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Thickening behaviour and shrinkage control of low profile unsaturated polyester resins

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The rheological and morphological changes of a low shrink unsaturated polyester resin during thickening and curing were investigated. The behaviour of low profile additive (LPA) could be modified by adding a thermo-breakable functional group to its molecule. The thickening reaction of the modified LPA with MDI was much faster than that of LPA with MgO, and the viscosity was stable for 3 months. Because of the thermo-decomposition of the thermo-breakable functional group, the thickened mixture of LPA-M with MDI lost its viscosity greatly at elevated temperatures. The unthickened LPA and thickened LPA-M/MDI samples showed clear phase separation, large internal surface areas and good shrinkage control. The thickened LPA/MDI samples showed little phase separation, very small internal surface area, and poor shrinkage control. The thickened LPA/MgO samples showed some phase separation and good shrinkage control at high moulding temperature. At low moulding temperatures, both phase separation and shrinkage control were poor. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

It is well known that the shrinkage of unsaturated polyester (UP) resins during curing can be controlled by adding small amounts of thermoplastics, often called low profile additives (LPAs). The effects of LPA type [1–4], its molecular weight [5,6], and concentration [7,8] on shrinkage control have been investigated by many researchers. It is generally agreed that the shrinkage control by LPA requires a strong phase separation between the LPA and the UP resins during curing [9–14].

UP resins used as sheet moulding compounds (SMC) and bulk moulding compounds (BMC) are generally thickened for easy handling before moulding, and good fibre carrying characteristics during moulding. Two thickening methods have been used in industry. One is based on Group IIA metal oxides or hydroxides, and the other is based on diisocyanate compounds. The carboxyl groups of UP and LPA molecules may form ionic bonds with the Group IIA metal oxides/hydroxides, while the hydroxyl and carboxyl groups of UP and/or LPA molecules may form covalent bonds with isocyanates through the formation of urethane linkage. Both mechanisms tend to increase the resin viscosity and turn the compound from a liquid to a soft solid.

The strength of the ionic bond between the carboxyl group and the oxide and/or hydroxide of Group IIA metal decreases greatly at elevated temperatures. Therefore, it is thought that the LPA and UP molecules can be released from the thickened matrix upon heating,

when the matrix is thickened with oxide and/or hydroxide Group IIA metals. MgO/Mg(OH)$_2$ is the most widely used thickener in industry, because of its low cost and high thickening efficiency [6,15]. The thickening reaction with MgO/Mg(OH)$_2$, however, is slow [16,18], and the viscosity of MgO/Mg(OH)$_2$ thickened resin is sensitive to humidity and temperature variations [17,18].

In contrast to the thickening with MgO, the thickening reaction of the UP resins with diisocyanate is fast, and after thickening the resin viscosity is stable for a prolonged time [6]. However, it is impossible to greatly reduce the compound viscosity upon heating because the UP and LPA molecules thickened with diisocyanates are chemically linked together. Another major disadvantage of isocyanate-thickened compounds is that thickening limits the phase separation between the LPA and the UP matrix, consequently, reduces the shrinkage control efficiency of LPA.

If the LPA molecules can be released easily from the UP matrix in the isocyanate-thickened compounds, such compounds would provide an ideal thickening behaviour, i.e. a fast viscosity rise during maturation, a stable viscosity during storage, and a good shrinkage control during moulding. In order to release LPA from the isocyanate-thickened matrix, thermo-breakable functional groups may be introduced to the LPA, UP or isocyanate molecules. These groups are stable during maturation, but may break at elevated temperatures. *Figure 1* shows schematically the bond-breakage by using this approach.

Azo-groups and peroxide groups are the well known thermo-breakable functional groups. These functional groups, however, cannot be used for our purpose

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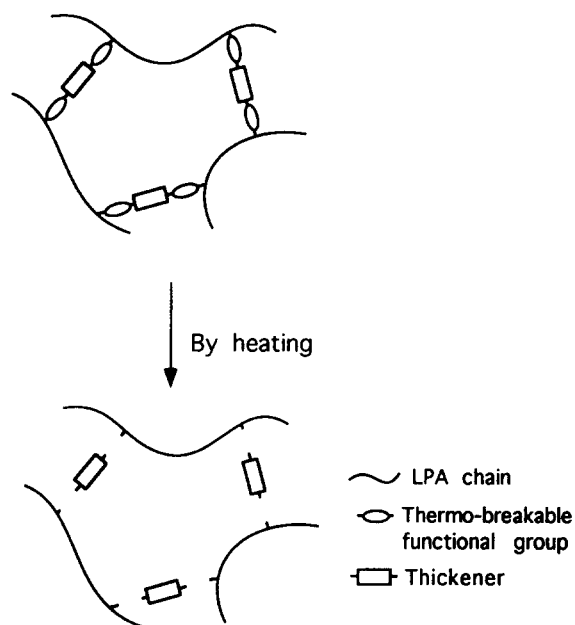
Figure 1 The schematic concept of thickening behaviour and viscosity control by using thermo-breakable LPA

HMDA : 1,6-hexanediamine
DKGA : 2,3-diketoglonic acid

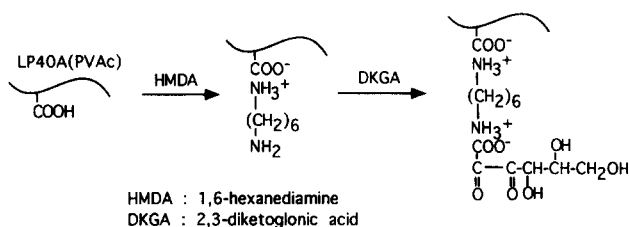**Figure 2** The synthesis process of thermo-breakable LPA

because they form radicals which may lead to unwanted polymerization among UP, styrene and LPA. Thus a diketo compound was chosen in this work because its decomposition temperature (around 100°C) is in the temperature range of SMC compression moulding and BMC injection moulding. There is also no radical formation in the system.

The purpose of this study is to develop a thermo-breakable LPA and to investigate the thickening and bond-breaking behaviours of MgO-thickened and diphenyl diisocyanate (MDI)-thickened UP resins containing either a standard LPA or a thermo-breakable LPA. Four systems were compared: an unthickened resin with the standard LPA, a MgO-thickened resin with the standard LPA, a MDI-thickened resin with the standard LPA, and a MDI-thickened resin with the thermo-breakable LPA. The viscosity changes during thickening and heating were measured by using a Brookfield viscometer. The morphology and internal surface area of cured samples were also measured. Shrinkage control of these materials were conducted through BMC moulding.

EXPERIMENTAL

Synthesis of thermo-breakable LPA (LPA-M)

A poly(vinyl acetate)-based LPA (LP40AS Union Carbide), which has some carboxyl groups was used as

the standard LPA in this study. It was also used to synthesize the thermo-breakable LPA (LPA-M) with a diketo compound.

Diketoglonic acid (DKGA) was chosen because of its harmless properties, and low cost. It can be easily grafted on LP40AS by using 1,6-hexanediamine. The synthesis process of this thermo-breakable LPA is shown in *Figure 2*. For the thermo-breakable LPA formed, there are three hydroxyl groups at the end of each branch. Thus, this material can be easily thickened with diisocyanates. The thickened chains can be separated from the matrix resin at the diketo group when the diketo group decomposes upon heating or at the amine salt.

Thirty wt% of LP40AS was dissolved in tetrahydro-furan (THF). 1,6-hexane diamine was added into the polymer solution and the solution was well stirred for 1 h. The molar ratio of the amine group to the carboxyl group ([-NH$_2$]/[-COOH]) was set at 2.2. The pH value of the solution was checked with a pH paper. Then, a diketoglonic acid/water solution prepared according to Penney and Zilvz[19] was added into the solution until the polymer solution was neutralized. This mixture was stirred for 2 h at room temperature. The modified LP40AS (LPA-M) was precipitated with hexane and dried under vacuum at room temperature.

Properties of LPA-M were characterized using a Fourier transform infra-red (*FT*i.r.) spectrometer (20 DX, Nicolet), and a differential scanning calorimeter (d.s.c., DSC2910, TA Instruments).

Thickening and curing

The UP resin and styrene (St) were thickened with MgO or MDI at room temperature in the dark. The composition of the four samples was as listed in *Table 1*. A commercially available UP resin (Q6585, Ashland) with a number-average molecular weight of 1580 was used. It consists of maleic anhydride and propylene glycol with an average of 10.13 C = C bonds per molecule. The acid value and the hydroxyl value of this UP resin are the same (about 35). The resin was shipped as a 65 wt% solution of UP in styrene. Extra styrene was

Table 1 The composition of the four samples

Run number[a]	LPA[b]	LPA-M	UP[c]	styrene	TBP	MgO	MDI
Unthickened LPA	15.0[d]	–	35.0	50.0	1.0	–	–
LPA/MgO	15.0	–	35.0	50.0	1.0	1.5	–
LPA/MDI	15.0	–	35.0	50.0	1.0	–	6.0–9.0
LPA-M/MDI	–	15.0	35.0	50.0	1.0	–	6.0–9.0

[a] Run number indicates the type of LPA/thickener used
[b] LPA, LP40AS
[c] UP, solid unsaturated polyester
[d] wt%

Table 2 The formulation of BMC panels moulded in this study

Material	Formula								
Sample number	1a	1b	1c	2a	2b	2c	3a	3b	3c
UP resin (Q6585)	93.33gm	93.33	93.33	93.33	93.33	93.33	93.33	93.33	93.33
LPA	25	25	25	25	25	25	0	0	0
LPA-M	0	0	0	0	0	0	25	25	25
Styrene	48.33	48.33	48.33	48.33	48.33	48.33	48.33	48.33	48.33
TBP (2%)	3.33	0	0	3.33	0	0	3.33	0	0
PDO (2%)	0	3.33	0	0	3.33	0	0	3.33	0
256 (2%)	0	0	3.33	0	0	3.33	0	0	3.33
MgO (2%)	3.33	3.33	3.33	0	0	0	0	0	0
MDI (9%)	0	0	0	15	15	15	15	15	15
Zinc stearate	6.66	6.66	6.66	6.66	6.66	6.66	6.66	6.66	6.66
CaCO₃ (Huber W4)	333	333	333	333	333	333	333	333	333
1.27 cm glass fibre (Vetrotex P-276)	50	50	50	50	50	50	50	50	50

added to the UP resin to adjust the molar ratio of styrene to the unsaturation of polyester molecules to 2:1 (about 41 wt% of UP in styrene). Fifteen wt% of solid LPA or modified LPA based on the total weight of UP resins, styrene and LPA or modified LPA was used in the formulation. For MgO, the thickener concentration was 1.5 wt%. For MDI, the thickener concentration varied from 6 to 9 wt%.

The thickened compounds were cured in a metal mould (229 mm × 181 mm × 6.5mm) with a cavity size of 30 mm in diameter and 1.5 mm in thickness for 10 min under 10.3 MPa in a laboratory press (Fred S. Carver). Curing temperatures were set at 150°C for reactions initiated with 1 wt% of *t*-butyl perbenzoate (TBP), 125°C for reactions initiated with 1 wt% of *t*-butyl peroctoate (PDO) and 80 and 60°C for reactions initiated with 1 wt% of 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)-hexane (Lupersol 256).

Material characterization

Viscosity measurement. The viscosity increase of the resin mixture (45 g) during thickening and the viscosity change of the thickened resin upon heating were measured using a Brookfield viscometer (RVTD, DV-1+ Viscometer, Brookfield Engineering Laboratories Inc.) with a No. 6 or No. 7 spindle at speed varying from 0.3 to 2.5 rpm. The sample was loaded in a glass tube (25 mm in diameter). While heating, the test tube with the thickened resin sample was placed in an oil bath with temperature set at either 100°C or 150°C. In order to inhibit the polymerization, there was no initiator in the resin samples. Instead 1 wt% of benzoquinone was added to the resin mixture for viscosity measurement.

Morphological observation. The cured samples were cracked at room temperature, soaked in dichloromethane for 3 h to remove LPA and dried overnight. The samples were then sputtered with gold (DESK II, Denton Vacuum Inc.) and the cross-section of the samples was observed with a scanning electron microscope (SEM, S-510, Hitachi) at 25 kV.

Internal surface area measurement. To measure the surface area of micro-voids in the cured resin, the cracked samples were pre-dried overnight in an oven at 120°C. The samples were then placed in a flask and further dried under vacuum for 18 h at 120°C. The internal surface area of samples was measured by the BET (Brunauer–Emmitt–Teller) technique with a BET analyser (Accusorb 2100E, MicroMeritics), with Krypton as an absorbent.

BMC moulding

To quantify the shrinkage control, BMC panels were prepared. A 150 ton hydraulic press with 30.48 cm × 30.48 cm Class A shear-edge mould was used in this study to mould the BMC panels. There are three different series in this study-regular LPA thickened with MgO and MDI and LPA-M thickened with MDI. In each series, three different initiators were used: (*t*-butyl perbenzoate TBP, Atochem), (*t*-butyl peroxy-2-ethyl hexanoate PDO, Atochem) and 256 (2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, Lupersol). The TBP samples were moulded at 150°C, the PDO samples were moulded at two different temperatures, −100°C and 120°C respectively, and the 256 samples were moulded at 80°C. These generated a 3 × 4 experimental matrix. 200% calcium carbonate and 10% 1.27 cm chopped glass fibres were added to each sample and they were thickened for 1 day before BMC moulding. The compositions of moulding samples are listed in *Table 2*.

A profilometer, Federal's Surfanalyzer 4000, was used for surface finish analysis. It provides total profile, roughness and multi-parameter measurement capability. Among all the parameters, the roughness average (*Ra*) is the most commonly used one. *Ra* is the arithmetic average height of roughness irregularities measured from a mean line within the sampling length (*L*). *Ra* provides a numerical value to quantify, distinguish and compare surface quality between different samples. In this study, all the samples were measured under the same parameters, and the total profiles and *Ra* of different samples were compared.

RESULTS AND DISCUSSION

Synthesis of LPA-M

The progress of each reaction was determined by the measurement of the pH value of solution. Because of the presence of carboxyl groups in LPA, the initial pH value of the solution of LP50AS and THF was 3. When 1,6-hexanediamine was added into the solution, the pH value was increased to 9. No crosslinked products were formed in the solution. The concentration of pendant amine groups in the formed polymer was measured by precipitating the polymer from the solution with *n*-hexane. The amine concentration was then determined by titration with 0.1 N aqueous HCl. If each carboxyl group of the LP40AS molecule would react with one of the two amine groups of a 1,6-hexanediamine molecule

to form a pendent amine group on the LPA chain, the molar ratio of the pendent amine groups to the initial carboxyl groups in LPA ($[-NH_2]/[-COOH]$) should be 1.0. The $[-NH_2]/[-COOH]$ value was found to be 1.08. Thus, it was concluded that all carboxyl groups in LPA had reacted with one end of amino groups of 1,6-hexanediamine to form pendent amine groups. These pendent amine groups were then reacted with the carboxyl groups of added DKGA. This was done by adding DKGA to the polymer solution until the solution was neutralized.

Figure 3 shows the *FT*i.r. spectra of the LP40AS before and after modification. After modification, the peaks at $1500\,cm^{-1}$ and $1670\,cm^{-1}$ were increased due to the introduction of 1,6-hexanediamine and 2,3-diketoglonic acid (DKGA) to LP40AS. A peak of keto groups was observed at $1050\,cm^{-1}$. A stronger peak around
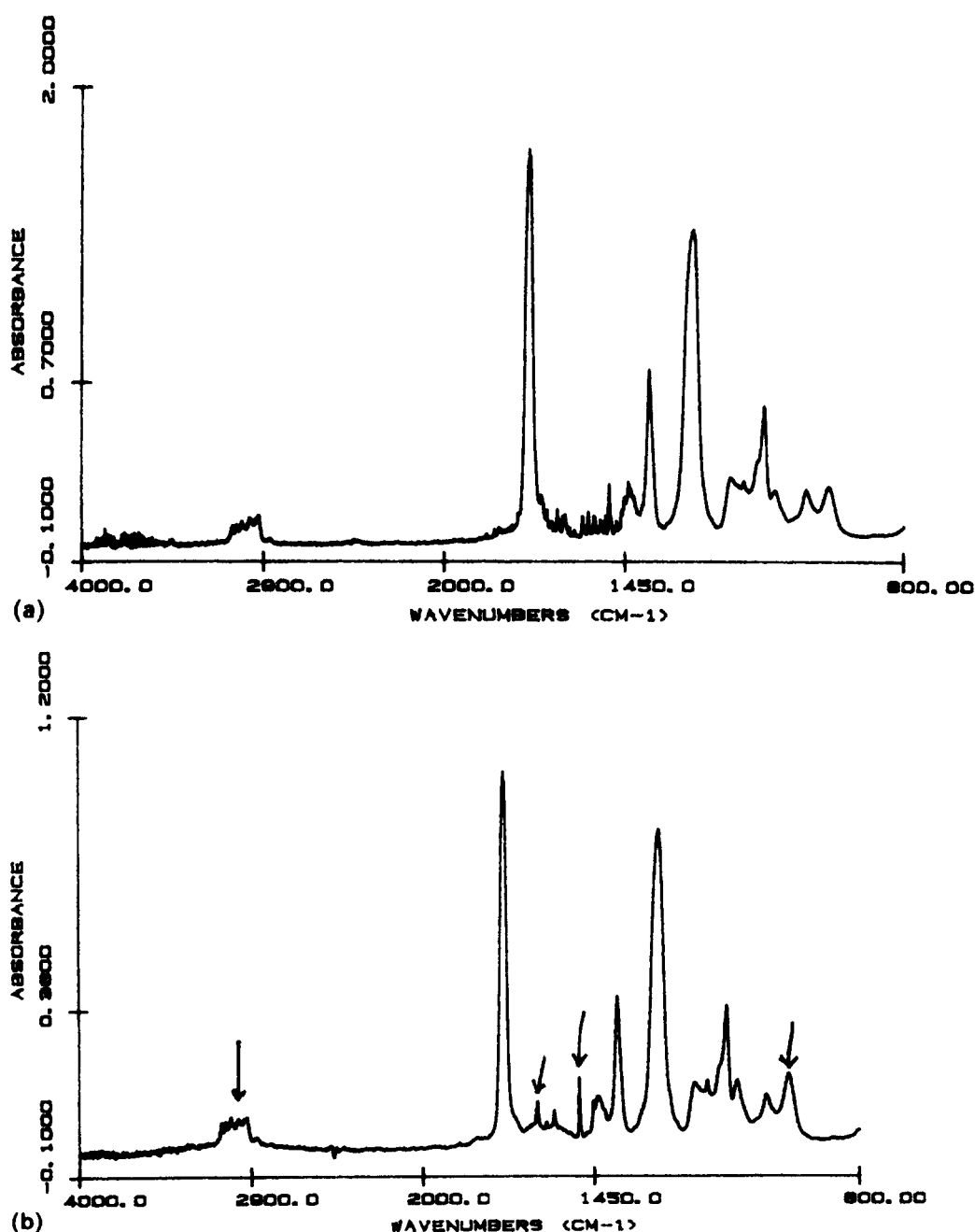

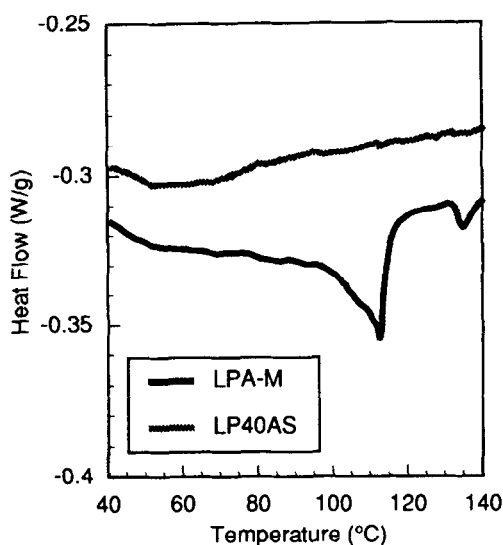**Figure 3** *FT*i.r. profiles of (a) LPA (LP40AS) and (b) LPA-M

Figure 4 D.s.c. curves of LPA and LPA-M

Figure 5 Viscosity changes of the samples during thickening

$3000\,cm^{-1}$ indicates the presence of strong hydrogen bonding because of the presence of amide and hydroxyl groups in LPA-M. These results confirmed that both 1,6-hexanediamine and DKGA have been linked to the LPA-M.

In order to investigate the thermodecomposition behaviour of the diketo groups in LPA-M, a d.s.c. measurement was conducted. *Figure 4* shows the d.s.c. profiles of LP40AS and LPA-M. The scanning rate was $10°C\,min^{-1}$. For LP40AS, no peaks were observed. After modification (LPA-M), a clear endothermic peak appeared above 80°C. The peak temperature (113.1°C) is very close to the thermodecomposition temperature of DKGA (125°C). The LPA-M sample shown in *Figure 4* was reheated in the d.s.c. and there was no endothermic peak. Thus, it is concluded that, upon heating the diketo groups in the modified LPA would start an irreversible decomposition at 80°C with a peak temperature around 113°C.

Viscosity changes during thickening and heating

Figure 5 shows the viscosity increase during thickening at room temperature for the LPA and the LPA-M based resins with either MgO or MDI as the thickener. The initial viscosity was 1.13×10^3 cP for all resins. The viscosity of LPA/MgO increased gradually, and reached 10^6 cP at around 600 h. After 600 h, the viscosity still increased slightly. This agreed well with the literature results[6]. After 650 h, the viscosity of the LPA/MgO sample became unstable and varied between 5×10^6 and 1×10^7 cP. For MgO-thickened UP resin, it has been reported that the thickening behaviour is controlled by two chemical structures[6,15]. These structures, shown in *Figure 6*, are sensitive to water content and can change easily by varying the humidity in the atmosphere. The unstable viscosity after the thickening was due to the chemical structure change of the thickened bonds.

In contrast, the viscosity of the LPA and the LPA-M based resins thickened with 6 wt% of MDI increased rapidly during the first 40 h, and then remained nearly unchanged for 3 months. Since the thickening behaviour is controlled by the chemical reaction between the isocyanate groups and the hydroxyl/carboxyl groups of
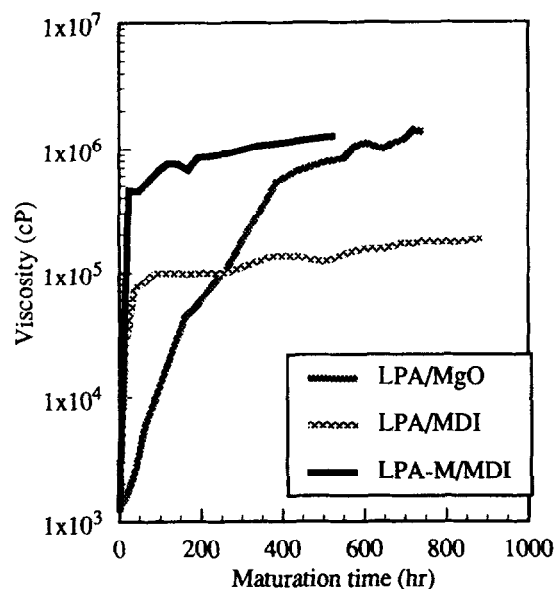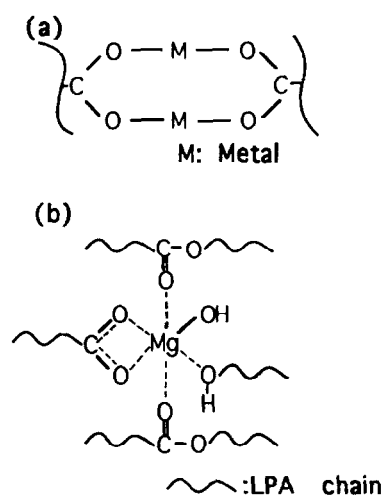

Figure 6 The chemical structure of thickened bonds between LPA and MgO and/or Mg(OH)₂: (a) metal ion with carboxylic group[15]; (b) complex aggregate structure[6]

LPA/LPA-M or UP, after the reaction is completed, the viscosity of the resin would remain unchanged. It was found that there was little difference of the thickening behaviour between the LPA and the LPA-M based resin thickened with MDI, except for the final viscosity value. The final viscosity of the LPA-M based resin $(1 \times 10^6$ cP) was larger than that of the LPA based resin $(1 \times 10^5$ cP). This is probably due to the difference of functional groups in LPA-M and LPA. The molar concentration of the hydroxyl groups in the LPA-M based system is nearly three times that of the carboxyl groups in the LPA based system. For 6 wt% of MDI, the molar ratio of the isocyanate groups in MDI to the thickenable functional groups in both LPA and UP (i.e. [-NCO]/([-COOH]+ [-OH])) was 0.93 for the LPA based resin and 0.84 for the LPA-M based resin. Furthermore, each LPA-M molecule has three hydroxyl groups which may result in crosslinking with MDI. Consequently, the final viscosity of the LPA-M based resin was larger than that of the LPA based resin.
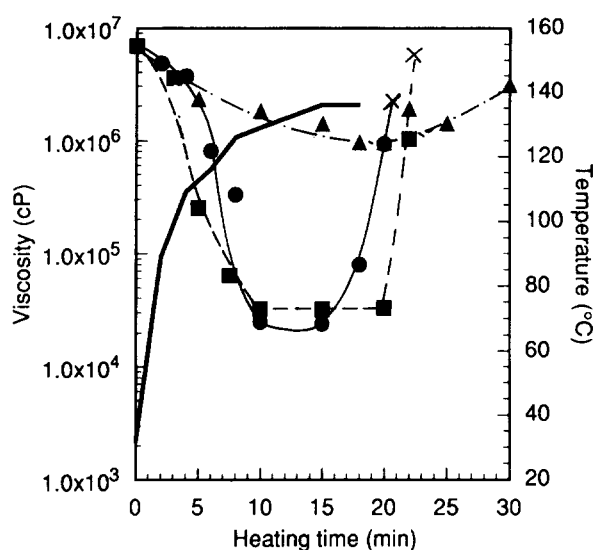
Figure 7 Viscosity changes of thickened samples during heating at 150°C. (▲) The LPA based resin thickened with 6% of MDI; (■) the LPA based resin thickened with 1.5% of MgO; (●) the LPA-M based resin thickened with 6% of MDI

In order to investigate the thermodecomposition behaviour of the thickened resin in the moulding process, the viscosity change of the thickened resins during heating was measured for LPA/MgO, LPA/MDI and LPA/MDI samples. The MDI concentration was set at 9 wt% (i.e. a stoichiometric value to the thickenable groups in the LPA-M based resin). To control the viscosity difference of the thickened resins, the heating of the thickened resins started when the sample's viscosity reached 8×10^6 cP during thickening.

Figure 7 shows the relationship between viscosity change, resin temperature and heating time. For the LPA/MDI based system, there is no thermo-breakable bond in the thickened resin. As expected, the viscosity of this sample decreased slightly from 8×10^6 cP to 1×10^6 cP by increasing the temperature from 25 to 136°C.

For the LPA/MgO based system, the viscosity started to decrease from very early stage of heating. The minimum viscosity reached was 3×10^4 cP. After 20 min, the viscosity of the sample increased drastically probably due to the thermal polymerization of UP and styrene.

For the LPA-M/MDI based system, the sample viscosity dropped slightly before temperature reached 100°C. Above 100°C, the viscosity decreased rapidly, indicating that the thermo-breakable groups started to decompose around 100°C. The minimum viscosity reached was 2.2×10^4 cP. After 15 min, the viscosity of the sample increased drastically. Compared to the LPA/MgO sample, the rate of viscosity drop of the LPA-M/MDI sample was smaller before 100°C but larger above 100°C. This indicates that the LPA-M/MDI based resin could keep its viscosity during the early stage of moulding when the compound temperature was below 100°C and could reach a lower viscosity than the conventional MgO or MDI thickened compounds when the material temperature was above 100°C in the mould.

If all thickened bonds were broken upon heating, the viscosity of the thickened resins should reach the initial viscosity of the unthickened resins (i.e. 1.13×10^3 cP).

This apparently did not occur. The minimum viscosities of the LPA-M/MDI based system and the LPA/MgO based system were both larger than the initial viscosity of the unthickened resins. In the LPA-M/MDI system, MDI may react with both LPA-M and UP. The chemical bonds between the UP and the MDI molecules would not break by heating, thus, resulting in a larger minimum viscosity. In the LPA/MgO based system, the ionic bonds between the MgO and the LPA/UP molecules may become weaker at elevated temperatures. They, however, may not completely break. Consequently, the minimum viscosity reached during heating was much higher than the initial viscosity of the unthickened resin.

Morphology of cured samples

The phase separation mechanism of low shrink UP resins has been explained by some researchers[13,14]. When the polymerization starts, the LPA becomes incompatible with the UP resin. This forces the UP microgels to coagulate and separate from the LPA rich phase. It is generally agreed that microvoids formed in the LPA-rich phase or in the interface between the LPA-rich and the UP-rich phases. These microvoids would compensate for the polymerization shrinkage of the UP resin. Both unthickened and thickened resins were cured with 1 wt% of TBP at 150°C for 10 min. The concentrations of the thickeners were 1.5 wt% and 9 wt% of MgO and MDI, respectively. To control the viscosity of the thickened resins, curing was conducted when the viscosity of all thickened resins reached about 2×10^7 cP. Before curing, all resin mixtures were transparent, except for the LPA/MgO sample. Because of the low solubility of MgO in the resin mixture, the LPA/MgO sample was turbid.

After curing, the unthickened and the LPA-M/MDI samples turned opaque. The cured sample of LPA/MgO was translucent, while the cured LPA/MDI sample remained largely transparent. If sample opacity is an indication of heterogeneous polymer structure and/or the presence of voids, these results suggested that a strong phase separation and microvoids formation have occurred in the unthickened and LPA-M/MDI samples, some phase separation and microvoids formation have occurred in the LPA/MgO sample, while little phase separation and microvoids formation have occurred in the LPA/MDI sample during curing. This order is reasonable, considering that LPA molecules were not linked to the UP resin in the unthickened sample, and could be easily separated from the thickened UP resin at elevated temperatures in the LPA-M/MDI system. Therefore phase separation between LPA and LPA-M and the cured UP resin was strong, and microvoids could be easily formed in these samples. In the thickened LPA/MgO sample, the ionic bonds could be weakened but not completely broken by heating. Consequently, phase separation and microvoids formation were not as strong as in the first two samples. In the thickened LPA/MDI sample, the LPA and the UP molecules remained chemically bonded during curing, therefore, little phase separation could occur.

Figure 8 shows the SEM micrographs of the cross-section of the cured samples. For the unthickened sample (*Figure 8a*), the structure of aggregated globules was clearly observed. The average diameter of the globules was 1.5 μm. For the LPA-M/MDI sample (*Figure 8b*), a structure of aggregated globules was also observed. The
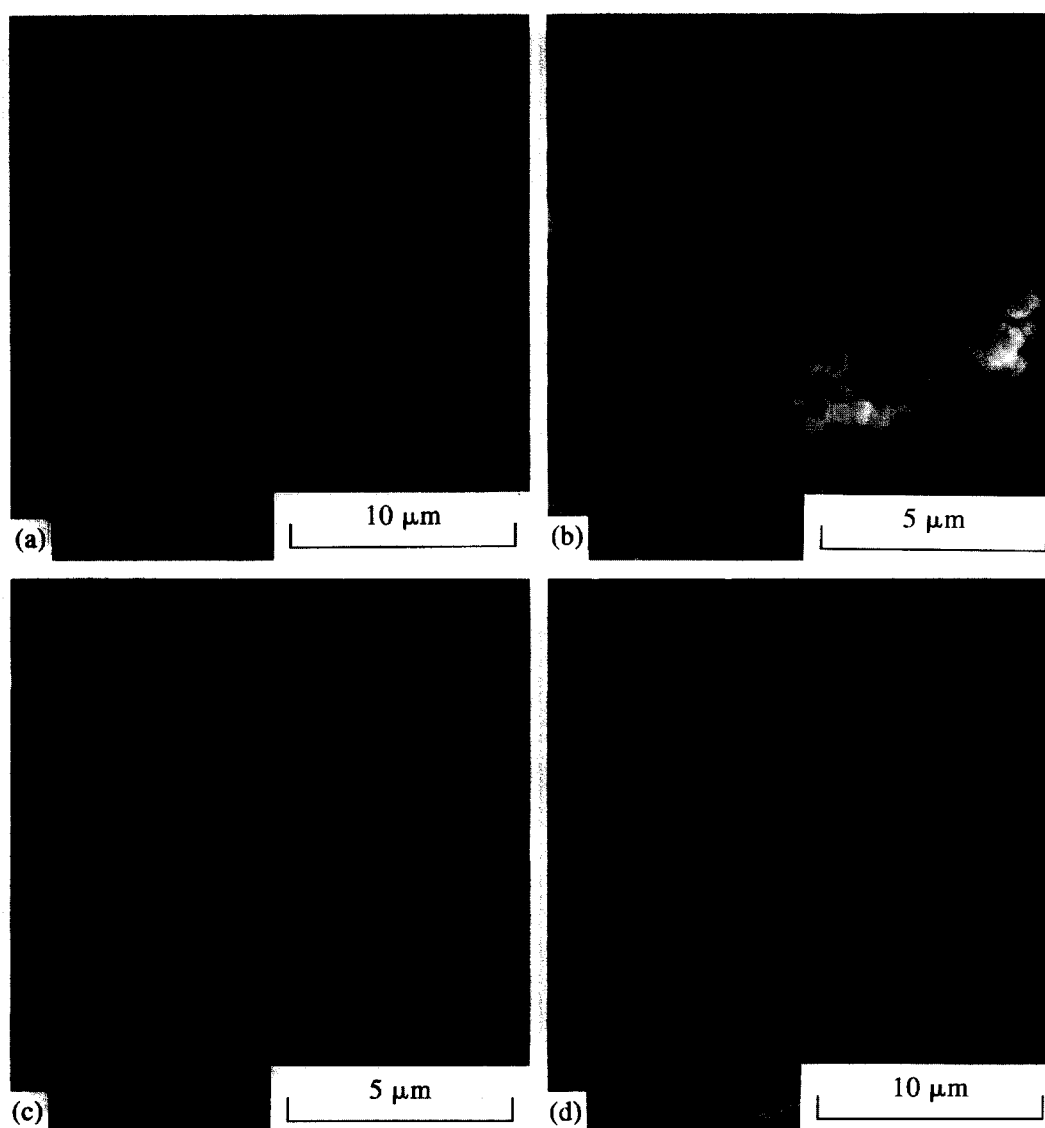
Figure 8 SEM micrographs of samples cured with TBP at 150°C: (a) the LPA resin without thickening; (b) the LPA-M resin thickened with MDI; (c) the LPA resin thickened with MgO; (d) the LPA resin thickened with MDI

diameter of the globules in the LPA-M/MDI sample (500 nm) was smaller than that in the unthickened sampled (1.5 μm). This is probably due to the change of compatibility between UP and LPA when LPA was modified. For the LPA/MgO sample (*Figure 8c*), the globular type structure could be seen, however, many globules were linked together. Thus, it is concluded that the performance of LPA on phase separation was reduced by thickening with MgO. For the LPA/MDI sample (*Figure 8d*), although there were some large globules, no clear phase separation could be observed. Most globules were linked to the continuous phase because the bonds between the LPA molecules and the UP resin could not be broken.

To quantify the amount of microvoids in the cured sample, the surface area measured by the BET technique has been found to be a good index[20]. For the BET technique, the volume of gas, V, adsorbed at pressure P is given as follows:

$$V = \frac{V_m C P}{(P_0 - P)[1 + (C - 1)(P/P_0)]} \qquad (1)$$

Where V_m is the volume of gas adsorbed in one complete

unimolecular layer, C and P_0 are constant and saturated pressure, respectively. Equation (1) can be rearranged as

$$V_a = \frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0} \qquad (2)$$

A plot of V_a against P/P_0 should give a straight line with its intercept being $1/V_m C$ and its slope being $(C - 1)/(V_m C)$. From the slope and the intercept, the two constants, V_m and C can be determined. By combining the covering area of one krypton molecule (21 Å^2) with V_m, the surface area can be calculated. In *Figure 9*, the relation between the pressure (P/P_0) and the absorbed volume (V_a) is shown. For all samples except the LPA/MDI samples, the absorbed volume of krypton is linearly proportional to the pressure. For the LPA/MDI sample, the surface area was too small to be measured with this equipment. The surface area of the LPA/MDI sample was estimated in the range of 0.1 to 0.2 m^{2}g^{-1}.

The surface area of the unthickened LPA sample showed a maximum value of 0.797 m^{2}g^{-1} among the four samples. The clear phase separation observed by SEM for
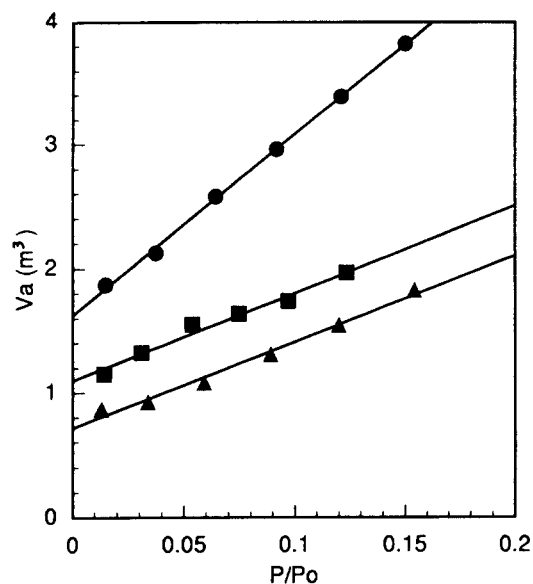
Figure 9 The relation between V_a vs. P/P_0 for cured samples. (■) The LPA resin without thickening; (▲) the LPA-M resin thickened with MDI; (●) the LPA resin thickened with MgO

the unthickened sample supports this result. The sample of LPA/MDI showed the minimum surface area due to poor phase separation. For the LPA/MgO sample, the surface area of $0.349 \, \mathrm{m^2 g^{-1}}$ was between that of the unthickened sample and that of the LPA/MDI sample. This again indicates that the effect of LPA on the shrinkage control was reduced by the MgO thickening.

For the three thickened samples, the LPA-M/MDI sample showed the largest surface area $(0.674 \, \mathrm{m^2 g^{-1}})$. This value is very close to that of the unthickened sample, which suggests that LPA-M may act as a better shrinkage controller than the LPA thickened with MgO.

In order to investigate the effect of temperature on sample morphology, the curing experiments were also carried out at 125°C for 10 min. The composition of the samples remained the same except that 1 wt% of PDO was used in order to keep the high reaction rate.

Figure 10 shows the SEM micrographs of cross-section of cured samples at 125°C. The unthickened sample turned from a transparent yellowish solution to a white opaque solid as in the case of 150°C curing. The morphology of the unthickened sample cured at 125°C is shown in *Figure 10a*. It shows clear phase separation with aggregation of globules. The average diameter of globules was $1.2 \, \mu m$, which is nearly the same as that cured at 150°C. The thickened sample of LPA/MgO turned from a slightly yellowish turbid mixture to a translucent white solid during curing. The LPA/MgO sample cured at 125°C was much more translucent than that cured at 150°C. The morphology of the LPA/MgO sample cured at 125°C is shown in *Figure 10b*. The flake-like structure indicates that phase separation in this sample was less than that cured at 150°C (*Figure 8c*). This implied that the shrinkage control performance of the LPA thickened with MgO may decrease when the curing temperature is reduced from 150°C.

The thickened sample of LPA-M/MDI turned from a transparent brown mixture to a slightly brown opaque solid during curing, which was similar to the case of 150°C curing. The morphology of the LPA-M/MDI
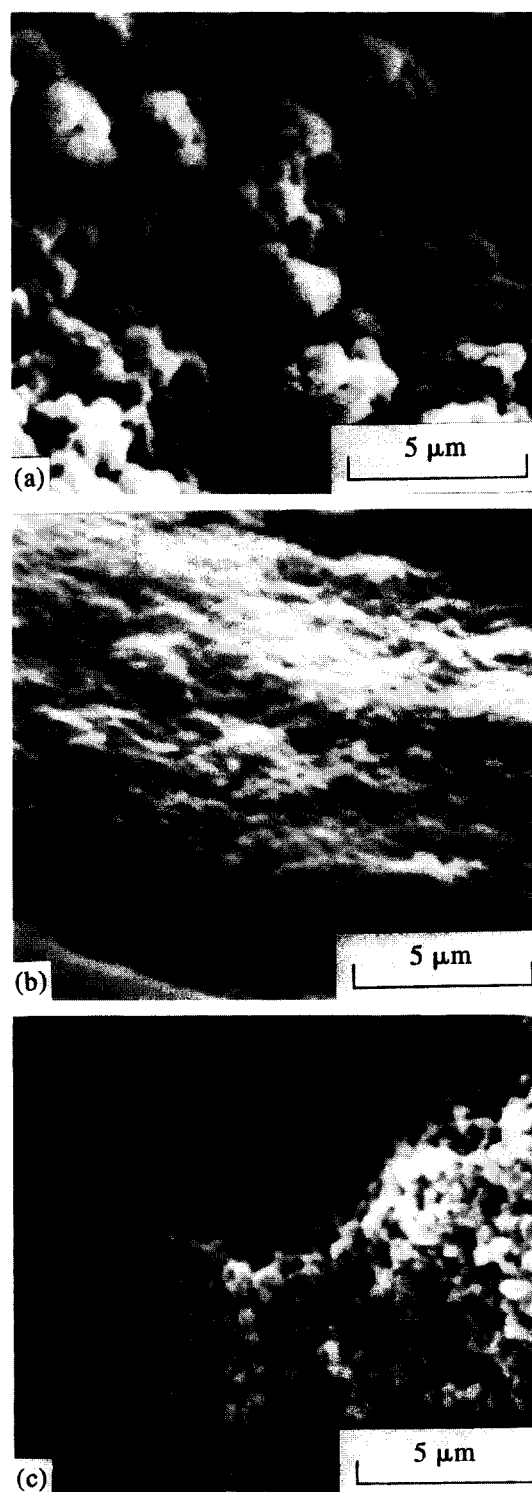
Figure 10 SEM micrographs of samples cured with PDO at 125°C: (a) the LPA based resin without thickening; (b) the LPA based resin thickened with MgO; (c) the LPA-M based resin thickened with MDI

sample cured at 125°C is shown in *Figure 10c*. The aggregation structure of globules with 500 nm in diameter is very similar to that of sample cured at 150°C (*Figure 8b*). From these results, we may conclude that the efficiency of LPA-M could remain the same when the curing temperature was reduced from 150 to 125°C.

To further investigate the effect of temperature on the morphology of LPA-M/MDI sample, the curing experiments were carried out at 80 and 60°C with 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane (Luper-
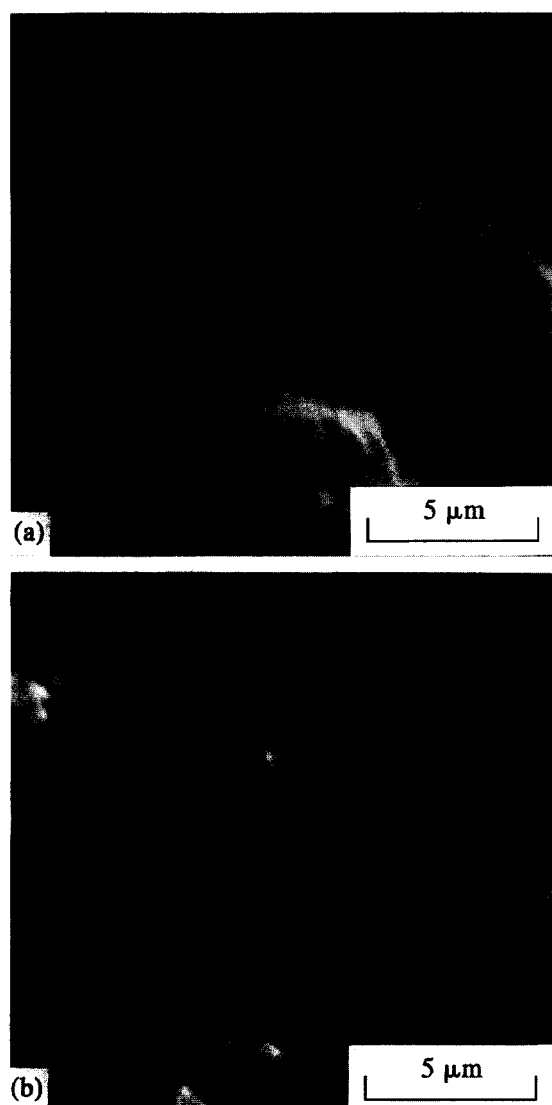
Figure 11 SEM micrographs of samples of the LPA-M based resin thickened with MDI cured at (a) 60°C and (b) 80°C
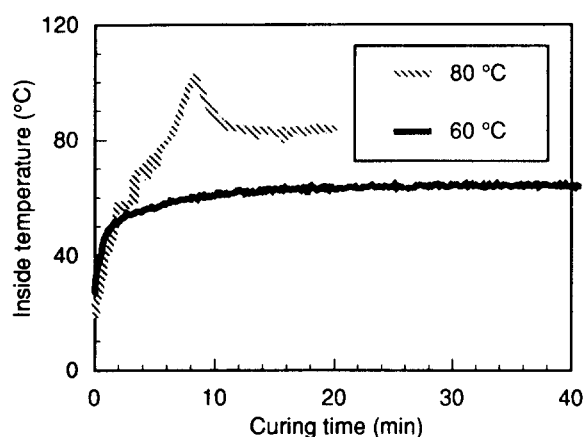

Figure 12 The resin temperature change during curing

sol 256) as the initiator. At 80°C, the cured sample also turned to an opaque solid. The sample cured at 60°C, however, was mostly translucent. *Figure 11* shows the micrographs of the LPA-M/MDI samples cured at 80 and 60°C. A clear phase separation can be seen in the 80°C cured sample, but not in the 60°C cured sample.

This indicates that most thickened bonds did not break at 60°C. Because of the reaction exotherm, the sample temperature could be much higher than the mould temperature during curing. To verify this, the temperature at the centre of the sample was measured by a thermocouple during curing. For the sample cured at 80°C, the inside temperature reached 103°C, while the maximum temperature for the sample cured at 60°C was only 64°C as shown in *Figure 12*. These results together with the d.s.c. curves shown in *Figure 4* confirm that the decomposition of thickened bonds in the LPA-M/MDI sample determined the morphology of the cured resin and the bond decomposition could be controlled by changing temperature.

BMC moulding

The weight of the charge placed in the mould was around 560 g with less than 2% variation. The mould surface temperature was also very consistent among the same initiator series. The moulding pressure varied from 20 to 30 tons, from run to run, but was constant within the run. Although the pressure varied between runs, the results of shrinkage control and surface quality did not seem to be affected.

The sample charge was placed at the centre of the mould cavity to ensure the same mould filling pattern for each sample. It was found that the LPA/MDI series had more difficulty filling up the mould cavity than the other two series. This is because the viscosity of the LPA/MDI series did not drop much during mould filling.

In order to obtain the temperature profile of the material during curing, the samples of the LPA-M/MDI series with different initiators were moulded in a 30-ton hydraulic press. The mould was simply a stack of 20.32×20.32 cm card boards with a 12.7×12.7 cm mould cavity. Each compound was shaped into two plies of 12.7×12.7 cm sample and inserted into the mould cavity. Two iron–constantan thermocouple wires, 0.0508 cm diameter (24 gauge), were placed into the sample, one between the two compound plies and the other near the top surface. The thickness of the samples was about 0.635 cm. The highest temperatures that can be reached were 220, 180, 130 and 110°C, respectively, for the mould surface temperatures of 150, 120, 100 and 85°C, respectively.

After moulding all the panels, the dimensions of the panels and the mould were measured to calculate the sample shrinkage.

Mould shrinkage is the comparison of the cold mould and the cold part dimensions and has units in length shrinkage per length part, or in percentage. The moulding shrinkage is determined by:

Shrinkage (cm/cm) $= (a - b)/a$

where:

$a = \sum$ lengths of four sides of the cold mould

$b = \sum$ lengths of four sides of the cold part

The value in *Table 3* is the average shrinkage value of three panels with the same formulation. A larger number means a larger shrinkage of the parts, and therefore, a smaller number means better shrinkage control. Several trends can be observed from *Table 3*. In the LPA/MgO series, the number increases as the temperature

Table 3 The average shrinkage values of BMC panels

	LPA/MgO ×10⁻³ (cm/cm)	LPA/MDI ×10⁻³ (cm/cm)	LPA-M/MDI ×10⁻³ (cm/cm)
150°C	1.00 ± 0.2	2.00 ± 0.1	1.40 ± 0.2
120°C	1.30 ± 0.1	1.7 ± 0.1	0.74 ± 0.05
100°C	1.78 ± 0.05	3.00 ± 0.2	1.00 ± 0.1
80°C	1.91 ± 0.05	1.80 ± 0.1	1.00 ± 0.2

Table 4 The values of roughness average (Ra) of BMC panels

	LPA/MgO	LPA/MDI	LPA-M/MDI
150°C	1.5 ± 0.5	2.8 ± 0.5	1.8 ± 0.5
120°C	2.3 ± 0.5	3.3 ± 0.5	2.0 ± 0.5
100°C	3.0 ± 0.5	3.5 ± 0.5	2.0 ± 0.5
80°C	4.0 ± 1.0	3.5 ± 1.0	1.8 ± 0.5

decreases. In the LPA/MDI series, the number is independent of temperature but generally is larger than that of the LPA/MgO series, which means a larger shrinkage. In the LPA-M/MDI series, the number is also independent of temperature but is closer to that of the high temperature LPA/MgO samples.

In *Table 4*, the values of roughness average (Ra) of BMC panels are listed. The number is the average value of three panels with the same formulation. A smaller number means a better surface quality. In the LPA/MgO series, the number increases as the temperature decreases. In the LPA/MDI series, the number is independent of temperature but generally is larger than that of the LPA/MgO series. In the LPA-M/MDI series, the number is also independent of temperature but is closer to the number of the high temperature LPA/MgO samples.

The BMC moulding results agree well with the analytical results stated earlier. It is clear that the modified LPA provides a better shrinkage control and surface quality than the regular LPA at low temperature-moulding.

CONCLUSIONS

The thickening behaviour and morphological changes of low profile unsaturated polyester (UP) resins, using either methyl diphenyl diisocyanate (MDI) or magnesium oxide (MgO) as a thickener were investigated. MDI-based compounds showed a rapid viscosity build-up during thickening and a stable viscosity control during storage. Upon heating, the viscosity decrease of MDI-based compounds was very small. The covalent bonding between the isocyanate groups and the hydroxyl or carboxyl groups of UP and LPA limited the phase separation between the UP and the LPA phases during curing. Consequently, the shrinkage control of MDI-based compounds was poor. MgO-based compounds, on the other hand, showed a slow viscosity build-up during thickening. The compound viscosity kept changing during storage. Upon heating, the viscosity decrease was substantial, however, the compound viscosity could

not be reduced to the initial viscosity level. Because the ionic bonding between MgO and the carboxyl groups of UP and LPA became weaker at elevated temperatures, some phase separation occurred during curing. Consequently, the shrinkage control of MgO thickened material was better than that of MDI thickened compounds, but not as good as that of unthickened compounds. When a thermo-breakable chemical with hydroxyl groups, such as diketo compounds, was grafted on the LPA, it was found that MDI-thickened material based on this modified LPA showed a fast viscosity build-up during thickening, a stable viscosity control during thickening, and a good shrinkage control during curing.

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