

Unsaturated Polyesters: Influence of the Molar Mass on the Cure with Styrene and the Properties of the Resulting Networks

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ABSTRACT: Fractions of an unsaturated polyester resin (UP), based on 1 mol maleic anhydride, 1 mol isophthalic acid, 1 mol propylene glycol, and 1 mol diethylene glycol, were obtained from an industrial reactor at various times during polyesterification. They were characterized by ¹H-NMR and chemical titration. Increasing the reaction time from 1 to 9 h led to an increase in (a) the number-average molar mass (M_n) in the range 484–1712 g/mol, (b) the maleic acid–fumaric acid isomerization from 85 to 95%, (c) the glass transition temperature (T_g) from 251 to 267 K, and (d) the compatibility with styrene. Several of these fractions were cured with styrene, in amounts ranging from S/E = 2–5 (molar ratio of C=C double bonds in styrene, S, and unsaturated polyester, E), using benzoyl peroxide as an initiator. Increasing M_n led to an increase in the T_g value and a decrease in the amount of moisture absorption. Both effects were explained by the decrease in the concentration of the polar end groups present in the UP chains. However, using a relatively high styrene fraction in the formulation (i.e., S/E = 5) led to cured products exhibiting reasonably high T_g values (approaching the pure polystyrene value) combined with a low moisture absorption. This constitutes a practical way to revalorize batches of UP resins with molar masses out of specification. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 755–760, 1997

Key words: unsaturated polyesters; styrene/UP ratio; water absorption; glass transition temperature

INTRODUCTION

Unsaturated polyester (UP) resins are one of the most widely used thermoset resins in polymeric composites, because of their good mechanical properties and relatively inexpensive prices. The curing reaction is a free-radical polymeriza-

tion of C=C double bonds present in the UP resin and in an unsaturated solvent which is usually styrene. With the addition of fillers and glass fibers, the resins are processed over a wide temperature range to form sheet-molding compounds (SMC), bulk-molding compounds (BMC), pultruded parts, etc.

UP resins are oligomers prepared by the esterification of diacids (or acid anhydrides) with diols, such that one of the starting monomers contains C=C double bonds in its structure. Usually, maleic anhydride plays this role. The reaction is a

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typical polycondensation characterized by a slow increase of the average molar mass of the UP resin with time. The end point is arbitrarily defined by the attainment of a particular acid value (conversion) or viscosity. On occasion, processors have to formulate their products with batches of UP resins which are out of the standard specifications, i.e., that have not been advanced enough in the polyesterification process. Although it can be expected that some properties of the cured products such as water absorption and the glass transition temperature will deteriorate, it is difficult to predict the sensitivity of these properties on the number-average molar mass (a measure of the attained conversion) of the UP resin. Moreover, it would be of interest to know which variables of the formulation can be modified to attenuate the expected deterioration in final properties.

The aim of this article was to show the influence of the number-average molar mass of a typical UP resin on the rate of cure with styrene and on the properties of the resulting products. Modifications in the final formulation that may attenuate the impact of using a low molar mass UP resin are discussed.

EXPERIMENTAL

Materials

UP resin fractions based on 1 mol maleic anhydride, 1 mol isophthalic acid, 1 mol propylene glycol, and 1 mol diethylene glycol were obtained from an industrial reactor at various times (from 1 to 9 h) during polyesterification. Several of these fractions were cured with styrene in amounts ranging from S/E = 2–5 (molar ratio of C=C double bonds in styrene, S, and unsaturated polyester, E). The cure was performed in a differential scanning calorimeter, heating from room temperature to 160°C (beyond the exothermic reaction peak), at 10°C/min. Benzoyl peroxide in the amount of 1.5 wt % was used as an initiator.

Techniques

The composition of UP resin fractions was determined by ¹H-NMR (Varian EM-390, 90 MHz, CDCl₃ solutions). Hydroxyl and acid values (*I*_{OH} and *I*_H, in mg KOH/g) were determined by chemical titration. From these values, the average hydroxyl (*f*_{OH}) and acid (*f*_H) functionalities, the

number-average molar mass (*M*_n), and the average functionality of unsaturations (*f*_{C=C}), were determined.

A Mettler TA 3000 provided with a thermal mechanical analyzer (TMA) was used to determine the glass transition temperature (*T*_g) of the starting UP resins and the products cured with styrene. A periodic force (cycle time = 12 s) was automatically applied over the sample while increasing the temperature at a constant heating rate of 10°C/min. *T*_g was defined as the onset value of the derivative change (for the cured products, a corresponding increase in the amplitude of oscillations was observed at *T* = *T*_g).

Differential scanning calorimetry (DSC, Mettler TA3000) was used to determine the reaction heat and the cure kinetics of UP–styrene formulations. The DSC was operated in the dynamic mode at 10°C/min under a nitrogen atmosphere. The reaction heat was obtained from the area of the exothermic reaction peak. A phenomenological *n*th-order kinetic expression was used to fit the rate of heat evolution as a function of temperature:

$$dx/dt = k(1 - x)^n \quad (1)$$

where $x = \Delta H(T)/\Delta H_T$ is the conversion of C=C double bonds, defined as the partial area at a certain temperature over the total area under the exothermic peak, and $k = k_0 \exp(-E/RT)$.

Specimens of the cured materials were kept at 23°C and 100% relative humidity for 4 days. After this period, an almost constant weight was reached. However, as discussed by Bellenger et al.,¹ it is difficult to define an equilibrium value of the water concentration in these systems, because it increases continuously at a very low rate. So, experimental data must be regarded as pseudoequilibrium values. The fraction of the absorbed water and the *T*_g of the preconditioned specimens were determined.

RESULTS AND DISCUSSION

Characterization of UP Fractions

Characteristics of the different UP fractions, determined by ¹H-NMR and chemical titration, are shown in Table I. Number-average molar masses varied in the range 484–1712 g/mol, with an in-

Table I Characteristics of UP Fractions Determined by $^1\text{H-NMR}$ and Chemical Titration

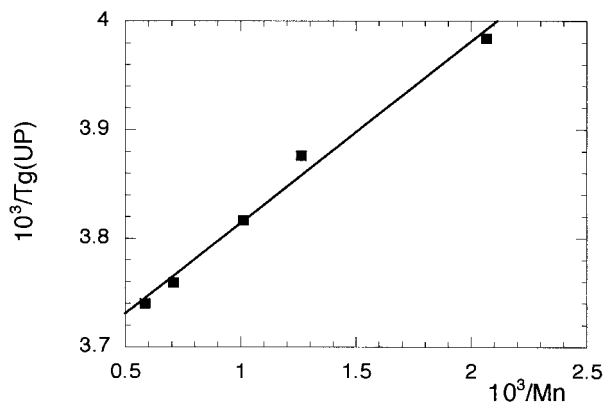
Sample <i>t</i> (h)	Molar Ratio (%) IPA : FA : MA	Molar Ratio (%) DEG : PG	Isom. (%)	I_{OH} (mg/g KOH)	I_{H} (mg/g KOH)	M_n (g/mol)	f_{OH}	f_{H}	$f_{\text{C}=\text{C}}$
1	51 : 42 : 7	52 : 48	85	160	73	484	1.4	0.6	1.2
3	52 : 42 : 6	52 : 48	87	82	59	792	1.2	0.8	1.9
5	52 : 43 : 5	51 : 49	90	67	47	990	1.2	0.8	2.4
7	52 : 45 : 3	52 : 48	94	43	36	1411	1.1	0.9	3.4
9	52 : 46 : 2	53 : 47	95	38	28	1712	1.1	0.9	4.1

IPA, isophthalic acid; FA, fumaric acid; MA, maleic acid; DEG, diethylene glycol; PG, propylene glycol; Isom., maleic acid-fumaric acid isomerization.

crease in the isomerization of maleic acid to fumaric acid, from 85% to 95%.

The average molar mass of the UP resin determined its compatibility with styrene. Increasing M_n led to an increase in the amount of styrene that could be added to the formulation. The UP resin with $M_n = 484$ was not soluble in the usual amounts of styrene ($S/E \geq 1$); for $M_n = 792$, the insolubility began at $S/E = 4$; for $M_n = 990$ and 1411, it was shifted to $S/E = 6$, whereas for $M_n = 1712$, insolubility began at $S/E = 7$. In this range of molar masses, the most important factor determining the compatibility with styrene is the concentration of chain ends (i.e., hydroxyl and carboxyl groups). The lower the molar mass, the higher the concentration of these groups and the lower the compatibility with styrene. Typical values of S/E in commercial formulations are in the range of 2–3. This determines a minimum value of M_n that can be used in practical applications.

The glass transition temperature of the UP resin increased with its number-average molar mass. Figure 1 shows a representation of $1/T_g$

**Figure 1** $1/T_g$ versus $1/M_n$ for the UP resin.

(UP) versus $1/M_n$, giving a linear plot. This means that the following equation proposed by Ueberreiter and Kanig² was verified:

$$1/T_g(\text{UP}) = 1/T_{g^\infty} + A/M_n \quad (2)$$

where T_{g^∞} is the limit of T_g (UP) when $M_n \rightarrow \infty$. The best linear correlation was obtained for $T_{g^\infty} = 274.2$ K and $A = 0.167$.

For an UP based on 0.54 mol isophthalic acid, 0.46 mol maleic anhydride, and 1 mol propylene glycol, eq. (2) was also shown to be valid with $T_{g^\infty} = 330$ K and $A = 0.155$.³ Therefore, the diethylene glycol present in our system produces a significant decrease in T_{g^∞} but does not practically affect the A value.

Cure of UP Fractions with Styrene

The set of UP resins with $M_n = 792, 990, 1411$, and 1712 was formulated with styrene, in amounts covering the range $S/E = 2-5$, and benzoyl peroxide (1.5 wt %). The cure in the DSC led to a single exothermic peak with a maximum in the range 110–122°C, depending on the particular formulation. The n th-order kinetic equation gave a good fitting of the DSC curves. Table II shows the resulting values of reaction heat and kinetic parameters.

The reaction heat did not depend on the M_n of the starting UP resin or the S/E value used in the formulation. This reflects the fact that there is only a small difference between the heats of polymerization and copolymerization among styrene derivatives and polyesters.⁴⁻⁷ In fact, the use of DSC to determine the overall polymerization kinetics of UP-S systems is based on that hypothesis.

The reaction heat was 64 ± 2 kJ/equiv, a

Table II Reaction Heat and Kinetic Parameters Arising from DSC Thermograms

S/E	M_n (g/mol)	ΔH_T (kJ/equiv)	n	E (kJ/mol)	k (117°C) (min ⁻¹ 10 ²)
2	792	65	1.69	168.7	2.9
2	990	65	1.74	172.8	5.0
2	1411	65	1.78	172.2	5.5
2	1712	63	1.72	175.9	6.4
3	792	63	1.47	141.7	2.0
3	990	63	1.50	144.7	2.2
3	1411	62	1.43	138.7	2.3
3	1712	64	1.51	144.0	2.4
4	990	65	1.39	123.3	1.3
4	1411	66	1.40	125.2	1.6
4	1712	63	1.39	126.8	1.6
5	990	64	1.26	107.3	0.9
5	1411	66	1.29	107.2	1.0
5	1712	64	1.33	112.7	1.2

S/E, molar ratio of unsaturations in styrene and the UP resin; M_n , number-average molar mass of the UP resin; ΔH_T , total reaction heat; n , reaction order; E , activation energy; k , specific rate constant.

value which is in close agreement with $\Delta H_T = 66$ kJ/equiv reported⁷ for a UP resin of different composition and formulated in a range of S/E values composed between 1.27 and 15. The constancy of the reaction heat also implies that the maximum conversion attained in the cure was independent of the molar mass of the starting UP resin.

Regarding the kinetic parameters, both the reaction order and the activation energy were approximately constant for a given set of S/E values. To eliminate the small variations in the activation energy, the specific rate constant was calculated at a constant temperature in the cure range, i.e., $T = 390$ K (117°C), close to the maximum of the DSC peak. The comparison of k values for a given S/E ratio indicates that the cure rate increased slightly with the molar mass of the UP resin. The effect was particularly evident for the lowest S/E value. A possible explanation is the increase in the fraction of fumarate double bonds when increasing M_n . It is known that fumarate polymers are subject to less steric influence in the *trans* form and are able to assume a planar configuration, displaying reactivities almost 20 times those of the maleate polymers in the copolymerization reactions with styrene.⁸ An alternative explanation for the increase in the cure rate with the molar mass of the UP resin is the higher compatibility with styrene. It may be speculated that mi-

crogels formed at low conversions in the UP-S copolymerization^{9,10} are swollen to a higher extent by the styrene monomer when M_n (UP) is increased. This could also explain the observed increase in reaction rate.

Characterization of Cured Products

Figure 2 shows the water absorption of the cured products as a function of the S/E ratio used in the formulation, when they were exposed to a 100% relative humidity environment at 23°C for 4 days. The water absorption decreased when increasing the molar mass of the UP resin and the S/E ratio. The first effect is due to the decrease in the concentration of the hydrophilic chain ends.¹ The second one arises from the hydrophobic nature of styrene.

Figure 3 shows the effect of water absorption on the glass transition temperature of cured products obtained with different M_n (UP) and S/E ratios. In every case, there was an increase in T_g with the S/E ratio used in the formulation, approaching the value of pure polystyrene (T_g close to 100°C). Conditioning the samples in a 100% relative humidity environment at 23°C for 4 days produced a decrease in the glass transition temperature. This decrease was amplified for low values of M_n (UP) and S/E ratios, in agreement with

the larger amount of absorbed water for these formulations.

From the results shown in Figures 2 and 3, it may be inferred that UP resins with low molar masses can still be used if they are formulated with larger styrene amounts than those usually recommended. For example, a UP resin with $M_n = 990$ g/mol, formulated with $S/E = 5$, led to a cured product a with T_g in the range 80–85°C and with a relatively low capacity of water absorption. Increasing M_n to 1712 g/mol led to a small increase in T_g (up to 88–90°C, depending on the water content).

CONCLUSIONS

The effects produced by the use of low molar mass UP resins on the crosslinking with styrene and on the properties of the cured products were analyzed. When the molar mass was very low (i.e., M_n values lower than about 500), the compatibility with styrene was reduced to such an extent that it was not possible to incorporate the minimum amount necessary to obtain a fully crosslinked network. For higher values of M_n , fully crosslinked materials could be obtained, as re-

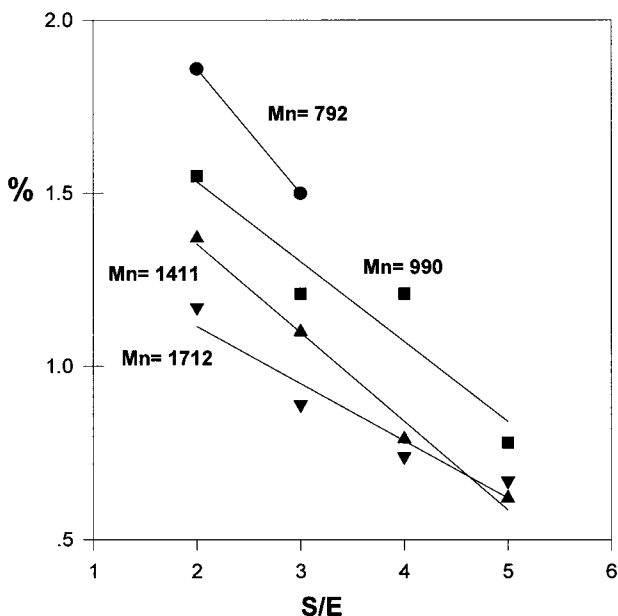


Figure 2 Water absorption (wet basis) of the cured products as a function of the S/E ratio used in the formulation, when they were exposed to a 100% relative humidity environment at 23°C, for 4 days. Lines correspond to different M_n values of the UP resin.

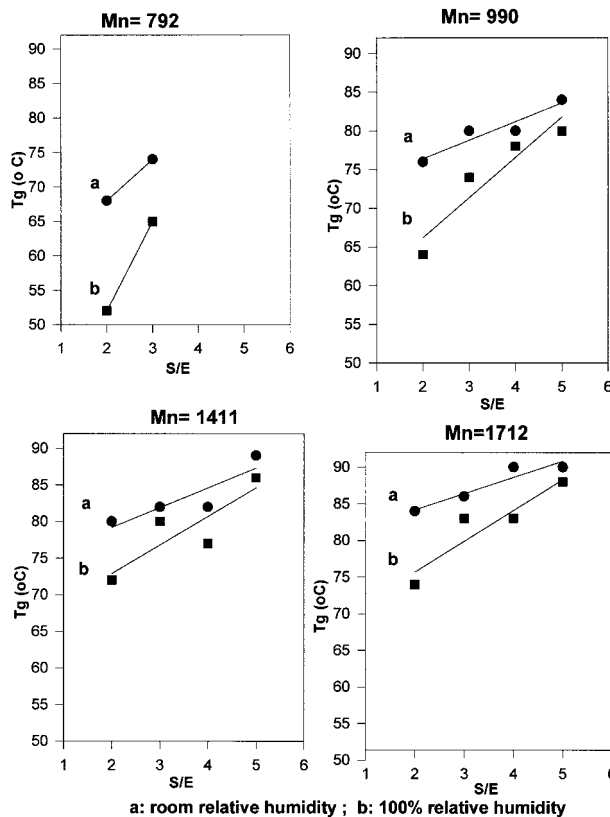


Figure 3 Effect of water absorption on the glass transition temperature of cured products obtained with different M_n (UP) and S/E ratios: (a) samples conditioned in the laboratory environment at 23°C; (b) samples conditioned in a 100% relative humidity environment at 23°C for 4 days.

vealed by the constancy of the total reaction heat. A slight increase in the cure rate with M_n was observed and explained by the larger isomerization of the low-reactive maleate to the high-reactive fumarate units (a secondary possible explanation was the increase in the swelling of microgels by the styrene monomer). Increasing M_n led to an increase in the T_g value and a decrease in the amount of absorbed water. Both effects were explained by the decrease in the concentration of the polar end groups present in the UP chains. However, using a relatively high styrene fraction in the formulation (i.e., $S/E = 5$) led to cured products exhibiting reasonably high T_g values (approaching the pure polystyrene value) combined with a low moisture absorption. This constitutes a practical way to revalorize batches of UP resins with molar masses out of specification.

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