Unsaturated Polyester Resins Based on Recycled PET: Preparation and Curing Behavior

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Received 31 December 1999; accepted 3 June 2000

ABSTRACT: The oligomers obtained from the glycolysis of Poly(ethlene terephthalate) (PET) waste were reacted with maleic anhydride to form a series of unsaturated polyester resins. The obtained resin was used to study the curing reaction with styrene by differential scanning calorimetry. The heats of reaction for styrene and polyester vinyl groups were measured by extrapolating the experimental results. Various kinetic parameters have been obtained using Kissinger expressions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1052–1057, 2001

Key words: glycolysis; recycling; PET; curing kinetics; DSC

INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used as films and fibers. Numerous processes have been proposed for recovering useful products from waste or scrap PET by depolymerizing or partially depolymerizing the polymer to lower molecular weight. The concept of preparing unsaturated polyester resin (UP) from the digested products of PET is well developed.[1,2]

The glycolysis of PET scrap with glycols and a catalyst by transesterification yields terephthalic oligomers. The oligomers may then be reacted with maleic anhydride and other dibasic acids to form unsaturated polyester resins. The use of PET waste is both inexpensive and effective way of incorporating terephthalic functionality into the backbone of a polyester resin. This is a consequence of the virgin terephthalic acid being more costly than PET scrap and having a high melting point that presents difficulties in synthesis. Another important feature is the use of the recycled material that aids in reducing the waste plastics volume, thus addressing an increasing environmental concern.[3]

Unsaturated polyesters (UP) have a leading role in the development of glass fiber-reinforced products and tremendous versatility with very low costs. Much work has been done in the area of glycolysis of PET waste and in the use of PET scrap in unsaturated polyester synthesis. The properties of the cured resin depend, as would be expected, on its composition but, in addition, they are markedly dependent on the extent of cure. Therefore, an understanding of the curing reaction is important for process control and optimization.

The kinetics of curing polyester resins is normally very complex because many reactive processes occur simultaneously. Although a considerable amount of research has been undertaken with regard to the cure kinetics of unsaturated polyester, little attention has been reported on UP resin obtained from PET waste.[4,5] In this article, a typical unsaturated polyester resin based on the glycolyzed PET products was prepared,

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Journal of Applied Polymer Science, Vol. 80, 1052–1057 (2001)

and the preliminary data on the curing behavior of resin obtained were reported.

EXPERIMENTAL

Materials

The recycled PET flakes were obtained from postconsumer soft-drink bottles that were washed and dried prior to use. The initiator for the curing reaction of the synthezed UP resins is *tert*-butyl peroxybenzoate with a purity of 98% and an active oxygen content of 8%. Propylene glycol (PG), maleic anhydride (MA), phthalic anhydride (PA), and tetrabutyoxy titanium were supplied by Junsei Chemical Co., Ltd without further purification.

Glycolysis of PET Waste

The PET waste was depolymerized in propylene glycol using 0.8% w/w tetrabutyoxy titanium, based on weight of PET, as catalyst. The reaction was carried out under reflux at 190°C for 6 h, and 210°C for 1 h in nitrogen atmosphere.

The glycolyzed products were then analyzed for hydroxyl number and the amount of free glycol as follows: (a) Determination of hydroxyl number: the hydroxyl numbers were determined by the conventional acetic anhydride/pyridine method.[6] (b) Determination of free glycol: a weighed quantity of the glycolyzed products was extracted with water and filtrated. The filtrate containing water, free glycol, and some soluble oligomers was concentrated by evaporation of water and then chilled to precipitate out the water-soluble oligomers. The residues remaining after the first and second filtrations were dried in a vacuum oven and weighed together. The difference between the original and the final weight represents the amount of free glycol removed by water extraction.

Preparation of Unsaturated Polyester Resins[7]

The UP resin was prepared by reacting the glycolyzed product with maleic anhydride at a value of the hydroxyl to carboxyl ratio of 1 : 1. The hydroxyl number of the glycolyzed product without separation of free glycol was used to determine the amount of maleic anhydride.

The resin used to analyze the curing kinetics was prepared by reacting 140 g GPET-3 with 98 g maleic anhydride, and was coded UPR.

The polyesterification reaction was carried out in a round-bottom flask equipping with a distillation condenser, a gas bubbler, a thermometer, and a stirring. The reactants were heated from the room temperature (28.5°C) to 190°C in 1.5 h. The temperature was then held for about 3 h, finally raised to 210°C, and maintained until the acid value reached about 50 mg KOH/g. The acid value was monitored during the reaction and determined by titrating the solution of weighed resin in acetone, with about 0.2 *N* standard alcoholic KOH solution using phenolphthalein indicator.

A conventional general-purpose resin was prepared by reacting maleic anhydride, phthalic anhydride, and propylene glycol, keeping MA to PA and the hydroxyl to carboxyl ratio at 1, and 1.1, respectively. This resulted resin was referred to UPP.

Differential Scanning Calorimetry

The calorimetry measurements are made on a SEIKO I-5000 series. Dynamic scans are performed at the heating rates of 2–20°C/min from 20–300°C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of UP Resins

The PET waste was depolymerized by glycolyzing it with PG. The characterization data of glycolyzed products were given in Table I. As can be seen, the extent of depolymerization increased with increasing amount of PG. In Figure 1, the change of acid value is plotted against reaction time for both systems. It is clear that the polycon-

Table I Characterization of Glycolyzed Products

		Analysis of Glycolyzed Product		
		Before Free Glycol Removal		After Glycol Removal
Glycolyed Product	PET/PG w/w	Free Glycol (%)	Hydroxyl Number	Hydroxyl Number
GPET-1	65/35	33.0	489.9	236.5
GPET-2	50/50	47.2	695.5	289.1
GPET-3	35/65	61.8	881.7	316.8

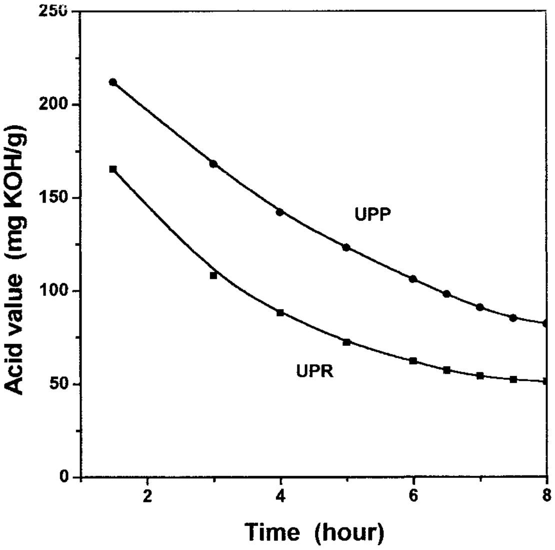

Figure 1 The acid vaule changes with reaction time.

densation of glycolyzed product with maleic anhydride was faster than that of the phthalic–anhydride-based resin certified by the reaction time to reach comparable conversion (acid value). It also means that the extent of depolymerization increases with the reaction time first, and finally reaches a equilibrium value, which is a general characteristic of condensation reactions. Therefore, the rate and extent of depolymerization, like many step reactions, will increase with increasing the amount of propylene glycol. It is consistent with the experimental results as mentioned above.

$$\text{PET} + \text{PG} \rightleftharpoons \text{DPET} \tag{1}$$

Normally, the glycolysis of PET waste occurs at random points along the chain, leading to the formation of glycolyzed products that are of unequal size. Balga and Wong measured the melting temperature for the fractions of glycolyzed products in ethylene glycol using DSC, and found it agrees very well with the melting point data of bis(hydroxyethyl) terephthalate (BHET) and dimers.[8] However, there is no marked melting onset temperature observed in our work. As reported by Vaidya and Nadkarni, the glycolyzed product contained a number of oligomers, and the molecular weight distribution was quite broad. These oligomers were linked through ester linkage, and the resulted unsaturated polyesters by reacting with maleic anhydride were compatible to styrene and can be cured with the conventional initiator systems.[9]

Table II **Heat of Reaction Measurement**

	Heating Rate (°C/min)				
Q_{total}	2	5	10	15	20
UPP (J/g)	373.8	385.6	401.2	395.6	379.8
UPR (J/g)	284.2	292.6	322.6	311.7	292.5

HEAT OF REACTION

As already mentioned, the curing of unsaturated polyester resins is complex, and includes several reactive processes. Assuming that the curing process only has a thermal effect and the heat produced by decomposition of initiator is negligible, the reaction advance will be directly proportional to the amount of heat generated and the maximum degree of curing reached when all double bonds that may react have done so.

The fraction of double bonds reacted during the curing reaction, or the relative degree of cure, at time t is defined as

$$a = \frac{Q_T}{Q_{\text{total}}} \tag{2}$$

where Q_T is the total heat of reaction up to time t or temperature T, and is calculated from

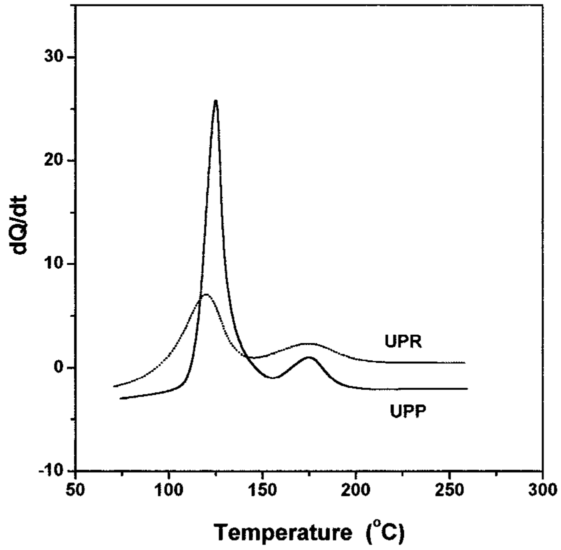

Figure 2 Typical dynamic DSC scans conducted at 10°C/min.

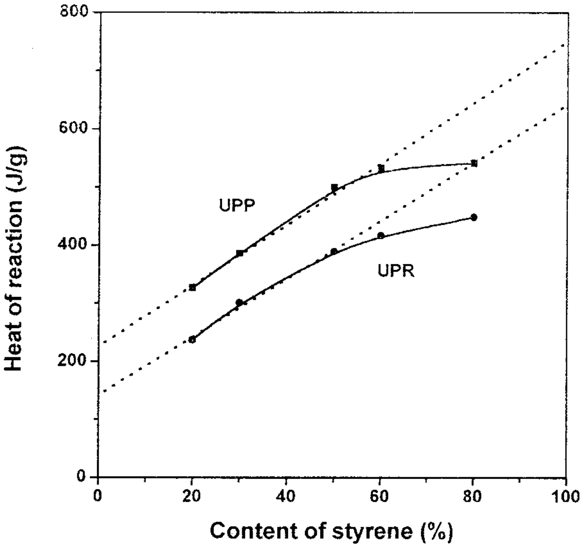

Figure 3 Heats of reaction as a function of the contents of styrene.

$$Q_T = \int_0^t \frac{dQ}{dt}\,dt = \frac{1}{\beta}\int_{T_0}^{T} \frac{dQ}{dt}\,dT \qquad (3)$$

where Q_{tot} is the total heat of reaction (derived from the whole area under the DSC curve), and β is heating rate. The experimental heats of reaction of UPP and UPR resins with 30% styrene for different heating rates are listed in Table II. The total measured heats of cure Q_{tot} were 385.8 J/g for UPP and 300.7 J/g for UPR.

A typical dynamic DSC thermograms was shown in Figure 2. As can be seen, the curves showed that there is similar curing processes occurring for both resins. The exotherm of reaction shows two peaks, related to the crosslink process and to the thermal polymerization of polyester–styrene, as described in previous works.[11–13]

The heats of reaction for unsaturated polyester obtained from glycolyzed PET waste was much lower than that from phthalic anhydride-based resin, as shown in Table I and Figure 3. It may be related to the complicated structure of glycolyzed product in which the molecular weight distribution was quite broad, and many kinds of fractions, including monomer and various molecular weight oligomers, were contained.

To determine the exothermic heat per mol of both polyester C=C double bonds reacted and styrene C=C double bonds reacted, we extrapolated the exothermic heats of reaction obtained by dynamic DSC experiments for different styrene contents. As can be seen from Figure 3, the extrapolation of experiment results to 100% styrene gives a reaction heat of 749.2 J/g from UPP resin and 639.4 J/g from UPR resin. For the extrapolation values of 224.2 J/g from UPP and 141.2 J/g from UPR, it is difficult to discover the physical meaning because the maleic autopolymerization reaction was considered difficult in the presence of styrene.

The mass per mol of double bonds can be calculated from the polyester resin compositions. Assuming that the heat of reaction per unit mass is proportional to the number of double bonds reacted, we estimated the theoretical heats of polymerization associated with the polyester C=C double bonds and C=C double bonds of styrene molecules. The mass per mol of double bond in the polyester was 362 g/g-mol for resin UPP, but it is not clear for resin UPR because the complicated compositions were contained in glycolyzed product. As can be seen from Table III, the results obtained in this present work were in good agreement with those reported in literature, except for the value of reaction heat for double bonds in polyester that was only calculated by extrapolating the experimental data to 0% of styrene.

Table III Comparison Between Heats of Reaction Obtained in this Study and Reported in the Literature

Heats of Reaction	Avella et al.[10]	Pusatcioglu et al.[14]	Polymer Handbook[11]	Ramis et al.[15]	Present Study UPP	Present Study UPR
Double bonds in styrene (kJ/mol)	71.1	71.1	66.9–71.1	75.2	77.7	66.5
Double bonds in polyester (kJ/mol)	67.3	93.6	58.5	78.6	83.4	117[a]

[a] This value was only calculated by extrapolating experimental results to 0% of styrene.

Table IV The Relationship Between Heating Rate (β) and Maximum Temperature of Exothermic Peak (T_p) for UPP and UPR Resins

Heating Rate, °C/min	UPP		UPR	
	T_{p1}, K	T_{p2}, K	T_{p1}, K	T_{p2}, K
2	—	—	365.1	435.5
5	390.6	444.0	383.0	441.1
10	403.2	454.5	393.4	449.0
15	409.8	458.7	397.9	453.7
20	416.7	463.0	412.0	460.6

Kinetic Analysis

The thermograms determined by DSC are analyzed by means of the simple Kissinger expression:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{R}\cdot\frac{1}{T_p} - \ln\left(\frac{AR}{E}\right) \tag{4}$$

where T_p is the temperature where maximum conversion rate occurs on DSC curve, E is curing activation energy, A is preexponential factor, and R is gas constant.

We can find that the curing of the unsaturated polyester systems produce multiple curing exotherms from Figure 2. Although many proposed expressions can be used to describe the curing reaction of thermosets[16–17]; however, the advantages of Kissinger method include simplicity, relative insensitivity to baseline and secondary reactions, and applicability to many types of reactions.[18] The peak temperatures for UPR were lower than those for UPP resin (Table IV), and reflected the higher curing rates in UPR system. It is possible due to the complicated compositions involved in UPR and the existence of organic metallic salt, which was used as a catalyst for glycolysis of PET waste.

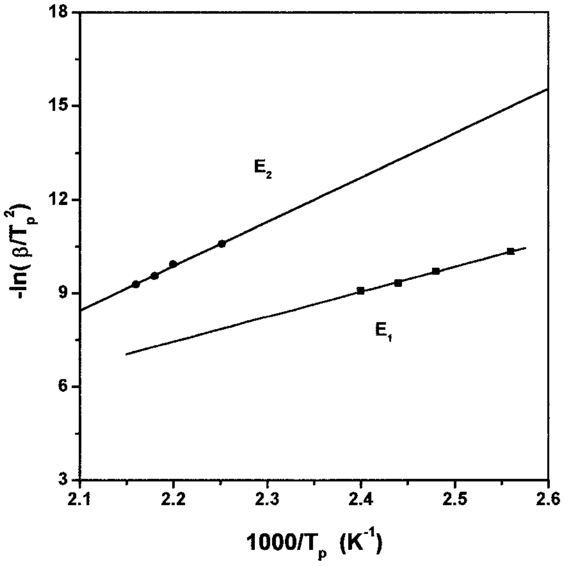

Figure 4 The plots of $-\ln(\beta/T_p^2)$ vs. $1/T_p$ for the UPR system.

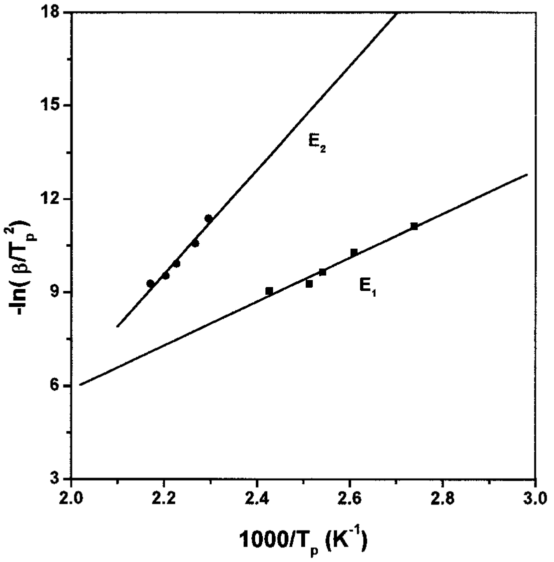

Figure 5 The plots of $-\ln(\beta/T_p^2)$ vs. $1/T_p$ for the UPP system.

Two values of activation energy can be obtained corresponding to different peaks according to eq. (4) for each system. Figures 4 and 5 plotted $-\ln(\beta/T_p^2)$ vs. $1/T_p$ for UPP and UPR systems. As mentioned above, the first peak may imply the crosslinking reaction between styrene and polyester molecules. The activation energies of 67.5 and 58.7 KJ/mol were much lower than that of 119.9 and 114.9 KJ/mol, which was related to a second peak. It means that the copolymerization of styrene and polyester occurs more easily. It is a fact revealed by many experiments. The kinetic rate constant K is calculated from the classic Arrhenius equation. A summary of activation energy E and kinetic constant K values for the curing behavior of both polyester resins was given in Table V. As expected, a lower value of activation energy for UPR system was obtained. It is similar to the change in the curing rate.

The values of the kinetic parameters have been obtained by some investigators. As expected and previously reported in the literature, the kinetic

Table V Kinetic Parameters for Both Resins

	k_1 (10^2 min^{-1})	k_2 (min^{-1})	E_1 (kJ/mol)	E_2 (kJ/mol)
Resin UPP	$2.82 \times 10^5 \exp(-E_1/RT)$	$4.55 \times 10^9 \exp(-E_2/RT)$	67.5	119.9
Resin UPR	$2.66 \times 10^7 \exp(-E_1/RT)$	$1.49 \times 10^{13} \exp(-E_2/RT)$	58.7	114.9

parameters obtained by different DSC methods do not match very well. The difference can be caused by different chemical composition of polyester resin and different initiator used in systems. For example, the activation energy usually decreases when an accelerator is used.[19]

CONCLUSIONS

Unsaturated polyester resin was prepared by reacting the glycolyzed PET waste with maleic anhydride. The heats of polymerization, associated with styrene and polyester double bonds, can be calculated by extrapolating the heats of reaction obtained from different styrene contents. Various kinetic parameters have been obtained using Kissinger expression from dynamic data. The thermograms show to peaks that were related to different reaction mechanisms. For the glycolyzed-based resin system, the low values of activation energy and heats of reaction were observed.

This work was supported by Han Yong Petrochemical Co., Ltd., Korea.

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