Curing of unsaturated polyester resins: effects of thickening agent

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The effects of thickening agent, magnesium oxide (MgO), on the curing behaviour of unsaturated polyester (UP) resins at 110°C were investigated by an approach of integrated reaction kinetics, rheology and morphology measurements using d.s.c., Fourier transform i.r. (*FT*i.r.) spectroscopy, a Haake viscometer, and SEM. For the UP resins thickened with 4% MgO at room temperature for 192 h, isothermal d.s.c. rate profiles at 110°C showed that the induction time, t_z, and the time to reach the maximum rate, t_m, were prolonged and the final overall C=C conversion was reduced when compared with those for the neat UP resins. For the thickened UP resins, *FT*i.r. measurements revealed that the conversion of styrene was always higher than that of polyester C=C bonds throughout the reaction. Rheokinetic data showed higher gelation time and gel conversion of total C=C bonds than for the neat UP resins. Also, SEM micrographs showed that the fractured surface after the cure appeared less smooth. Finally, all the experimental results have been elucidated in light of the formation of thickening-induced microdomains of aggregates for polyester chain segments prior to cure, as observed by SEM micrographs, and the associated reduction of reactivity for styrene and, especially, polyester C=C bonds in these microdomains during the cure.

(Keywords: unsaturated polyesters resins; thickening; curing)

INTRODUCTION

The carboxylic acid end groups in unsaturated polyester (UP) resins are able to react with oxides and/or hydroxides of Group IIA metals, such as MgO and $Mg(OH)_2$, which quite often will result in at least a 1000-fold increase in viscosity (up to $> 10^6$ cP or 10^3 Pa s) in 2–3 days. Such a maturation or thickening process of UP resins is an essential step that precedes curing in the processing of sheet moulding compound (SMC), where the rate of thickening and the resulting viscosity determine the mouldability of the compound[1–4].

The reaction mechanism of the maturation process using MgO has been studied extensively[5–10] and is the subject of several review publications[3,11]. Three major theories have been proposed. The first one postulates a two-stage reaction where a basic salt is formed by the reaction between one MgO and one polyester carboxylic acid end group, followed by complexation of carbonyl and/or hydroxyl oxygens present on the polyester with available coordination sites on the magnesium of the basic salt[5,6]. The second one postulates the formation of chain extension and chain entanglement, where the dicarboxylic acid end groups on a polyester chain react with MgO generating very high molecular weight species or neutral salts through condensation polymerization, resulting in a large increase in viscosity due to the chain entanglement[7]. The third one postulates the formation of neutral salts by the further reaction of basic salts (the basic salt formation being the same as that in the first theory) with extra carboxylic acid end groups, followed by aggregation of magnesium ions in the same way as has been found for other ionomers[8–10].

The effects of thickening on the curing of UP resins have been investigated by many researchers[12–15]. Curing was carried out either in sample pans of differential scanning calorimeters using isothermal[13,15] and non-isothermal[12] modes or in metallic moulds[14]. It was generally observed that[12,15] in the cure of thickened UP resins, the heat of reaction decreased when compared with non-thickened ones. However, the reported results regarding effects of thickening on the reaction rates are quite controversial. For the thickened UP resins, while some[12,13] reported that the induction time, t_z, and the time to reach the maximum reaction rate, t_m, in the cure reaction were shorter than those of non-thickened UP resins, the opposite trend was also found[14]. On the other hand, Yu and Ma[15] found that during the initial period of thickening, t_z and t_m increased as the degree of thickening increased, while the trend was reversed in the latter period of thickening.

Most of the above studies of thickening effects on the curing of UP resins were based on macroscopic observations solely from d.s.c. measurements. An in-depth elucidation of the findings from a microscopic point of view were essentially lacking. In this study, an integrated reaction kinetics, rheology and morphology measurement was carried out for UP resins with and without thickening. The progress of microstructure formation during reaction and its effects on the reaction kinetics and rheokinetics are discussed.

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EXPERIMENTAL

Materials

The UP resin used contained isophthalic acid, fumaric acid and propylene glycol in a molar ratio of 1:1.70:2.65 (by ^{1}H n.m.r.). The acid value and the hydroxyl number of the resin were found to be 24.1 and 28.4, respectively, by end-group titration, which gives a number-average molecular weight of 2140 g mol^{-1}. On average, the calculated number of C=C bonds in each polyester molecule was 7.72. The styrene content in the UP resin (37.4% styrene) was determined by evacuating styrene monomers in the vacuum oven at room temperature. The initial viscosity of the resin was measured to be 1320 cP using a Haake viscometer (Couette, SVII). Based on the characterization results, extra styrene was added to the resin so that the molar ratio of styrene to polyester C=C bonds was adjusted to be 2/1.

In this study, MgO (starmag-150 MgO powder, Konoshima) was employed as the thickening agent. The average particle size diameter and the density were 0.35 μm and 0.48 g ml^{-1}, respectively, as given by the manufacturer. For the sample solution with MgO, 4 wt% MgO was added. After the residual water in the UP resin was determined by titration using the Karl-Fischer method, the molar ratio of polyester carboxylic end groups, MgO and H_2O in the sample solution prior to thickening was calculated to be 1.00:3.57:0.90. The cure reaction was initiated by 1 wt% t-butyl perbenzoate (TBPB) at 110°C. All the materials were employed as-received without further purification.

Instrumentation and procedure

Characterization of UP resins during thickening. In studying the thickening behaviour of UP resins prior to curing, the sample solution containing MgO was placed in a 50 ml flask, and capped with a glass stopper to prevent evaporation of the styrene monomer. The sealed bottle was then placed in a thermostatically controlled water bath, maintained at 25°C ± 1°C, for a thickening period of ~200 h. At different degrees of thickening, samples were taken for measurement of both viscosity and acid number. The viscosity of the partially thickened sample was determined by using a Haake viscometer (model RV20/M10) with a cone-and-plate measuring unit (PK1, 1°) at room temperature, while the acid number was determined by titration as described by Han and Lem[8]. The i.r. spectra for partially thickened samples at several selected times were also obtained.

D.s.c. The reaction kinetics of partially thickened UP resins were also measured by a Dupont 9000 differential scanning calorimeter with a 910 pressurized d.s.c. cell at atmospheric pressure. All the reactions were conducted in hermetically sealed aluminium sample pans with sample weights ranging from 6 to 10 mg. It should be noted that in removing the partially thickened sample for the measurements, loss of styrene monomer would be inevitable. Since the possible change of sample compositions could thus affect the cure kinetics and heat of reaction[12,16], the sample preparation procedures for partially thickened UP resins prior to d.s.c. experiments were modified as follows. First, the sample solution containing MgO was placed in 10–12 d.s.c. sample pans. After sealing the sample pans, they were transferred into a thermostatically controlled water bath at 25°C simultaneously for thickening. At different degrees of thickening, the sample pan was taken from the bath and placed into the d.s.c. sample cell. Isothermal reaction rate *versus* time profiles were measured at 110°C. Isothermal d.s.c. runs were ended when there was no further exotherm. Samples were then reheated from room temperature to 210°C in the scanning mode with a heating rate of 2.5°C min^{-1} to determine the residual reactivity in the isothermally cured samples. Resins were also cured in the scanning mode with a heating rate of 2.5°C min^{-1}. The total heat of reaction was calculated from the area under the scanning d.s.c. curve. If we make three assumptions that the density and heat capacity of the resin change little with reaction from liquid to solid within the temperature range used, that heats of polymerization associated with styrene and polyester C=C bonds are approximate, and that the reaction can be complete as long as the temperature is high enough for a long period of time, the overall reaction rate can be directly obtained from the rate of heat release measured by d.s.c. as follows[17]:

$$\frac{d\alpha}{dt}=\frac{1}{\Delta H_T}\left(\frac{d\Delta H_t}{dt}\right) \tag{1}$$

and

$$\alpha=\frac{1}{\Delta H_T}\int_0^t \frac{d\Delta H_t}{dt}\,dt=\frac{\Delta H_t}{\Delta H_T} \tag{2}$$

where $d\alpha/dt$ and α are the overall reaction rate and total conversion at a given time, ΔH_t is the heat release before time t, and ΔH_T is the total heat release, which is usually taken as the heat release from the direct scanning d.s.c. run (i.e. $\Delta H_T = \Delta H_S$).

Fourier transform i.r. (FT*i.r.*) *spectroscopy.* In this study, a Fourier transform i.r. spectrometer (Digilab, FTS-40) with a resolution of 4 cm^{-1} in the transmission mode was also used for on-line conversion measurements of styrene and polyester C=C bonds during the reaction. Sample solution (~0.8 mg) was pasted between two KBr plates, which were then transferred to a liquid sampling cell, a temperature-controlled flow-through cell (TFC, Harric Scientific), where the possible loss of volatile species such as styrene monomers during measurement could be prevented. As soon as the TFC was mounted on a sample holder located in the i.r. chamber, the isothermal reaction of the sample was measured continuously at 110°C under atmospheric pressure for the entire course of the reaction. Four consecutive 1 s scans were taken at each sampling time, and their average was transformed into a frequency-domain spectrum. The sampling interval was 45 s. Measurement was ended when there were no changes in absorbance peak areas. All i.r. spectra were expressed in absorbance units, where the individual reaction conversions of styrene and polyester C=C bonds could be determined as a function of time.

In the analysis of i.r. spectra, all the absorbances were based on peak areas. Changes of absorbance at 912 cm^{-1} (C–H out-of-plane bending in CH_2=CHR for styrene) and 982 cm^{-1} (C–H out-of-plane bending in CHR=CHR for polyester) were employed to calculate conversions of styrene and polyester vinylene groups, respectively. The absorbance at 1730 cm^{-1} (C=O stretching) was chosen as an internal standard. The absorbance at 695 cm^{-1} (C–H out-of-plane bending in benzene ring of styrene)

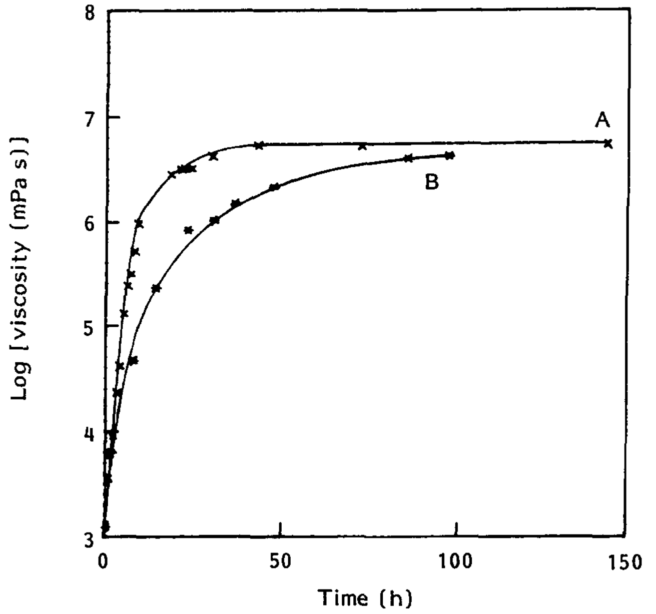

Figure 1 Variation of resin viscosity as a function of time during thickening: (A) at 25°C; (B) at 18°C

was also measured to correct for styrene loss. However, by using the TFC, no styrene loss was found during the continuous monitoring. Since the peaks at 982 and 992 cm^{-1} (C–H out-of-plane bending in CH_2=CHR for styrene) overlapped, a simple subtraction method was used to separate the individual peaks[18].

For the thickened sample by 4% MgO, the change of peak area at 982 cm^{-1} would also be affected by further thickening or state change of the sample during the cure at 110°C[19], where -OOC–HC=CH–COO- units were involved in either case. Hence, the change of absorbance at 982 cm^{-1} could not reflect the conversion of polyester vinylene groups due to curing. In this case, the reaction of thickened resin cured in the d.s.c. cell was stopped at a preset time by rapidly chilling the sample pan in liquid nitrogen for 5 min. Sample from each d.s.c. pan cured to various degrees of overall conversion was then pasted between two KBr plates and *FT*i.r. spectroscopy was employed to measure the conversion of styrene. Finally, the conversion of polyester vinylene groups was calculated from the styrene conversion by *FT*i.r. spectroscopy and the overall conversion by d.s.c.

Morphology. In the morphological study, sample from each d.s.c. pan cured to various degrees of overall conversion was broken into several pieces and dissolved in dichloromethane for 1 day to remove all soluble materials. The undissolved sample was placed on a filter paper and dried at room temperature for 1 day. The dry sample was then gold-coated for morphological measurement. Hitachi S-2400 and Jeol JSM-6300 scanning electron microscopes with accelerating voltages of 20 kV were used to observe the fractured surface of each sample at magnifications of 1000–5000 ×.

Rheological measurements. For rheological measurements during curing, a Haake viscometer (model RV20/M10) was used to measure the viscosity change prior to gelation. Sample solution (2–3 g) was placed inside a Couette SVII type of measuring unit, and the viscosity *versus* time profile was then measured under atmospheric pressure at 110°C. The gelation time may be determined when the sample viscosity started to rise sharply. Instead of comparing the viscosity measurement data with the reaction conversion data measured by d.s.c. or *FT*i.r. spectroscopy on the basis of the same cure time, the gel conversion of the sample solution was measured directly as follows. Sample solution (2 g) was first sealed in a 50 × 6 mm thin aluminium disc mould. Several such moulds were then placed simultaneously into a thermostatically controlled silicone oil bath at 110°C. By referring to the viscosity *versus* time profile measured by the Haake viscometer, the reaction of resin cured in the mould was stopped at each preset time by removing one of the disc moulds from the oil bath and quenching it in liquid nitrogen for 5 min to prevent any further reaction. Six to eight partially cured samples at various degrees of cure were thus obtained. Using a Haake viscometer with a cone-and-plate measuring unit (PK1, 1°), the viscosity of partially cured samples at room temperature was measured.

For the overall conversion of the partially cured samples, a d.s.c. run in scanning mode from 25 to 210°C at a heating rate of 2.5°C min^{-1} was carried out to measure the residual reaction exotherm. The overall conversion can then be calculated as follows:

$$\alpha_s = \frac{\Delta H_{S,0} - \Delta H_{S,t}}{\Delta H_{S,0}} \tag{3}$$

where α_s is the overall conversion for the partially cured sample at 110°C for a reaction time t, $\Delta H_{S,0}$ is the total heat release from the d.s.c. scanning run for the unreacted sample solution, and $\Delta H_{S,t}$ is the residual heat release from the d.s.c. scanning run for the partially cured sample at 110°C for a reaction time t.

Sample from each disc mould cured to various degrees of conversion was also pasted between two KBr plates and *FT*i.r. spectroscopy was employed to measure the conversions of styrene and/or polyester C=C bonds.

RESULTS AND DISCUSSION

Characteristics of UP resins during thickening

Figure 1 shows the variation of resin viscosity as a function of time during thickening at 18 and 25°C. At 25°C, the resin viscosity increased very rapidly for the first 10 h, showing a linear relationship between log viscosity and time, and then levelled off after 40 h. At a lower thickening temperature, the trend of viscosity variation was similar, but the thickening rate became slower. The viscosity would not reach a plateau value until after 100 h at 18°C. The faster thickening rate at a higher temperature is due to the enhanced diffusion rate of MgO to the carboxylic acid groups of UP resins in the thickening process[5].

Figure 2 shows the variation of acid number for UP resins during thickening at 25°C. Since the decrease of acid number is an indicator of the extent of the thickening reaction between MgO and carboxylic acid groups in UP resins as revealed by a viscosity increase, the variation of acid number as a function of time essentially corresponded to that of the viscosity change shown in *Figure 1*.

Figure 3 shows *FT*i.r. spectra for UP resins thickened for various times at 25°C. As the thickening progressed, the absorption band at 3440–3540 cm^{-1} and the absorption peak at 3695 cm^{-1} appeared and became stronger, which is due to the O–H stretching caused by the formation of H_2O molecules. Also, part of the absorption peak at 1730 cm^{-1} due to the C=O stretching of the neutral COOH group in UP resins gradually shifted to 1650 cm^{-1} to 1550 cm^{-1} as a result of the formation of carboxylate anions, COO^-, in the thickening process.

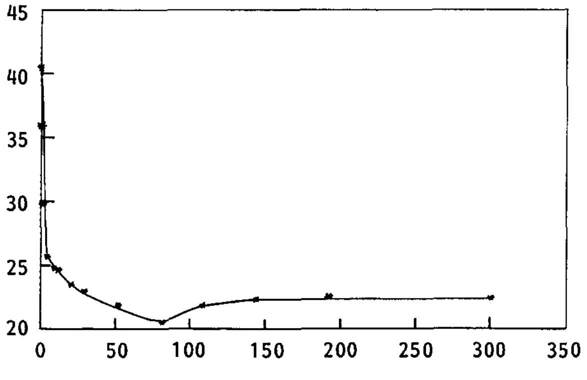

Figure 2 Variation of acid number for UP resin as a function of time during thickening at 25°C

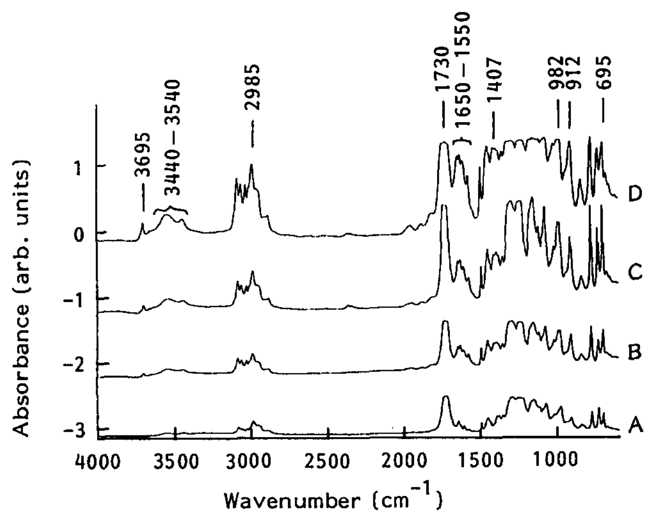

Figure 3 *FT*i.r. spectra for UP resins thickened for different times at 25°C: (A) 0 h; (B) 53 h; (C) 73 h; (D) 96 h

Curing kinetics

Figure 4 shows the effect of thickening on d.s.c. reaction rate profiles of UP resins cured at 110°C. As a result of thickening, the t_z and t_m were markedly prolonged. Although the duration of thickening time would affect t_m in a somewhat irregular manner, a longer time of thickening could generally result in an increase in t_z (*Table 1*). The latter is because the initiator efficiency, f, would decrease as the viscosity of the reaction medium increases due to the cage effect[20], leading to a reduction in the rate of formation of initiator radicals and, in turn, an increase in t_z.

The effect of increasing thickening time would generally cause a lower isothermal heat of reaction, ΔH_{iso}, and a lower final conversion, α_{iso} (*Table 1*). An ~10% decrease in α_{iso} was found for the resin thickened for 192 h when compared with the non-thickened one.

Figure 5 shows detailed reaction kinetics measured by *FT*i.r. spectroscopy for the thickened UP resins (192 h

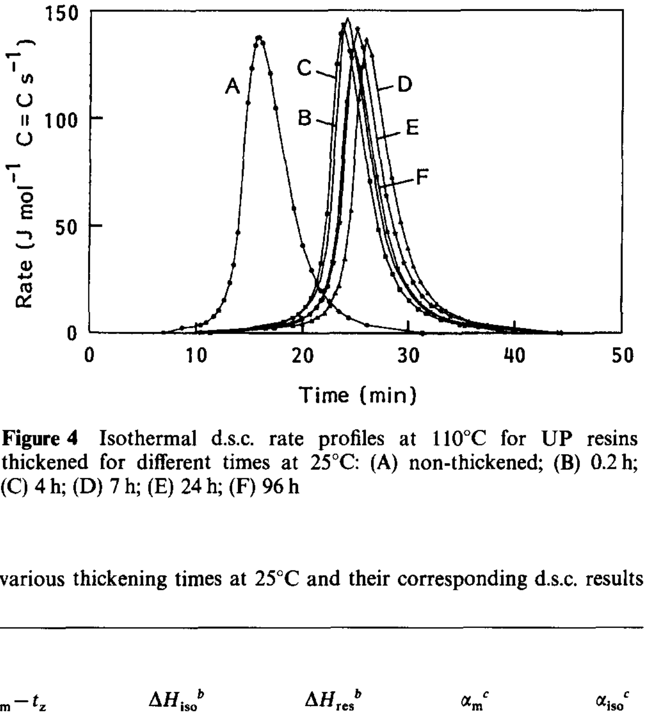

Figure 4 Isothermal d.s.c. rate profiles at 110°C for UP resins thickened for different times at 25°C: (A) non-thickened; (B) 0.2 h; (C) 4 h; (D) 7 h; (E) 24 h; (F) 96 h

Table 1 Summary of viscosity data measured at 25°C for UP resins with various thickening times at 25°C and their corresponding d.s.c. results for isothermal reactions at 110°C

Thickening time (h)	Viscosity (Pa s)	t_z^a	t_m^a	$t_m - t_z$	ΔH_{iso}^b	ΔH_{res}^b	α_m^c	α_{iso}^c
Non-thickened	0.9	7.0	15.8	8.8	275.2	30.0	26.8	76.7
0.2	2.3	8.7	24.1	15.4	277.4	35.7	26.6	77.3
4.0	32.3	10.6	23.7	13.1	262.0	38.0	25.3	73.0
7.0	243.2	11.3	25.9	14.6	256.9	37.5	24.0	71.6
10.0	1259	11.3	25.2	13.9	271.7	35.8	24.7	75.7
24.0	2530	10.4	25.4	15.0	271.1	36.4	26.2	75.6
80.0	5278	12.2	24.7	12.5	245.4	40.6	24.5	68.4
96.0	5437	12.0	23.6	11.6	238.2	37.2	22.3	66.4
192.0	5497	12.2	23.2	11.0	235.0	36.5	21.9	65.5

[a] t_z is the induction time (min) and t_m is the time to maximum rate (min)

[b] The units of ΔH_{iso} and ΔH_{res} are J g^{-1} resin, where ΔH_{iso} is the heat release for isothermally cured sample and ΔH_{res} is the heat release by rescanning the isothermally cured sample at 2.5°C min^{-1} from room temperature to 210°C

[c] α_m (%) is the conversion at the time to maximum rate, and α_{iso} (%) is the overall conversion based on the ΔH_S of non-thickened sample as 100% conversion (i.e. $\alpha_{iso} = \Delta H_{iso}/\Delta H_S$), where ΔH_S is the heat release at 2.5°C min^{-1} scanning rate from room temperature to 210°C and equals 358.72 J g^{-1} (= 13.86 kcal mol^{-1}) C=C for the non-thickened sample

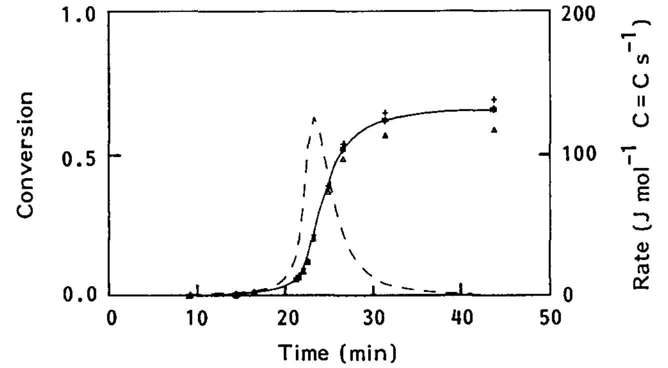

Figure 5 Conversion profiles of overall C=C bonds (*, measured by d.s.c.), styrene (+, measured by *FT*i.r.), and polyester C=C bonds (Δ, calculated from $3\alpha_{tot}-2\alpha_{st}$) for thickened UP resins (192 h at 25°C) cured at 110°C. The d.s.c. reaction rate (---) and overall conversion profiles based on ΔH_S of non-thickened sample (——) are also plotted for comparison

at 25°C) cured at 110°C. The conversion of styrene C=C bonds, α_S, was always higher than that of polyester C=C bonds, α_E, throughout the reaction. This is in contrast to that of non-thickened UP resin system[16,19], as indicated by the relative conversion profiles of α_S *versus* α_E shown in *Figure 6*, where the conversion of polyester C=C bonds exceeded that of styrene in the early part of the reaction (i.e. prior to 40% conversion), while the trend was reversed in the latter part of the reaction.

For the thickened UP resin system, the average mobility of the C=C units in big polyester molecules would be more severely curtailed when compared with that of the non-thickened one. This is because for the former system, the participation of -OOC-HC=CH-COO- units in polyester during the thickening process could lead to complex formation or domain formation that would hamper the mobility of the C=C units in polyester. Therefore, from the start of the reaction, the number of styrene vinyl groups consumed for every polyester vinylene reacted in the copolymer structure (i.e. the average crosslink length of styrene[18], *n*, through which the vinylene groups either in two adjacent polyester molecules or in the same polyester molecule are connected) could be greatly enhanced due to an increase of the relative mobility of C=C units in the small styrene molecule compared to that in the big polyester molecule. A higher α_S than α_E even in the early stage of the reaction would then result.

Figure 6 also shows that the thickening effect could lead to a reduction in the final conversions of both styrene and polyester C=C bonds (69.0% *versus* 74.2% for α_{st}; 58.5% *versus* 62.9% for α_{pes}). The trend of decrease in the final conversion of overall C=C bonds due to thickening (65.5% *versus* 70.5% by *FT*i.r.) was consistent with that obtained from d.s.c. measurements (65.5% *versus* 76.7%).

Morphology

Morphologies of the thickened and non-thickened UP resins during the cure were somewhat different, as shown below, where all of the morphology studies were conducted on d.s.c. specimens. It should be noted that for the morphologies found in the fracture surface of d.s.c. specimens which were cured *in situ*, they reflected the microstructure build-up which was undissolved by the solvent up to a certain monomer conversion. Although the sample had lost some of its mass in the solvent treatment procedure before being examined by SEM, the true morphology in the polymerizing system at the time of cessation of cure could still be revealed or inferred from the morphology observed by SEM. This is because the characteristics of the established microstructure for the partially cured sample would not be affected much by the solvent extraction procedure.

Figures 7 and *8* show SEM micrographs of the fractured surface for thickened (192 h at 25°C) and non-thickened UP samples, respectively, cured at 110°C to various conversions. *Figure 7a* shows that, for the sufficiently thickened sample prior to curing, many microdomains were scattered in local spots, which could result from the aggregation of polyester chain segments through the linking and coordination of MgO during the thickening of UP resins.

In the very early stages of reaction (conversion $\alpha = 0.01\%$), a loosely crosslinked network spanned the system for both samples (*Figures 7b* and *8a*), while the crosslinking reaction also proceeded in the spherical microdomains of polyester aggregates exclusively for the thickened sample.

As the reaction progressed ($\alpha < 7\%$), clear and discrete microgel particles could be easily identified for the non-thickened sample (*Figure 8b*), while for the thickened sample, microgel particles tended to be fused together and existed within and on the surface of the local microdomains of polyester aggregates (*Figure 7c*).

At the peak of the d.s.c. rate profile ($\alpha \approx 23\%$), a densely crosslinked network was distributed throughout the system for both samples (*Figures 7d* and *8c*). Some microdomains could still be seen for the thickened sample.

In the latter stages of reaction ($\alpha = 70$–75%) for both samples, microgel structures in local spots were intimately overlapped via crosslinking to form a compact microstructure and appeared flake-like as a whole, where the complex 'river markings' were caused by crack plane jumping during fracture. For the thickened sample, the

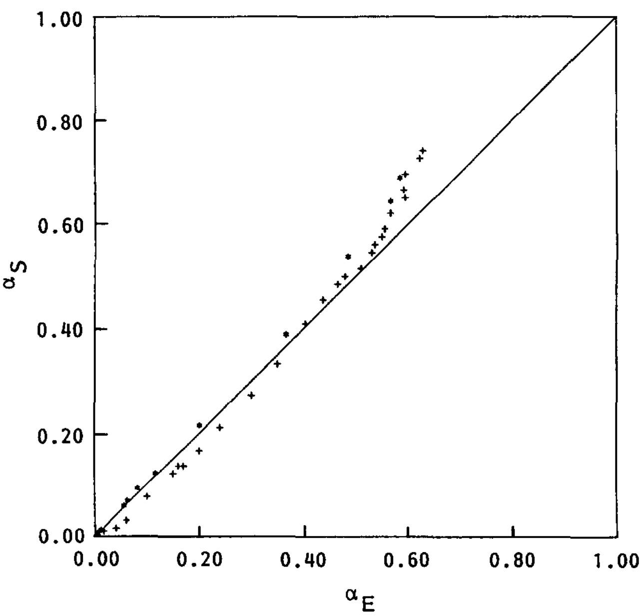

Figure 6 Relative conversion profiles of styrene (α_S) *versus* polyester C=C bonds (α_E) for non-thickened (+) and thickened (*, 4% MgO) UP resins cured at 110°C

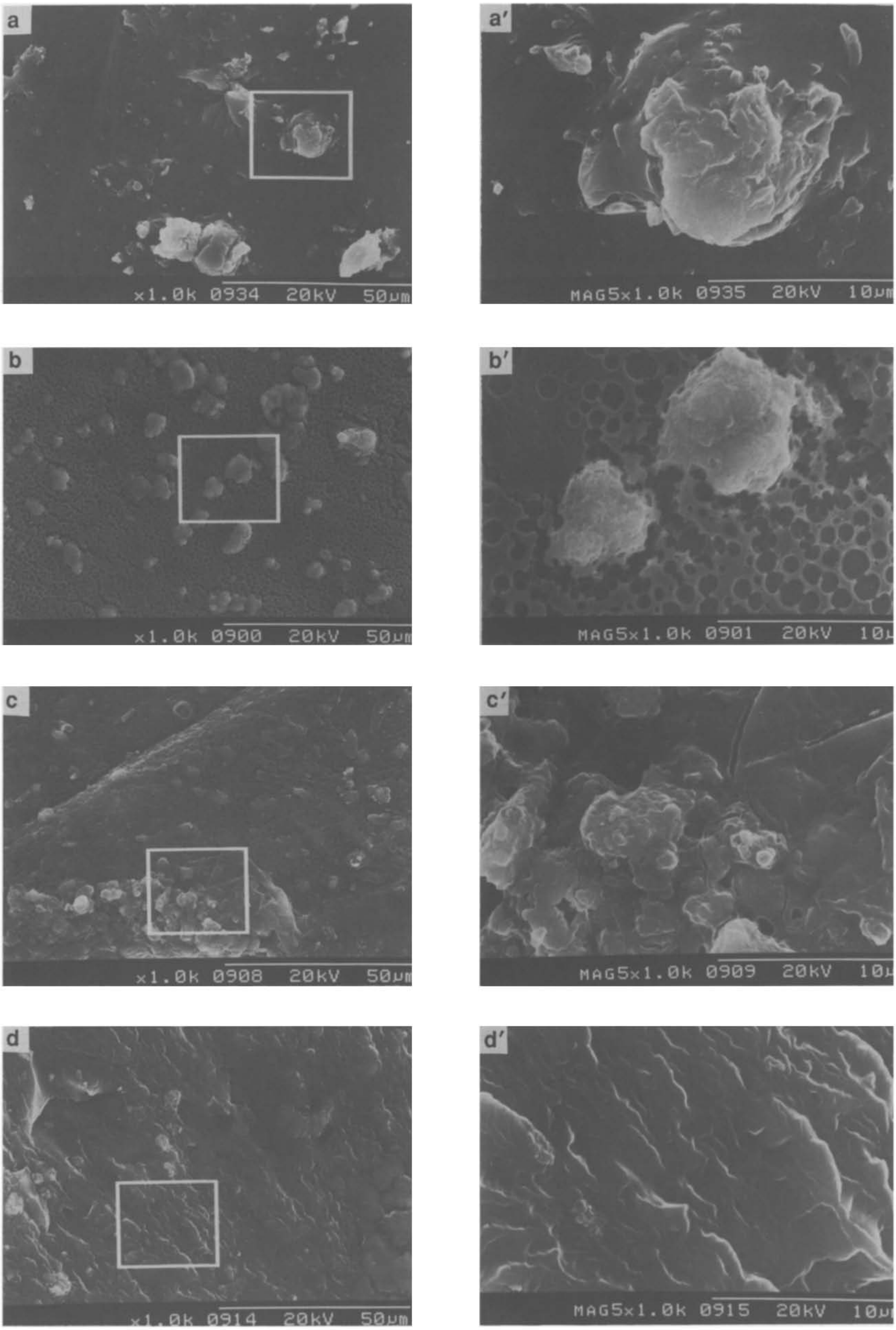

Figure 7 SEM micrographs of the fractured surface for thickened UP samples (192 h at 25°C) cured isothermally at 110°C to various conversion levels: (a) before curing; (b) $\alpha = 0.01\%$; (c) $\alpha = 2.5\%$; (d) $\alpha = 23.0\%$; (e) $\alpha = 68.7\%$. The micrographs on the right show the boxed area in the micrographs on the left at higher magnification

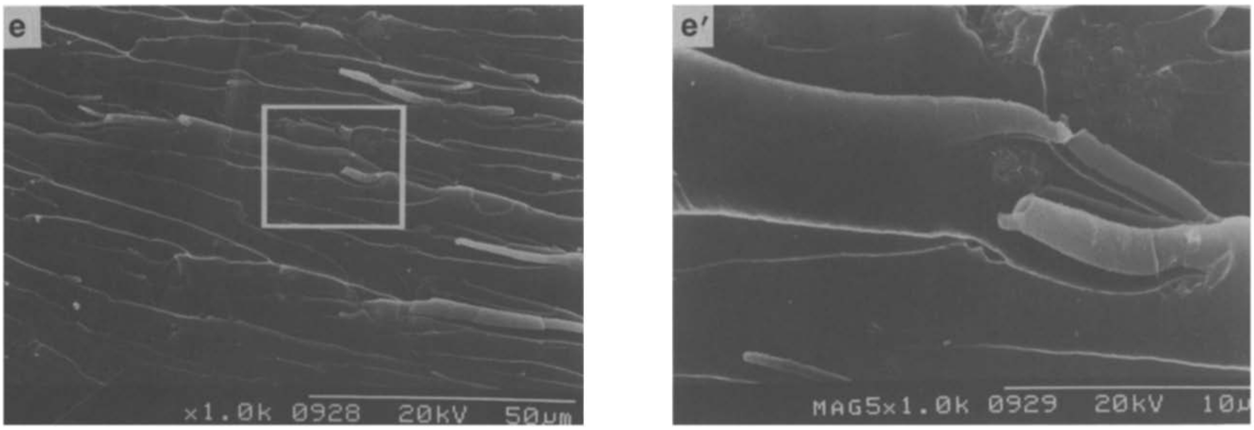

Figure 7 *Continued*

flake-like microstructure was less oriented, its surface appeared less smooth and some microdomains were still sparsely scattered.

Rheokinetics

Figure 9 shows the viscosity variation *versus* time profiles for non-thickened and thickened UP resins during cure at 110°C. It is seen that for both samples the viscosity decreased with time up to a certain time since the sample in the measuring unit was heated up from room temperature to 110°C, remaining unreacted, and the viscosity decreased as a result of increasing temperature. Once the sample started to cure, the viscosity increased with cure time and eventually exhibited a sharp increase near gelation. Since the time to reach infinite viscosity in *Figures 9a* and *b* cannot be obtained accurately due to limitations of the instrument used, to facilitate the determination of gelation time, the ratio of the initial viscosity to the viscosity during cure was plotted against the cure time (not shown) for both samples. By extrapolating the viscosity ratio to zero, the gelation times can then be determined and are presented in *Table 2*. The gel time by such on-line measurements was found to be larger (24.8 min *versus* 13.8 min) for the thickened sample. Another off-line measurement of viscosity *versus* time using a cone-and-plate measuring unit (see below) exhibited the same trend for t_{gel} (21.5 min *versus* 6.1 min).

It should be noted that the gel time, t_{gel}, can be regarded as a summation of the induction time, H_{t_z}, and the cure time up to gelation, $t_{\mathrm{gel}}-H_{t_z}$, both of which were delayed for the thickened sample as shown in *Table 2*. Hence, the thickening effect would reduce not only the rate of formation of initiator radicals prior to cure but also the rate of crosslinking of monomers in the cure, causing an increase in H_{t_z} and $t_{\mathrm{gel}}-H_{t_z}$, respectively. Reaction kinetics from d.s.c. results of t_z and t_m-t_z in *Table 1* also showed the same trend caused by the thickening effect. (The true gelation point would be generally located around the midpoint of the sharp rise in the d.s.c. reaction rate profile prior to the maximum peak[21].)

In order to obtain accurate gel conversions, partially cured samples up to gelation for the non-thickened and thickened UP resins cured at 110°C were quenched in liquid nitrogen to stop any further reaction. The viscosity and reaction conversions were measured at room temperature. *Table 3* shows the variations of viscosity and reaction conversions with time, where the last column lists the gel time, gel conversion of total C=C bonds measured by d.s.c., and gel conversions of styrene, polyester C=C bonds, and total C=C bonds measured by *FT*i.r. spectroscopy. Under the thickening effect, gel conversion of total C=C bonds, α_s or α_{tot}, is increased (11.6% *versus* 9.8–10.4%). This is due to the enhancement of the gel conversion of styrene, α_{st} (13.5% *versus* 9.7%) more than the reduction of the gel conversion of polyester C=C bonds, α_{pes} (7.8% *versus* 10.4%).

Effects of thickening-induced microdomain formation on reaction kinetics, gelation and final morphology

For the UP resins thickened with MgO, many microdomains (*Figure 7a*), resulting from the aggregation of polyester chain segments through the linking and coordination of MgO, would be generated, where the mobility of polyester C=C bonds could be reduced considerably as mentioned earlier. As the thickening progressed, the molar ratio of styrene to polyester C=C bonds in these microdomains would become lower than in the original resin matrix (i.e. 2/1) since the concentration of polyester C=C bonds in a unit volume of the microdomains is getting higher as a result of the gradual aggregation of polyester chain segments consisting of –OOC–HC=CH–COO– units.

During the subsequent cure reaction at 110°C, the styrene swelling effect on microgel structures[16] at the microdomains with molar ratio $<2/1$ would be inadequate, which could lead to more styrene and polyester C=C bonds to be trapped in the compact microdomains after curing. Although outside the microdomains, the molar ratio would be $>2/1$, the enhancement of the final conversions due to the favourable swelling effect of styrene there could not make up for the depression of the final conversions in the microdomains. Consequently, the final conversions of styrene, polyester and total C=C bonds (α_S and α_E in *Figure 6* and α_{iso} in *Table 1*) for the entire system as a whole could be reduced, when compared with those of the non-thickened sample.

Gelation is defined as when a single molecule, connected by ordinary covalent bonds, extends throughout the polymerization system[22]. For the UP resins system, where microgel formation is the main feature in the cure[16,23], it is proposed that at the gelation point the microgel particles tend to interconnect with each other

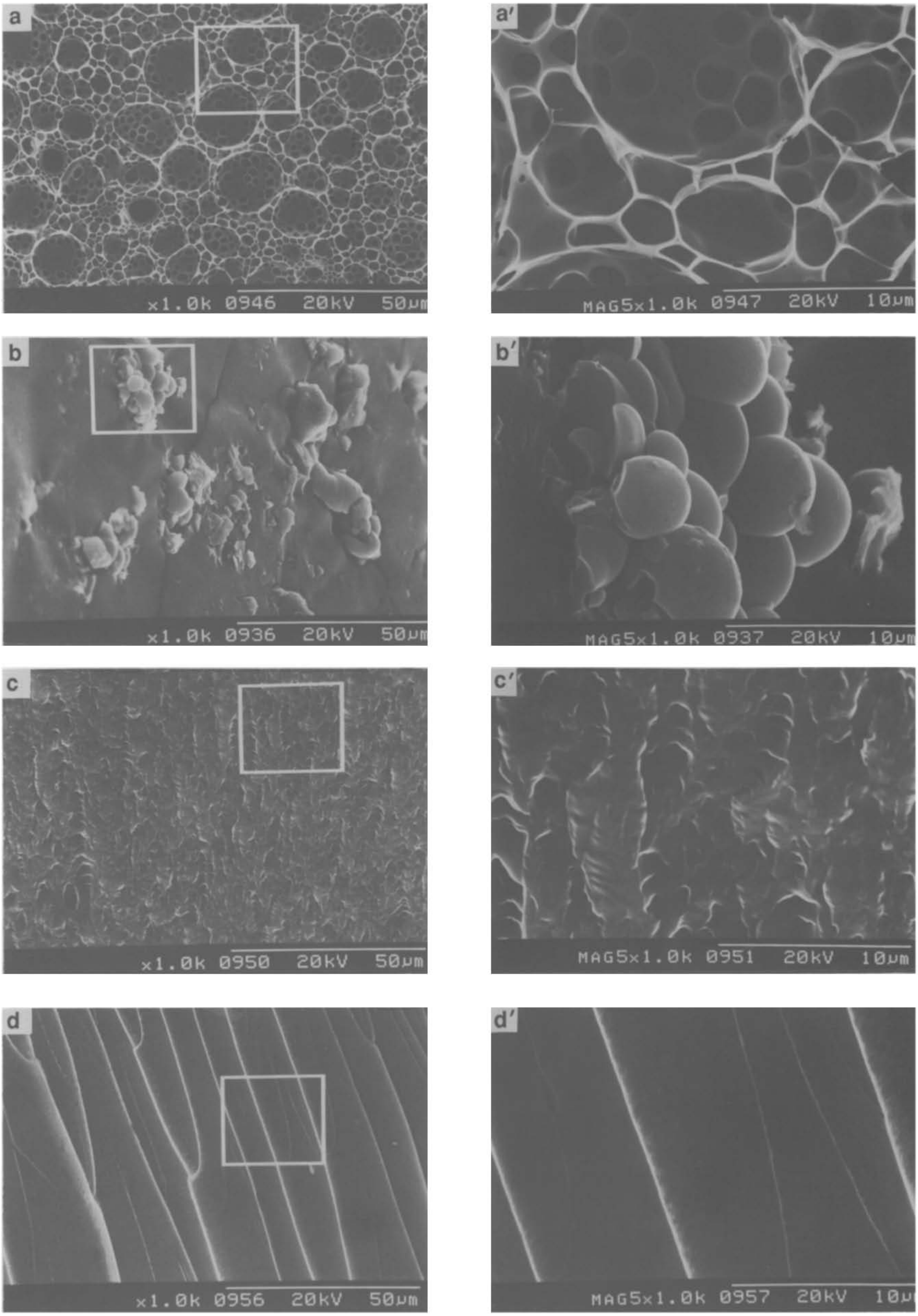

Figure 8 SEM micrographs of the fractured surface for non-thickened UP samples cured isothermally at 110°C to various conversion levels: (a) $\alpha=0.01\%$; (b) $\alpha=6.8\%$; (c) $\alpha=22.2\%$; (d) $\alpha=75.7\%$. The micrographs on the right show the boxed area in the micrographs on the left at higher magnification

via intermicrogel crosslinking reactions and percolate through the whole system for the first time[24].

For the thickened UP resins, with many microdomains scattered around the system, the inter-crosslinking of microgel particles throughout the system at gelation would inevitably have come across some of the microdomains. The lower reactivity of styrene and, especially, polyester C=C bonds in the microdomains could thus prolong the gel time when compared with the non-thickened system (*Table 2*).

For the UP resins system, the gel conversion of overall C=C bonds would reach a minimum at molar ratio = 2/1[21,25]. Either decreasing or increasing the molar ratio of styrene to polyester C=C bonds could raise the gel conversion. For thickened UP resins, since the molar ratios inside and outside the microdomains of polyester aggregates would be <2/1 and >2/1, respectively, a higher gel conversion of overall C=C bonds could then result (*Table 3*). A lower gel conversion of polyester C=C bonds for the thickened UP resins would be essentially due to the lower reactivity of polyester C=C bonds in

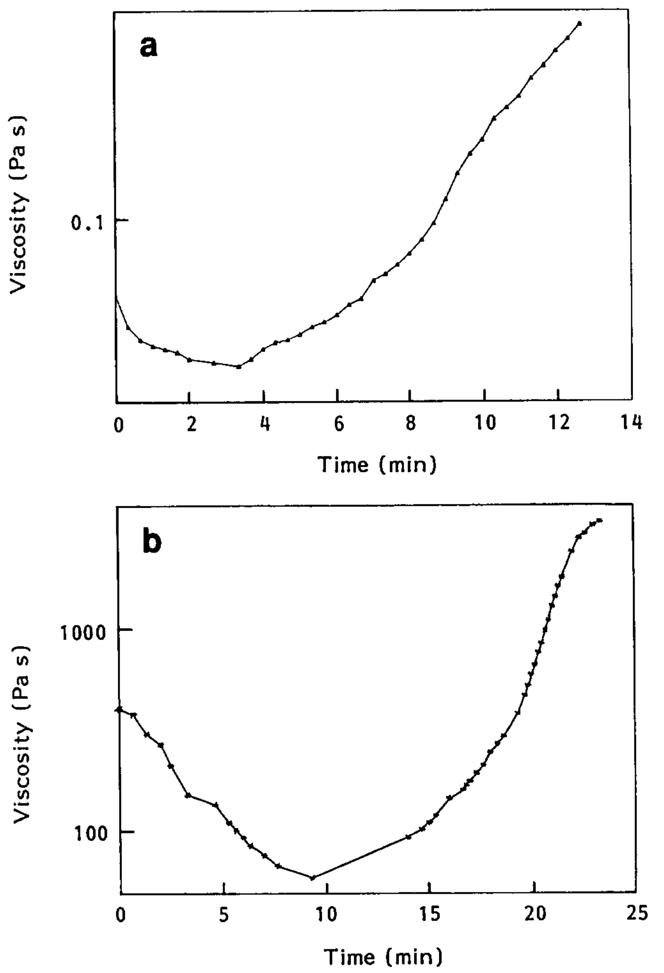

Figure 9 Viscosity variation *versus* time profiles for UP resins cured at 110°C before the gelation: (a) non-thickened sample; (b) thickened sample (192 h at 25°C)

Table 2 Gelation time data for non-thickened and thickened (192 h at 25°C) samples cured at 110°C

	Non-thickened resin	Thickened resin
t_{gel} (min) (SVII)	13.8	24.8
H_{t_z} (min)[a]	3.4	9.4
$t_{gel}-H_{t_z}$ (min)[b]	10.4	15.4
t_{gel} (min) (cone-and-plate)	6.1	21.5

[a] H_{t_z} is the induction time revealed by the onset of viscosity rise in the measurement by the Haake viscometer with SVII measuring units

[b] $t_{gel}-H_{t_z}$ is the actual cure time up to gelation

Table 3 Viscosity and reaction conversions for the partially cured samples up to gelation for non-thickened and thickened (192 h at 25°C) UP resins cured at 110°C. The measurements were carried out at room temperature

Point	1	2	3	4	5	6	Gel point[a]
Non-thickened							
t (min)	3.0	4.0	5.0	6.0	15.0	-	6.1
Viscosity, η (N s m^{-2})	2.33	2.60	5.01	100.7	solid	-	∞
η_0/η	0.51	0.46	0.24	0.01	-	-	0
D.s.c. conv.[b]							
α_s	0.0119	0.0128	0.0498	0.0953	0.319	-	0.098
*FT*i.r. conv.							
α_{st}	0.0273	0.0312	0.0476	0.0910	0.308	-	0.097
α_{pes}	0.0330	0.0355	0.0584	0.112	0.310	-	0.118
α_{tot}	0.0292	0.0326	0.0512	0.0979	0.309	-	0.104
Thickened							
t (min)	10.0	12.0	14.0	16.0	18.0	24.0	21.5
Viscosity, η ($\times 10^4$ N s m^{-2})	1.1	1.6	2.7	4.6	7.6	solid	∞
η_0/η	0.48	0.33	0.20	0.11	0.07	-	0
D.s.c. conv.							
α_s	0.0052	0.0116	0.0554	0.0624	0.0818	0.201	0.116
*FT*i.r. conv.							
α_{st}	0.006	0.012	0.058	0.068	0.092	0.216	0.135
α_{pes}[c]	0.0036	0.0108	0.0498	0.0516	0.0612	0.171	0.078

[a] The last column lists the gel time, gel conversion of total C=C bonds measured by d.s.c., and gel conversions of styrene, polyester C=C bonds, and total C=C bonds measured by *FT*i.r., which were obtained by plotting the viscosity ratio, η_0/η, *versus* time, d.s.c. conversion and *FT*i.r. conversions, respectively, followed by extrapolating the corresponding curve to zero viscosity ratio

[b] α_s is the conversion of total C=C bonds measured directly by d.s.c. for the partially cured sample; α_{st}, α_{pes}, and α_{tot} are the conversions of styrene, polyester C=C bonds, and total C=C bonds, respectively, measured directly by *FT*i.r. for the partially cured sample

[c] By calculation, $\alpha_{pes}=3\alpha_s-2\alpha_{st}$

the microdomains. Since the relative mobility of styrene to polyester C=C bonds is higher for the thickened resin than for the non-thickened resin as mentioned earlier, a higher gel conversion of styrene could arise.

For the thickened UP resins, the fractured surface after the cure appeared less smooth (*Figures 7e* and *8d*). This could be attributed to the fact that the final monomer conversion in the microdomains (molar ratio $<2/1$) would be appreciably lower than that in the other areas (molar ratio $>2/1$), and the solvent treatment procedure prior to SEM observation could extract more unreacted monomers and leave more holes in the microdomains.

CONCLUSIONS

Thickening of UP resins with MgO could lead to the formation of microdomains of aggregates for polyester chain segments through the linking and coordination of MgO. In the microdomains, the molar ratio of styrene to polyester C=C bonds would be lower than that in the original resin matrix (i.e. 2/1), resulting in an inadequate styrene swelling effect on microgel structure during cure. Since the aggregation of polyester chains and the inadequate styrene swelling effect in the microdomains could reduce the reactivity of styrene and, especially, polyester C=C bonds considerably therein, a longer gel time and lower final conversions of styrene, polyester and total C=C bonds would result when compared with those of the non-thickened system.

For the thickened UP resins, a higher gel conversion of total C=C bonds would be due to a deviation of the molar ratio from 2/1 both inside (i.e. $<2/1$) and outside (i.e. $>2/1$) the microdomains, where the molar ratio $=2/1$ for UP resins could lead to a minimum gel conversion of total C=C bonds. Also, a higher conversion of styrene than that of polyester C=C bonds throughout the reaction for the thickened resins would be essentially due to the enhanced relative mobility of styrene to polyester C=C bonds in the microdomains of polyester aggregates. As a result of a lower final monomer conversion in the microdomains scattered around the system, a less smooth fractured surface after cure could arise.

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