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The properties of unsaturated polyester based on the glycolyzed poly(ethylene terephthalate) with various glycol compositions

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Abstract

Unsaturated polyester (UP) based on the glycolyzed poly(ethylene terephthalate) (PET) with propylene glycol (PG), diethylene glycol (DEG) and their mixture was prepared and the influence of glycol compositions on the chemo-rheological behavior and the mechanical properties was studied. The glycolyzed products showed broad bimodal distribution in their molecular weights and the larger molecular weight oligomers were obtained with increasing DEG contents in DEG and PG mixtures. The gelation time of UP was delayed with increasing DEG contents. After 1 h curing, the final conversion level increased as the DEG contents increased. The tensile modulus decreased and the toughness of cured products increased with increasing DEG contents due to the flexibility of ether linkage in the DEG unit. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Glycolysis; Unsaturated polyester

1. Introduction

Recently, recycling of polymers has received a great deal of attention [1]. Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics which is used to manufacture films and bottles for packaging. The overall world consumption of PET amounts to about 13 million tons, of which 9.5 million tons are processed by the textile industry, 2 million tons are consumed in the manufacture of audio and video tapes, and 1.5 million tons are used in the manufacture of various types of packaging—mainly bottles and jars [2]. PET does not create any direct hazard to the environment, but due to its substantial volumes in the plastics waste stream and its high resistance to the atmospheric and biological agents, it could be thought of as a noxious material. Therefore, the recycling of PET will not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy. Products made from recycled plastics can result in 50–60% energy saving as compared to making the same product from virgin resin [3].

In a recent study, Nadkarni et al. [4,5] suggested the synthesis of unsaturated polyester (UP) resin from PET waste and also investigated the kinetics of glycolysis on several glycols. Baliga and co-workers [6] carried out the glycolysis of PET with ethylene glycol (EG) using various metal-acetate catalysts. They found that glycolyzed products had 1–3 repeating units depending on the catalyst used. After synthesis of UP based on waste PET was suggested, researchers [7,8] tried to apply this unsaturated polyester to polymer concrete by replacing Portland cement as a concrete binder. Aslan et al. [9] compared the composite sheet containing unsaturated polyester developed in recycled PET to the analogous composite made of virgin unsaturated polyester resin. Abdel-Azim et al. [10] investigated the compressive strength of the polymer concrete using unsaturated polyester based on recycled PET. As shown above, the most previous works about recycling of PET were concentrated on the glycolysis. This is because polyols produced by glycolysis can be used for producing other polymers such as UP or polyurethane.

In this work, we tried to compare the properties of unsaturated polyester prepared by glycolysis of PET with propylene glycol (PG) and diethylene glycol (DEG) and their mixture. The cure behavior and the tensile properties of

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Table 1
The sample codes and preparation method of the glycolized products and unsaturated polyesters (glycolized products result from the glycolysis of PET with glycol mixture. Glycolized products and maleic anhydride were polycondensated for unsaturated polyester)

Unsaturated polyesters	Glycolized products	PET (mol/repeating unit)	Glycol mixture (DEG/PG, mol/mol)	Maleic anhydride (mol)
U0	G0	0.365	0/1.84	1.60
U25	G25	0.365	0.46/1.38	1.60
U50	G50	0.365	0.92/0.92	1.60
U75	G75	0.365	1.38/0.46	1.60
U100	G100	0.365	1.84/0	1.60

the cured resin based on the glycolyzed PET were investigated.

2. Experimental

2.1. Materials

PET pellets for the bottle with a number average molecular weight of 20 000 and a weight average molecular weight of 50 000 (H-2214 grade) were supplied from SAEHAN Inc. GR-grade PG obtained from Shinyo Pure Chemicals was used for glycolysis. DEG was obtained from Kanto Chemicals. Zinc acetate and maleic anhydride were supplied by Shinyo Pure Chemicals. Styrene monomer was obtained from Junsei Chemicals. Benzoyl peroxide supplied by Fluka AG was used as an initiator for curing the unsaturated polyester resins.

2.2. Glycolysis of PET

In the experimental runs, 70 g (0.365 mol/repeating unit) of PET pellets were added to 1.84 mol of PG so that the molar ratio of PET repeating unit to PG is 1:5.04. Various compositions of PG and DEG were considered. These mixtures, together with 0.5 wt.% zinc acetate based on weight of PET as transesterification catalyst, were charged to a glass reactor. The reactor was heated for 3 h at 175°C, and then held for 5 h at 225°C [11]. The reaction was carried out under reflux in nitrogen atmosphere. After 8 h, the contents in the reactor were allowed to cool to room temperature.

2.3. Preparation of unsaturated polyester resin

The UP resins were prepared by reacting the glycolyzed products with maleic anhydride at fixed value of the glycolyzed products including free glycol to maleic anhydride molar ratio of 1.1. The glycolyzed product indicates PET depolymerized with glycols. The polyesterification reaction was carried out in a glass reactor having a partial condenser and stirring assembly. The reactants were heated to 150°C and were then held for about 24 h to complete the reaction.

2.4. Curing reaction of unsaturated polyester

The UP resins were dissolved in styrene monomer at 60°C for 30 min. The amount of styrene was 35 wt.% of resin. In order to cure the resin, benzoyl peroxide (BPO, 1 wt.% of the resin) was added as an initiator. In the differential scanning calorimetry (DSC) studies of the isothermal curing kinetics of thermosetting resins, one assumes that the amount of heat generated during the curing reaction is directly proportional to the degree of reaction of the sample at that time [12] and then one relates the rate of cure, $d\alpha/dt$, to the rate of heat generated, dQ/dt, by

$$\frac{d\alpha}{dt} = \frac{1}{Q_T}\left(\frac{dQ}{dt}\right)_T \tag{1}$$

where Q_T represents the total heat generated. Integrating Eq. (1) with respect to time, one can obtain the relative degree of cure, α,

$$\alpha = \frac{1}{Q_T}\int_0^t \left(\frac{dQ}{dt}\right)dt \tag{2}$$

The measurements of the heat of reaction were conducted using DSC 2010 (TA Instruments) with nitrogen as the flushing gas at 50 ml/min. At a specified temperature, the isothermal experiment was completed (Q_M), and then the sample was quenched using liquid nitrogen. After the sample was stabilized at room temperature, the residual heat of reaction (Q_R) was measured under a constant heating rate of 10°C/min to 250°C. We can then evaluate total heat of reaction ($Q_T = Q_M + Q_R$).

2.5. Measurements

The molecular weight of the glycolyzed products and UP were measured by Waters Gel Permeation Chromatography (GPC). All samples are dissolved in tetrahydrofuran (THF) of HPLC grade at the constant concentration 0.1 wt.%. After filtration of samples, 200 μl of each sample was injected into ultrastyrogel columns. At that time, the flow rate of carrier solvent was 1.00 ml/min. Monodisperse polystyrene was used as the reference.

The rheological behaviors during the isothermal curing were also analyzed by using rheometer (PHYSICA RHEO-LAP 120) at 80°C. Disposable parallel plate cell having 50 mm diameter was used in the dynamic shearing test. In all cases, the gap size fixed at 0.5 mm.

Tensile tests were carried out using Instron Universal Test Instrument (Model 4201) at room temperature.

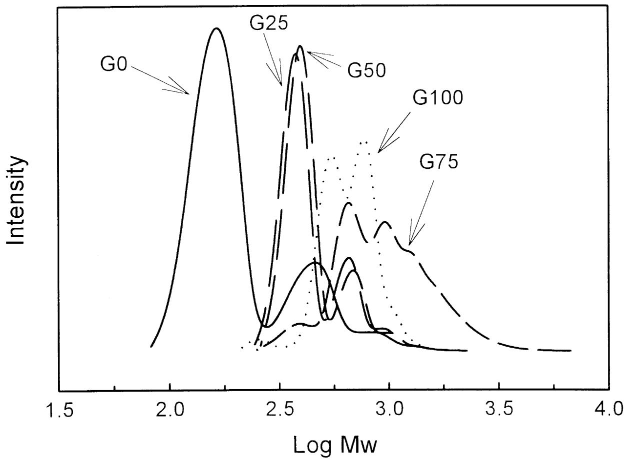

Fig. 1. The GPC data of the glycolized products with various glycol compositions.

Samples were made in accordance with ASTM D1708. Tensile tests were performed under the condition that the cross-head velocity of tensile tester was set at 1 mm/min and the initial gauge length is fixed at 22 mm.

The dynamic mechanical properties were studied by Rheometic Scientific Dynamic Mechanical Thermal Analyzer (DMTA). Samples mounted in the flexural mode were run with dual cantilever bending at the strain amplitude of 0.01 mm. For temperature scanning of the cured resin, samples were prepared approximately 30 mm long, 10 mm wide and 1.2–2 mm thick. The samples were analyzed from −30 to 230°C at a heating rate of 5°C/min and a frequency of 1 Hz.

3. Results and discussion

3.1. Glycolysis of PET

The glycolysis was carried out with at five glycol compositions. The glycolyzed products were obtained by reacting PET with DEG/PG mixtures having 0, 25, 50, 75 and 100 mol% of DEG. The molar ratio of glycol to PET was keep constant in all depolymerization reactions of PET. The sample codes of the glycolyzed products are given in Table 1.

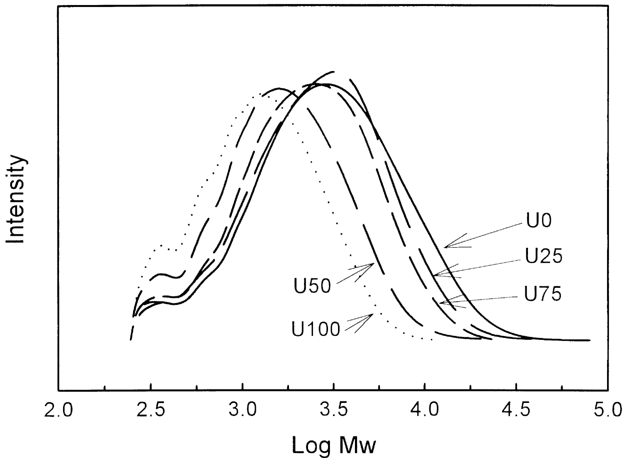

Fig. 2. The GPC data of synthesized unsaturated polyesters.

Fig. 1 shows the gel permeation chromatography (GPC) data of the glycolyzed product using various glycol compositions. The peak weight average molecular weight of the glycolyzed product increases with increasing amount of DEG in glycol composition, varying from 180 to 690. This molecular weight range is comparable to the molecular weights of oligomers that have 1–3 monomeric units. There are two main peaks (bimodal shape) in each glycolyzed product; it may be the glycolyzed products composed of mainly two kinds of components. We have not identified the definite components of the glycolyzed products, which can be done for example, using ^{13}C NMR. The second peak increases as the DEG contents increase. These results imply that the extent of depolymerization decreases with increasing amounts of DEG in the glycol mixtures.

3.2. The characteristics of unsaturated polyester

The glycolyzed products were polycondensed with maleic anhydride in order to synthesize the unsaturated polyester. The sample codes of the synthesized UPs by reacting glycolyzed products and free glycol with maleic anhydride are listed in Table 1. Fig. 2 shows the GPC data of these samples. The range of peak molecular weight of UPs was about 1120–1770. A decreasing tendency of molecular weight with increasing DEG contents was observed. It results from the difference of the reactivity between PG and DEG with maleic anhydride. At the composition of more than 50% DEG, the reactivity decreases considerably, resulting in the decrease of the molecular weight of the UP. The glass transition temperatures of the synthesized UPs obtained from DSC measurements are shown in Fig. 3. The decreasing tendency of glass transition temperatures with increasing DEG contents may be due to the flexibility of DEG units and molecular weights of UP resins.

3.3. Curing of unsaturated polyester

Unsaturated polyesters can be dissolved in a polymerizable monomer such as styrene. They are long chain linear polymers containing a number of reactive monomer. The polymerizable monomer, which also contain C=C reactive double bonds, acts as a curing agent by bridging adjacent polyester molecules at their unsaturation positions.

There are several accepted methods to determine the gel point from the rheological study of crosslinked polymers. In the first method, the polymer in its liquid state is subjected to shear flow. The measured viscosity increases with increasing extent of reaction until the stress reaches the limit of the instrument or until the material breaks. However, it is hard to measure this high shearing viscosity. Therefore, the gel point is sometimes defined as the point at which the relative viscosity reaches 10^3 or 10^4 Pa s [13,14]

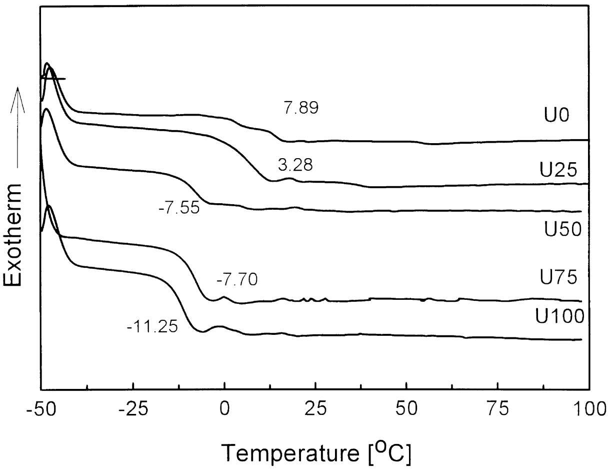

Fig. 3. The glass transition temperatures of synthesized unsaturated polyesters.

even though it is less scientific. In the second method, small amplitude oscillatory shear gives the components of the complex modulus during the crosslinking process. Tung and Dyne [15] reported that the time at which the crossover of storage modulus (G') and loss modulus (G'') occurs during isothermal curing can be taken as the gel point. Actually, the gel point detection method of Tung and Dyne is frequently used for its simplicity. But, Winter [19] suggested that there is only one class of network polymers for which gel point coincides with the crossover of G' and G'' by modeling the rheological behavior at the gel point. This class of polymers exhibits, when reaching gel point, power law relaxation $G(t) \approx t^{-n}$ with a specific exponent value $n = 1/2$. Therefore, some polymers have different exponent value, $n \neq 1/2$, in which case the crossover occurs before the gel point (for $n < 1/2$) or after (for $n > 1/2$).

Oscillatory rheological studies were performed in order to correlate the viscosity with overall cure behavior. Fig. 4 shows the variation in G' and G'' with curing time for U0 resin at 80°C. Both G' and G'' increase as curing reactions. G' monotonically increases with curing time and is leveled off whereas G'' goes through a local maximum, corresponding to the vitrification [16], and then leveled off. The gel point determined from $G' = G''$ is about 4.5 min. Similar patterns are detected in the other compositions. Fig. 5 gives the results of complex viscosity measured as a function of the cure time at 80°C. The crosslinking reactions between unsaturated polyester C=C bonds and styrene significantly modify the resin's viscosity behavior as expected. At an early stage of curing, the viscosity increases slowly, but increases very rapidly later, tending to approach a very large value. The gelation determined from $\eta_{\text{complex}} = 10^4$ was somewhat delayed as DEG content increases. This may be attributed to the increase of the distance between the curable double bonds. In the case of U0 resin, the gel point is about 5.6 min. The gel points determined from $G' = G''$ for UP resins appear somewhat earlier than those determined from $\eta_{\text{complex}} = 10^4$. In other words, this behavior is included in the region of ($n \neq 1/2$ or $n < 1/2$)

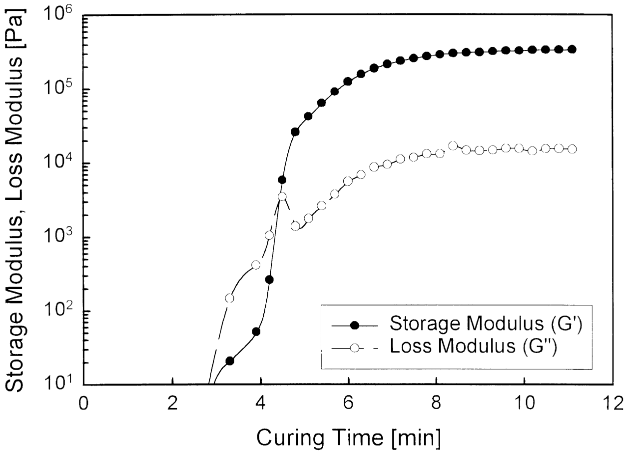

Fig. 4. Storage modulus (G') and loss modulus (G'') of U0 resin during cure at 80°C.

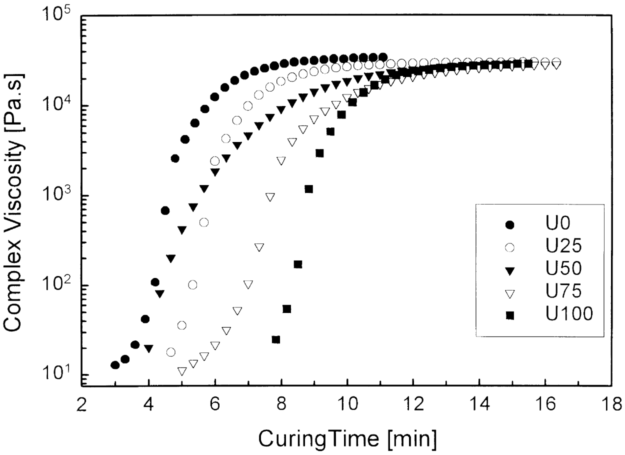

Fig. 5. Variation of complex viscosities with cure time at 80°C.

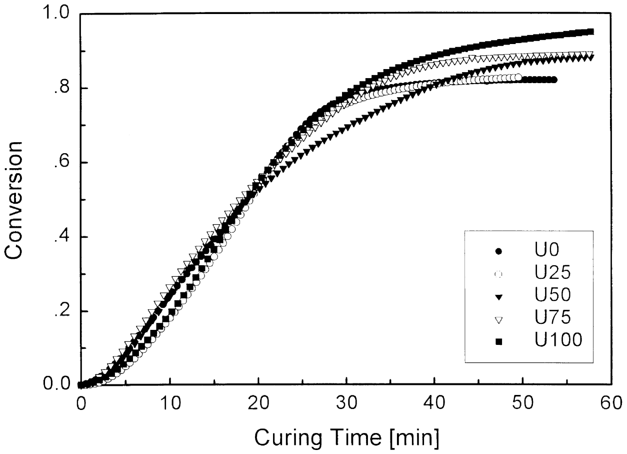

Fig. 6. Variation of curing conversion with cure time at 80°C.

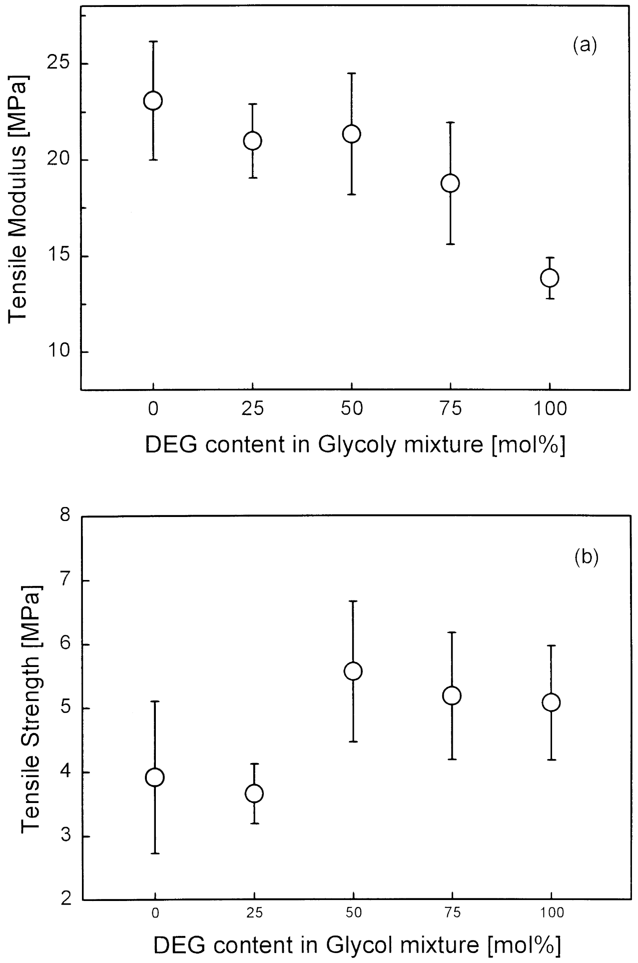

Fig. 7. Tensile modulus (a) and strength (b) of cured resins with the DEG content.

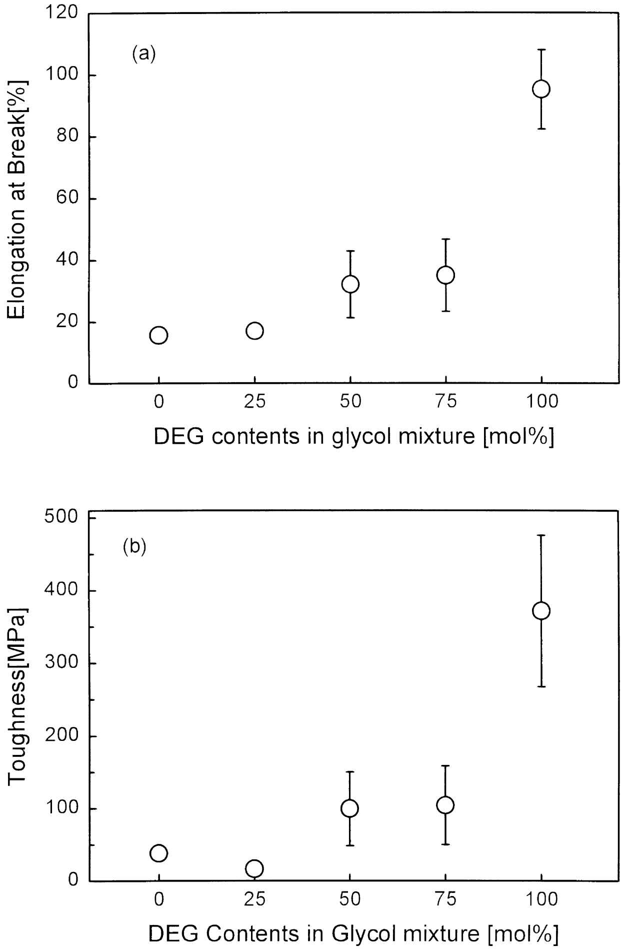

Fig. 8. Elongation at break (a) and tensile toughness (b) of cured resins with the DEG content.

according to Winter [19]. Similar patterns are shown for unsaturated polyester systems [14,17].

The extent of reaction with time is shown in Fig. 6. The overall extent of cure on each composition reaches 0.80–0.87. The curing conversion increases with the increase in DEG content. It is thought that a flexible DEG unit in a network structure increases the mobility of the C=C units and styrene monomers by lowering the T_g of the reaction medium. In other words, it would be effective for the retardation of vitrification.

3.4. Mechanical properties

Tensile modulus and tensile strength of the cured resin based on glycolyzed PET are shown in Fig. 7(a) and (b), respectively. Tensile moduli decrease as the DEG content increases. It is due to the flexibility of the cured resin because DEG has aliphatic ether linkage. The unfilled, cured, brittle UP resins are prone to stress cracking and brittle fracture [9]. The tensile strength depends on the composition of DEG. Low contents of DEG cause the brittleness of resin, which results in its low strength.

Both the elongation at break and the tensile toughness were greatly increased with the content of DEG as shown in Fig. 8(a) and (b). This result also tells us that the DEG units impart flexibility to the cured resin. This may be attributed to the increase of distance of each crosslinked points in the cured resin and the flexible long linear ether linkages, which enables the chains to move more freely. Diethylene glycol has a longer chain length than propylene glycol. This effect appears in the synthesized unsaturated polyester. The unsaturated polyester chain with DEG unit has a longer distance between the reactive double bonds than with the PG unit. This enables the cured resin to have a lower crosslinking density. The DEG unit is more flexible than the PG unit due to the ether linkage. These two reasons explain the toughness imparted to the cured chain.

A sinusoidal load was applied to the sample and the real (E') and imaginary (E'') moduli were measured. The ratio E''/E' is defined as the loss tangent or the damping (tan δ). The tan δ peak temperature is taken as the glass transition temperature (T_g). Fig. 9 shows the tan δ of the cured resins. The tan δ peak decreases with increasing DEG content except for 25% DEG. This is another evidence that DEG

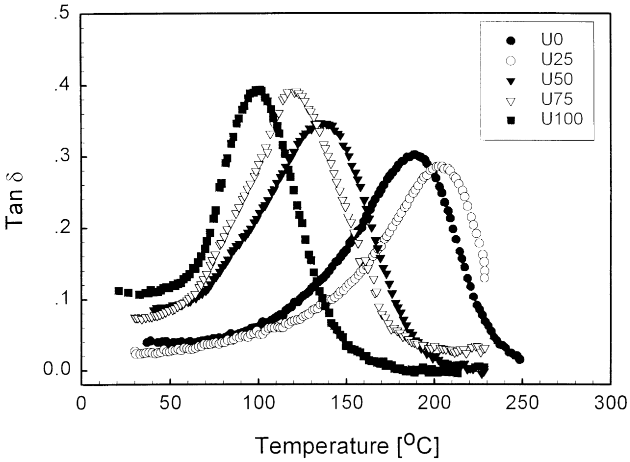

Fig. 9. The loss tangent, tan δ, peaks of cured resins.

units in the cured UP network enable chains to move more freely and give flexibility to the cured network. However, the sample with 25% DEG has the highest T_g. At present, it is difficult to explain why it has the highest E' and therefore high crosslinking density.

4. Conclusions

It appears that it is feasible to treat PET by glycolysis with PG and DEG mixtures. The extent of depolymerization decreases with increasing amount of DEG and the gelation time is also delayed. The cured resin based on the glycolyzed PET has a tensile strength similar to the typical hand lay-up mat laminate polyester resin. The tensile toughness was greatly enhanced by incorporating DEG units.

Unsaturated polyesters are used extensively as matrices in fiber-reinforced composite systems. They are particularly useful in sheet-molding compounds (SMC) and bulk-molding compounds (BMC) for manufacture of automotive parts [18]. In this study, it was possible to control the extent of depolymerization, gelation time and brittleness of unsaturated polyester resin using different glycol compositions. Therefore, it is thought that unsaturated polyesters obtained from recycled PET would be applicable to the FRP resin, SMC and BMC by offering versatility in processing and enhanced properties.

Acknowledgements

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