Cure of unsaturated polyester resins: 2. Influence of low-profile additives and fillers on the polymerization reaction, mechanical properties and surface rugosities

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The effects of poly(vinyl acetate) (PVAc) and $CaCO_3$ on the cure kinetics, mechanical properties and surface rugosities of unsaturated polyester (UP) resins were studied. When the ratio of styrene to UP unsaturation was kept constant, PVAc did not have any effect on cure kinetics, maximum conversion or glass transition temperature of the crosslinked UP resin. The addition of $CaCO_3$ led to a decrease in the induction period of the copolymerization, without any significant action on the subsequent cure rate. The addition of PVAc was only effective in promoting an excellent copy of the mould surface at concentrations higher than the critical one leading to co-continuous structures (8 wt% for the formulation used in the present study). The use of PVAc at concentrations beyond the critical value did not produce further improvements in the surface quality. The simultaneous use of both PVAc and $CaCO_3$ in UP formulations led to materials with very low strength and impact resistance, and with only a moderate ability to reproduce the mould surface.

(Keywords: unsaturated polyester resins; poly(vinyl acetate); low-profile additives; fillers; cure kinetics; mechanical properties; surface roughness)

INTRODUCTION

Low-profile additives (LPAs) are used in unsaturated polyester (UP) formulations to improve the surface quality of the moulded part, compensating for resin shrinkage. Acid-terminated poly(vinyl acetate) (PVAc) is widely used as an LPA, particularly in sheet moulding compound (SMC) formulations. Phase separation occurs at the very beginning of the reaction[1,2]. At low concentrations of PVAc the final morphology is composed of discrete particles of the LPA dispersed in the cured UP matrix; at concentrations higher than a critical value, a co-continuous structure is obtained[3,4]. These co-continuous regions promote cavitation in response to tensile stresses arising from internal thermal — and cure — contractions in the presence of mechanical constraints[5]. This explains their action as LPAs.

Fillers are normally used in SMC and BMC (bulk moulding compound) formulations to improve the elastic modulus and reduce costs. Calcium carbonate is widely used for these purposes.

Although the effects of both LPAs and fillers on the cure kinetics were reported in several papers[6–13], results are still controversial. While Kubota[6] found a very small effect of a low-profile additive (cellulose acetate butyrate) on the cure kinetics, Han and coworkers[8–12] reported lower reaction rates and final degrees of cure when using an LPA. A decrease in the final conversion was also reported by Kiaee *et al.*[13]. However, as PVAc is available in a styrene solution, most of the reported results show both the influence of PVAc and the simultaneous change in the ratio of styrene (S) to UP double bonds (E).

Regarding the effect of $CaCO_3$, there is a consensus that it accelerates the rate of cure[6–8]. A decrease in the final conversion with increase in filler content was also observed[6].

The aims of the present paper are: (a) to study the effect of PVAc and $CaCO_3$ on the cure kinetics, while keeping constant the ratio of unsaturations (S/E); and (b) to analyse the influence of PVAc and $CaCO_3$, individually and combined in a single formulation, on mechanical properties and surface rugosities. The effect of different morphologies (discrete particles of LPA *versus* co-continuous structure) will be discussed.

EXPERIMENTAL

Materials

The unsaturated polyester (UP) resin was a commercial

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product based on 2 mol maleic anhydride, 1 mol isophthalic acid, 2.34 mol propylene glycol and 1.17 mol dipropylene glycol. The double-bond content was 3.02×10^{-3} mol g^{-1} and the acid value was 17 mg KOH g^{-1}. It was available as a solution containing 30 parts by weight of styrene monomer to 70 parts of resin. Extra styrene was added to obtain a ratio of styrene (S) to UP double bonds (E) equal to S/E = 2.7. This particular value lies in the range of S/E values where the maximum glass transition temperature (T_g) of cured products was obtained[14].

The initiator was benzoyl peroxide (BPO) in an amount of 1.5 wt%.

The low-profile additive was LP40A (Union Carbide), a 60/40 mixture of styrene with an acrylic-acid-terminated poly(vinyl acetate) (PVAc). In order to keep the ratio S/E equal to 2.7, the maximum amount of PVAc that could be incorporated into the formulations was 13.2 wt% (the addition of higher amounts would have required partial evaporation of styrene from the UP or the PVAc solutions). When preparing formulations with lower concentrations of PVAc, extra styrene was added to get S/E = 2.7 in every case.

The mineral filler was a finely ground limestone ($CaCO_3$) with particles in the range 1–25 μm, with a mean of 15 μm.

Blending of all ingredients was carried out at room temperature with manual stirring. In order to prepare specimens for mechanical tests, solutions were degassed, poured into a glass plate mould provided with spacers of different thicknesses, and cured in an oven at a constant temperature in the 65–140°C range, followed by a post-cure at 140°C for 30 min. Cure times were selected so as to obtain the maximum conversion after the post-cure step[14].

Techniques

Scanning electron microscopy studies (SEM, Philips 505) were carried out on Au-coated fracture surfaces, produced after immersion in liquid nitrogen. A previous etching in dichloroethylene or methyl ethyl ketone, for 30 min, was used to dissolve most of the PVAc present in the fracture surface (together with the sol fraction[1]).

Differential scanning calorimetry (d.s.c., Mettler TA3000) was used to obtain conversion *versus* time curves at constant temperatures. The induction period was defined as the time necessary to observe a significant departure of the d.s.c. signal from the baseline. Dynamic scans were used to determine the influence of additives on the overall heat of reaction. The T_g of cured materials was measured by thermal mechanical analysis (t.m.a., Mettler TA3000), as described in a previous paper[14].

Flexural experiments were conducted at room temperature using a three-point-bending assembly attached to a mechanical testing machine (Instron 1125). Sample dimensions and crosshead speed were selected according to ASTM standard method D790. Values of flexural modulus E and flexural strength at failure were obtained from the resultant load–displacement curves.

Impact tests were carried out at room temperature using a Charpy three-point-bending pendulum (Tonindustrie), according to DIN-53453 standard procedure.

Surface rugosities were measured using a Talysurf 5-120 device (Rank–Taylor–Hobson). It basically consists of a pick-up provided with a special point that measures the vertical distances between 'hills' and 'valleys' present in the surface along a certain length of the specimen. The average surface rugosity R (μm) is defined as the average of maximum heights observed in five different measurements. In order to prepare the specimens for this characterization, one of the plaques of the mould was replaced by a special glass plaque with a very low surface rugosity. The ability of different formulations to copy this low-rugosity surface was then established.

RESULTS AND DISCUSSION

Morphologies generated in PVAc–UP formulations

The phase separation process taking place in PVAc–UP formulations has been studied by several researchers[1–4]. A change from particulate to co-continuous morphology occurred at a PVAc concentration between 8 wt% and 16 wt% for one system[3], and at a concentration of 5 wt% for another formulation[4].

The effect of varying PVAc concentration on morphologies generated in our system is shown in *Figure 1*. At 2 wt% and 4 wt% PVAc the LPA is randomly dispersed as discrete particles. At 5 wt% PVAc a transition to the co-continuous structure begins to take place. At 8 wt% PVAc the structure becomes co-continuous. The nodules are crosslinked polyester microparticles, forming a continuous macronetwork which is insoluble in organic solvents. The PVAc, which was washed out by the previous etching in a solvent, was distributed around the microparticles and formed the other continuous phase.

Specimens with 5 wt% or less PVAc were translucent, whereas those having 8 wt% or more PVAc were opaque. In fact, this constitutes a rapid way to characterize the critical PVAc concentration at which the co-continuous structure is obtained.

Influence of PVAc on cure kinetics

Table 1 shows the overall heats of reaction as a function of the PVAc content. On a total mass basis, the addition of PVAc decreases the heat of polymerization. However, when expressed per mole of double bonds (or per unit mass of resin devoid of PVAc), the heat of reaction becomes constant within experimental error. This means that the final conversion of double bonds does not depend on the PVAc content.

Figure 2 shows conversion *versus* time curves for formulations containing various percentages of PVAc, cured at 85°C. It is observed that when the S/E ratio is kept constant, there is no significant influence of the LPA on the cure kinetics. A similar result was obtained by Kubota[6] using cellulose acetate butyrate as a low-profile additive. Lower reaction rates reported by other authors[8–12] may be ascribed to variations in the S/E ratio among the various formulations and/or to a fractionation of the initiator (used in small amounts) in the PVAc-rich phase segregated during the polymerization.

The glass transition temperature of the crosslinked UP was not affected by the presence of PVAc in the formulation (T_g was close to 130°C for every formulation). This means (a) that PVAc was fully segregated from the UP matrix and (b) that PVAc did not significantly affect the structure of the resulting network. Our results are contrary to the statement that the T_g values of UP matrices are, in general, lowered by low-profile additives[15].

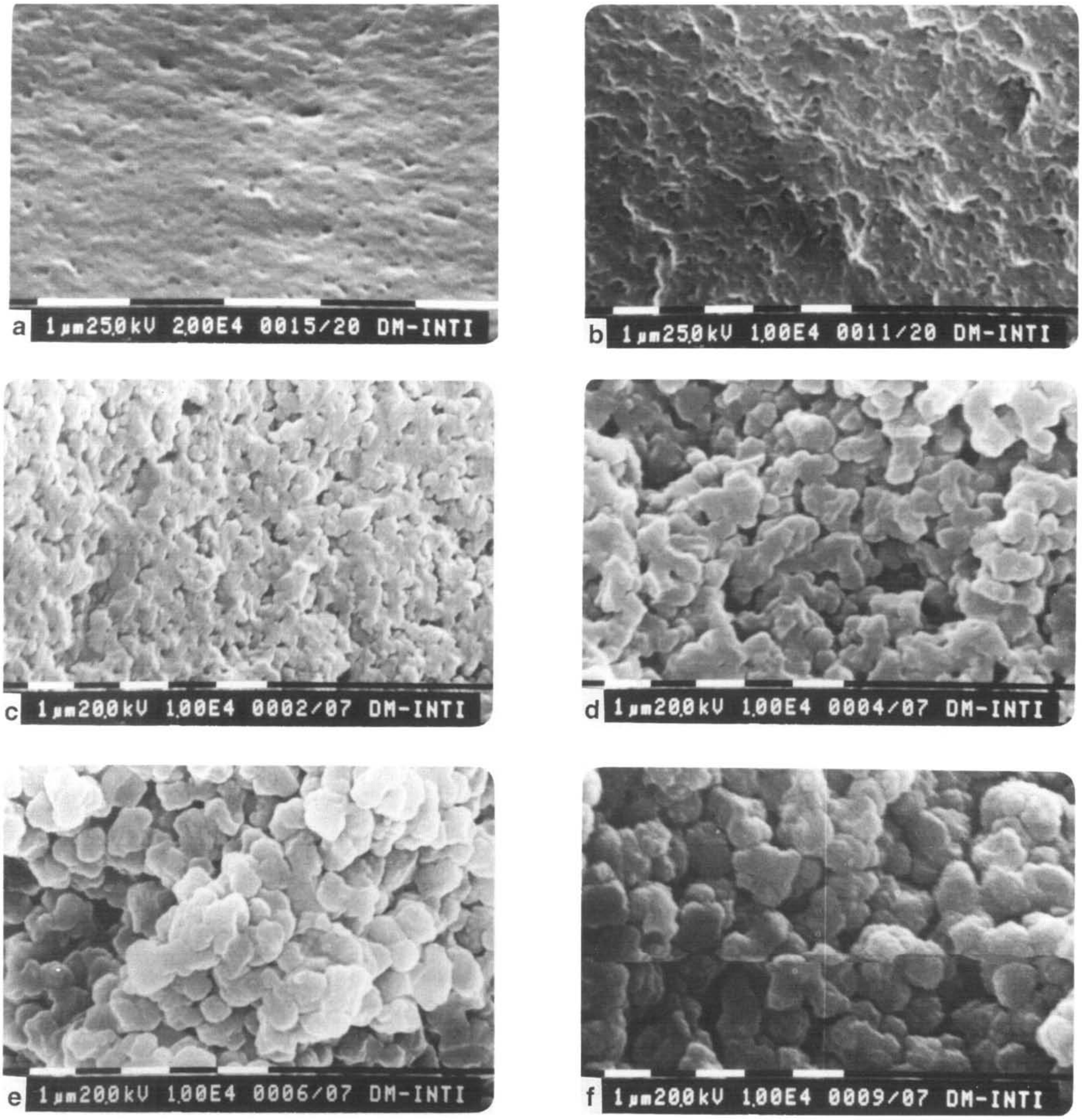

Figure 1 Scanning electron micrographs of fracture surfaces corresponding to blends containing a constant ratio of S/E=2.7 and various concentrations of PVAc: (a) 2%, (b) 4%, (c) 5%, (d) 8%, (e) 11% and (f) 13.2%

Table 1 Overall heat of reaction as a function of PVAc content for formulations with S/E=2.7

PVAc (wt%)	ΔH (J g^{-1})	ΔH (J mol^{-1})
0	404	66.1
5	377	65.0
8	371	65.9
11	351	64.5
13	345	65.3

Influence of CaCO$_3$ on cure kinetics

Formulations with S/E=2.7 and containing various amounts (wt%) of CaCO$_3$ were cured at 75°C in the d.s.c. *Table 2* shows the resulting induction times (the mass of sample was always the same to avoid any effect of varying the oxygen/resin ratio in the d.s.c. pans)[16].

The decrease in the induction time with the increase in CaCO$_3$ content is the main effect of the filler on the kinetics. The slopes of the conversion *versus* time curves after the beginning of the reaction were practically not affected. Our results are consistent with previous experimental observations revealing that the rate of cure is increased in the presence of a filler[6–8]. However, we suggest that the action of CaCO$_3$ is to reduce the inhibition period. This may be due to a preferential adsorption of the inhibitors present in the formulations, including dissolved oxygen, which is a usual co-inhibitor of these formulations[16].

The overall heats of reaction arising from dynamic

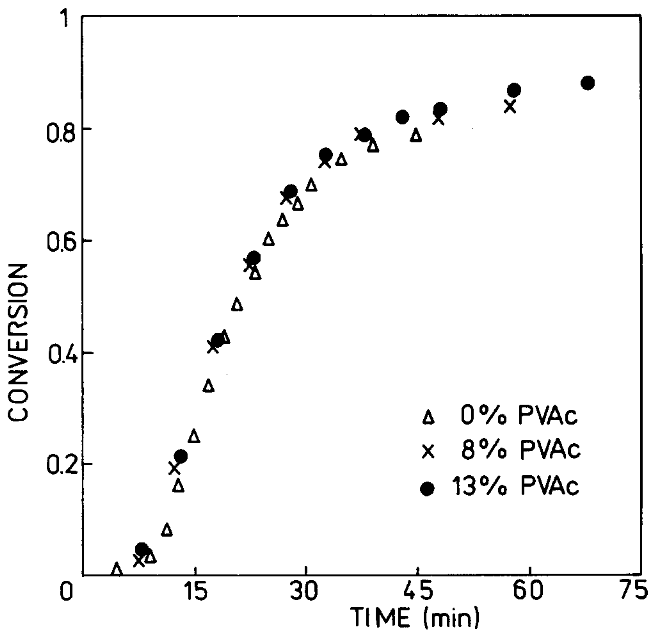

Figure 2 Conversion *versus* time curves for formulations containing a constant ratio of S/E = 2.7 and various concentrations of PVAc, cured at 85°C

Table 2 Induction times at 75°C and overall heats of reaction arising from dynamic d.s.c. runs, as a function of the $CaCO_3$ content in the formulation (S/E = 2.7)

$CaCO_3$ (wt%)	Induction time (min)	ΔH (J mol^{-1})
0	26	66.1
20	23	67.6
40	18	61.9
60	6	59.7

Table 3 Influence of PVAc and $CaCO_3$ on mechanical properties of crosslinked UP resins (S/E = 2.7)

Formulation	Flexural modulus (GPa)	Flexural strength at failure (MPa)	Impact energy (arbitrary units)
Resin (S/E = 2.7)	3.8	110	3
Resin + 60 wt% $CaCO_3$	8.7	50	1.5
Resin + 13.2 wt% PVAc	3.0	65	2
Resin + 60 wt% $CaCO_3$ + 13.2 wt% PVAc	6.3	30	1

d.s.c. runs are also shown in *Table 2*. Although a small decrease in the heat evolved per mole of double bonds is observed, in agreement with results reported by Kubota[6], this fact must be taken with caution owing to the effect on the recorded heat of the great incidence of small fluctuations in the actual amount of filler. This was confirmed by the fact that the final T_g was not affected by the $CaCO_3$ content, within experimental error.

Influence of PVAc and $CaCO_3$ on mechanical properties

Table 3 shows the influence of both LPA and filler on mechanical properties. The addition of 13.2 wt% PVAc produces a decrease in flexural modulus, flexural strength at failure and impact energy, as reported by other authors[4,15]. The co-continuous resin/PVAc blend is very weak from the mechanical point of view.

The addition of a filler increases the elastic modulus but leads also to a significant decrease in both the flexural strength and the impact energy. The easy debonding of the crosslinked UP resin from the filler surface (*Figure 3*) gives an explanation of the weakness of these structures.

The addition of both PVAc and $CaCO_3$ leads to a composite with a higher elastic modulus than the one of the pure resin alone, but showing a dramatic decrease in both the flexural strength and the impact energy.

Influence of PVAc and $CaCO_3$ on surface rugosities

Table 4 shows the effect of additives on average surface rugosities R (μm). The glass plaque used as a reference had a value of $R = 0.05\ \mu$m. The crosslinked UP resin without additives could not copy the reference glass plaque, and showed a value of $R = 0.29\ \mu$m. Addition of PVAc led to a significant improvement of the surface quality. For PVAc concentrations lying in the range giving co-continuous structures, the surface quality was almost the same as that of the mould, i.e. $R = 0.06$–$0.08\ \mu$m. Increasing the PVAc content over the critical value did not produce any improvement in the surface quality.

Addition of $CaCO_3$ led to a significant increase in the surface rugosity. By adding PVAc to these formulations, there was an improvement but the performance was far from that obtained with samples devoid of filler.

These observations show that the action of an LPA is better evaluated through direct measurement of surface rugosities of moulded parts instead of the usual indirect

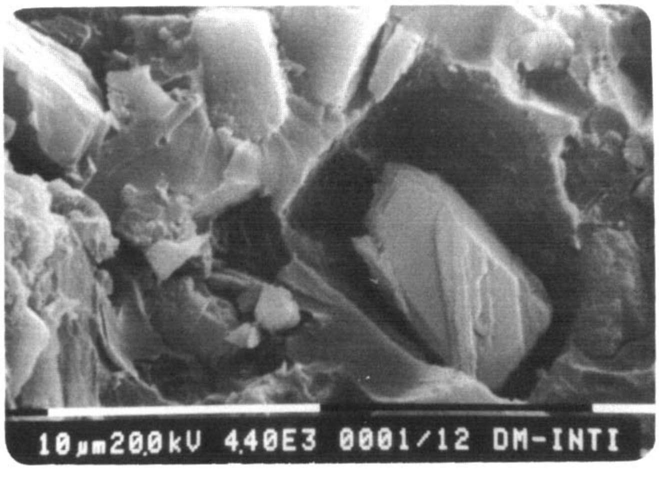

Figure 3 Scanning electron micrograph of a fracture surface for a formulation with S/E = 2.7, containing 60 wt% $CaCO_3$. The debonding of filler particles from the crosslinked resin is evident

Table 4 Effect of additives on average surface rugosities R (μm)

Sample	R (μm)
Reference glass plaque	0.05
Crosslinked resin	0.29
Resin + 5% PVAc	0.14
Resin + 8% PVAc	0.07
Resin + 11% PVAc	0.06
Resin + 13% PVAc	0.08
Resin + 60% $CaCO_3$	0.44
Resin + 60% $CaCO_3$ + 11% PVAc	0.17
Resin + 60% $CaCO_3$ + 13% PVAc	0.18

measurement of shrinkage during cure, i.e. simultaneous addition of PVAc and $CaCO_3$ can produce an excellent behaviour in shrinkage experiments[5], but not such good behaviour in reproducing the mould surface.

CONCLUSIONS

The addition of PVAc to UP formulations is only effective in promoting an excellent copy of the mould surface at concentrations higher than the critical one leading to co-continuous structures (8 wt% for the formulation used in the present study). An easy way to determine this critical concentration is by the transition from translucent to opaque cured products. The addition of PVAc beyond the critical concentration is useless, i.e. it does not give a further improvement in the surface quality.

When keeping the ratio S/E constant, PVAc did not show any significant effect on cure kinetics, maximum conversion or structure of the crosslinked UP resin (as revealed by a constancy in the value of T_g).

A particular effect of $CaCO_3$ addition is to decrease the induction period of the copolymerization without any significant action on the subsequent cure rate. This may be ascribed to preferential adsorption of inhibitors present in the formulation (including dissolved oxygen which acts as a co-inhibitor).

The simultaneous use of both PVAc and $CaCO_3$ in UP formulations leads to materials with very low strength and impact resistance and with only a moderate ability to reproduce the mould surface (although shrinkage may be reduced as desired)[5].

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