Polymer Bulletin 34, 377–383 (1995)

Polymer Bulletin

Synthesis and characterization of some novel unsaturated polyester resins containing amide groups

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Received: 26 May 1994/Revised version: 4 January 1995/Accepted: 23 January 1995

Summary

An ethylenically dibasic acid amide was prepared by reacting anthranilic acid with maleic anhydride and characterized by various methods. The unsaturated dibasic acid amide was used for preparing three novel unsaturated polyesters with ethylene glycol (EG), diethylene glycol (DG) and tetraethylene glycol (TG), respectively. The molecular weights of the prepared polyesters were determined by the end group analysis. These polyesters were diluted with styrene / acrylonitrile (AN) mixture to prepare curable resins with inhibited premature gelation. The effect of the structure of the resins on their curing behavior and mechanical properties has been investigated.

Introduction

It has long been known that polymerizable unsaturated polyester resin compositions and specially those derived from mixtures of esters of glycols and ethylenically unsaturated dicarboxylic acids readily react between the ethylenic groups of the polyesters to form useful polymeric products. A mixture of a polyester of maleic or fumaric acid with ethylene glycol, together with an ethylenically unsaturated compound, such as styrene, is an example of such a high-reactive mixture. Such a mixture will commence to gel (i.e., to copolymerize) almost at once, even at room temperature. This undesirable inherent characteristic of copolymerizable mixtures to react prematurely was recognized by Ellis who, in US Patent No. 2,255,313, proposed to inhibit or otherwise control such premature reaction by the addition of an α-cellulose to the composition. Ellis' discovery, while not entirely satisfactory, proved that premature gelation could be inhibited. Subsequently, with the growth of the field of application of copolymerizable resinous compositions in the plastics art, an intensive search was begun for improved means for controlling and/or reducing this tendency of polymerizable compositions to undergo premature reaction (1). The stability of the unsaturated polyester in the latter study was based on adding an amidine salt.

This search centered on providing stable polymerizable compositions comprising an ester of a glycol and ethylenically unsaturated dibasic acid amide and

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mixtures of such esters with copolymerizable ethylenically unsaturated monomer (styrene). The aim of incorporating the amid group, in each building block of the polymer chain, is to elevate the stability of the polymerizable compositions. A further object is to test the characteristics of the obtained resins .

Experimental

All the reagents used were Merck reagent grade otherwise will be specified. Differential thermal analysis was carried out by the aid of DTA cell manufactured by Theta Industries Incorporation, New York, USA. Infrared analysis was performed by Perkin-Elmer spectrometer, model 621. The NMR study was accomplished by Jeol 100 MHz instrument. Solution of 10% of the sample in DMSO, was used, and tetramethylsilane was used as internal reference signal.

***Synthesis of N(2-carboxy phenyl) β-carbamoyl acrylic acid (CPCA)*:** This dibasic acid which has the formula, $HOOC-C_6H_4-$ NH-CO-CH=CH-COOH, was prepared by condensation of anthranilic acid with maleic anhydride according to the method described in reference (2). In this respect a solution of 0.1 mol. maleic anhydride in 100 ml dry benzene was added to a hot solution of 0.1 mol. anthranilic acid dissolved in 100 ml. dry benzene. The mixture was refluxed under continuous stirring while a slow stream of nitrogen gas was applied. The pale yellow precipitate which has been formed, after 1hr reaction time, was filtered and washed several times with hot benzene to remove unreacted anthranilic acid and maleic anhydride. The final product was recrystallize from ethyl alcohol to produce the pure CPCA (yield = 95%).

Synthesis of unsaturated polyesters (UP). The UP resins were prepared by reacting the appropriate amounts of unsaturated dibasic acid (CPCA) and glycol (ethylene glycol (EG), diethylene glycol (DG) and tetraethylene glycol (TG) obtained from Aldrich). The ratio of diacid : glycol was 1 : 1.1 in all cases. Three UP resins were prepared in a one-liter resin kettle equipped with a stirrer, nitrogen gas inlet tube, thermometer and steam and cold water condensers connected in series. Heat was supplied with a standard resin kettle mantle and a thermowach attachment on the thermometer was used to maintain a near constant temperature. The reagents, i.e., glycol and diacid were added to the resin kettle at room temperature and were stirred under nitrogen while being heated to 195°C. Generally a 10 mole-% excess glycol was used to ensure a high hydroxyl to acid number ratio as described in our previous publication (3). At 195°C, a small amount of xylene was added to assist refluxing and this temperature was maintained until water evolution ceased in about 5 hr. Afterwards, the condensers were removed, and the excess glycol and xylene were removed by sparging with nitrogen for 0.5 hr at 195°C. The unsaturated polyester resins were analyzed for acid and hydroxyl values (4, 5), for the sake of calculating the molecular weights via end group analysis, before blending these with the proper monomer to get 40% w/w monomer in the resin.

Determination of peak exotherm. The curing exotherms of unsaturated polyester resins were measured, by Digitron digital differential thermometer, type K, model 3202 with a resolution of 0.1° C, as described in the previous work (6). 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 over the curing reactions. The formulation used for curing was resin / initiator / accelerator = 100 / 2 / 0.2 (parts by weight) (6).

Mechanical properties. The compressive stress-strain diagrams were measured using a Zwick mechanical testing machine as described in the previous work (6).

Results of analysis

The following data were obtained for CPCA: melting point measured by DTA (onset =189°C cf. Fig. **1**); R_f = 0.4 [on "Silufol" plate, eluent: ethylacetate: petroleum ether (vol. ratio 1:1)]. The acid number (determined in acetone solution) = 480 mg KOH/g (theoretical: 477 mg KOH/g). The significant IR absorption bands of CPCA were found at 3400 (s), 3080 (w & broad), 1600, 1690 and 720 (s) cm^{-1} for -OH (carboxyl), -CH=CH- (maleate), C=O (carboxyl), C=O (amide) and benzene ring substitution, respectively.

The IR spectra of UP resins showed typical absorption bands at 3200 (w), 3078 (w & broad), 1720 (s), 1690, 1220, 960 (s) and 720 (s) cm^{-1}. The strong absorption band at 3200 cm^{-1} in the spectrum of CPCA is characteristic of -OH group. For the UP this absorption is weak indicating the esterification. Additional evidence of the ester structure is deduced from the ester absorption band at 1720 cm^{-1} (7). Bands at 1220 and 960 cm^{-1} are due to C=O vibrations of the ester group. Band at 3078 is conform to -CH=CH-. The typical band due to benzene ring substitution in polyesters appears at 720 cm^{-1} (8).The band at 1690 cm^{-1} is relating to C=O vibration of the amide group.

The main NMR resonances (chemical shifts, ppm.) of CPCA were found as follows: 6.2 - 6.4 (two doublets), 7 - 8.5 (multiplete) and 12.0 (singlet) assigned for -CH=CH- (maleate), aromatic protons and -OH proton. In their study on UP from maleic anhydride and 1,5-pentanediol, Larez et al. (7), afforded a value of 6.25 ppm. (singlet) for the chemical shift of -CH=CH-. Meanwhile, in the present study, the NMR resonance for the same group is represented by two doublets in the range 6.2 - 6.4 ppm. This difference in the NMR resonance could be attributed to the symmetric and asymmetric structure of their polymer repeating unit and CPCA, respectively.

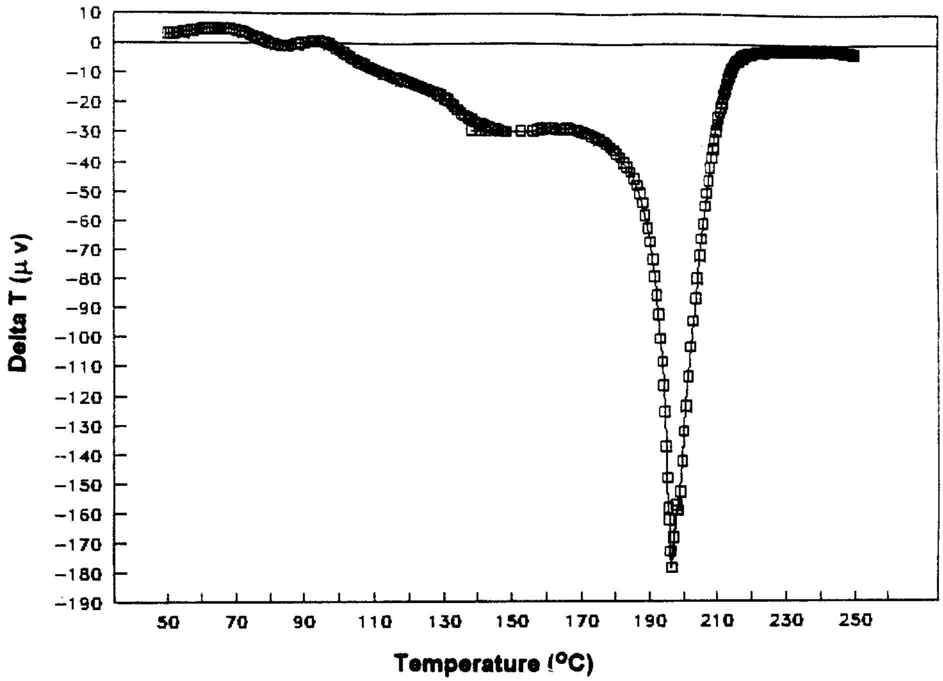


Fig. (1) DTA scan for CPCA

Discussion

Unsaturated polyester resins, prepared by melt polycondensation on the basis of phthalic anhydride, maleic anhydride, and different glycols, have been described recently (3). The present work is an attempt to synthesize UP resins from CPCA as unsaturated dibasic acid and different glycol systems. The CPCA was used to achieve a regular spacing between the unsaturation as well as invoking an amide group in each building block of the unsaturated polyester chain. Implement of amide groups in the polymer chain was aimed to prevent premature gelation of uncatalyzed polymerizable UP resins and accelerate the rate of cure of such resins after the addition of a polymerization catalyst.

Ordinarily it is desirable that the unsaturated polyester polymerizable into an infusible resin so that the proportion of unsaturated components should be such that the polyester contains an average of more than one double bond per polymer molecule (1). The molecular weights of the prepared polymers were determined by the end group analysis. The resultant values are tabulated in Table **1** in conjunction with the acid number of the prepared polyesters. The highest molecular weight, M_n = 2947, was obtained for formula P1 for which EG was used. In the present study, each dibasic acid contains double bond derived from maleic anhydride which has been reacted with the anthranilic acid to form the CPCA molecule. Accordingly, the molecular weights listed in Table **1** reveal that P1, P2 and P3 contain 10, 9 and 8 double bonds/polyester chain, respectively. This finding indicates that the affinity of glycols to react with CPCA reduces with increasing the molecular weight of these glycols leading to a less degree of polymerization.

The solubility of the prepared UP resins in different monomers and monomer mixtures was tested. It has been found that styrene is very poor solvent, while the best solvent for these resins is acrylonitrile (AN) in admixture with styrene (40% AN). It seams that AN enhance the solvation power of styrene monomer. This finding is supported by the cosolvancy effect (9). The prepared UP resins were dissolved in the styrene / AN mixture and the resultant formulae designated here as P1, P2 and P3 for the resins synthesized from EG, DG and TG, respectively.

The curing exotherms of formulae P1-P3 were measured. Since the amount of heat evolved upon curing depends on the sample size, it was desirable to consider this parameter. For this reason it was very important to use glass bottles of the same volume in all measurements to achieve the repeatability of the measurements and affording legitimate comparative study. The heat evolved during cure was plotted versus time in Fig. **2**. The maximum curing temperature, T_{max}, and the time, t_{max}, required to reach the maximum curing temperature were obtained from the graph and tabulated in Table **1**. It can be seen that T_{max} reduced from 58°C to 52°C when EG was replaced by DG. A further reduction to 47°C was obtained upon using TG for constructing the UP resin. This could be attributed to the effect of equivalent polymerizable double bonds (EPDB) where it is the highest in case of P1. As may be seen in Fig. **2** the curing induction period increases by increasing the molecular weight of the glycol incorporated in the polymer chain. This leads to an increase of the time required for complete curing (t_{max}).

Table (1) Acid number (mg. KOH / g polymer), molecular weights, curing behavior and mechanical properties of the synthesized unsaturated polyesters (formulae P1 - P3)

No	Acid No.	M wt.	EPDB	t_{max}(min.)	T_{max}(°C)	σ_u (MPa)	E (GPa)
P1	25.8	2947	0.273	11.0	58.0	148.4	0.861
P2	28.7	3010	0.219	18.5	52.2	137.0	0.781
P3	32.3	3392	0.157	28.0	47.0	128.8	0.532
$^+$1e	17.9$^+$	2438$^+$	0.265	21.0$^+$	108.0$^+$	146.6	0.856

$^+$ data for formula No. 1e published in reference [10]

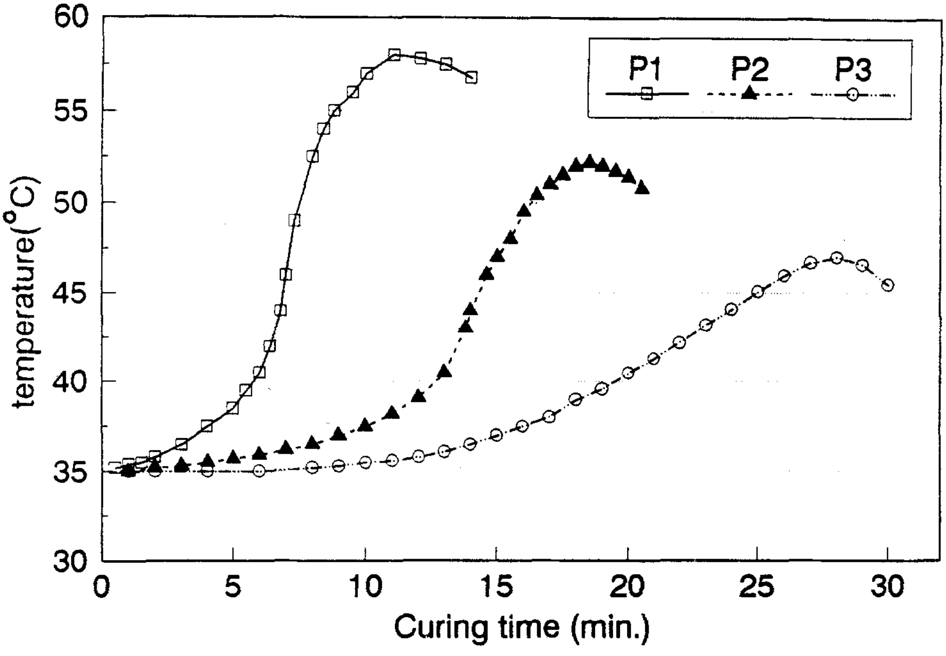
In our previous publication (10), a series of UP resins based on phthalic anhydride maleic anhydride and EG or EG combined with other higher glycols was prepared. The structure of formula No. 1e in this series is similar to the structure of P1 except that the UP chains in the latter formula contain amide groups. The characteristics of formula 1e are shown in last raw in Table 1. Comparing the curing characteristics of these two formulae reveals that inclusion of the amide group accelerates the curing reaction and markedly reduces the heat evolved during cure. This finding afford a new piece of evidence that the structure affecting the amount of heat liberated while curing as well as the curing time.

The compressive strength, σ_u, and the Young's modulus of the cured resins (P1-P3) are also listed in Table 1. The corresponding values for formula 1e were measured and listed in the same table. Comparing the data of P1 and 1e announces that the amide group has no appreciable influence on the mechanical properties. Meanwhile, the EPDB is an important factor to be accounted for.

Conclusion

The present results illustrate that although the inclusion of the amide group markedly accelerates the curing reaction and reduces the heat evolved during cure; this group has no appreciable influence on the mechanical properties.

Fig.(2) Curing exotherms of UP formulae P1-P3.



References

1. Edwin WM, Jerome GK (1958) US Patent No. 2,846,411.
2. Vogel AI (1974) Practical Organic Chemistry, Longman London, p 377.
3. Abdel-Azim AA, Nasr ES, Farhat MS (1994) Polym J 26(4): 423
4. Sorenson WR, Campbell TW (1968) Preparative Method of Polymer Chemistry, Interscience , New York, p.155.
5. Urbanski J, Czerwinski W, Janika K, Majewska F, Zowall H (1977) Handbook of Analysis of Synthetic Polymers and Plastics, Ellis Horwood, Chester, England .
6. Nasr ES, Abdel-Azim AA (1992) Polym advanc Technol 3: 407
7. Larez V, Cristobal J, Perdomo MGA (1991) Polym Bull 26: 313
8. Lehtinen A, Era Mustonen T, Anttalainen E (1980) Makromol Chem, Rapid Commun 1: 499
9. Abdel-Azim AA, Heikki T, Juha M, Franciska S (1993) Polym J 25(7): 671.
10. Abdel-Azim AA, Mahmoud BH, Farhat MS (1994) Polym advanc Technol 5: 269