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Effects of inhibitor and cure promoter on unsaturated polyester cure and mechanical properties

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The fast growth of unsaturated polyester (UPE) use in new fields of application demands of fabricators a good knowledge of every formulation parameter on the resin properties. UPEs using various anhydrides, glycols, fillers and low-profile additives have already been studied [1–5] but there is less work on polymerization inhibitor and cure promoter problems [6, 7]. Because a mixture of UPE and vinyl monomers is reactive even at room temperature, polymerization inhibitors are blended to prevent premature reaction or gelation under a wide variety of storage and processing conditions. To control the gel time and final crosslinking, room-temperature promoters are added. Our purpose is the optimization of UPE room-temperature cure formulations for canoe manufacture. The techniques usually used to investigate UPE crosslinking are infrared spectroscopy [1, 2], differential scanning calorimetry (DSC) [8, 9, 15] and rheometry analysis [9, 10]. The mechanical behaviour of cured material is tested by the three-point bending test [3].

UPE curing is a free-radical copolymerization between polyester unsaturated groups and styrene double bonds. The kinetics of copolymerization seems to be near-azeotropic during the first stage of reaction [7, 11], where the free-radical concentration remains constant and depends on the initiator concentration and cure promoter. Intramolecular reactions link adjacent polyester chains molecules and form spherical structures called microgels [12]. This first stage of reaction may also be sensitive to inhibitors because of their free-radical consumption. As copolymerization proceeds, the concentration of microgels increases and leads to macrogelation. At this stage of reaction there is a dramatic increase in free-radical concentration that is called autoacceleration [13]. After gelation the reaction is no longer near-azeotropic, and styrene conversion proceeds faster than polyester unsaturation conversion. Styrene is then the only molecule able to diffuse into microgel particles at this later stage of cure. The rate of styrene conversion depends on the initiator and cure promoter rates [7]. Inhibitor influence was not studied, but we can presuppose that it is an important factor in UPE cure.

In this letter the reaction kinetics is investigated by viscosimetric gel-time measurements. The final conversion is calculated from DSC and mechanical

performance tested with the three-point bending method. The experimental plan allows us to study the relative influence of several parameters on UPE cure.

Unsaturated polyester resins were studied without fibres. They were made from mixtures of maleic anhydride (AM) or orthophthalic anhydride (AP) and propylene glycol and diluted in 40% styrene. Diallyl phthalate (DAP) could be added as specified in Table I. UPE resins at level 1 had a molar ratio AM/AP = 2/1 and level 2 contained only maleic anhydride. Their molecular weight determined by gas-phase chromatography was $M_n = 2400 \text{ g mol}^{-1}$, and $I_a = 20 \text{ mg KOH g}^{-1}$. Standard formulations of UPE contain about 100–200 p.p.m. of free-radical inhibitor. To prevent premature gelation during polyesterification our resins were never given less than 35 p.p.m. benzoquinone (BQ). The maximum amount used was 155 p.p.m. di-*tert*-butyl hydroquinone (DTBHQ) or *tert*-butylcatechol (TBC). Inhibitors were Aldrich products. Two free-radical initiators (Butanox M50 and LPT, AKZO) which are methylethylketone peroxides in a phthalate solution were used to start the cure reaction. Cobalt octoate was used as cure promoter at 6% in a phthalate solution (AKZO).

Each UPE resin studied was formulated according to an experimental plan. An L16 Tagushi matrix [14] was used with eight factors having each of two possible values. The chosen experimental factors are listed in Table I. In the L16 matrix columns 1, 2, 4,

TABLE I Experimental factors and their values

Factors	Columns attributions	Level 1	Level 2
AM/AP ratio	8	2/1	1/0
Monomer	12	Styrene	Styrene + 10% DAP
Peroxide	11	Butanox M50 ^a	Butanox LPT ^a
Peroxide concentration (%)	1	1	2
Inhibitor	4	BQ + TBC	BQ + DTBHQ
Inhibitor concentration (p.p.m.)	6	35 ^b	155
Cure promoter concentration (%)	5	0.15	0.30
Post-cure	2	None	48 h at 50 °C

^aAKZO commercial peroxides.

^b35 p.p.m. is the minimum concentration of inhibitor to avoid gelation during polyesterification.

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5, 6, 8, 11 and 12 are allocated to factors and columns 3, 7, 9, 10, 13, 14 and 15 represent interactions between factors. Experimental results were computed with a fractional factorial design that allowed us to calculate the magnitude of the main effects and the two-factor interactions.

Factor effects that were appreciable for gelation time (Fig. 1) were the inhibitor concentration and inhibitor type. Other factors like cure promoter or initiator concentration were not found as important as the inhibitor in the UPE cure kinetics. The gel time extended from 2.2 to 25.2 min for our tested formulations. 155 p.p.m. of inhibitor raised the gelation time and could even lead to two separate gelation phenomena, which is not beneficial for cured resin performance. The use of 35 p.p.m. inhibitor was often weak in preventing gelation during long room-temperature storage. For high inhibitor concentrations the choice of inhibitor is very important. As a general rule the quinones are good high-temperature inhibitors while hydroquinones are good low-temperature inhibitors. In our formulations benzoquinone was added to prevent gelation during polyesterification and TBC or DTBHQ to improve resin storage. The use of BQ with TBC increased the gelation time while BQ with DTBHQ reduced it.

UPE formulations seem to support longer storage with BQ-DTBHQ mixtures. TBC is a good inhibitor that is still active at high temperature [6] while DTBHQ is only efficient at room temperature. The use of UPE resins for room-temperature cure applications forces inhibitors to be efficient when no initiator is added, and to let the reaction proceed when the temperature increases with a reaction exotherm. The best inhibitor mixture for our formulations was BQ-DTBHQ. For linear polymerization, inhibitors have a well-known retardant effect but the final polymer can often reach its optimal properties in a longer time. For thermoset materials things are different, because gelation occurs at low conversion and reduces the molecular mobility. The curing reaction is in some cases stopped before autoacceleration takes place and this leads to a poorly crosslinked material.

The calculated final conversion (Fig. 2) after 48 h room-temperature reaction varied from 38 to 99%. When annealing was conducted during 48 h in a 50 °C oven the minimum degree of conversion obtained was 86%. One important factor was initiator concentration that increased the crosslinking for 2% peroxide. The increase of free-radical concentration (depending on the initial initiator concentration) increased the rate of intermicrogel reaction. This is due to closely overlapped microgels (polyester C=C bond conversion is high at the first stage of reaction) restricting styrene monomers from diffusing into microgels. Styrene conversion goes faster in the intermicrogel reaction, leading to a higher UPE crosslinking density. An interaction between initiator concentration and annealing shows us that annealing is only useful in the case of low initiator concentration. The final conversion of 1%

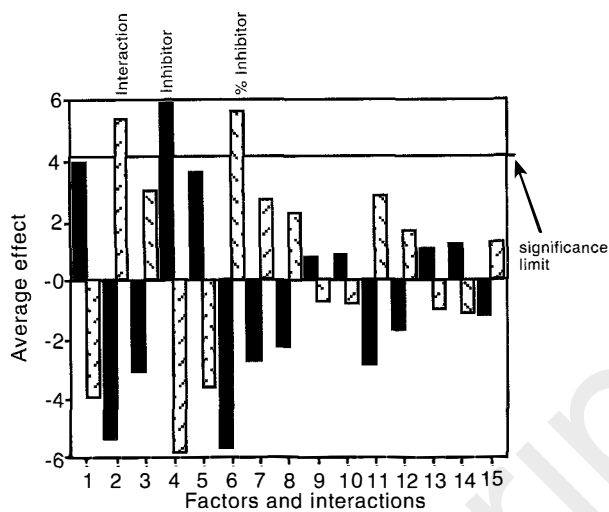


Figure 1 Taguchi experimental plan results for UPE gel time. Average effects and significance limit are calculated with factors at (■) level 1, (□) level 2.

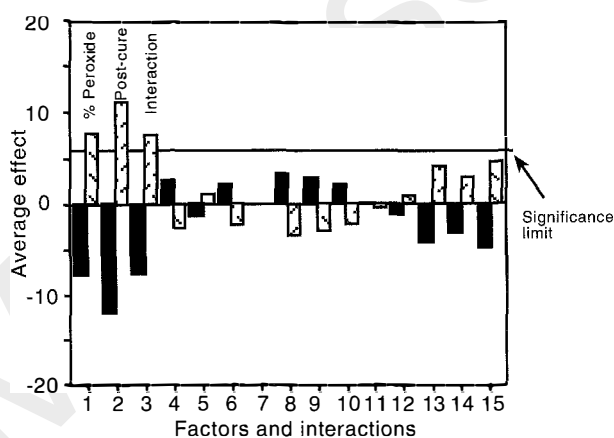


Figure 2 Taguchi experimental plan results for UPE final conversion. Average effects and significance limits are calculated with factors at (■) level 1, (□) level 2.

peroxide formulations after annealing was the same as for the 2% formulations without annealing. For high initiator concentrations, styrene conversion goes fast and then increases the crosslinking density. For low peroxide concentration, styrene conversion is stopped at a lower conversion rate and annealing allows styrene molecules to diffuse into microgels to increase the crosslinking.

Inhibitors and cure promoters have an appreciable effect on the final UPE conversion. High promoter concentration leads to a high crosslinking density while a high inhibitor concentration lowers it. When annealing is conducted on UPE cured material these factors have no effect because of free styrene diffusion.

The final UPE conversion was about 90% for most of the formulations, but we needed to ask whether the mechanical performance was the same for all cured materials (Fig. 3). The flexure modulus calculated for cured resins with a three-point bending test extended from 200 to 5800 MPa after 48 h cure at room temperature. Influential factors were the initiator and inhibitor concentration, and the extent of annealing. These factors also influenced

the final conversion before annealing. However, when a post-cure was conducted the inhibitor effect on crosslinking density was no longer appreciable but was appreciable on flexure modulus. This means that the way that the copolymerization reaction proceeds has an influence on the mechanical performances of cured resins. Even if residual styrene is able to increase the final conversion during annealing, the flexure modulus will not reach such high values as when styrene conversion proceeds faster during the room-temperature reaction. The BQ + DTBHQ mixture increases the flexure modulus after room-temperature curing. The addition of diallyl phthalate in UPE formulations leads to low flexure moduli due to the poor miscibility of styrene and DAP.

The curing of unsaturated polyester needs to take into account factors such as free-radical initiators and cure promoters. The inhibitor mixture is also influential on the cure kinetics and mechanical properties. Benzoquinone–di-*tert*-butyl hydroquinone mixtures provides a high reaction rate and high flexure modulus for cured material. Post-curing is a good way to improve the final conversion, but the mechanical properties will not reach such high values as for fast initial cure formulations.

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References

1. V. C. J. LAREZ and G. A. PERDOMO MENDOZA, *J. Appl. Polym. Sci.* **43** (1991) 1605.
2. M. PAAUW and A. PIZZI, *ibid.* **42** (1991) 1377.
3. G. CHRETIEN, "Matériaux composites" (Lavoisier, Paris, 1986) p. 65.
4. G. D. CHEEVER, *J. Coating Technol.* **50** (1978) 645.

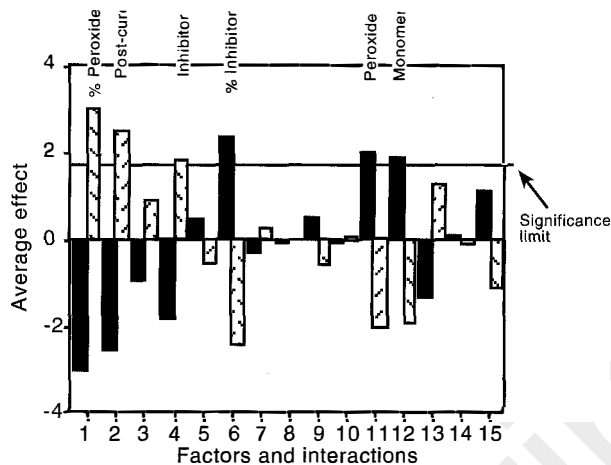


Figure 3 Taguchi experimental plan results for UPE flexure modulus. Average effects and significance limit are calculated with factors at (■) level 1, (□) level 2.

5. M. R. KAMAL and S. SOUROUR, *Polym. Eng. Sci.* **13** (1973) 59.
6. G. A. SCHULTZ, in Proceedings of 26th annual Technical Conference on Reinforced Plastics, Vol. 4b (1971) p. 1.
7. Y. J. HUANG and J. S. LEU, *Polymer* **34** (1992) 295.
8. S. Y. PUSATCIOGLU, A. L. FRICKE and J. C. HASSLER, *J. Appl. Polym. Sci.* **24** (1979) 937.
9. M. J. M. ABADIE and D. SAKKAS, *Eur. Polym. J.* **28** (1992) 873.
10. G. TIEGHI, M. LEVI and A. FALLINI, *Polymer* **33** (1992) 3748.
11. F. R. TOLLENS and L. J. LEE, *ibid.* **34** (1993) 29.
12. Y. S. YANG and L. J. LEE, *ibid.* **29** (1988) 1793.
13. M. R. KAMAL and S. SOUROUR, *Polym. Eng. Sci.* **13** (1973) 59.
14. J. F. SCUOTTO, D. MATHIEU, R. GALLO and R. PHAN-TAN LUU, *Bull. Soc. Chim. Belg.* **94** (1985) 897.
15. C. D. HAN and K. W. LEM, *J. Appl. Polym. Sci.* **28** (1983) 743.