ELSEVIER

European Polymer Journal 37 (2001) 1075–1078

EUROPEAN POLYMER JOURNAL

Short communication

Reaction mechanism of an unsaturated polyester system containing thickeners

Mangeng Lu [a], Mija Shim [b], Sangwook Kim [a,*]

[a] *Department of Chemical Engineering, The University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, South Korea*

[b] *Department of Life Science, The University of Seoul, Seoul 130-743, South Korea*

Received 3 September 1998; received in revised form 8 August 2000; accepted 4 September 2000

Abstract

The thickening process and curing reaction of unsaturated polyester resins were characterized by viscosity measurement and differential scanning calorimetry when a thickener was involved. Various kinetic parameters were determined by means of dynamic and isothermal experimental data and rheological process. The different values of activation energy reflected the different reaction mechanisms occurred in the curing course. Under isothermal conditions, polymerization reaction is one-order and diffusion-controlled reaction becomes significant when high concentration of thickener was applied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated polyester; DSC; Curing reaction; Kinetics

1. Introduction

Unsaturated polyesters (UPs) have a leading role in the development of glass fiber reinforced products and tremendous versatility with very low costs. The use of UPs in bulk and sheet molding compounds results in composite materials that have high strength, dimensional stability, and very good surface quality [1].

Sheet and bulk molding compounds are chemically thickened compositions. This is generally achieved with group IIA metal oxides and hydroxides, especially with MgO. It is thought that it first interacts with the carboxylic acid group on chains. Then a complex is formed with the salt thus formed and the carboxylic acid groups of other chains, leading to an increase in viscosity [2–4].

Many works on the thickened mechanisms have been performed, but the effects of the thickeners on the curing of UPs and their composites are still not fully clear. Moreover, as well known, the properties of thermosetting polymers and their composites very much depend on the curing process. The determination of the kinetic parameters characterizing the curing process of thermosets can be conducted by differential scanning calorimetry (DSC) measurements [5–10]. In this paper, isothermal and dynamic DSC data, as well as rheological process were used to evaluate the curing process and kinetic parameters for an UP/MgO system.

2. Experimental

The resin used in this study is a commercial UP based on propylene glycol, phthalic anhydride, and maleic acid (POLYCOAT OS-108 for SMC, Aekyung Chemical Co., Ltd.). The resin was supplied with a acid number 19.0, and a styrene content of 32.6%. The molar ratio of isophthalic acid, fumaric acid and propylene glycol is 1:1.74:2.49 by ^{1}H NMR. The initiator for the curing reaction is tert-butyl peroxybenzoate with a purity of 98%. The thickener is a light magnesium oxide with the concentrations of 1–10 wt.%. The thickener was dried prior to use.

---

[*] Corresponding author. Tel.: +82-2-2210-2447; fax: +82-2-2210-2310.

E-mail address: swkim@uoscc.uos.ac.kr (S. Kim).

PII: S0014-3057(00)00198-1

The thickening behaviour of UP resins prior to curing was measured using a Brookfield Synchro-Lectric Viscometer at 20°C. For rheological measurements during curing, a Brookfield (Model DV-II+) Viscometer was used to measure the viscosity change prior to gelation. The gelation time was determined when the sample viscosity started to rise sharply [11].

The calorimetry measurements were made on a SEIKO I-5000 series. Dynamic experiments were performed at heating rates of 5–20 $\min^{-1}$ for a temperature range of 20–300, and isothermal scans are measured at four temperatures between 80°C and 110°C in a nitrogen atmosphere. More details about calibration procedure and thermal conditions can be found elsewhere [6].

3. Results and discussion

3.1. Viscosity variation

The viscosity of the samples containing thickeners increases with maturation time, and then reaches a practical constant. Increasing the content of thickener can result in a higher viscosity since the resin viscosity increase was resulted from the combination of carboxylic groups and MgO [12,13]. Fig. 1 shows the viscosity variation as a function of time for non-thickened and thickened UP resins during cure at different temperatures. The viscosity for both systems decreases with time at the first several minutes, the so-called reduce-period. In fact, during the early stage of cure, the long-chain polyester molecules tend to form a spherical-type microgel structure, and the microgels are only locally distributed and crosslinking is intramicrogel dominated at the early stage. Therefore the viscosity variation in this period is mainly caused by increasing temperature. After that time, the samples start to cure and the viscosity of systems increases rapidly, eventually reach gel [14].

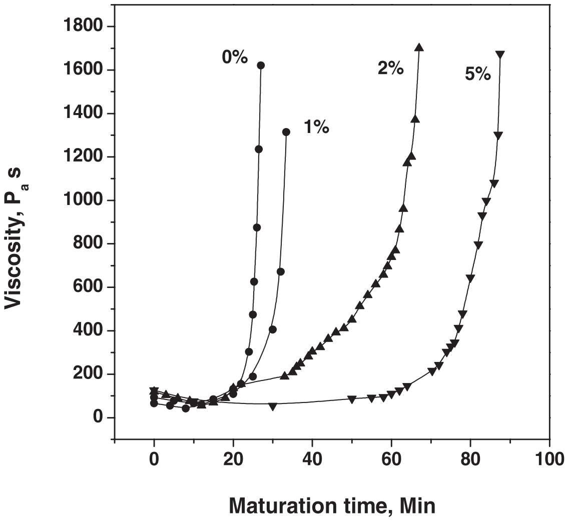

Fig. 1. Viscosity variation as a function of time for UP resins with different contents of thickener cured at 80°C before gelation.

As shown in Fig. 1, the thickened systems show longer gel time because of the high viscosity and the lower reactivity of styrene and, especially, polyester C=C bonds in the microdomains, where the concentration of polyester C=C bonds is getting higher as a result of the gradual aggregation of polyester chain segments consisting of –OOC–CH=CH–COO– units.

3.2. Reaction kinetics

The heat of reaction can be markedly affected by thickeners (Table 1). The values of curing heat slightly decrease with increasing the contents of thickener under isothermal conditions, although extra reaction heat can be generated by the interaction of magnesium ion and carboxyl group. It may be attributed to the relatively decrease of concentration of double bonds, and the much more increase in viscosity of system by chemically thickening.

The dynamic DSC curves are analyzed by means of the simple Kissinger expression by plotting $-\ln(\beta/T_p^2)$ against T_p^{-1}, where β is heating rate, T_p, is the tempera-

Table 1
Kinetic parameters from dynamic scans

Contents of MgO (%)	Dynamic scans					Isothermal scans			
	Heat of reaction ($J g^{-1}$)	$\ln A_1$ ($\min^{-1}$)	$\ln A_2$ ($\min^{-1}$)	E_1 ($kJ mol^{-1}$)	E_2 ($kJ mol^{-1}$)	Heat of reaction at 100°C ($J g^{-1}$)	n	$\ln A$ ($\min^{-1}$)	E_a ($kJ mol^{-1}$)
0	385.8	12.6	22.2	67.5	119.9	248.6	1.08	33.1	115.8
1	372.4	19.4	30.2	67.0	139.9	238.9	1.17	30.2	106.4
2	368.5	20.5	31.6	91.0	144.7	241.6	1.10	32.8	116.2
5	394.0	22.0	28.8	95.9	134.8	220.7	0.82	32.4	115.5
10	371.6	23.7	29.2	101.5	136.3	188.4	0.94	24.9	88.3

ture where maximum conversion rate occurs on DSC curve [15]. The activation energy calculated of 67.5 kJ mol^{-1} to the first peaks is much lower than that of 119.9 kJ mol^{-1} to the second peaks for the pure UP system. It means that the copolymerization of styrene and polyester is much easier than the thermal polymerization. It is a fact revealed by many experiments. It is interesting that the values of activation energy corresponding to the first peaks increased with increasing the contents of thickeners, but kept practically constant for the second peaks. It said that the thickener only affects the copolymerization process of styrene and polyester. It is reasonable since the thermal polymerization is mainly governed by reaction temperature. These results cannot be observed in isothermal experiments where the reaction between styrene and polyester double bond is predominant. In the case of the isothermal experiments, we can estimate the value of n and $\ln k$ for a given experiment by assuming a n-order reaction process.

As a result of thickening, the reduction time and the time to reach the maximum reaction rates in the isothermal curing reaction increased when compared with non-thickened ones. It may be because the initiator efficiency would decrease as the viscosity of the system increases due to the cage effect, such leading to a reduction of formation rate of initiator radicals. However, some controversial results have been reported in literature [4,16].

The values of activation energy for isothermal cures in Table 1 were between the values obtained from the first and second peaks in dynamic experiments. One can consider that thermal polymerization involves in the isothermal curing process since a long curing time was required to reach completion. As can be seen, the value of activation energy for the sample containing 10% of thickener markedly decreased in isothermal condition. Such a decrease in apparent activation energy has been frequently observed in heterogeneous reactions [17]. Therefore, when a large amount of thickener was applied, the diffusional factors become significant because of its high viscosity.

The kinetic parameters also can be derived from the rheological method. The dependence of polymeric viscosity on temperature can be determined by an Arrhenius equation [18]:

$$\eta = A\exp(-E_r/RT) \tag{1}$$

where E_r is activation energy of the rheological process.

Assuming that the viscosity η is inversely proportional to the gel time t_g and using the logarithm of equation (1) results:

$$\ln(1/t_g) = -E_r/RT + \ln A' \tag{2}$$

where A' is pre-exponential factor in min^{-1} (t_g is expressed in min).

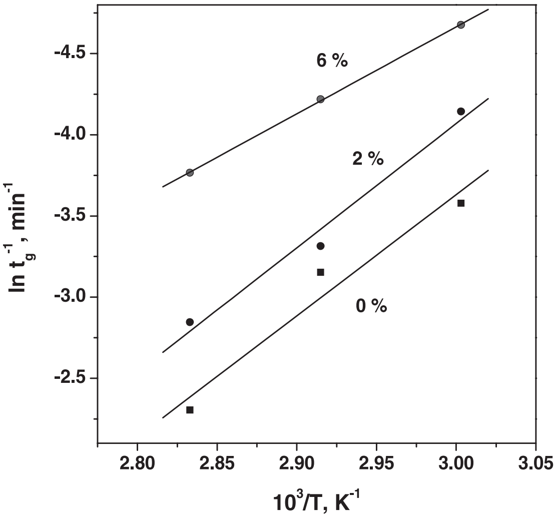

Fig. 2. Graphical determination of the kinetic parameters for gel time.

Plotting $\ln(1/t_g)$ versus $1/T$ (Fig. 2), the kinetic parameters E_r and A' were calculated. The values of activation energy were 62.0, 65.7 and 57.3 for 1%, 2% and 5% MgO thickened systems, respectively, which approximate to the values from the first peaks by dynamic analysis. It is reasonable since the reactions revealed from gel time and the first peak by dynamic scans have a same mechanism, representing a chemical-controlled reaction process.

4. Conclusions

The above discussion demonstrates how the thickener used in molding compounds can affect the curing reaction of UP resin systems. The heats of reaction and various kinetic parameters have been obtained from dynamic and isothermal data. The values of activation energy may reveal the reaction mechanisms occurred in the curing process. At high curing temperatures, thermal polymerization may take place. Under general isothermal conditions polymerization is a first order reaction, but the complete cure has not been reached because of the vitrification or diffusion difficult.

Acknowledgements

This work was supported by Han Yang Petrochemical Co., Ltd. in Korea.

References

[1] Salomone JC. Polymeric materials encyclopedia, vol. 11. Boca Raton, FL: CRC Press; 1996.

[2] Alve FB. J Polym Sci 1971;9:2233.

[3] Rodriguez EL. J Appl Polym Sci 1990;40:1847.

[4] Yu TL, Ma SC. J Macromol Sci-Pure Appl Chem 1993; A30:293.

[5] Lu MG, Shim MJ, Kim SW. Polym Eng Sci 1999;39:724.

[6] Kim SW, Lu MG, Shim MJ. Polym J 1998;30:90.

[7] Lu MG, Shim MJ, Kim SW. Thermochem Acta 1998;323: 37.

[8] Lee DS, Han CD. Polym Eng Sci 1987;27:955.

[9] Gillham JK. Polym Eng Sci 1979;19:676.

[10] Lem KW, Han CD. Polym Eng Sci 1984;24:175.

[11] Huang Y-J, Wen Y-S. Polymer 1994;35:5295.

[12] Reiko S, Wai-Ming JK, Lee LJ. Polymer 1996;37:3567.

[13] Rodriguez E. J Appl Polym Sci 1990;40:1847.

[14] Yang YS, Lee L. Polym Eng Sci 1991;31:321.

[15] Singer HE. Anal Chem 1957;29:1702.

[16] Hang YJ, Hsu TJ, Lee LJ. Polymer 1985;26:1247.

[17] Hill G. An introduction to chemical engineering kinetics and reactor design. Wiley: New York; 1977 [Chapter 12].

[18] Yang YS, Suspene L. Polym Eng Sci 1993;31:321.