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Thermal Property and Curing Behavior of Unsaturated Polyester Resins Based on Recycled Poly(ethylene terephthalate)

Ju Hyun Kim, Sung Geun Kim and Dai Soo Lee*

Department of Chemical Technology, Chonbuk National University, Chonju, 561-756, Korea

Tae Seok Park, Jungahn Kim and Kwang Ung Kim

Division of Polymer Science and Engineering, Korea Institute of Science and Technology,
P.O.Box 131, Cheongryang, 130-650, Korea

ABSTRACT: Unsaturated polyester (UPE) resins of different molecular weight or different degree of unsaturation were prepared from recycled poly(ethylene terephthalate) (RPET). The thermal properties and curing behaviour of the UPE resins based on RPET were studied by employing differential scanning calorimeter. Glass transition temperature (T_g) of the cured UPE resin was dependent on T_g of the uncured resin and molecular weight between the crosslink points. The rate of cure was not changed much while final degree of cure during isothermal cure decreased with increasing molecular weight of the UPE resin. It was also observed that the rate of cure of the UPE resin decreased with decreasing degree of unsaturation of the UPE resin. It is postulated that curing behaviour of the UPE resins based on RPET depends on thermal properties and degree of unsaturation as the curing is a diffusion controlled free radical polymerization. The curing behaviour of the UPE resins based on RPET was analyzed by employing the diffusion controlled free radical polymerization scheme and was found to be similar to the curing behaviour of conventional UPE resins.

Introduction

Recently, recycling of post consumer plastics has been attracting the attentions of many researchers as the consumption of plastics for packaging is increasing. Plastics for packaging include engineering plastics as well as commodity polymers. Poly(ethylene terephthalate)(PET) is one of the versatile engineering plastics which is used to manufacture films and beverage bottles for packaging. The amount of PET resin used for beverage bottles in Korea was about 60,000 tons in 1995. To meet the growing demands of recycling PET bottles, a few recycling plants of PET bottles are being operated in Korea. PET bottles collected are crushed, washed and seperated into fragmented PET chips in the plants. Successful recycling usually requires development of various applications of recycled products in the markets.

Applications of the recycled PET (RPET) resin may include manufacturing low grade fibers, unsaturated polyester (UPE) resins, and polyurethanes. According to Rebeitz *et al.*, the UPE resins based on RPET were useful as a matrix resin of polymer concretes.[1,2] Vaidya and Nadkarni studied the preparation of the UPE resins, based on RPET and reported that the UPE resins based on RPET were more reactive than conventional UPE resins.[3,4] But there is few information in the literatures on relationships between molecular structures and curing behaviour of the UPE resins based on RPET. Understanding thermal properties and curing characteristics is necessary for proper applications of the UPE resins based on RPET. In this paper, effects of molecular weights and degree of unsaturation on the thermal properties and curing behaviour of the UPE resins based on the RPET are reported.

Experimental

Carbonated beverage bottles made of PET body, high density polyethylene (HDPE) base-cup, and lables were collected, washed with water, and crushed into small fragments using a crusher. The fragments of PET were seperated from crushed mixtures of PET, HDPE, and various lables with adhesives by density difference in water and washed again. The PET collected was dried in a vacuum oven overnight at 100 ℃. Glycolysis of the RPET was carried out using propylene glycol (PG) at 200 ℃ for 8 hours. In the glycolysis of the RPET, zinc acetate (0.5 % by weight of the PET) was added as a catalyst, following the method employed by Vaidya and Nadkarni.[5] Various UPE resins were prepared from products of glycolysis, maleic anhydride (MAH) and adipic acid (AA). PG, MAH, AA and zinc acetate used for the experiments were reagent grades. In Table I, recipes of the UPE resins and number average molecular weights (M_n) of the UPE resins are summarized. Assuming that all terminal of the UPE resins are hydroxyl groups, the M_n were estimated from the hydroxyl values (*H.V.*) of the resin by the following relationships:

$$M_n = \frac{1.12\times10^5}{H.V.} \qquad (1)$$

The resins were diluted with styrene monomer to make 44 % (by wt.) styrene solution after the polymerizations, and hydroquinone (0.5 % by weight of the resin) was added as an inhibitor for storage stability.

In order to cure the resin, benzoyl peroxide (BPO, 1 wt.% of the resin), was added as an initiator. Exotherms during isothermal cure of the resins at 90, 100 and 110 ℃ were obtained by employing a differential scanning calorimeter (DSC: DuPont Thermal analyzer 2000). The DSC was also employed to measure glass transition temperature (T_g) of the resin after post cure. For the post cure, the isothermally cured resin was heated from room temperature to 220 ℃ at 10 ℃ per minute in the DSC.

Results and Discussion

Properties of the thermosetting polymers such as the UPE resins are largely influenced by the degree of crosslinking and T_g. According to Nielson[6], T_g's of thermosets are determined generally by molecular weight between crosslinked points (M_c) as follows:

$$T_g = T_{go} + \frac{3.9\times10^4}{M_c} \qquad (2)$$

where T_{go} is glass transition temperature of the resin before cure. In Table II, T_g's of the UPE resins based on RPET are given. It was observed that the T_g's of the UPE resins measured by DSC (T_{gm}'s) were lower than T_g's calculated by equation (2) (T_{gc}'s). However, change of the T_{gm}'s followed the same trends as the T_{gc}'s. It is speculated that the T_{gc} of the UPE resin was higher than the T_{gm} due to the assumption in the calculation of T_g that all double bonds in the resin were reacted to make crosslinked networks during cure. In fact, the curing of the resin must have been incomplete even after post cure as the curing was a highly diffusion controlled reaction. It was found that the T_g of the UPE resin increased with increasing molecular weight of the resin and decreased with decreasing

Table I. Sample Code and Properties of the UPE Resins Based on RPET

sample code	recipe of UPE resin (by molar ratio)				hydroxyl value (mgKOH/g)	M_n
	PET*	PG	MAH	AA		
A-1	1.0	1.4	1.0		110.10	1.0×10^3
B-1	1.0	1.2	1.0		75.58	1.5×10^3
C-1	1.0	1.1	1.0		50.05	2.2×10^3
B-10	0.8	1.2	1.0		75.43	1.5×10^3
B-11	0.8	1.2	0.95	0.05	80.75	1.4×10^3
B-12	0.8	1.2	0.95	0.10	87.96	1.3×10^3
B-13	0.8	1.2	0.85	0.15	81.39	1.4×10^3
B-14	0.8	1.2	0.80	0.20	77.65	1.4×10^3

*Molar ratio of repeat unit.

degree of unsaturation of the UPE resin. It is postulated that increasing molecular weight resulted in increase of T_{go}, decrease of M_c and increase of T_g of the cured UPE resin. On the other hand, decreasing degree of unsaturation resulted in the decrease of T_{go}, increase of M_c, and decrease of T_g of the cured UPE resin.

As the curing of the UPE resin is exothermic, exotherms during cure of the resins were analyzed to study the curing behaviour of the UPE resins. For the analyses of the exothermic properties, ultimate heats of cure of resins should be known. According to Han and Lee[7], there were unreacted double bonds in UPE resins which could be confirmed by infra-red spectrum after post cure. They obtained ultimate heat of cure of resins from the total degree of cure and heat of cure measured, respectively. The ultimate heat of cure of UPE resins obtained by Han and Lee showed reasonable aggreements with heat of reaction for copolymerization of diethyl fumarate and styrene reported by Horie *et al.*.[8] Thus, the heat of copolymerization of diethyl fumarate and styrene reported by Horie for corresponding styrene/fumarate ratio of the UPE resin was used as ultimate heat of cure (Q_{UT}) of the resins in this study. Table III gives a summary of the Q_{UT}'s for the UPE resins investigated. Rate of cure ($d\alpha/dt$) and degree of cure (α) were obtained from rate of heat generation (dQ/dt) as follows:

$$\frac{d\alpha}{dt}=\frac{1}{Q_{UT}}\left(\frac{dQ}{dt}\right)_T \tag{3}$$

$$\alpha=\frac{1}{Q_{UT}}\int_0^t\left(\frac{dQ}{dt}\right)_T dt \tag{4}$$

Exothermic properties of the resins during cure were analyzed using the Q_{UT}'s given in Table III and the relationships given above.

Figure 1 shows $d\alpha/dt$ versus cure time for A-1 and C-1. Note that molecular weight of C-1 is larger than that of A-1 in Table I. It was observed that the peaks of $d\alpha/dt$ for B-1 and C-1 were similar to each other. It seems that rate of cure of the resin is hardly affected by the molecular weight of the UPE resin based on RPET. In Figure 2, α versus cure time for A-1 and C-1 are shown. It was observed that final degrees of cure of A-1 were higher than those of C-3. It is worthwhile to note that the T_g's of A-1 and C-1 are 80 ℃ and 110 ℃, respectively in Table II. Thus, it is speculated that curing reaction of C-1 might be more restricted than that of A-1 during the diffusion con-

Table II. Glass Transition Temperatures of the UPE Resins Based on RPET

sample code	T_{go}[a] (℃)	T_{gm}[b] (℃)	T_{gc}[c] (℃)
A-1	-8.0	80	107.6
B-1	-0.7	104	121.8
C-1	15.8	110	138.0
B-10	-1.9	107	132.7
B-11	-5.8	90	121.6
B-12	-4.7	89	115.5
B-13	-8.6	76	104.6
B-14	-11.9	65	94.4

[a] T_g of the uncured resin.
[b] T_g of the resin measured by DSC after post cure.
[c] T_g of the resin calculated by equation (2).

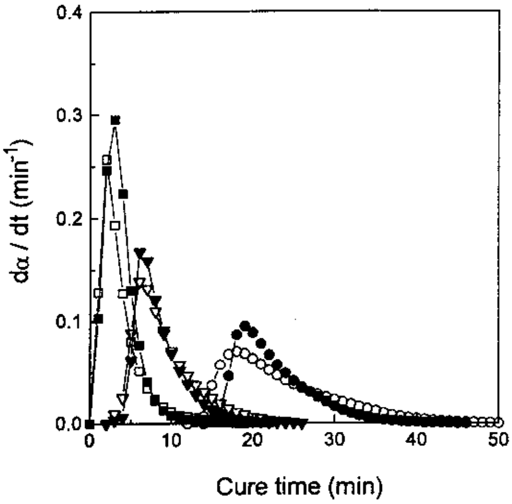

Figure 1. $d\alpha/dt$ versus cure time for A-1 (open symbols) and C-1 (closed symbols) at different isothermal temperatures (℃): (○) 90; (▽) 100; (□) 110.

Table III. Ultimate Heat of Cure (Q_{UT}) for the UPE Resins Based on RPET

sample code	A-1	B-1	C-1	B-10	B-11	B-12	B-13	B-14
Q_{UT} (cal/mole)	91.91	92.87	93.38	95.64	95.56	95.44	95.33	95.21

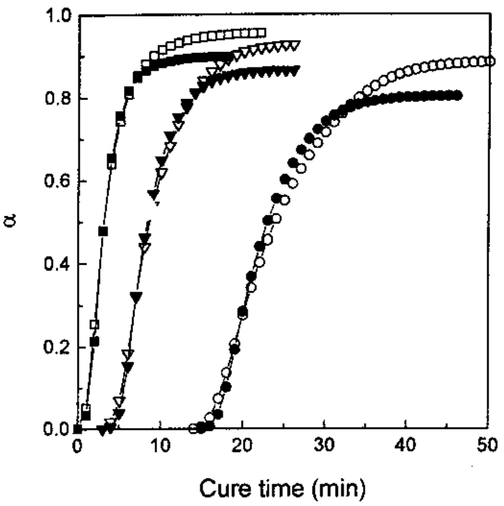

Figure 2. α versus cure time for A-1 and C-1 at different isothermal temperatures. The symbols are the same as in Figure 1.

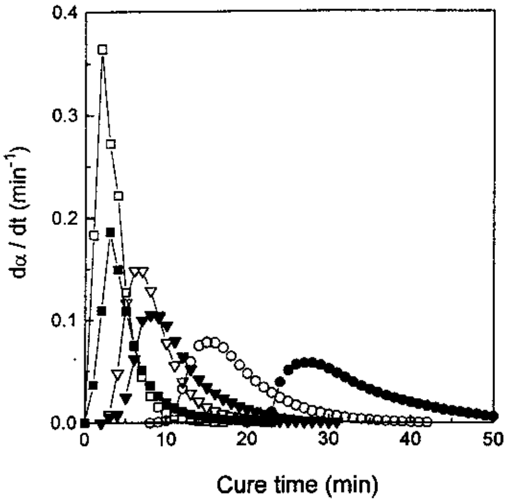

Figure 3. $d\alpha/dt$ versus cure time for B-10 (open symbols) and B-14 (closed symbols) at different isothermal temperatures (℃): (○) 90; (▽) 100; (□) 110.

trolled isothermal cure at 90 ℃, 100 ℃ and 110 ℃ and final degrees of cure of C-1 were lower than those of A-1.

Figure 3 shows $d\alpha/dt$ versus cure time for of B-10 and B-14. Note that MAH was partially replaced by AA in the preparation of B-14 and the degree of unsaturation of B-14 was low compared with B-10. It is seen that the peaks of $d\alpha/dt$ for B-10 appeared at a stage of cure earlier than those of B-14 and the peak values of $d\alpha/dt$ of B-10 are larger than those of B-14. It seems that the rates of cure of B-10 are higher than those of B-14 due to the higher double concentration of B-10 compared with B-14. In Figure 4, α versus cure time for B-10 and B-14 are shown. It was observed that final degrees of cure of B-14 are higher than those of B-10 at 90 ℃ but there were little differences at 100 ℃ and 110 ℃. Note that the ratio of styrene/fumarate of B-14 is larger than that of B-10 as AA was introduced in B-14. In general, the curing of UPE resin is facilitated with increasing the ratio of styrene/fumarate. The higher final degree of cure of B-14 than that of B-10 at 90 ℃ may be attributable to the higher styrene/fumarate ratio of B-14 than that of B-10.

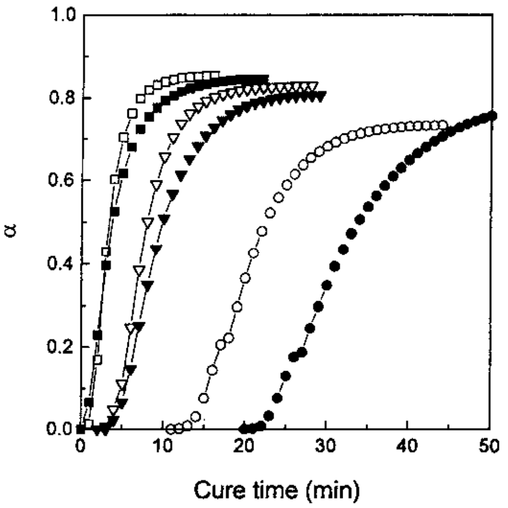

Figure 4. α versus cure time for B-10 and B-14 at different isothermal temperatures. The symbols are the same as in Figure 3.

The curing of the unsaturated polyester resin is a free radical polymerization. Thus, the mechanistic kinetic model proposed by Stevenson[9] was used to obtain kinetic parameters for the curing of the UPE resins based on RPET. The system Equations for the cure are as follows:

$$d[Z]/dt = -k_z[Z][R.] \tag{5}$$

$$d[I]/dt = -k_d[I] \tag{6}$$

$$d[R.]/dt = 2fk_d[I] - k_z[Z][R.] \tag{7}$$

$$d\alpha/dt = k_p(1-\alpha)[R] \tag{8}$$

Table IV. Kinetic Parameters of the UPE Resins Based on RPET

sample code		A-1	B-1	C-1	B-10	B-12	B-14
k_{po} (L/mol min)	9 ℃	177	223	349	214	144	115
	100 ℃	226	239	353	244	168	121
	110 ℃	231	279	377	264	171	125
m	90 ℃	0.53	0.69	0.70	0.69	0.65	0.62
	100 ℃	0.54	0.72	0.69	0.74	0.64	0.62
	110 ℃	0.62	0.72	0.75	0.71	0.72	0.69
A_o (L/mol min)		3.1×10^4	1.6×10^4	1.5×10^3	1.2×10^4	4.0×10^3	5.7×10^3
E_p (kcal/mol)		3.70	3.08	1.06	2.90	2.39	1.15

in which $[Z]$ is the inhibitor concentration, $[I]$ is the initiator concentration, $[R.]$ refers radical concentration (the sum of concentrations of polyester radical, styrene radical, and initiator radical), k_z is the rate constant of inhibition, k_d is the rate constant of initiator decomposition, f is initiator efficiency, and k_p is the rate constant of propagation reaction. Based on the results of previous studies,[7] we assumed that the propagation reaction, the curing of the resin, began after inhibitors were exhausted and the termination reaction rate was zero as it was negligibly small compared to propagation reaction rate. As the curing reaction is diffusion controlled, k_p was assumed to follow the relationships:

$$k_p = k_{po}\,[1-(\alpha/\alpha_f)]^m \qquad (9)$$

in which α_f is the final degree of cure, and m is a constant. The rate constant k_{po} follows the Arrhenius relationship as follows:

$$k_{po} = A_o \exp(-E_p/RT) \qquad (10)$$

where A_o is a pre-exponential factor, E_p is the activation energy of the propagation reaction, R is the universal gas constant, and T is the absolute temperature. In solving Equations (5)-(8), we need the value of initiator efficiency. We used the expression for f suggested by Bisenberger[10] which is as follows:

$$f=\frac{f_o^2[1-(\alpha/\alpha_f)]^2}{2(1-f_o)([I]/[I]_o)}\{[1+\frac{4(1-f_o)([I]/[I]_o)}{f_o^2[1-(\alpha-\alpha_f)^2}]^{1/2}-1\} \qquad (11)$$

where f_o is the initial value of the initiator efficiency and $[I]_o$ is the initial concentration of initiator. In carrying out the computation, we have used the following numerical values available in literatures[11]: $[I]_o=4.541\times10^{-2}$(M/L); $f_o=0.2$. The rate constant of initiator decomposition, k_d, was estimated from the following expression:

$$k_d = k_{do} \exp(-E_d/T) \qquad (12)$$

in which $k_{do}=2.928\times10^{16}(\text{min}^{-1})$, and $E_d=1.546\times10^4$(K) for benzoyl peroxide. Table IV gives a summary of the kinetic parameters for the curing of the UPE resins based on the kinetic model described in Equations (5)-(12). It is of interest to note that the values of m are 0.5~0.7 which are in close agreement to the values of m for conventional UPE resins, reported by Lee and Han.[12] It was found that activation energies (E_p's) of the curing reaction of the UPE resins decreased by increasing the molecular weight or by decreasing degree of unsaturation of the UPE resin.

Conclusions

Thermal properties and exothermic curing behaviour of the UPE resins based on RPET were studied and kinetic parameters of the cure were obtained, based on the mechanistic model for free radical polymerization. The curing behaviour of the UPE resins based on RPET seemed to be similar to those of conventional UPE resins. The rate of cure was not changed so much, whereas final degrees of cure during isothermal cure of the UPE resins based on RPET decreased with increasing molecular weight of the resin. The rate of cure of the UPE resin decreased with decreasing degree of unsaturation of the UPE resin. It is postulated that curing behaviour of the UPE resins based on RPET depends on thermal properties and that the degree of unsaturation, as the curing is a diffusion controlled free radical polymerization.

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