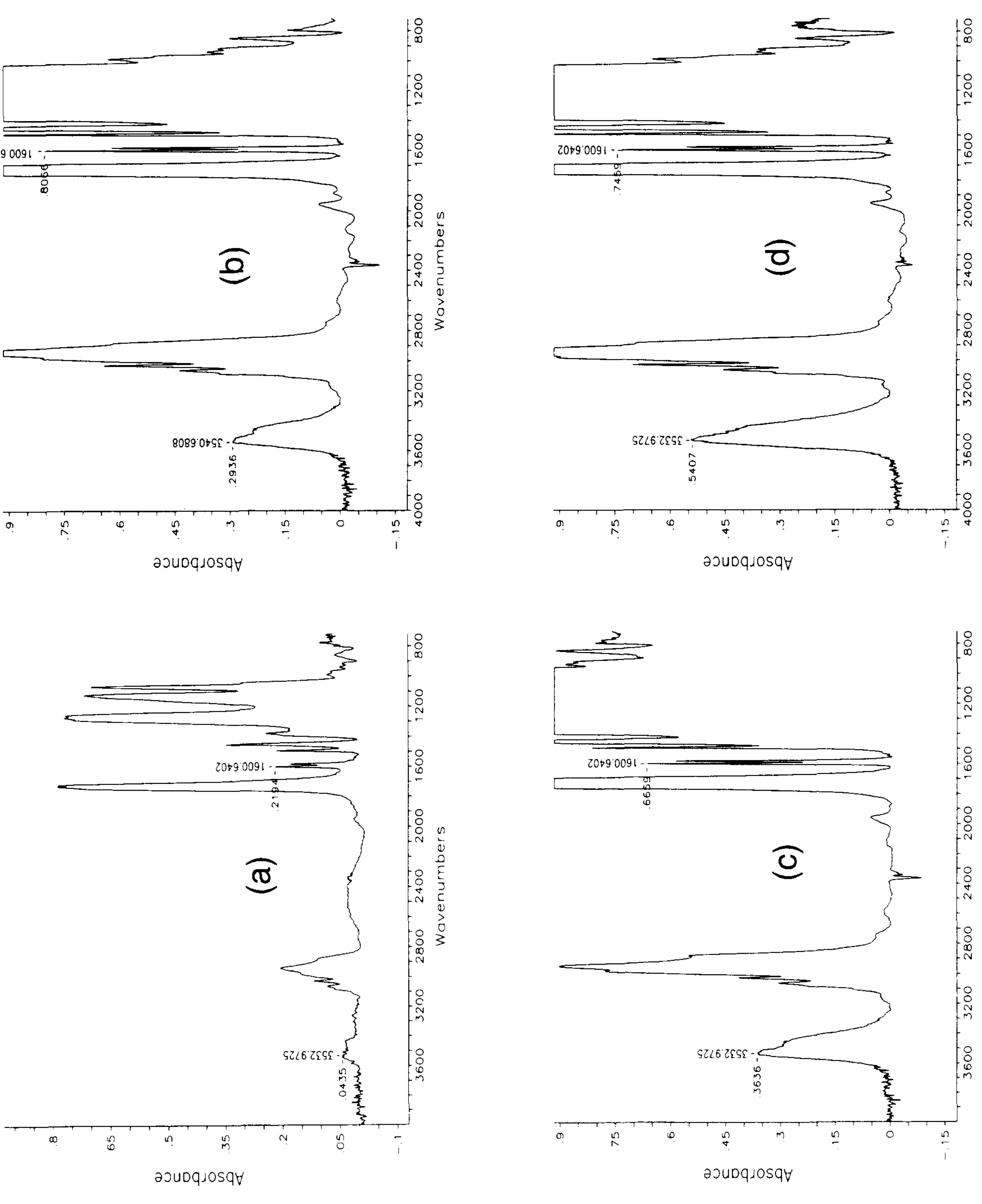


Figure 1 Micro-i.r. spectra of degraded UP resin: (a) neat resin; (b) UP degraded for 3 h at 170°C; (c) UP degraded for 3 h at 170°C and 1 h at 225°C; (d) UP degraded for 3 h at 170°C and 4 h at 225°C

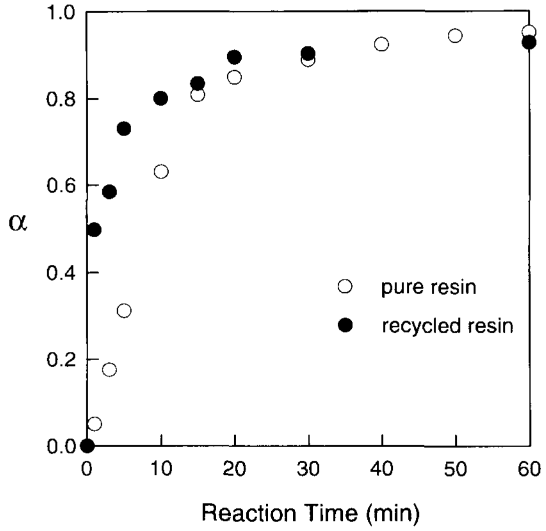


Figure 2 Extent of reaction with cure time

5 cm long, 1.2 cm wide and 0.3 cm thick. The average impact strength was reported as the average of at least five specimens.

Discussion

D.s.c. was used to investigate the cure of the unsaturated polyester resin. Experiments were conducted in both dynamic and isothermal modes. The total heat generated during isothermal and dynamic experiments, Q_{iso} and Q_{dyn}, respectively, was measured, and the maximum extent of conversion, $\alpha_{\text{ult}}(T)$, was calculated using equation (1):

$$\alpha_{\text{ult}}(T) = Q_{\text{iso}}/Q_{\text{dyn}} \tag{1}$$

It was assumed that the rate of conversion, $\mathrm{d}\alpha/\mathrm{d}t$, is proportional to the rate of heat generated during cure, $\mathrm{d}Q/\mathrm{d}t$, and can be calculated from equation (2), where Q_{ult} is the total heat generated during a dynamic run:

$$(\mathrm{d}\alpha/\mathrm{d}t)_T = (\mathrm{d}Q/\mathrm{d}t)_T/Q_{\text{ult}} \tag{2}$$

Rate data were analysed using equation (3), a modified form of a kinetic model suggested by Kamal *et al.*[6], and used extensively to study the cure of polyesters by Han and Lem[7–9]:

$$\mathrm{d}\alpha/\mathrm{d}t = k_1(\alpha_{\text{ult}} - \alpha)^m + k_2\alpha^m(\alpha_{\text{ult}} - \alpha)^n \tag{3}$$

The parameters k_1 and k_2 are rate constants, and the quantities m and n identify, empirically, the order of the reaction. Consistent with prior literature, we assume $(m + n) = 2$. The total heat of reaction of the unsaturated polyester, determined from a dynamic d.s.c. experiment, is in the range of 260–270 J g^{-1}.

The rate of conversion is strongly dependent on temperature, and the maximum reaction rates are obtained within 20 min at 70°C, 10 min at 80°C and 1 min at 90°C. The percentage conversion at the point of maximum reaction rate is about 60%, and is independent of temperature. *Table 1* is a summary of the kinetic parameters k_1, k_2, m and n. The rate constants k_1 and k_2 increase with temperature, but could not be measured accurately at 90°C due to the fast reaction. The reaction order parameters m and n are approximately equal and independent of temperature.

'Recycled' resin was produced from components added sequentially in a series of steps and in the following proportions: 15 wt% of ground UP, 30 wt% of PG, 26 wt% of maleic anhydride and 29 wt% of styrene. Finely ground cured UP resin was first heated in PG at 170°C for 3 h and 225°C for specified times. The micro-i.r. spectra of degraded UP are shown in *Figure 1*. A peak at 1600 cm^{-1} confirms the presence of the C=C bond of benzene, and does not change during reaction. A peak at 3532 cm^{-1} confirms the presence of hydroxyl groups at the chain ends of the UP resin. The relative amount of hydroxyl groups at a specific reaction time is calculated from equation (4):

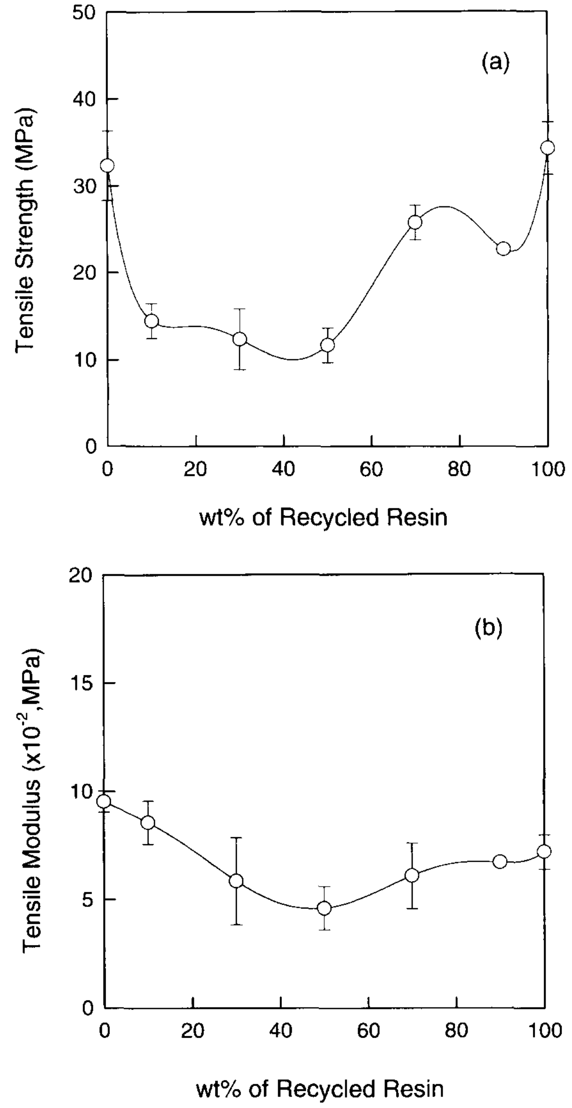


Figure 3 (a) Tensile strength of mixtures of neat and recycled resins. (b) Tensile moduli of mixtures of neat and recycled resins

$$\mathrm{OH}(\%)_{\text{rel}} = \{(A_{3532}/A_{1600})_{t=t} - (A_{3532}/A_{1600})_{t=0}\} / (A_{3532}/A_{1600})_{t=t} \tag{4}$$

The relative amounts of hydroxyl groups are 45.5, 63.1 and 72.6%, for the degraded UP at 170°C for 3 h, at 170°C for 3 h followed by 225°C for 1 h, and 170°C for 3 h followed by 225°C for 4 h, respectively. The UP/PG resin (3 h at 170°C, 4 h at 225°C) was then reacted with maleic anhydride at 150°C for 24 h. After reaction, the styrene was added and the resulting 'recycled' resin was cured. The extents of reaction as a function of time at

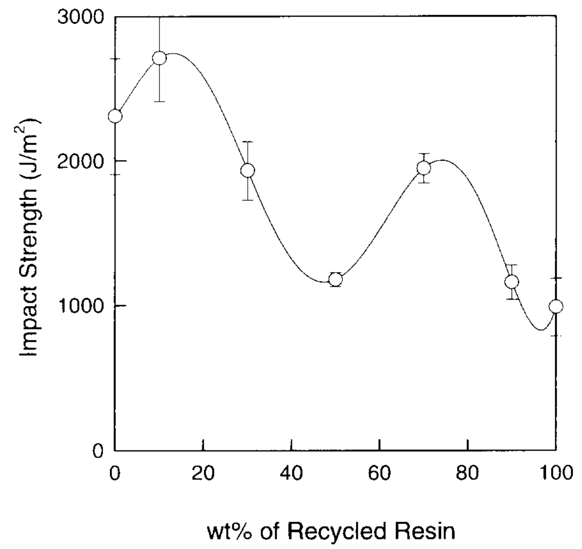
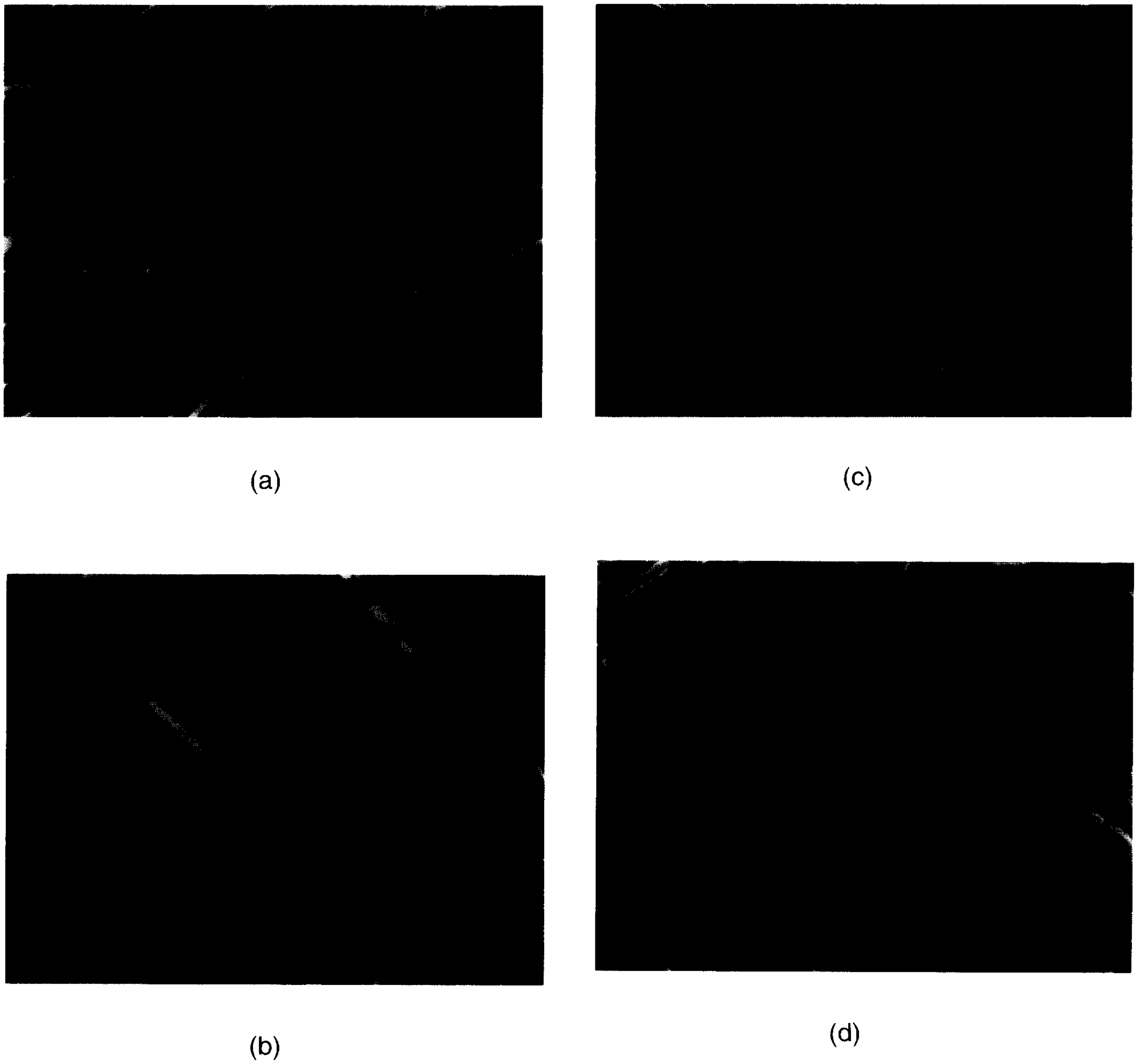


Figure 4 Impact strength of mixtures of neat and recycled resins

80°C for both the neat and recycled resins are shown in *Figure 2*. The curing reaction for the recycled resin is faster than that of neat resin, and its maximum rate of reaction rate is reached at a lower conversion than that of the neat resin. The glass transition temperatures of the cured neat and recycled UPs were 65 and 57°C, respectively. The glass transition temperature of a 50/50 wt% mixture of the two was approximately the same as that of the recycled resin.

The tensile strength and modulus of the cured neat and recycled resins and their mixtures are shown in *Figures 3a* and *3b*. The tensile strength of the cured recycled resin is slightly higher than that of the neat one, while its tensile modulus is lower. Both the tensile strength and modulus of cured UP resins are affected by the chemical structure of the glycols employed in their manufacture. Generally, commercial UP resins contain a propylene/ethylene glycol mixture, and the ratio of the two determines the mechanical properties. The higher percentage of PG in the recycled resin results in the increase of the tensile


(a) (c)

(b) (d)

Figure 5 SEM micrographs of fracture surfaces: (a) neat UP; (b) 90/10 wt% neat/recycled; (c) 50/50 wt% neat/recycled; (d) 10/90 wt% neat/recycled

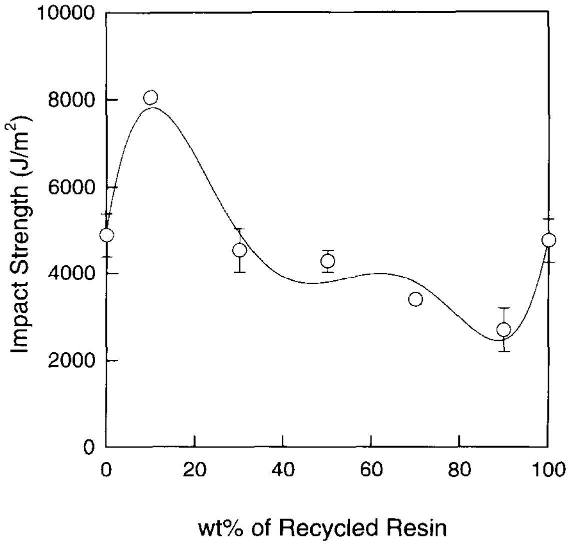


Figure 6 Impact strengths of mixtures of neat and recycled UP containing 15 wt% of glass fibre

strength and decrease of the tensile modulus. The tensile strengths and moduli of the mixtures are inferior to those of the cured neat and recycled UPs, with the 50/50 wt% mixture showing the minimum value. Impact strengths of the mixtures are shown in *Figure 4*. In order to relate the impact strengths to the morphologies of the mixtures, the fracture surfaces of impact specimens were examined using scanning electron microscopy (SEM). The fracture surface of neat UP is shown in *Figure 5a*. It has a basic 'longitudinal' texture[10] consisting of low ridges and shallow grooves, elongated from left to right, which is commonly observed for cross-linked polymers[11-13]. The fracture surface of the 90/10 wt% neat/recycled mixture is shown in *Figure 5b*. The spacing between grooves is roughly 50 μm, which is larger than that in the neat resin (roughly 10 μm), and may account for its slightly higher impact strength. The fracture surface of the 50/50 wt% mixture is shown in *Figure 5c*. It has a spacing between grooves of roughly 1–2 μm, which correlates with its lower impact strength, relative to that of the neat resin. The fracture surfaces of the 30/70 wt% neat/recycled resin mixture (*Figure 5d*) and the recycled UP are substantially different than the others, indicating a ductile, inhomogeneous fracture mechanism, resulting in multilayered fracture surfaces.

The addition of 15 wt% of chopped glass fibre, with an average length equal to 0.64 cm, to the recycled resin increases the impact strength by more than a factor of two (*Figure 6*). The mixture containing 10 wt% of recycled resin has the highest impact strength of all the mixtures tested, while the others have impact strengths lower than those of the glass fibre filled constituent resins.

In conclusion, it appears feasible to recycle thermoset polyester resins by glycolysis of the cured material and reconstitution of the product by the addition of maleic anhydride and styrene. The mechanical properties of mixtures of the recycled resin with neat unsaturated polyesters will depend on the components used in the glycolysis reaction, but the resulting products will have properties suitable for many applications.

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