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Mechanical properties and curing characteristics of unsaturated polyesters synthesized for large casting

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Summary

A series of unsaturated polyesters (UP) based on phthalic anhydride (PHA), succinic acid (SU), adipic acid (AD), sebacic acid (SE),maleic anhydride (MA), ethylene glycol (EG), diethylene glycol (DG), triethylene glycol (TG), and styrene (Sty) were prepared. The molecular weights of the prepared polyesters were determined by the end group analysis. The effect of the structure of the resin on its mechanical and curing behavior has been investigated. On the basis of the experimental study, we concluded : (1) the maximum curing temperature, T_{max}, is related to the molecular weight of the glycol incorporated in these castings. In this context, T_{max} was found to decrease with increasing the molecular weight. Meanwhile, the time to peak temperature, t_{max}, was increasing; (2) the values of T_{max}, Young's modulus and compressive strength were found to be influenced to a large extent with the type of the saturated acid as well as the molecular weight of the glycol embodied in these resins. A relation representing the variation of compressive strength, σ_u, as a function of equivalent polymerizable double bonds, EPDB, was derived. It was assumed that this equation can be used to predict the compressive strength for any particular UP formula from its theoretical EPDB value.

Introduction

Unsaturated polyester resins are produced by reacting an unsaturated dibasic acid or a mixture thereof with a saturated dibasic acid with a polyhydric alcohol. The product is then dissolved in a vinyl monomer. These unsaturated polyester resins are cured by the aid of an organic peroxide (1). Few years ago, some work described a technique for producing polyester resins based on recycled poly(ethylene terephthalate), PET (2, 3). The properties of polymer concrete obtained from the latter type of resins were extensively studied and were found to be comparable to polymer concrete made from chaste materials (4 - 7).

The high exothermic curing reaction has been a considerable problem when large objects are cast from high polymeric resins. The heat liberated tends to rise the mold temperature and accelerate the curing reaction and sways the physical and mechanical properties of the thermosetting material. Therefore, the control of the rate of heat generation and the temperature variations during the processing of these materials are very important in order to achieve the desired degree of cure of the product. However, the rate of the polymerization reaction is dependent upon the temperature and the type and the concentration of the monomer and initiator used. In the previous study the concentrations of initiator and accelerator were established (1). However, this work pertains to the preparation of thermosetting materials and testing their applicability for casting large sized objects by liken the heat of curing and the mechanical properties of the final product. This is accomplished by using different types of aromatic and aliphatic dibasic acids, such as PHA, SU, AD and SE in conjunction with a various combinations of polyhydric alcohols, such as EG, DG or TG, for constructing the unsaturated polyesters. These variations in the structure is aimed to optimize the quality of the final product., namely, the mechanical properties and the heat evolved during the cross-linking operation.

Experimental

1. ***Materials.*** polyhydric alcohols (EG, DG and TG) , phthalic anhydride (PHA), maleic anhydride (MA), dibasic acids (SU, AD and SE) and styrene (Sty) were reagent grade and used without further purification. All Chemicals were obtained from Aldrich.

2. ***Preparation of unsaturated polyesters (UP).*** The UP resins were prepared by reacting the appropriate amounts of saturated, unsaturated acid or acid anhydrides, and glycols according to the ratios tabulated in Table 1. sixteen UP were prepared by the method described in ref. (7). The unsaturated polyester resins were analyzed for acid and hydroxyl values (7,8), for the sake of calculating the molecular weights via end group analysis, before blending these with Sty monomer.

3. ***Determination of peak exotherm.*** The curing exotherms of unsaturated polyesters were measured, by Digitron digital differential thermometer, type K, model 3202 with a resolution of 0.1° C, as described in the previous work (1). To achieve the reproducibility of the measurements and affording a comparative study, the volume and the shape of the curing glass bottles, used in all experiments, were kept constant. The curing zero time was considered as the moment at which the initiator is added to the reaction mixture at 35°C. The maximum curing temperature was taken as the highest value in the temperature/time curve, peak exotherm temperature (T_{max}), whereas t_{max} is the time required to acquire T_{max}. The concentration of methyl ethyl ketone peroxide, MEKP (initiator), and cobalt octoate, CO (accelerator), were kept constant allover the curing reactions.

Table (1) Composition of different formulae of unsaturated polyester resin

No	composition							
	Acid (mol)					Glycol (mol)		
	PHA	SU	AD	SE	MA	EG	DG	TG
1	0.5	.	.	.	0.5	1.1	.	.
2	0.5	.	.	.	0.5	0.55	0.55	.
3	0.5	.	.	.	0.5	0.55	.	0.55
4	0.5				0.5	.	0.55	0.55
5	.	0.5	.	.	0.5	1.1	.	.
6	.	0.5	.	.	0.5	0.55	0.55	.
7	.	0.5	.	.	0.5	0.55	.	0.55
8	.	0.5	.	.	0.5	.	0.55	0.55
9	.	.	0.5	.	0.5	1.1	.	.
10	.	.	0.5	.	0.5	0.55	0.55	.
11	.	.	0.5	.	0.5	0.55	.	0.55
12	.	.	0.5	.	0.5	.	0.55	0.55
13	.	.	.	0.5	0.5	1.1	.	.
14	.	.	.	0.5	0.5	0.55	0.55	.
15	.	.	.	0.5	0.5	0.55	.	0.55
16	.	.	.	0.5	0.5	.	0.55	0.55

The formulation used for curing was resin /initiator / accelerator = 100 / 2 / 0.2 (parts by weight) (1).

4. ***Mechanical properties.*** The compressive stress-strain diagrams were measured using a Zwick mechanical testing machine as described in the previous work (1).

Results and discussion

Molecular weight : The molecular weights of the prepared polymers were determined by the end group analysis. Since methods of end group analysis count the number of molecules in a given weight of sample, they yield the number-average molecular weight for polydisperse materials. The method becomes insensitive at high molecular weight (above 25000), as the fraction of end groups becomes too small to be measured with precision (9). End group analysis in condensation polymers usually involves chemical methods of analysis for functional groups. Carboxyl and hydroxyl groups in polyesters (10, 11) are usually titrated with a titrable reagent. The resultant molecular weights are tabulated in Table 2 in conjunction with the acid number of the prepared polyesters. The highest molecular weight, M_n = 2960, was obtained for formula

No. 13 for which the EG was used as a unique glycol for constructing the unsaturated polyester. We believe that the accuracy of the determined values is good enough since the highest molecular weight is less than 25000 as previously established (9). When 1,5-pentanediol was used in conjunction with maleic anhydride, for synthesis of UP, Larez et al. (12) have obtained an unsaturated reasonably high molecular weight polyester, M_n= 3307, as compared with that obtained with lower glycols (13, 14). Horie et al. (15) have obtained polyester fumarate resins by reacting fumaric acid, succinic acid and diethylene glycol. The resultant molecular weight's range being 2700 - 3300 and found to depend on a large extent to the variation of the fumaric - to - succinic. In the present study, the reaction of MA, SU and different glycols yielded polyester resins having molecular weight ranging between 1785 and 2288. The highest molecular weight (M_n= 2288) was obtained when EG was used as a unique glycol for preparing the UP upon using SU as saturated dibasic acid.

The choice of saturated acid (aliphatic or aromatic) and glycols offers great latitude in the design of polymer backbones. The cross-linking density of the cured product depends to a great extent to the type of the glycol and the acid used in constructing the resin.

***Curing behavior*:** Examples of the curing exotherms for some of the present formulae are given in Fig.1. From these, as well as, the exotherms not illustrated, the values of T_{max} and t_{max} were derived and tabulated in Table 2. It should be pointed out that the maximum curing temperature is related to three different parameters: 1) type of saturated acid, 2) molecular weight of the saturated acid and glycol, and 3) the equivalent polymerizable double bonds (EPDB) of the unsaturated polyester resin.

(a) Effect of acids : The unsaturated acid, MA, was used to provide the unsaturation necessary for curing while the saturated acid governs the spacing of such unsaturation. The influence of the acid type on the heat evolved upon curing UP is illustrated in Table 2. Comparing the formulae containing EG as a sole glycol component in the main chain of the polymer (formulae 1,5,9 and 13) reveals that the polymerizable equivalent double bonds, EPDB, depends to a large extent on the type of the acid used. For this set of UP formulae, it can be seen that EPDB decreases with increasing the molecular weight of the dibasic acid, accordingly t_{max} increases and T_{max} decreases. A similar phenomenon is detected for other glycol combination systems.

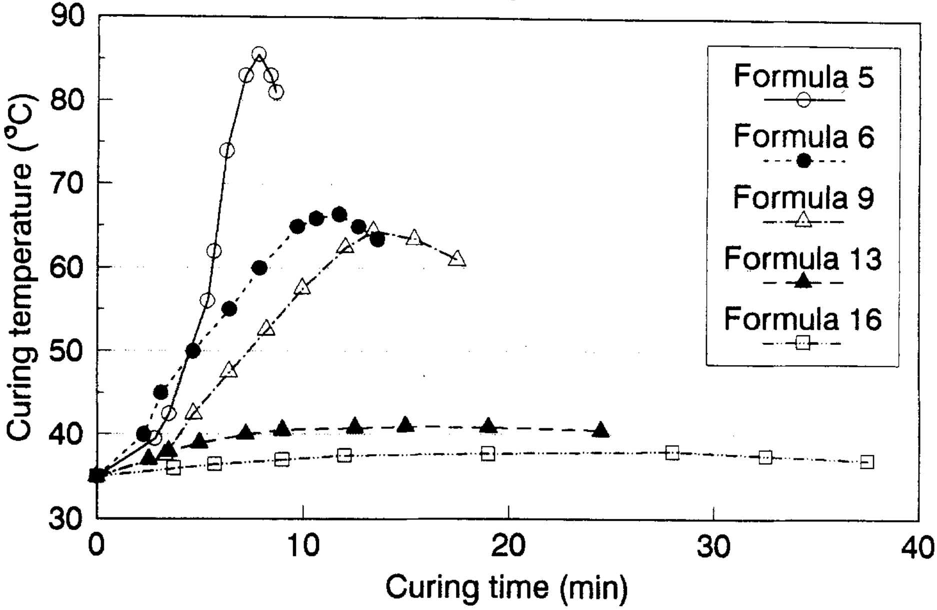
(b) Effect of glycols : One of the parameters which influence the heat generation upon curing the UP is the type of the glycols incorporated in the polymer. In this context, linear polyester fumarates of different EPDB values were prepared by assorting the glycol combinations. Comparing the formulae containing PHA as one of the components in the main chain of the polymer, reveals that T_{max} reduces with increasing the average molecular weight of the glycol system. When EG is used alone (formula No. 1), T_{max} recorded the highest value (70.5°C). This value considerably reduces to 49° C and 41° C on replacing half of the quantity of EG with DG and TG (formulae No. 2 and 3) respectively. It is of interest to note that the value of T_{max} (38.5° C), for the formula contains DG+TG, (formula No. 4) is lower than that for the formula contains EG + TG since the molecular weight of DG is higher than that of EG.

It is obvious that the variation of the types of glycols and their combinations leads to different behavior of exothermic temperature. This may be virtue to the differences in the molecular weights of the repeating units of the unsaturated polyesters. Consequently, this molecular weight's variation leads to a disparity in EPDB. With respect to the other three sets of resins, for which SU, AD and SE were used instead of PHA, the variation of T_{max} with the type of glycol shows the same behavior as that already discussed in the foregoing section. Values of t_{max} for different resins under investigation are also shown in Table 2. It is seen that values ranging between 7.8 and 28 min. are obtained. Here it should be pointed out that a faster curing reaction is obtained when EG is used as a sole glycol. Meanwhile, the other types of glycols and their combinations, even with EG, produce unsaturated polyester resins having longer curing times combined with less heat evolved.

Table (2) Acid number, molecular weights, curing behavior and mechanical properties of unsaturated polyesters (formulae 1 - 16)

No	Acid No.	M wt.	EPDB	t_{max}(min.)	T_{max}(° C)	σ_u (MPa)	E (GPa)
1	17.95	2438	0.265	8.0	70.5	178.7	0.878
2	18.7	2123	0.237	16.0	49.0	153.0	0.828
3	22.3	2010	0.214	15.0	41.0	141.9	0.763
4	19.07	2230	0.195	18.0	38.5	104.0	0.720
5	17.8	2288	0.278	7.8	85.5	189.4	0.992
6	19.7	1980	0.244	11.7	66.5	162.7	0.655
7	23.8	1758	0.218	12.75	43.0	142.6	0.560
8	18.3	1998	0.197	20.75	42.0	111.1	.
9	16.0	2512	0.258	13.4	64.5	175.4	0.792
10	17.9	2148	0.228	18.5	41.3	148.1	0.582
11	18.9	1889	0.205	18.8	41.5	124.9	0.400
12	18.0	2131	0.186	27.0	40.1	79.8	.
13	15.3	2960	0.224	15.0	41.0	146.0	0.682
14	16.2	2484	0.202	19.25	40.3	120.2	.
15	18.1	2152	0.184	23.0	38.5	71.9	.
16	17.5	2399	0.168	28.0	38.0	31.3	.

Fig.(1) Selected Curing Exotherms for Unsaturated Polyester Formulae



Mechanical properties: The values of Young's modulus, E in GPa, and compressive strength, σ_u in MPa, were derived from the stress - strain curves for different cured resins. The data are grouped in Table 2. It can be seen that for each set of resins, i.e. those resins based on the same saturated dibasic acid, the values of E and σ_u are reducing with increasing the molecular weight of the glycol. Similarly, for the resins based on the same glycol, the same behavior, regarding to E and σ_u, is obtained. Values of E ranging between 0.4 and 0.992 GPa are obtained here. The obtained values run in harmony with the values reported by Rebeiz et al. (5). They assigned E values of 0.3 and 1.24 GPa for two different UP resins based on recycled poly(ethylene terephthalate).

Careful inspection of the data quoted in Table 2 divulge that it is possible to derive a relation representing the variation of σ_u as a function of EPDB. The data were fitted to the equation: $\sigma_u=94.25+(80.22/EPDB)-(15.29/EPDB^2)$ for which the correlation coefficient is 0.9907. This equation leads to the speculation that one can predict the compressive strength for any particular UP formula by calculating its EPDB value. The regular increase in σ_u with increasing EPDB is being a credit of increasing the cross-linking density. It has been mentioned before that the EPDB depends to a large extent to the molecular weight of both acid and glycol incorporated in the UP molecule. Accordingly, it is obvious that σ_u depends on the molecular weight of the components of UP resin.

An attempt to derive a relation between the Young's modulus, E, and EPDB was performed. This exertion was ineffectual due to the scattering of the data points. However, a general trend of reducing E with reducing EPDB was noticed. When the value of EPDB reduces to 0.197 or less, no Young's modulus is obtained and the resin switches from rigid form to flexible form. This situation is always available when DG and TG are combined with an aliphatic dibasic acid. The flexibility of such resins is attributed to the long chain of both DG and TG. However, when EG is used instead of DG, in the second and third sets, the average length of the glycols is lessened and the rigid character is introduced. It can be seen that the shortening in length is compensated, in the fourth set, by the long SE chain. Consequently, all cured resins comprises DG, TG and SE are flexible.

The above mentioned discussion leads to the speculation that the introduction of a tenuous network of primary chemical-bond crosslinks to the aliphatic chains does not completely restrict the local freedom of motion of these chains. Accordingly, as the length of the polymer segment increases, many conformations can be held and the flexibility increases. This situation is, due in the first set, to the steric hindrance of the phenyl group of PHA, embedded in the polymer segment.

Conclusion

The exotherm temperatures and curing time of unsaturated polyester resins can be controlled by using two types of glycols having different molecular weights for constructing the unsaturated polyester resins. It has been established that the maximum curing temperature is related to the molecular weight of the glycol incorporated in the unsaturated polyester. In this context, T_{max} decreases with the increase in molecular weight, meanwhile, the time to peak temperature t_{max} increases. Similarly, the exotherm temperatures and curing time of unsaturated polyester resins can be manipulated per processing requirements by varying the type of the saturated dibasic acid incorporated in manufacturing the resin. Inclusion of aliphatic dibasic acid with higher molecular weight in conjunction with EG intensively reduces T_{max}. Unsaturated polyester resin, having EG combined with a higher molecular weight glycol would be best suited for processes like large object molding, where a low temperature is desirable. These formulae would definitely benefit the large moulding industries by offering versatility in processing and properties over conventional resins.

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