Cure of unsaturated polyester resins: 1. Heat of copolymerization and glass transition temperature

Juan C. Lucas

CITIP (Center of Technological Investigations for the Plastic Industry), INTI (National Institute of Industrial Technology), Parque Tecnológico Migueletes, c.c. 157, (1650) San Martín, Argentina

and Julio Borrajo and Roberto J. J. Williams*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J.B. Justo 4302, (7600) Mar del Plata, Argentina

An unsaturated polyester (UP) resin based on maleic anhydride, isophthalic acid, propylene glycol and dipropylene glycol was cured with variable amounts of styrene, using benzoyl peroxide as initiator. Differential scanning calorimetry was used to determine heats of copolymerization, thermal mechanical analysis was employed to measure glass transition temperatures and Fourier-transform infra-red spectroscopy was used to follow the individual conversions of styrene (S) and UP double bonds (E). A heat of copolymerization equal to $66 \, \text{kJ mol}^{-1}$ was obtained, independently of the initial S/E ratio. Taking the overall conversion into account, the theoretical value for complete conversion of double bonds was estimated as $69 \, \text{kJ mol}^{-1}$. These values are in good agreement with literature values for the copolymerization of diethyl fumarate and styrene ($65-70 \, \text{kJ mol}^{-1}$) and styrene homopolymerization ($68.5-73 \, \text{kJ mol}^{-1}$). The maximum glass transition temperature (T_g) was obtained for formulations with S/E between 2 and 3, undergoing a near-azeotropic copolymerization. A single relationship between T_g and overall conversion was obtained for different cure temperatures.

(Keywords: polyester resin; heat of reaction; glass transition temperature; azeotropic copolymerization)

INTRODUCTION

The crosslinking of unsaturated polyester (UP) resins with styrene (S) has received the attention of many authors. The heat evolved in this copolymerization is usually expressed in units of energy per unit mass[1-9], and reported values range between $275 \, \text{J g}^{-1}$ (ref. 5) and $502 \, \text{J g}^{-1}$ (ref. 9). This extended range is the consequence of the variable concentration of double bonds in different formulations (both of styrene, S, and of unsaturated polyester, E) and the different conversions attained in the cure.

A more fundamental value of the heat of copolymerization is obtained by using units of joules per mole of double bonds (J mol^{-1}). Yang and Lee[9] reported heats of reaction for two different formulations equal to 60.9 and $61.3 \, \text{kJ mol}^{-1}$. However, as the final overall conversion was not reported, the theoretical heat of copolymerization cannot be calculated.

It is generally accepted that there is only a small difference between the heats of polymerization and copolymerization among styrene derivatives and polyesters[3,10,11]. In fact, the use of differential scanning calorimetry (d.s.c.) to determine the overall polymerization kinetics of UP-S systems is based on that hypothesis.

Reported values for the heat evolved in styrene homopolymerization[12] lie between 68.5 and $73 \, \text{kJ mol}^{-1}$. For the homopolymerization of the diethyl ester of fumaric acid (taken as a model system of UP resins), the reported value[12] is $65 \, \text{kJ mol}^{-1}$. For the copolymerization of the diethyl ester of fumaric acid with styrene, reported values are between 65 and $70 \, \text{kJ mol}^{-1}$ for the whole ratio of compositions of both comonomers[11].

One of the aims of the present paper is to determine actual (at the maximum conversion attained in the cure) and theoretical (at complete conversion) values of the heat of copolymerization (in J mol^{-1}) for a typical unsaturated polyester. The influence of the S/E ratio will be discussed.

On the other hand, the influence of the S/E ratio and the polymerization temperature on the glass transition temperature of the cured materials will be analysed. The representation of the polymerization in a X_S (conversion of styrene double bonds) vs. X_E (conversion of UP double bonds) diagram[13] will be used to discuss the experimental trends.

EXPERIMENTAL

Materials

The unsaturated polyester (UP) resin was a commercial product recommended for BMC (bulk moulding

---

compound) and SMC (sheet moulding compound) applications. Its composition, determined by ^{1}H n.m.r. was: 2 mol maleic anhydride, 1 mol isophthalic acid, 2.34 mol propylene glycol and 1.17 mol dipropylene glycol. The double-bond content was 3.02×10^{-3} mol g^{-1} (mostly fumarate unsaturations arising from maleic anhydride isomerization). The acid value was 17 mg KOH/g, as reported by the supplier. It was available as a solution containing 30 parts by weight of styrene monomer to 70 parts of resin. Extra styrene was added to establish the desired S/E ratio (molar ratio of both types of unsaturations).

The initiator was benzoyl peroxide in an amount of 1.5% based on total mass. This concentration was enough to give a single peak of reaction when scanning at a constant heating rate in d.s.c. The use of a smaller amount of initiator led to the appearance of an exothermic peak at high temperatures, ascribed to thermally initiated polymerization[4,14].

Blending of all ingredients was carried out at room temperature with normal stirring.

Thermal analysis

A Mettler TA 3000 provided with d.s.c. and t.m.a. (thermal mechanical analysis) was used. D.s.c. was employed to obtain the overall heat of reaction at a constant heating rate of 10°C min^{-1}, as well as conversion vs. time curves at constant temperature. T.m.a. was used to determine the glass transition temperature (T_g) of products cured to different extents of reaction in the d.s.c. cells. A periodic force (cycle time = 12 s) was automatically applied over the sample while increasing temperature at a constant heating rate (10°C min^{-1}). The increase in the amplitude of the oscillations revealed that the sample had reached its T_g. Figure 1 shows a typical run (T_g was defined as the onset value of the amplitude change).

Infra-red spectroscopy

An FTi.r. spectrometer (Nicolet, model 5SXC) with a resolution of 4 cm^{-1} in the transmission mode was used to follow the concentration of both types of unsaturations along the polymerization. One drop of mixture was placed between two sodium chloride plates, which were mounted on a sample holder located in the FTi.r. instrument. A Beckmann CTC temperature chamber was

used to maintain the reaction temperature at the required value. Three consecutive 1 s scans were taken at each sampling time, and their average was stored on a floppy disk. The sampling interval was varied between 1 and 4 min depending on the cure temperature and the conversion level.

The consumption of styrene monomer (S) was followed by measuring the change in peaks at 912 and 992 cm^{-1}, while the consumption of C=C double bonds of the polyester (E) was followed by the change in the peak at 982 cm^{-1}. The simple subtraction method proposed by Yang and Lee[13] was used to decouple the overlapping bands at 982 and 992 cm^{-1}. The C–H peak at 2942 cm^{-1} was chosen as the internal standard. Absorbances were calculated in terms of peak areas, and conversions were determined from the change of the normalized absorbance.

RESULTS AND DISCUSSION

Heat of copolymerization

Table 1 shows the overall heats of reaction for formulations containing different molar ratios of double bonds, S/E. The average value of the heat of copolymerization, expressed per mole of unsaturations, is 66 kJ mol^{-1}. There is no dependence of the heat of copolymerization on the S/E ratio, within experimental error ($\pm 5\%$). This is consistent with the information available in the literature, discussed in the 'Introduction'.

The theoretical heat of copolymerization at complete conversion was obtained by measuring the actual conversion of cured samples by FTi.r. The styrene conversion was $X_S = 0.97-0.98$, and the conversion of C=C bonds in the UP was $X_E = 0.93 \pm 0.03$, resulting in an overall conversion between 0.94 and 0.97. The theoretical heat of copolymerization between styrene and fumarate unsaturations of the UP may thus be estimated as 69 kJ mol^{-1}. This is in very good agreement with values reported for the copolymerization of diethyl fumarate and styrene[11] (65–70 kJ mol^{-1}), and for the homopolymerization of styrene[12] (68.5–73 kJ mol^{-1}).

As $X_E < X_S$ at the maximum extent of reaction, it may be inferred that a fraction of the polyester C=C bonds remains trapped in the highly crosslinked network structure and does not enter reaction even at temperatures above T_g. This topological effect has been discussed in the literature[15,16].
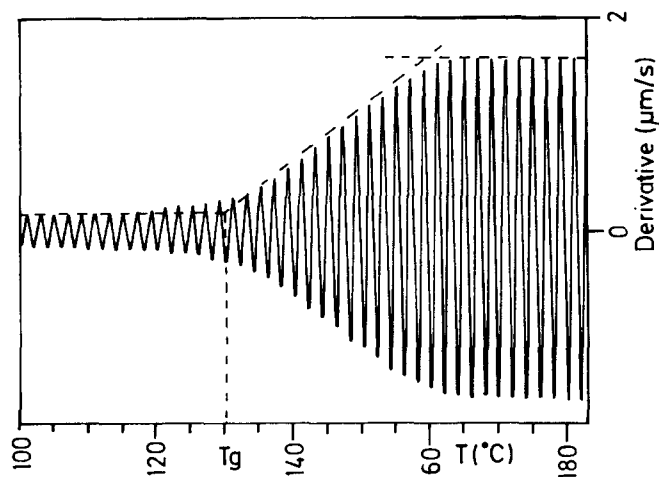

Figure 1 T.m.a. thermogram of a cured product under a periodic force. T_g is defined as the onset value of the amplitude change

Table 1 Overall heats of reaction for formulations containing different molar ratios of double bonds, S/E

S/E	ΔH (J g^{-1})	ΔH (J mol^{-1})
1.27	312	63.2
1.5	341	65.7
1.75	355	65.3
1.87	374	67.8
2	377	66.9
2.25	393	66.5
2.5	397	66.1
2.7	404	66.1
3	429	68.2
4	442	65.3
5	451	63.6
6	485	65.7
7	491	64.4
15	546	64.4

Glass transition temperature

The T_g of samples containing various S/E ratios and cured in the d.s.c. up to the maximum conversion was determined by t.m.a. *Figure 2* shows the presence of a maximum around 130–135°C for S/E values between 2 and 3. A sharp drop in T_g is observed for S/E values lying outside this range. For high styrene contents T_g gets close to the value for polystyrene, i.e. about 100°C.

A ratio of S/E close to 2 is the usual recommendation for typical UP formulations. This criterion should be extended to the range of S/E values between 2 and 3, where a maximum T_g is obtained. For a UP based on 1 mol maleic anhydride, 1 mol isophthalic acid, 1 mol propylene glycol and 1 mol diethylene glycol, Bucknall et al.[17] recently reported the presence of a broad maximum in T_g for S/E values between 1.57 and 3.83.

The individual conversions of styrene (X_S) and UP double bonds (X_E), for formulations containing different S/E ratios and cured at 75°C, were followed by FTi.r. *Figure 3* shows the results for S/E = 2, 2.5 and 3. The ratio S/E = 2.5 leads to an azeotropic copolymerization, i.e. S and UP double bonds are incorporated into the polymer in the same ratio as the initial S/E value. Then, the reaction path in X_S vs. X_E coordinates follows the 45° line. Of interest is the fact that the maximum T_g value seems to be related to formulations undergoing copolymerization at near-azeotropic conditions.

For S/E = 2, styrene is in defect with respect to the azeotropic composition. So, the curve lies above the 45° line. The opposite happens for S/E = 3. At high conversions there is an up-bending of the curves, meaning that the relative rate of styrene consumption increases significantly. At these conversions diffusional limitations affect the UP unsaturations, which are part of the polymer network, much more than the free styrene monomer. However, post-cure at 140°C led to high conversions of both types of unsaturations, i.e. $X_S = 0.97$–0.98 and $X_E = 0.90$–0.96.

Formulations with S/E = 3 were cured in the d.s.c. at three different constant temperatures, 90, 105 and 115°C.
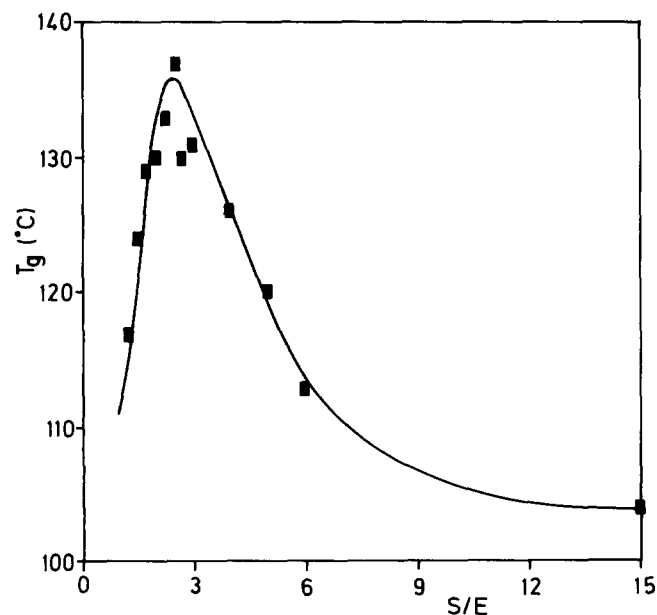
Figure 2 Glass transition temperature as a function of the ratio of styrene and unsaturated polyester double bonds in the initial formulation
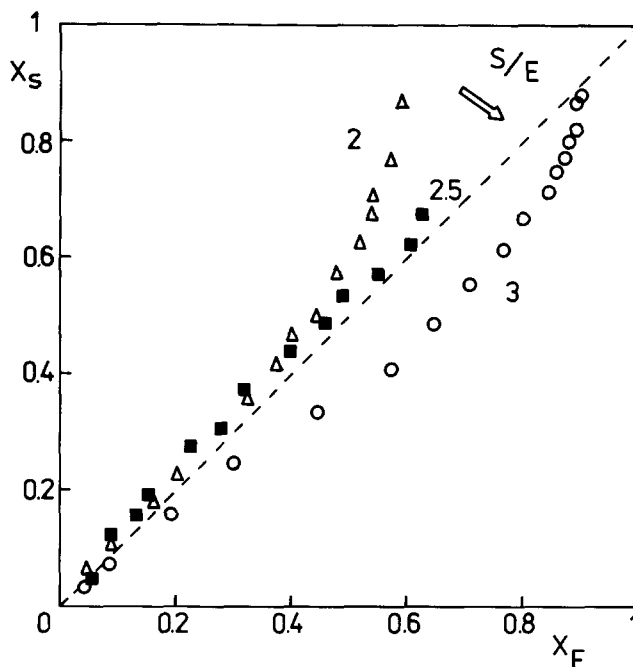
Figure 3 Styrene conversion (X_S) vs. polyester double bond conversion (X_E) for formulations with different S/E ratios, cured at 75°C
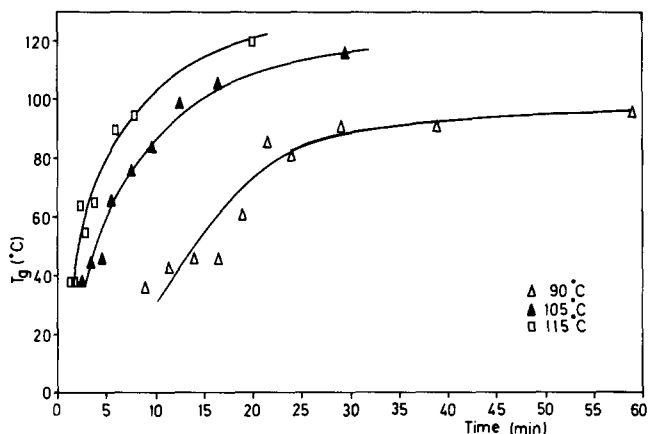
Figure 4 Glass transition temperature vs. time for samples with S/E = 3, cured at different temperatures
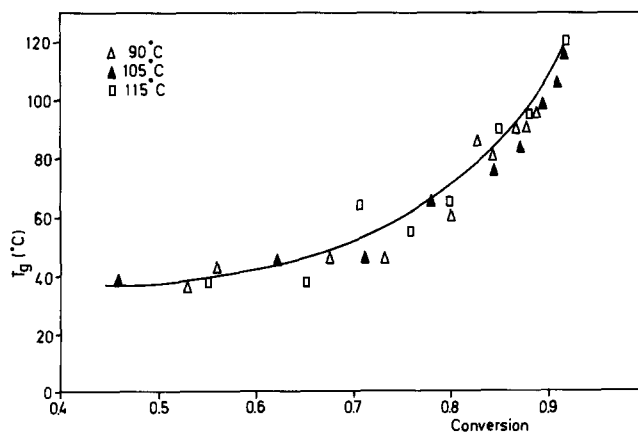
Figure 5 Glass transition temperature vs. conversion for samples with S/E = 3, cured at different temperatures

Conversion vs. time curves were obtained up to a maximum conversion limited by vitrification. On the other hand, the evolution of T_g vs. time was obtained by stopping the reaction at particular times, immersing the

d.s.c. pans in liquid nitrogen to arrest polymerization, and measuring T_g by t.m.a. (a different sample was used for every cure time).

Figure 4 shows T_g vs. time curves at three different cure temperatures. When T_g reaches T_{cure}, the further increase of T_g is severely retarded due to the onset of vitrification. *Figure 5* shows a similar representation in terms of conversion, in the 0.4–1 conversion range. Within experimental error, every point lies on the same curve. As T_g is very sensitive to the network structure, it may be concluded that the cure temperature does not affect significantly the copolymerization reaction. In fact T_g is influenced by the initial S/E ratio.

CONCLUSIONS

The heat of copolymerization of styrene (S) and fumarate double bonds of UP resins (E) was estimated as $69 \, \mathrm{kJ \, mol^{-1}}$, independently of the S/E ratio. This is in good agreement with values reported for the copolymerization of diethyl fumarate with styrene and for styrene homopolymerization.

The maximum T_g of cured materials was obtained for formulations with S/E ratios ranging between 2 and 3, which led to near-azeotropic copolymerizations. The relationship between T_g and conversion, for a fixed value of S/E, did not depend on cure temperature. Therefore, factors affecting the T_g value were the initial S/E ratio and the final conversion attained.

REFERENCES

1   Kamal, M. R., Sourour, S. and Ryan, M. E. *Soc. Plast. Eng. Tech. Pap.* 1973, **19**, 187
2   Kamal, M. R. and Sourour, S. *Polym. Eng. Sci.* 1973, **13**, 59
3   Kubota, H. *J. Appl. Polym. Sci.* 1975, **19**, 2279
4   Cuadrado, T. R., Borrajo, J., Williams, R. J. J. and Clara, F. M. *J. Appl. Polym. Sci.* 1983, **28**, 485
5   Han, C. D. and Lem, K. W. *J. Appl. Polym. Sci.* 1983, **28**, 3155
6   Han, C. D. and Lem, K. W. *Polym. Eng. Sci.* 1984, **24**, 175
7   Batch, G. L. and Macosko, C. W. *Soc. Plast. Eng. ANTEC Tech. Pap.* 1987, **33**, 974
8   Han, C. D. and Lee, D. S. *J. Appl. Polym. Sci.* 1987, **33**, 2859
9   Yang, Y. S. and Lee, L. J. *J. Appl. Polym. Sci.* 1988, **36**, 1325
10   Joshi, R. M. *J. Polym. Sci.* 1962, **56**, 313
11   Horie, K., Mita, I. and Kambe, H. *J. Polym. Sci. (A-1)* 1969, **7**, 2561
12   Ivin, K. J. in 'Polymer Handbook', 2nd Edn. (Eds J. Brandrup and E. H. Immergut), Wiley, New York, 1975, p. II-421
13   Yang, Y. S. and Lee, L. J. *Macromolecules* 1987, **20**, 1490
14   Bergmark, P. and Flodin, P. *Polymer* 1987, **28**, 1662
15   Horie, K., Mita, I. and Kambe, H. *J. Polym. Sci. (A-1)* 1970, **8**, 2839
16   Yang, Y. S. and Lee, L. J. *Polymer* 1988, **29**, 1793
17   Bucknall, C. B., Partridge, I. K. and Phillips, M. J. *Polymer* 1991, **32**, 786