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Low temperature cure of unsaturated polyester resins with thermoplastic additives

III. Modification of polyvinyl acetate for better shrinkage control

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Abstract

Copolymers of vinyl acetate and acid monomers were synthesized by emulsion polymerization and applied as shrinkage control additives in the polymerization of unsaturated polyester (UP) and styrene at low temperatures. The presence of acid groups on the copolymer chain changes the selectivity of the cobalt promoter, and in turn, the relative reaction rate in the thermoplastic-rich and the UP-rich phase during polymerization. The kinetic results from differential scanning calorimeter showed that the copolymer containing stronger carboxyl groups tended to attract more cobalt promoter and led to a higher reaction rate in the thermoplastic-rich phase. The dilatometry results confirmed that the increased reaction rate in the thermoplastic-rich phase led to an earlier formation of microvoid and, consequently, less volume shrinkage of the resin during polymerization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated polyester resin; Polyvinyl acetate; Low profile additive

1. Introduction

Interest in the development of low shrinkage or “low profile” unsaturated polyester (UP) resins for low temperature applications has grown considerably in industry in recent years because of the increased applications of new composite manufacturing processes such as low pressure compression molding of sheet molding compound (SMC), resin transfer molding (RTM) and vacuum infusion liquid composite molding (e.g. SCRIMP). The concept of “low profile” refers to the formation of a uniform and smooth surface without flaws such as sink marks, surface waviness and fiber print-through caused by polymerization shrinkage. Low profile additives (LPAs) are generally thermoplastics such as polyvinyl acetate, poly(methyl methacrylate), thermoplastic polyurethane and saturated polyester. They do not participate in the free-radical copolymerization between UP vinylene group and styrene double bond. However, they do cause the formation of a two-phase structure during polymerization, which is generally regarded as the key factor of the shrinkage control or “low profile” mechanism. The low profile mechanism and the effect of LPA type, molecular weight and concentration on the shrinkage control performance of various resin systems have been subjects of extensive studies [1–7], however, most of the work was conducted for resins cured at high temperatures.

In Parts I and II [8,9], we reported the effects of LPA and resin structure on the shrinkage control of resins cured at low temperatures in terms of volume change, morphological change and phase behavior. It was found that the formation of a large scale co-continuous structure constructed by LPA- and UP-rich regions, or an LPA-rich dominated particulate-like structure, is very important for LPA to be effective as a shrinkage control agent. The sample morphology is fixed at the gel point with a conversion lower than 5%. However, microvoid formation that leads to shrinkage compensation takes place in the later stages of cure when the resin conversion approaches the final value. In this study, a hypothesis based on the reaction partition is proposed to explain why volume expansion takes place so late during polymerization. Modified polyvinyl acetates are synthesized according to this hypothesis and their applications as LPAs at low temperature cure explored.

2. Phase separation and reaction partition

The phase separation process during the copolymerization

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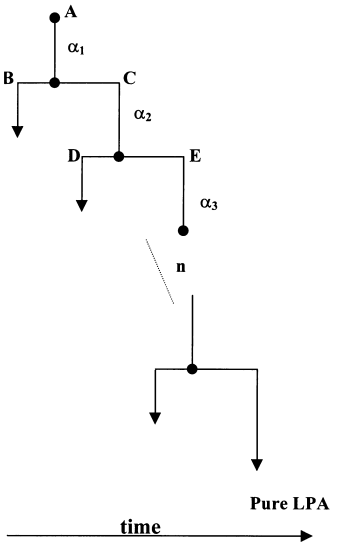

Fig. 1. Schematic of the evolution process of phase separation.

of UP and styrene in the presence of LPAs is quite complicated. The phase structure of the system changes continuously during the reaction [2], and hence the ternary phase diagram can only be established for the initial compatibility of the reactants [5].

Conceptually, the formation and evolution of the LPA-rich phase during polymerization can be qualitatively represented by Fig. 1. The UP/styrene/LPA system starts as a homogeneous mixture A. The phase separation occurs when a conversion α_1 is reached, because of the incompatibility between LPA and the reacted UP. The new phase B is UP-rich with very low LPA concentration. The new phase C contains most of the LPA, together with a certain amount of styrene monomer and UP resin. Thus, further phase separation will mainly occur in phase B. This structure evolves continuously until gelation. After this the macro-scale structure is fixed, but localized phase separation may occur in the two primary phases when the reaction continues.

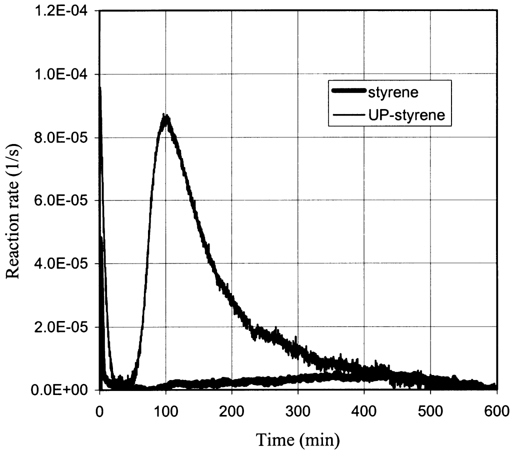

Fig. 2. A comparison of the reaction rate of styrene homopolymerization and UP-styrene copolymerization. Curing agent: 1.5% MEKP, 0.5% cobalt octoate, 300 ppm benzoquinone. Temperature: 35°C.

Table 1
The viscosity increases due to the addition of cobalt octoate for a LPA and a UP resin, which contain carboxyl groups

Viscosity (cP)[a]	LPA-A[a]	UP	PVAc (pure)
Without cobalt octoate	1.96×10^4	9.09×10^2	3.95×10^3
With cobalt octoate	9.53×10^4	2.02×10^3	3.93×10^3

[a] Acrylic modified PVAc, with carboxyl groups.

The phase separation process results in the partition of reactants. Experimentally, the composition of each phase could not be determined easily because of the continuous phase separation during curing. Some indirect measurements, such as phase equilibrium and separation without reaction, were carried out by Huang and Su [10] for UP systems containing different types of LPAs, such as PMMA and PVAc. Their results suggest that the styrene C=C bond and UP C=C bond ratio in the LPA-rich layer is very high.

Similar to monomers, other reaction agents such as promoters and initiators are also partitioned into two phases during phase separation. Thus, reaction rates in both phases are affected not only by the partition of monomers, but also by the partition of the promoter and the initiator. The rate of monomer consumption in each phase may be different due to the differences in monomer and curing agent compositions.

A series of experiments was carried out to verify the aforementioned hypothesis. The UP resin used was Q6585 from Ashland Chemical. The properties of this resin have been described in Part I [9]. The reaction kinetics of styrene homopolymerization and UP-styrene copolymerization (the ratio between the resin double bond and the styrene double bond was adjusted to 2.0 by adding extra styrene) were measured by a differential scanning calorimeter (DSC). The detailed operational procedure can be found in Part II [9]. The curing agents included 1.5% methyl ethyl ketone peroxide (MEKP, Aldrich Chemical) as intitiator, 0.5% cobalt octoate (Pfaltz & Bauer) as promoter and 300 ppm benzoquinone (Aldrich Chemical) as inhibitor. As shown in Fig. 2, the UP-styrene copolymerization is much faster than the styrene–styrene homopolymerization. This implies that the UP-rich phase would gel very fast at the early stage of reaction. However, the LPA-rich phase consisting of a large amount of styrene monomer and non-reactive LPA would react much slower, and may continue to remain in the liquid state after macro gelation [4,10].

The selectivity of the cobalt promoter towards the two phases was also studied. The two thermoplastics studied were acrylic modified polyvinyl acetate (with carboxyl group), PVAc-A from Union Carbide, and a pure PVAc from Aldrich Chemical. It was found that the selectivity of the promoter towards the two phases was quite different.

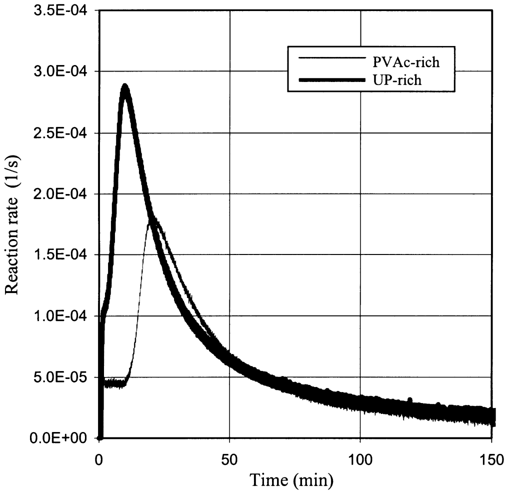

Fig. 3. Comparison of reaction rates at 35°C of the upper (LPA-rich) and the lower (UP-rich) phases of resin A with 3.5% LPA-A, phase separated at −2°C.

When a styrene solution of PVAc-A was mixed with a cobalt type promoter, the solution turned gel-like immediately. This suggests that there exists a certain bonding between the PVAc-A molecule and the cobalt promoter. When the UP resin and the cobalt salt were mixed, a similar viscosity increase was also observed, except that the level of increase was less because of the lower molecular weight of the polyester resin itself. Here, a Rheometrics Dynamic Analyzer (RDA) was used to evaluate the viscosity rise of PVAc-A, UP resin and pure PVAc with and without the presence of 0.5% cobalt promoter. The viscosity was measured at room temperature and at a shear rate of 1 s^{-1}. A comparison of the three is given in Table 1. No viscosity change was observed for the pure PVAc. This phenomenon is quite similar to the thickening mechanism in SMC and BMC compounding, where the alkaline earths, such as magnesium and calcium oxide and hydroxide, are used as thickeners. The high viscosity obtained from the thickening arises from the complexation of carbonyl oxygens of the polyester with available coordination sites of the magnesium of the basic salt [3]. A similar complexation between the carboxyl group of LPA/UP resin and cobalt salt is the source of viscosity increase.

To study this phenomenon further, formulated UP resin, with 6% PVAc, styrene, cobalt promoter and inhibitor were mixed simultaneously so that a transparent (single-phase) mixture was obtained. The mixture was then forced into phase separation by decreasing the temperature to −2°C. It appeared that most of the cobalt promoter went into the UP-rich phase, as the lower phase (UP-rich) was pink (color of cobalt ion), and the upper phase (LPA-rich) was colorless. The two phases were separated, and their reaction rate was measured by DSC at 35°C with 1.5% MEKP. The results show that the polymerization rates of the two phases were quite different, as shown in Fig. 3.

These results suggest that the carboxyl groups of the polyester molecules may attract more cobalt promoter than the carboxyl group of LPA molecules. One possible explanation is that the concentration of the carboxyl group of polyester is much higher than that of the LPA carboxyl group. The other reason is that the acid strength of the polyester carboxyl group is higher than that of LPA, because the polyester carboxyl groups are end groups, while the LPA carboxyl groups are pendant groups. After phase separation, most of the cobalt ions choose the polyester-rich phase. The LPA-rich phase is relatively promoter-lean, which may significantly lower the reaction rate of this phase by influencing the initiator decomposition rate. It should be noted that in the actual reaction, the composition of each phase, and in turn the reaction rate, may not be the same as that obtained here, but the basic trend should be the same. In our optical microscopy experiment [9], it was observed that the UP-rich phase was solid after macro gelation, while the LPA-rich phase was still liquid-like when the sample was pressed. This phenomenon confirms that the LPA-rich phase may react more slowly than the UP-rich phase.

2.1. Modification of PVAc for better shrinkage control

The slow reaction in the LPA-rich phase may have significant effect on both the microvoid formation and shrinkage control. As demonstrated in Part II [9], the volume expansion caused by the formation of microvoids takes place long after gelation, when the resin system is in a solid state for a long time. It is speculated that the low reaction rate in the LPA-rich phase is responsible for the volume expansion occurring at such a late stage. This hypothesis is based on the fact that the LPA-rich phase consists of a large amount of styrene monomer and tends to remain in the liquid state for a long period during polymerization. The stress build-up and microcracking are unlikely when the LPA-rich phase is fluid-like. While a liquid-like material is not favored for microcracking, a solid with very high modulus would also suppress the crack initiation and growth. Ideally, the reaction rate in the LPA-rich phase should be higher than that in the UP-rich phase such that the LPA-rich phase may form a soft solid quickly during curing. When the UP-rich phase starts to react, the internal stress generated by polymerization can be released quickly by microcracking in the surrounding LPA-rich phase or at the interface. Consequently, volume expansion may occur earlier with better shrinkage control as a result.

One method to achieve this goal is to synthesize vinyl acetate copolymers with comonomers containing stronger acid groups. The increase of the acidity of LPA may improve the reactivity of the LPA-rich phase by attracting more promoter, and thereby accelerate the reaction rate in that phase. However, the introduction of carboxyl group would decrease the compatibility between LPA and styrene. Therefore, an optimized content of acid comonomer needs to be determined between a balance of decreasing compatibility and increasing reaction rate.

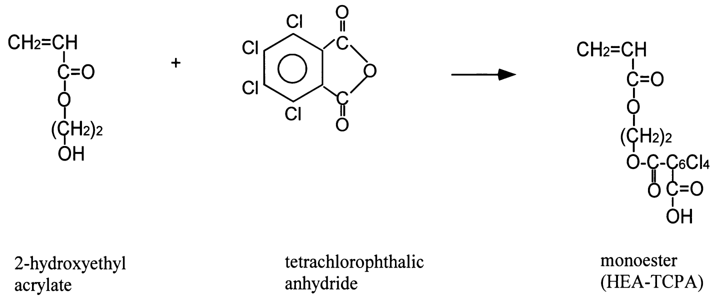

Fig. 4. Synthesis path of the monoester of 2-hydroxylethyl acrylate and tetrachlorophthalic anhydride.

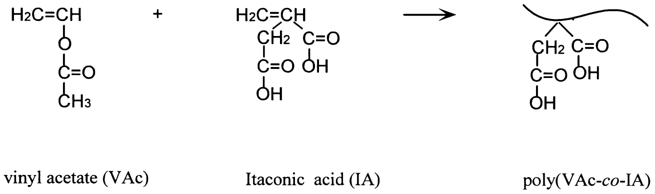

Fig. 5. Reaction scheme of the synthesis of poly(VAc-*co*-IA).

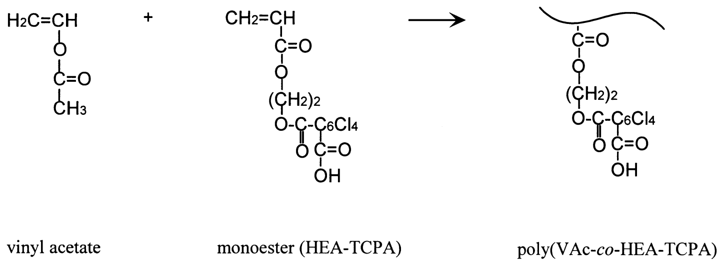

Fig. 6. Reaction scheme of the synthesis of poly(VAc-*co*-HEA-TCPA).

3. Experimental

3.1. Preparation of monomers

Two acid monomers, an itaconic acid (IA, Aldrich Chemical) and a monoester of 2-hydroxyethyl acrylate and tetrachlorophthalic anhydride (HEA-TCPA) were incorporated into the PVAc main chain. Itaconic acid is about twice as acidic as acrylic acid and more reactive than maleic or fumaric acid. Its two carboxyl groups allows the introduction of larger amounts of acidity into the copolymer even at rather low comonomer concentrations.

The monoester of 2-hydroxyethyl acrylate and tetrachlorophthalic anhydride is not commercially available. The acidity of tetrachlorophthalic anhydride is much stronger than that of itaconic acid because the four chloro substituents are the acid-strengthening groups which activate the ring toward nucleophilic substitution. The synthesis process of the monoester is shown in Fig. 4. Tetrachlorophthalic anhydride (Aldrich Chemical) was first mixed with 2-hydroxyethyl acrylate (Aldrich Chemical) in a flask. The mixture was then stirred continuously for about 72 h in a water bath, in which the temperature was maintained at about 48°C to avoid potential side reactions such as the formation of diester at high temperatures. The final mixture of reactants and products was filtered and transferred to a separation funnel and washed with double distilled water. The unreacted tetrachlorophthalic anhydride was separated from the product through filtration, whereas the unreacted 2-hydroxyethyl acrylate (soluble in water) was eliminated by discarding the water phase. The monoester obtained is a light yellow liquid and is unsolvable in water.

Vinyl acetate was used as-received from Aldrich Chemical.

3.2. Synthesis of copolymers

The reaction schemes of the copolymer synthesis are presented in Figs. 5 and 6. Both the comonomers can be introduced into the PVAc main chain directly through the breaking of carbon=carbon bond. The experimental set-up consisted of a five-neck reaction kettle, a reflux condenser, two addition funnels, a gas injector, a thermometer, a mechanical stirrer and a heating mantle. The temperature was controlled within ±2°C through a temperature controller. The general ingredients used are listed in Table 2, in which the mole percent of comonomers varied from 0 to 5% of total monomer phase. The initiator used was potassium

Table 2
General ingredients for the synthesis of the copolymers

Compound	Weight	Percent (mol.%)[a]
Deionized water	100	–
NP-40	20	–
Vinyl acetate	133.3–107	100–95
Itaconic acid	0–2	0–1
HEA-TCPA	0–26.33	0–5
Potassium persulfate	0.607	–
Deionized water	50	–

[a] The mole percent of the monomer is based on the monomer phase only.

persulfate (KPS, Aldrich Chemical), and a non-ionic surfactant, NP-40 from Union Carbide, was employed.

A semi-continuous emulsion process was adopted for copolymer synthesis because of its better control of copolymer composition. Before the reaction, deionized water and surfactant were introduced into the reactor and stirred until the surfactant dissolved in water. An initial charge, about 10 wt.% of monomer phase, was added into the reactor, emulsified sufficiently, and purged with N_2 for 30 min. The temperature was then raised to the desired level (i.e. 75°C), and the initial part of the initiator that was dissolved in a small amount of water was fed into the reactor. The initial charge was polymerized for about 30 min, and the remaining monomers and initiator solution were fed into the reactor continuously within 3 h. After the feeding, the polymerization was continued batchwise for another half an hour. The final latex was broken by adding sodium chloride and stirring rigorously at 85°C. The solid product was washed with water to eliminate the surfactant and salt, dried in an oven, and stored for further characterization.

3.3. Characterization

The composition of the copolymer (the content of acid groups) was determined by titration. A sample with known weight was first dissolved in acetone, and then titrated with 0.01 N alcoholic (methanol) caustic solution.

The molecular weights of the copolymers were measured by gel permeation chromatography (GPC, Water 150C). The measurement was conducted at room temperature with tetrahydrofuran as solvent. The dual detector system consists of an ultraviolet (UV) detector and a differential refractometer (RI) in sequence along the flow direction. The GPC curves were analyzed using the calibration curve obtained with standard samples of monodispersed polystyrene to estimate the molecular weight.

3.4. Cure kinetics

The resin conversion and the reaction rate of UP resins with the copolymers as LPAs were measured by DSC. Again, the ratio between the resin double bond and the styrene double bond was adjusted to 2.0 by adding extra styrene. The level of initiator (MEKP), promoter (cobalt octoate) and inhibitor (benzoquinone) used was 1.5%, 0.5% and 300 ppm, respectively. The detailed operational procedure is the same as described in Part II [9].

3.5. Dilatometry study

The volume change of resins containing the copolymers as LPAs was examined by a dilatometer. The detailed construction and operation procedures can be found elsewhere [7]. The sample weight varied from 5 to 6 g. The measurements were made under a pressure of 0.69 MPa (100 psi) and 35°C.

4. Results and discussion

4.1. Material characterization

Table 3 shows the acid content of copolymers obtained by dissolving copolymers in acetone, and then titrated by potassium hydroxide in methanol. One can see that the acid content of the copolymer is slightly lower than the actual feeding ratio in the synthesis, suggesting that the incorporation of acid comonomers is incomplete.

Table 3
The composition of copolymers examined by titration

	VAc/HEA-TCPA	VAc/HEA-TCPA	VAc/IA
Monomer ratio (mole)	98/2	95/5	99/1
Monomer ratio (wt.%)	8.71	19.80	1.50
Copolymer composition (wt.%)	6.75	17.82	1.36

Table 4
Weight average molecular weights of the synthesized polymers

PVAc	Poly(VAc-co-HT)[a] 98/2	Poly(VAc-co-HT)[a] 95/5	Poly(VAc-co-IA) 99/1
1.87×10^5	1.07×10^5	1.35×10^5	1.38×10^5

[a] poly(VAc-co-HT): poly(VAc-co-HEA-TCPA).

Table 5
Formulations for the dilatometry experiments using synthesized polymers as LPAs

Compounds	1	2	3	4
Resin A	6.197	6.197	6.197	6.197
Styrene	2.302	2.302	2.302	2.302
PVAc	1.5	–	–	–
Poly(VAc-co-HEA-TCPA) (98/2)	–	1.5	–	–
Poly(VAc-co-IA) (99/1)	–	–	1.5	–
Poly(VAc-co-HEA-TCPA) (95/5)	–	–	–	1.5
MEKP	0.15	0.15	0.15	0.15
Cobalt octoate	0.05	0.05	0.05	0.05
Benzoquinone (ppm)	300	300	300	300

The molecular weight of the homopolymer and the copolymers was measured by GPC. The solvent used was tetrahydrofuran, and the evolution flow rate was set at 1 ml/min. The results are listed in Table 4. The vinyl acetate homopolymer has the highest molecular weight among the four polymers. It appears that the addition of acid comonomer tends to slightly decrease the molecular weight of the copolymer. Our previous results [9] indicate that the molecular weight of the LPA can affect the low profile performance of LPAs. However, for PVAc, changing the molecular weight from 190 000 to 90 000 only shifts the first transition point from 3.5 to 4% (i.e. Table 1 in Ref. [8]); therefore, the differences shown in Table 4 are assumed to be negligible.

4.2. Dilatometry study

Table 5 gives the formulations of the samples used in the dilatometry study. Again, the styrene double bond versus UP double bond ratio was adjusted to 2. Benzoquinone (300 ppm) was used as the inhibitor. The initiator system included 1.5% MEKP and 0.5% cobalt octoate. Each sample contained 6% PVAc polymer or copolymer, and was cured at 35°C and 0.6 MPa (100 psi).

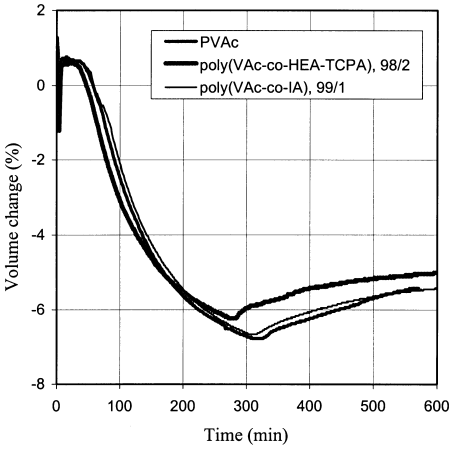

Fig. 7. The volume change profiles of resin A with the acid modified LPAs (6%) cured at 35°C.

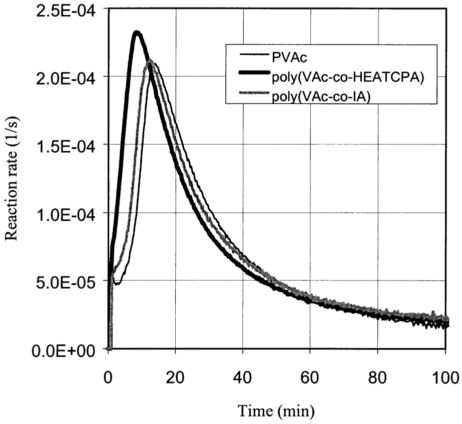

Fig. 8. Comparison of the reaction rate of the LPA-rich phase of three samples containing different LPAs cured at 35°C.

The volume changes as a function of the reaction time (for samples with copolymers) are compared with those with pure PVAc in Fig. 7. All the three samples showed volume expansion but at different times. For the sample containing HEA-TCPA modified PVAc, the volume expansion took place earlier than the other two, i.e. 280 and 315 min. The sample with pure PVAc exhibited the latest expansion. The final shrinkage of the sample with HEA-TCPA modified PVAc was also lower than the other two.

Increasing the content of acid comonomers from 2 to 5% did not improve the shrinkage control. On the contrary, no volume expansion was observed. This can be attributed to the fact that too much increase of COOH group greatly decreases the compatibility of the copolymer with styrene and UP resin. It was difficult to dissolve the copolymer in styrene, and the solution was found to be slightly cloudy.

To confirm the dilatometry results, the reaction rate in the LPA-rich phase needs to be measured and compared among different systems. As the actual reaction rate in each phase

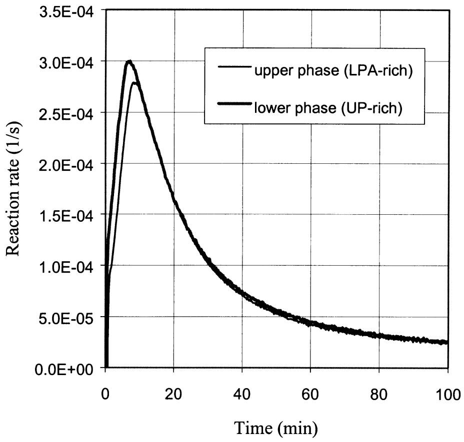

Fig. 9. Comparison of reaction rates of the upper (LPA-rich) and the lower (UP-rich) phases of resin A containing 6% poly(VAc-co-HEA-TCPA) (98/2) at 35°C.

(LPA- and UP-rich) cannot be measured directly during curing, the same “temperature quenching” method employed previously was used here. The same formulations as in the dilatometry test were prepared (the initiator and inhibitor were excluded) and stored at −2°C. The systems were forced to phase separate by decreasing the temperature. Two layers were found after the phase equilibrium. The upper phase was LPA-rich and the lower was UP rich. According to visual observation, the upper phase of the sample containing HEA-TCPA modified LPA had the strongest pink color, whereas the sample with pure PVAc was colorless, suggesting that the former attracted more cobalt into the LPA-rich phase. However, in comparison with the lower phase, the upper phase of all the three samples was still promoter-lean. Kinetic studies were conducted on the upper phase of each sample at 35°C by using DSC. Fig. 8 shows the reaction rate of the three upper phase mixtures. As expected, the sample with HEA-TCPA modified LPA, which has the earliest volume expansion, had the highest reaction rate. The reaction of the sample with IA modified LPA was slightly faster than that with pure PVAc, which implies that the carboxyl group of IA is weaker in competing with the UP carboxyl groups than that of HEA-TCPA.

In comparison with the reaction in its UP-rich phase, the reaction in the LPA-rich phase of the sample with HEA-TCPA modified LPA is still slow (Fig. 9), but the difference between the two phases is smaller in comparison with Fig. 3. This indicates that changing the selectivity of the promoter can improve the shrinkage control, but in a limited range because the LPA-rich phase has less carboxyl groups and higher styrene/UP ratio than those in the UP-rich phase.

These results confirm our hypothesis discussed in the previous section. That is, the late stage volume expansion during curing is caused by the low reaction rate in the LPA-rich phase. Changing the selectivity of cobalt promoter by modifying the LPA structure increased the reaction rate in the LPA-rich phase; consequently, the volume expansion point was shifted to an earlier stage and better shrinkage control was achieved.

5. Conclusion

In this paper, a hypothesis is proposed to explain the late stage volume expansion of UP/styrene/LPA systems at low temperature cure. It suggests that the slow reaction in the LPA-rich phase is the main reason for the microvoid formation occurring in the later stages of polymerization. The low reaction rate in the LPA-rich phase is a direct result of two factors: low promoter concentration and high styrene/UP ratio. The low promoter level in the LPA-rich phase is caused by the selective partition of the promoter due to the complexation between the cobalt ion and the carboxyl groups of UP and LPA.

Copolymers of vinyl acetate and acid monomers such as itaconic acid and HEA-TCPA were synthesized for the purpose of changing the selectivity of the cobalt type of promoter toward the LPA- and UP-rich phase during phase separation. The kinetic results confirmed that the LPA containing carboxyl groups tended to attract more cobalt promoter and had a higher reaction rate than the LPA without carboxyl groups. The dilatometry results demonstrated that in comparison with the unmodified LPA, samples with acid modified LPA showed earlier volume expansion during curing, as a result of faster reaction in the LPA-rich phase.

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