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Modification of unsaturated polyester resins for viscosity control

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Thermally breakable functional groups based on diketogulonic acid and salt formation between amine and carboxy groups were grafted onto the chains of unsaturated polyester (UP) molecules. These functional groups are stable at room temperature but can be broken at elevated temperatures. They can also react with isocyanates. The modified UP resin showed a fast viscosity rise during thickening and a stable viscosity during room temperature storage. Upon heating the thickened resin, we found that the viscosity was reduced to much lower than the viscosity of the regular resins. With a combination of modified and unmodified resins, the viscosity changes of the UP compounds can be controlled during moulding. Published by Elsevier Science Ltd.

(Keywords: unsaturated polyester resin; diketo compounds; amine salt)

INTRODUCTION

Unsaturated polyester (UP) resins are some of the most widely used thermoset polymers. Their major applications are for composite products manufactured by compression moulding in the form of sheet moulding compounds (SMCs) or bulk moulding compounds (BMCs), injection moulding in the form of BMCs, resin transfer moulding (RTM), casting and manual lay-up. For SMCs and BMCs, the materials are generally thickened for easy handling and good fibre-carrying characteristics during mould filling. Common thickeners for UP resins are group IIA metal oxides or hydroxides and diisocyanate compounds. For the metal oxides or hydroxides, the thickening process proceeds via the formation of ionic bonds by the reaction of the alkaline oxides or hydroxides with the carboxy end-groups of the UP molecules. For the diisocyanates, covalent bonds are formed with the hydroxy and carboxy end-groups of the UP molecules through the formation of urethane linkages during the maturation process.

Magnesium oxide (MgO) and magnesium hydroxide ($Mg(OH)_2$) are the most popular thickeners used in industry because of their low cost and high thickening efficiency[1,2]. However, the maturation process based on MgO or $Mg(OH)_2$ is slow and the viscosity of the thickened compound is sensitive to humidity and temperature variations[3,4]. On the other hand, the thickening process based on diisocyanates is fast and the thickened compound has a stable viscosity. However, the viscosity drop of the thickened compound is fairly small during moulding owing to strong covalent bonding.

An ideal viscosity profile for moulding of SMCs or BMCs is shown in *Figure 1*. The desirable viscosity varies at different stages. The compound viscosity should increase quickly during thickening and should remain stable afterwards to provide a long shelf life. During the moulding process, a higher initial viscosity is desirable since it can provide a better fibre-carrying capability. Near the end of mould filling, the charge becomes very thin and thus requires a much higher pressure for further material flow in order to fill the details and the corners of the mould cavity. Accordingly, a lower viscosity is necessary.

In recent years, there has been a growing interest in industry to develop compounds which can be moulded at very low press pressures (6.9×10^5–$1.7 \times 10^6\,N\,m^{-2}$ (100—250 psi) instead of 5.5×10^6–$2.1 \times 10^7\,N\,m^{-2}$ (800–3000 psi)) such that low cost, non-steel moulds can be used. A commercially available low pressure moulding compound, Crystic Impreg[5], has been developed for this purpose. Crystic Impreg is based on a crystalline unsaturated polyester made by reacting symmetric glycols such as neopentyl glycol, 1,6-hexanediol and 1,4-cyclohexanedimethanol with fumaric acids. At room temperature, the crystallinity of the unsaturated polyester may serve as a thickener for the compound, whereas when the compound temperature is raised above 60°C, the crystal may melt, and the compound viscosity may drop substantially. This type of maturation can be considered as a physical thickening process, in contrast to the chemical thickening process based on the group IIA metal oxides and hydroxides or diisocyanates. The matured compound is very stable and can be stored at room temperature for a prolonged time period. However, owing to the sharp crystalline melting transition, the viscosity of the compound may become too low at elevated temperatures to carry the fibres effectively during moulding.

In this study, a modified unsaturated polyester was synthesized to vary the rheological changes of resins

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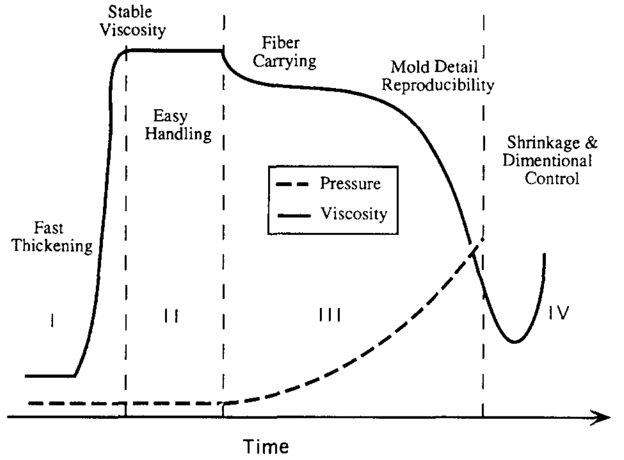


Figure 1 Ideal viscosity profile for SMCs or BMCs during moulding: (I) thickening; (II) storage; (III) mould filling; (IV) curing

during thickening and moulding. A thermally breakable diketo group[6] was introduced onto the unsaturated polyester molecules through salt formation. This group, together with the salt, may break at elevated temperatures, and therefore reduce the compound viscosity upon heating. Temperature and shear effects on the viscosity changes were investigated.

EXPERIMENTAL

Materials

The unsaturated polyester resin (B95) was supplied by Cook Composites and Polymers. The B95 resin is a maleic anhydride and propylene glycol based UP with mostly carboxy groups on both ends. It has a number average molecular weight of 1500 and an average of 9.5 C=C bonds per UP molecule. Styrene (ST) (Aldrich Chemical) was used as received. At higher temperatures, t-butyl peroxybenzoate (TBP, Atochem) with a molecular weight of 194, an activation energy of 33.0 kcal mol^{-1} (1 cal = 4.2 J) and a half-life at 101°C of 10 h was used as the initiator. At lower temperatures, t-butyl peroxy-2-ethylhexanoate (PDO, Atochem) with a molecular weight of 216, an activation energy of 34.0 kcal mol^{-1} and a half-life at 77°C of 10 h was used as the initiator.

Synthesis of the modified unsaturated polyester (MUP)

Amine-terminated unsaturated polyester. The B95 resin was dissolved in dichloromethane (DCM) to form a

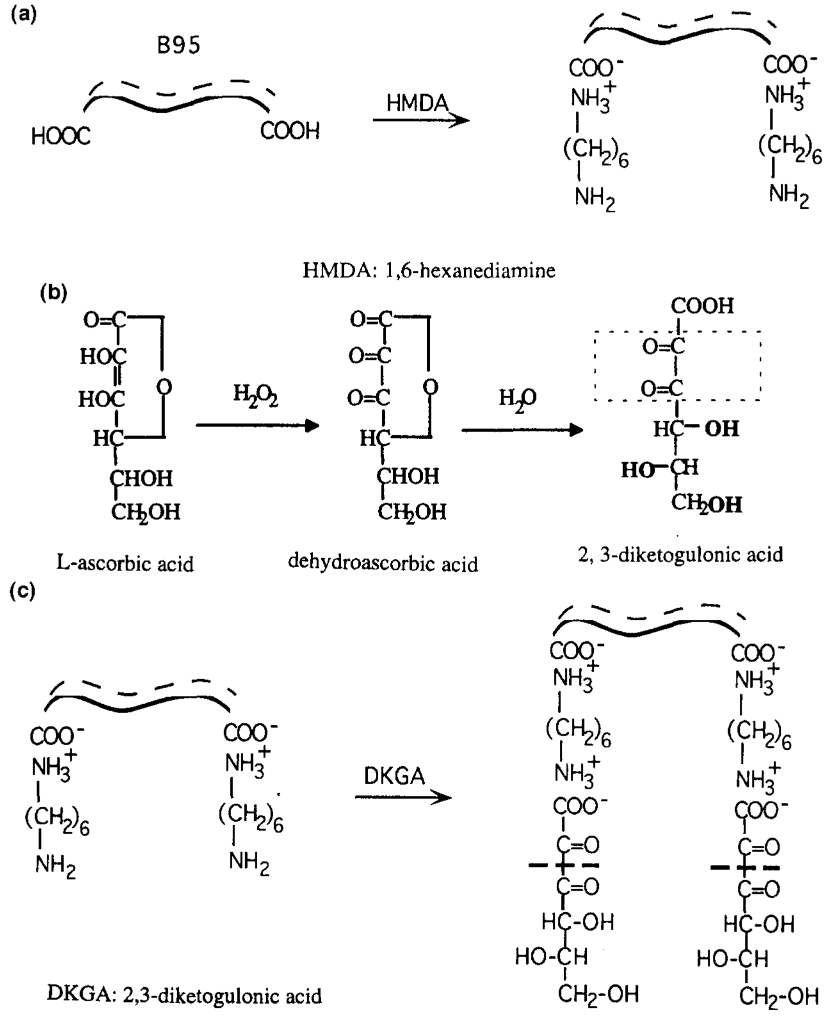
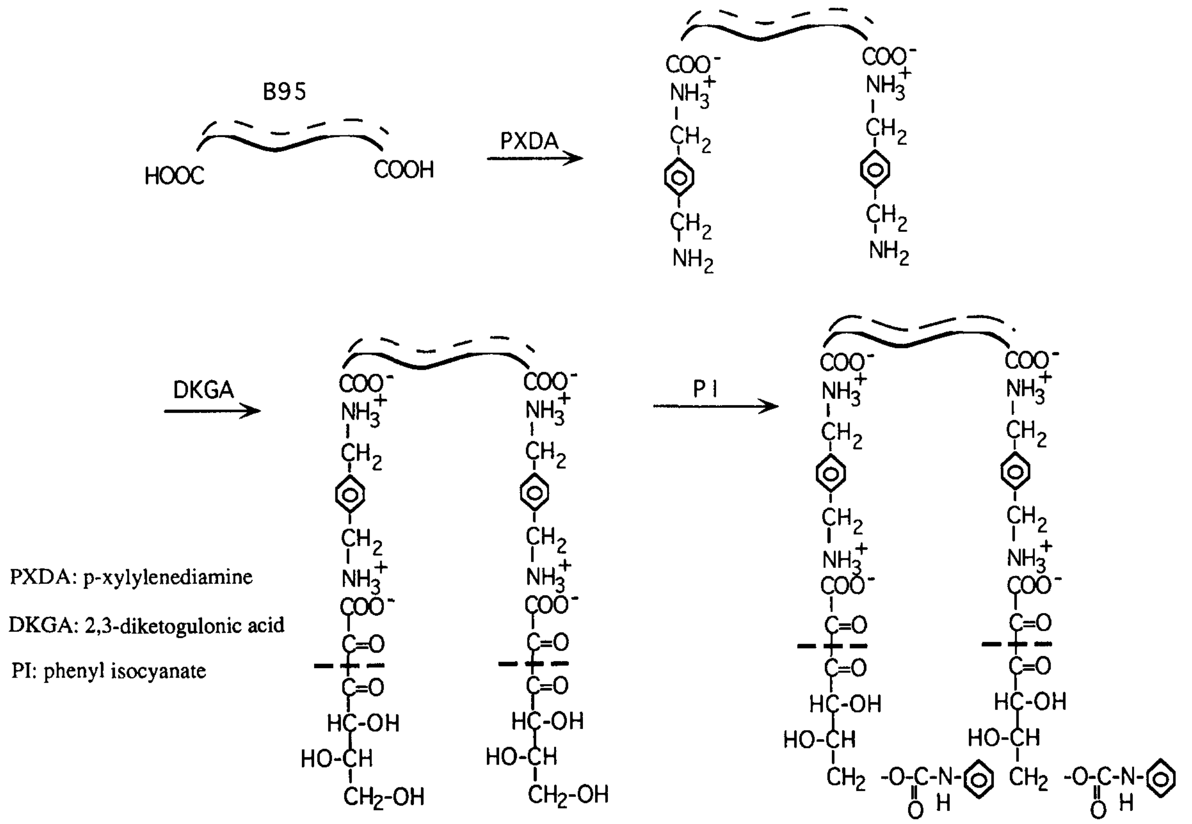


Figure 2 Schemes for (a) the reaction of B95 with HDAM, (b) the synthesis of 2,3-diketogulonic acid (DKGA) and (c) the reaction of B95–HDAM with DKGA



PXDA: p-xylylenediamine

DKGA: 2,3-diketogulonic acid

PI: phenyl isocyanate

Figure 3 Capping reaction and the final structure of the MUP

33 wt% polymer solution. To form the amine-terminated UP, we added 1,6-hexanediamine (HDAM) in a molar ratio of amine groups to carboxy groups ($[NH_2]/[CO_2H]$) of 2.2 to the polymer solution. The solution was stirred for 0.5 h until the pH turned basic (i.e. a pH of around 9). The reaction scheme is shown in *Figure 2a*.

Diketogulonic acid. Ascorbic acid was used to synthesize the diketogulonic acid (DKGA) containing a thermally breakable diketo group[6,7] (see *Figure 2b*). An aqueous solution of 33% ascorbic acid was reacted with hydrogen peroxide overnight at room temperature to form the diketogulonic acid. The diketogulonic acid, however, may be further oxidized to form L-xylosone, L-threonic acid and oxalic acid in the presence of hydrogen peroxide[8]. Therefore, the final product may be a mixture of diketogulonic acid with several other acids.

Modified unsaturated polyester. The MUP was prepared by the reaction of the amine-terminated UP resin and the diketogulonic acid in a molar ratio of 1 (see *Figure 2c*). The polymer solution was stirred for about 2 h at room temperature until the solution pH turned neutral. The final product was a mixture of the MUP, DCM and water. The solution was then placed under vacuum at about 35°C until all the solvents were evaporated. The dried polymer was checked using a differential scanning calorimeter (DSC 2910, TA Instruments) and a Fourier transform infra-red (*FT*i.r.) spectrometer (model 20 DX spectrometer, Nicolet) to make sure that there was no solvent left.

The modified UP resin based on 1,6-hexanediamine was found to have a low compatibility with styrene. The maximum achievable styrene concentration in the mixture of resin and styrene was 43 wt%, i.e. the maximum molar ratio of styrene to the C=C bonds of the modified UP was 1.5. This is because 1,6-hexanediamine is not very soluble in styrene. The strong hydrogen bonding of the six hydroxy groups of the modified UP also tended to reduce the styrene compatibility. Another major drawback of this modified UP was that the viscosity drop of the thickened resin was small upon heating, owing to the presence of a large number of hydroxy groups which tended to form a highly branched polymer when the resin was thickened with diisocyanates.

In order to solve these problems, we made several changes. Firstly, an aromatic diamine, *p*-xylylenediamine, was used to replace 1,6-hexanediamine in the modification. With this aromatic diamine, the compatibility of the modified UP and styrene was improved. A molar ratio of 2 between styrene and the C=C bonds of the modified UP could be achieved. Secondly, to reduce the hydrogen-bonding effect, we used phenyl isocyanate to cap some of the hydroxy groups on the modified UP resin. Tests were done for capping one, two and four hydroxy groups. The capping process was carried out after the modified UP was dissolved in styrene. The viscosity of the resin did not change considerably when one hydroxy group was capped on the modified UP. When two or four hydroxy groups were capped, the viscosity of the resin reduced greatly. However, capping four hydroxy groups on the modified UP molecule tended to reduce the thickening activity too much, and consequently the maturation process with diisocyanates became very long (more than 50 h). Therefore, capping

Table 1 Compositions of samples used in this study

Sample	UP (wt%)	MUP (wt%)	ST (wt%)
100% UP	43.2	0.0	56.8
30% MUP/70% UP	31.5	13.5	55.0
40% MUP/60% UP	27.4	18.3	54.3
100% MUP	0.0	50.0	50.0

of two hydroxy groups on the modified UP was chosen in this study. The final version of the MUP was mixed with 50 wt% styrene to make the molar ratio of styrene to the C=C bonds of the MUP equal to 2. Capping some of the hydroxy groups also improved the solubility of the MUP in styrene. The capping reaction and the final chemical structure of this MUP are shown in *Figure 3*.

Preparation of thickened resin

The MUP/ST solution or a mixture of MUP/ST and UP/ST solutions was thickened with 1.5 wt% MgO or 3–8 wt% diphenyl diisocyanate (MDI) at room temperature. The molar ratio of styrene to the C=C bonds of the UP resin was always set at 2. *Table 1* lists the formulations of the compounds used in this study.

Viscosity measurement

The viscosity change during the maturation or the heating process was monitored using a Brookfield viscometer (RVDT, DV-I+ Viscometer, Brookfield Engineering Laboratories Inc.) with spindle 6 and/or 7 at 0.5 rev $\min^{-1}$ speed. The sample was loaded in a glass tube (25 mm in diameter). For heating, the test tube containing the thickened resin sample was placed in an oil bath with the temperature set at 150°C. In order to inhibit the polymerization, we used no initiator in the resin samples. Instead, 0.5 wt% benzoquinone was added for this series of viscosity measurements.

A rheometer developed by Rheometrics Inc. (a modified RDA II) in the steady shear mode was used in this study to evaluate the rheological changes of the resins under various shear rates. Viscosity was measured with the samples being heated from room temperature to 110°C with 1 wt% PDO as the initiator. Two serrated aluminium plates, 7.9 mm in diameter, were used as a sample cell. The gap between the two plates was set at 1.1 mm. Experiments were conducted at different shear rates ranging from 0.01 to 10 s^{-1}.

The reaction kinetics were measured using differential scanning calorimetry (d.s.c.). The reactions were conducted in volatile aluminium sample pans capable of

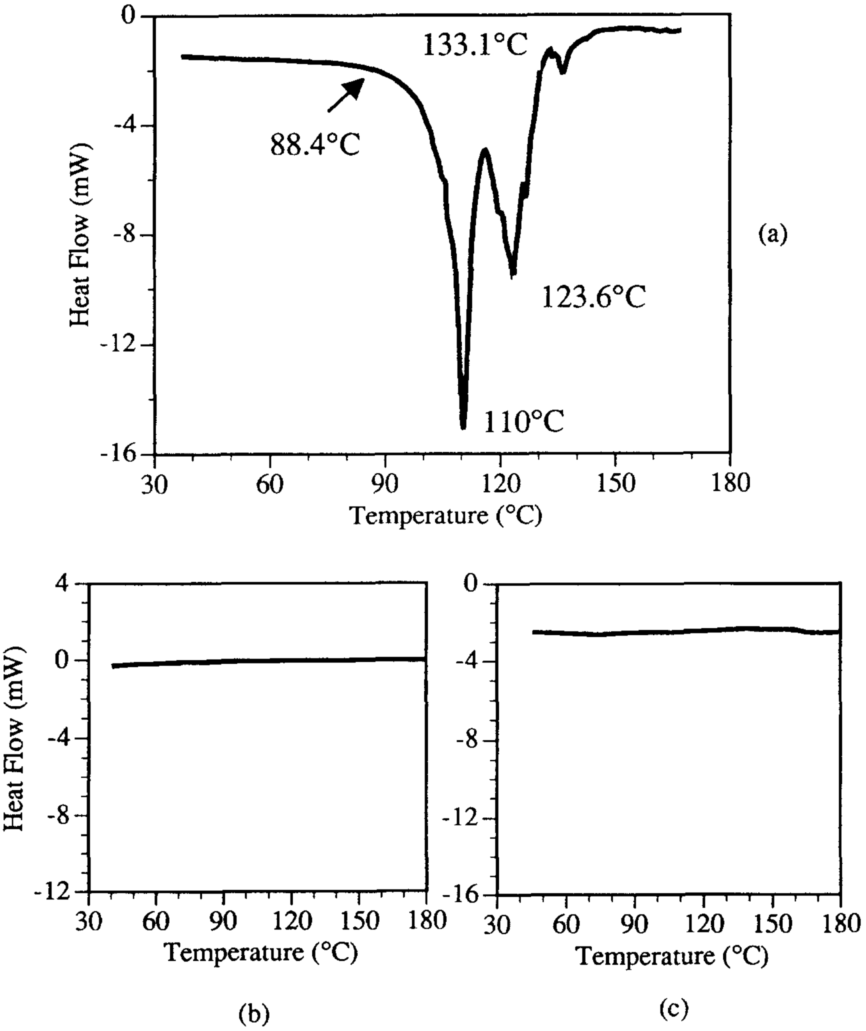


Figure 4 D.s.c. curves for (a) the MUP, (b) the residual scan of the sample in (a) and (c) the UP

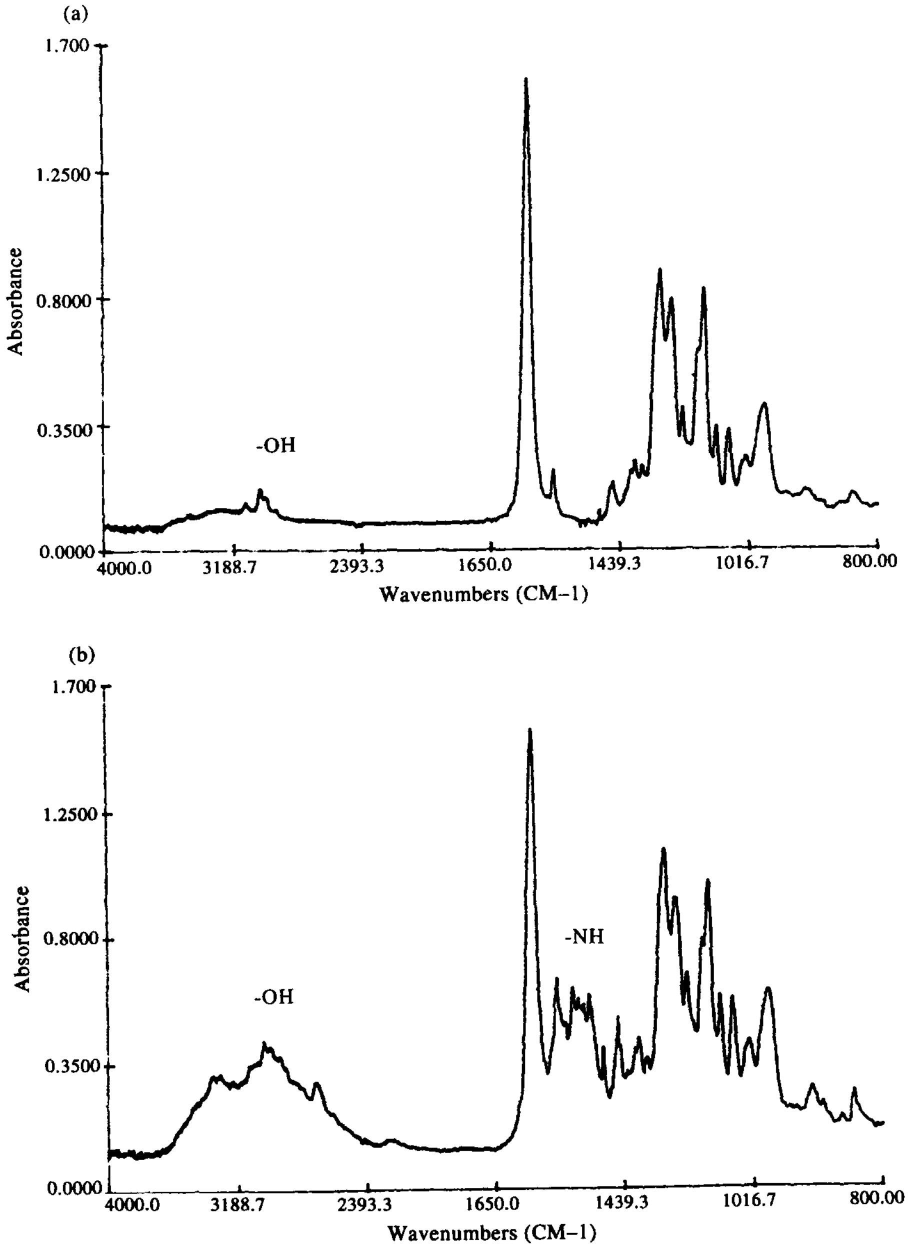


Figure 5 Comparison of the *FT*i.r. spectra of the (a) unmodified and (b) modified UP resins

withstanding at least 2 atm (1 atm = 101 325 Pa) internal pressure after sealing. The reactions were carried out in the scanning mode from room temperature to 200°C at a heating rate of $10^\circ C\,min^{-1}$.

RESULTS AND DISCUSSION

Characterization of the MUP

The MUP resin was checked with d.s.c. scanning runs at a heating rate of $10^\circ C\,min^{-1}$. *Figure 4a* shows that an endothermic peak appeared from 88 to 133°C, which indicates bond breaking in that temperature range. *Figure 4b* shows a repeat scan of the same sample; evidently, the endothermic peak has disappeared. For further verification, the same experiment was carried out for the unmodified UP resin, and the results showed that there were no endothermic peaks (*Figure 4c*). On the basis of these results, it is concluded that a thermally breakable bond has been introduced into the MUP resin and that the decomposition temperature is around 110°C. The structures of the UP before and after modification were also checked with *FT*i.r. *Figure 5* shows a comparison of the i.r. spectra of the unmodified and modified UP resins. For the MUP, a fairly broad peak appeared around $3000\,cm^{-1}$ for the multiple hydroxy groups in the MUP and amine salt. New peaks showing salt formation between amine and carboxy groups appeared in the range $1500-1700\,cm^{-1}$.

The bond breakage temperature was affected by maturation. *Figure 6* shows that the endothermic peak was broadened and the peak was delayed by adding the thickener. This may be explained in terms of an increase in molecular weight of the thickened MUP system.

Maturation process

The ideal thickening behaviour of the UP resin would involve the material reaching the saturated viscosity quickly and remaining stable afterwards. Generally,

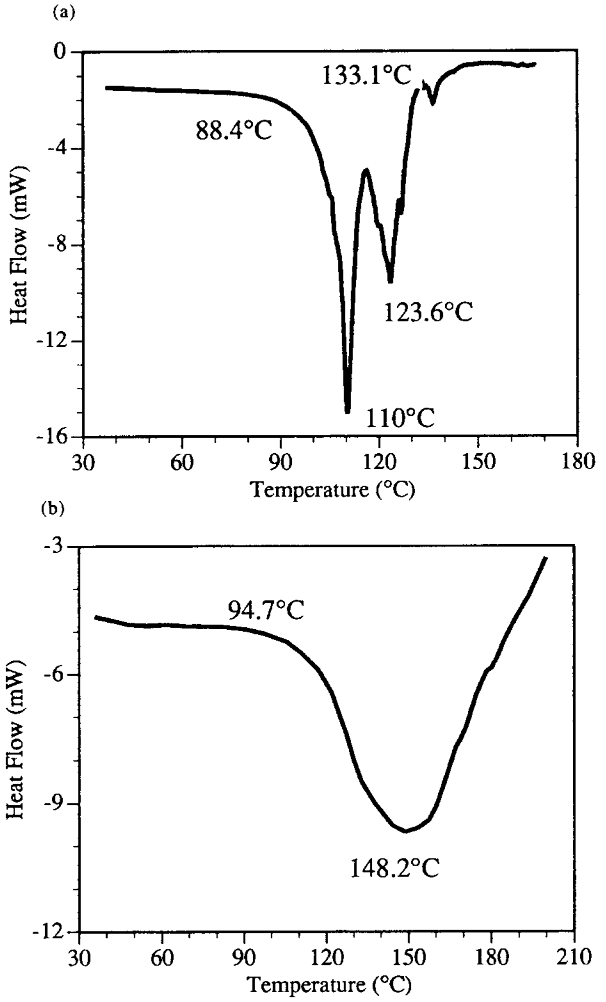


Figure 6 Comparison of d.s.c. scanning data for (a) unthickened and (b) thickened MUP resins

diisocyanate-thickened UP systems exhibit such behaviour. *Figure 7* shows a comparison of the maturation processes of UP/ST systems thickened with MgO or MDI and the MUP/ST system thickened with MDI. For the UP/ST/MgO system, the viscosity increased gradually. It took more than 200 h to reach 7.0×10^6 cP (1 P = 0.1 N s m^{-2}). After that, the viscosity still increased slowly and tended to fluctuate. On the other hand, the maturation process based on MDI was much faster and the resin viscosity remained stable after thickening. This is because urethane linkages formed were stable.

As shown in *Figure 7*, the MUP thickened with MDI showed the same thickening behaviour as the UP/ST/MDI system. However, the amount of MDI needed to give the same saturated viscosity was different. For a saturated viscosity of $8.5 \times 10^6 - 9 \times 10^6$ cP, the unmodified UP/ST system required 8 wt% MDI, i.e. a molar ratio of isocyanate groups to carboxy groups of 1.15, while only 3 wt% MDI was needed for the MUP/ST system, i.e. a molar ratio of 0.25. The difference is due to the introduction of multiple hydroxy groups onto the UP molecules, which tended to form highly branched polymers. Thus, a smaller amount of thickener was needed to achieve the same saturated viscosity.

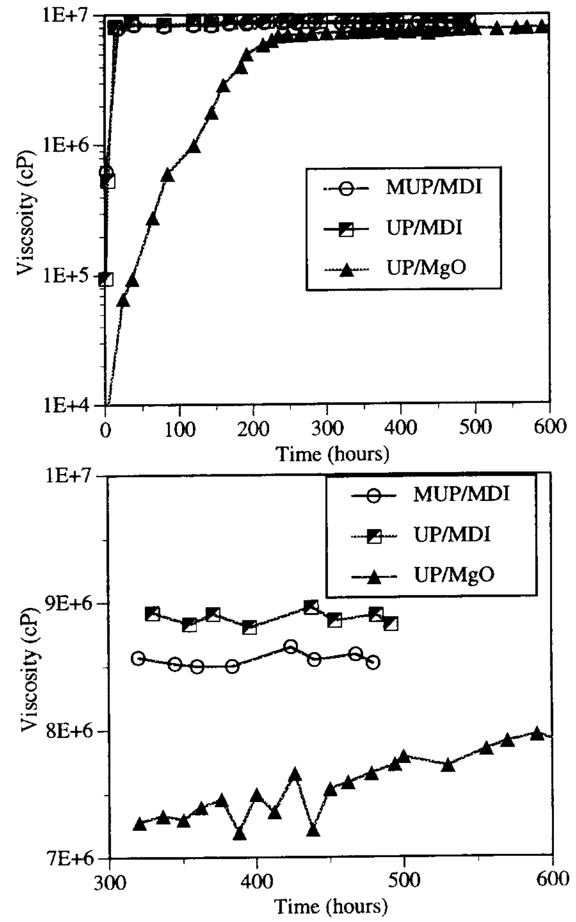


Figure 7 Viscosity changes during the maturation processes of 100% MUP/ST/3% MDI, 100% UP/ST/8% MDI and 100% UP/ST/1.5% MgO

Viscosity change during heating

In order to understand the viscosity changes during heating for the MUP resin, we compared the systems UP/ST/MDI, UP/ST/MgO and MUP/UP/ST/MDI with three different weight concentrations of MUP. The amounts of MDI added were different in order to give similar saturated viscosities. *Figure 8* shows the viscosity changes during heating for these samples, as measured by the Brookfield viscometer. The sample compositions are listed in *Table 2*. The viscosity of the UP/ST/MDI system was reduced slightly upon heating from 1.5×10^7 to 3.4×10^6 cP as the temperature was raised from room temperature to 120°C. The UP/ST/MgO system showed a viscosity drop from 9.5×10^6 to 2.1×10^5 cP when the temperature was increased from 25 to 120°C. This difference in behaviour can be explained in terms of the nature of the different bonds formed during thickening. The molecules in the MDI-based system were linked by covalent bonds, which are stable at high temperatures. In contrast, the ionic bonds formed in the MgO-based system would become unstable at elevated temperatures. As shown in *Figure 8*, the viscosity of both systems increased after about 900 s, at which point the temperature was about 110°C. This viscosity increase may have been the result of considerable styrene evaporation and thermally induced polymerization in the resin system, despite the presence of benzoquinone.

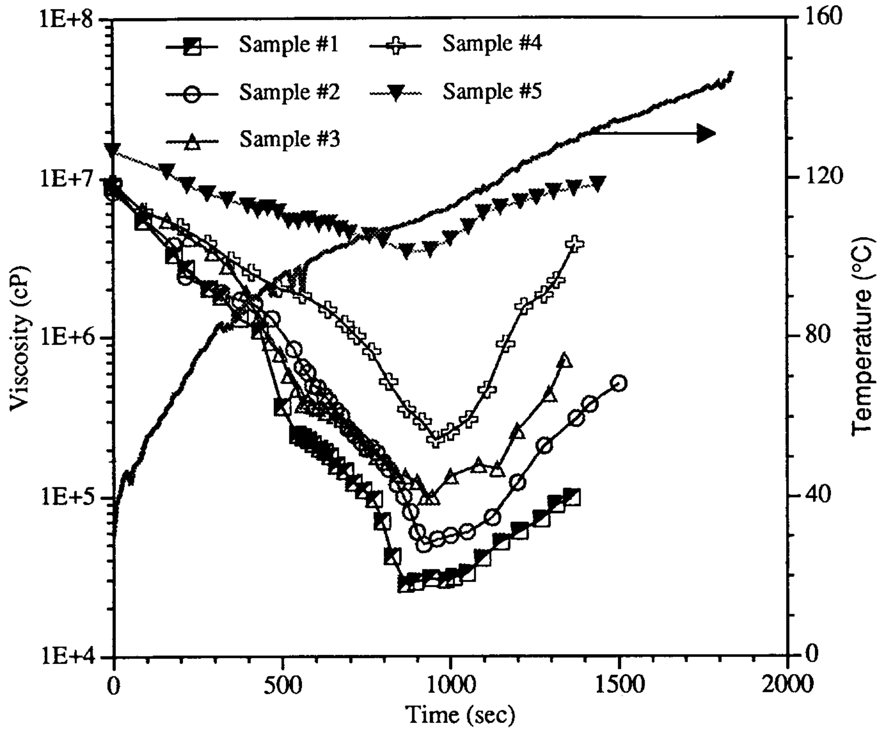


Figure 8 Viscosity changes during heating (the sample compositions are listed in *Table 2*)

Table 2 Comparison of viscosity changes

Sample	UP (wt%)	MUP (wt%)	Unthickened viscosity, μ (cP)	Thickener	Starting viscosity, μ_s (cP)	Minimum viscosity, μ_m (cP)	μ_s/μ_m
1	0.0	100.0	1.3×10^4	3 wt% MDI	9.0×10^6	2.8×10^4	321.2
2	60.0	40.0	8.2×10^3	5 wt% MDI	8.2×10^6	5.0×10^4	164.0
3	70.0	30.0	7.3×10^3	6 wt% MDI	9.1×10^6	1.0×10^5	91.0
4	100.0	0.0	1.3×10^3	1.5 wt% MgO	9.5×10^6	2.1×10^5	45.2
5	100.0	0.0	1.3×10^3	8 wt% MDI	1.5×10^7	3.4×10^6	4.5

Among the three MUP-based samples, the viscosity decreased more as the amount of MUP increased. For the 100% MUP/ST/MDI system, the viscosity decreased from 9×10^6 to 2.8×10^4 cP as the temperature increased from room temperature to 120°C. The viscosity showed a gradual drop in the beginning, then a sharp change around 95°C, indicating that the thermally breakable bonds had started to break. When the temperature was further increased, the lowest viscosity was reached at 108°C; after that, the viscosity started to increase owing to the evaporation of styrene and thermally induced polymerization of the MUP/ST system. The initial and the lowest viscosities of the 40% MUP/60% UP/ST/MDI and 30% MUP/70% UP/ST/MDI systems were 8.2×10^6 and 5×10^4 cP and 9.1×10^6 and 1×10^5 cP, respectively. Also, a rate change in viscosity drop was found around 95°C for these two samples. The lowest viscosities were found at 110 and 111°C, respectively, for these two samples.

The resin viscosity should drop to the initial value of the unthickened material (see *Table 2*) if all the thickening bonds are broken upon heating. The minimum viscosities of the UP/ST/MgO and UP/ST/MDI systems were both much larger than the initial viscosities of the unthickened resins. In the UP/ST/MgO system, the ionic bonds between MgO and the UP molecules may become weaker at elevated temperatures. However, they may not break completely. Consequently, the minimum viscosity reached during heating is much higher than the initial viscosity of the unthickened resin. For the 100% MUP system, the lowest viscosity, at 2.8×10^4 cP, was slightly higher than the viscosity of the unthickened system (1.3×10^4 cP). This indicates that although most thermally breakable bonds were broken, there were still some larger molecules formed perhaps from the urethane linkages of MDI and the hydroxy groups of the MUP molecules.

Shear effects on the gelation of the UP system

During mould filling, the compound is under a certain shear force. The dependence of the compound viscosity and gelation time on the shear rate or shear stress is an important issue since the UP compounds are non-Newtonian fluids and will become solids during moulding. *Figure 9* shows the viscosity changes of the unthickened sample and two thickened samples under different shear rates as measured using the RDA II at room temperature. All samples showed shear thinning.

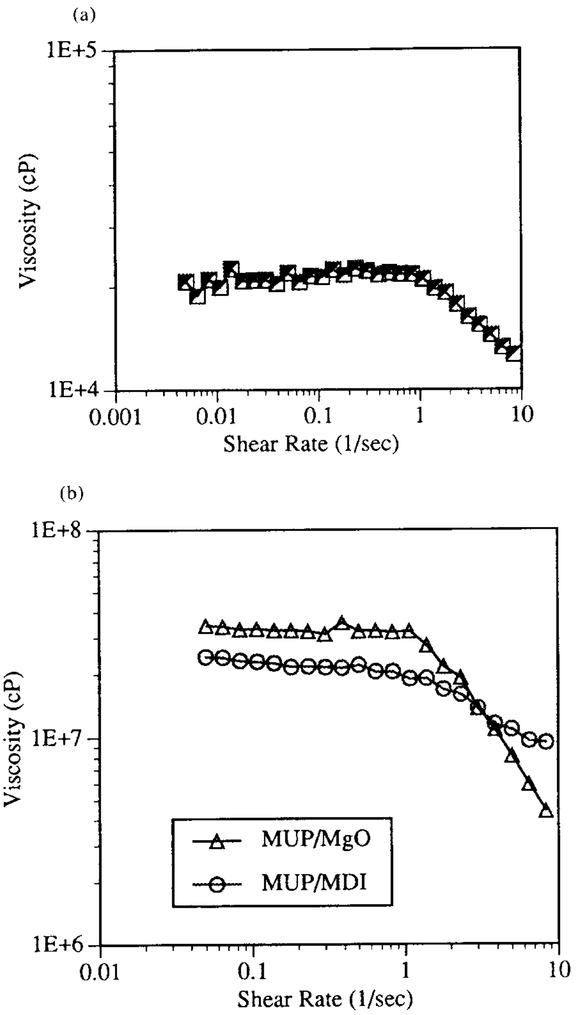


Figure 9 Shear effects on the room temperature viscosity of (a) unthickened and (b) thickened MUP resins

For the thickened samples, the viscosity of the MDI-thickened system showed less dependence on the shear rate than the viscosity of the MgO-thickened system. This is probably a result of the covalent bonding of the urethane linkage being stronger than the ionic bonding of MgO. Therefore, the shear force results in less influence on the MDI-thickened samples than on the MgO-thickened samples.

Figure 10 shows the viscosity changes during heating for the unthickened UP system at four different shear rates. The gelation time was around 160 s under the lowest shear rate, 0.1 s^{-1}, but increased to 230 s when the shear rate was increased to 5 s^{-1}. This implies that the unthickened compounds would have a longer flow time in a manufacturing process with higher shear rates, e.g. injection moulding as opposed to compression moulding. This shear rate dependence of the gelation time has been investigated in previous work[9]. It was found that the polymers formed in the reaction of a UP resin and styrene had a bimodal molecular weight distribution[10]. The smaller ones were the primary polymers formed from the radical polymerization of monomers, often referred to as 'microgels'. Because of the multifunctionality of the UP molecules, the microgels had many pendent C = C bonds, which made them highly reactive. The larger polymers observed were believed to be the result of polymerization between microgels[11]. Under shear flow, the formation of the larger polymers was delayed. Because resin gelation depended mostly on the formation of larger polymers, the gelation time became longer at higher shear rates.

The MgO-thickened system, however, did not show the same behaviour. As shown in *Figure 11*, the gelation time was largely independent of the shear rate. For the thickened MUP/ST/MDI system, a strong dependence of the gelation time on the shear rate was again observed as shown in *Figure 12*. Since the ionic bonds in the MgO-thickened system would not be totally broken upon heating, most molecules in the system were connected during polymerization. This might have prevented the formation of a bimodal molecular weight distribution. Consequently, there was little shear effect on the gelation time. On the other hand, the thermally breakable bonds would break at elevated temperature and release the UP molecules in the MDI-thickened MUP system; therefore, the polymer formation in this system should be similar to that in the unthickened UP compound. As a result, a strong shear rate dependence of the gelation time was observed in this system.

Compound viscosity design

With the different rheological characteristics of UP and MUP thickened by MgO or MDI, it is possible to design a compound based on a mixture of these materials to achieve a desirable viscosity profile. Examples are shown in *Figure 13*. The viscosity in each case was measured using the RDA II under a shear rate of 0.1 s^{-1}. For the system of 100% UP resin thickened with MgO (*Figure 13b*), a significant viscosity drop was observed at the beginning of the heat treatment caused by the relaxation of ionic bonds at elevated temperature. The viscosity increased after 30 s when the reaction started. On the other hand, for the system of 100% MUP thickened with MDI (*Figure 13c*), the resin viscosity decreased gradually at the beginning of the heat treatment, and the viscosity continued to drop despite the commencement of the resin reaction. This implies that the effect of the bond breakage of the thermally breakable groups was larger than the effect of the resin reaction in this stage. The viscosity started to increase after 140 s when the resin reaction dominated the viscosity change. For the system of 35% MUP mixed with 65% UP and thickened with MgO (*Figure 13a*), the viscosity showed a substantial drop at the beginning of the heat treatment, similar to that of the UP/ST/MgO system. The viscosity remained low for about 60 s before it started to increase, similar to the MUP/ST/MDI system. The early viscosity drop was due to the relaxation of MgO bonds, while the viscosity remained low because of bond breakage in the thermally breakable groups. These examples show that different viscosity profiles can be designed with different combinations of the resins and thickeners according to the needs of the applications.

Curing behaviour

The curing behaviour of the UP-based and MUP-based systems was investigated by d.s.c. The d.s.c. scanning data followed typical bell-shaped reaction curves for the unthickened UP/ST system and the

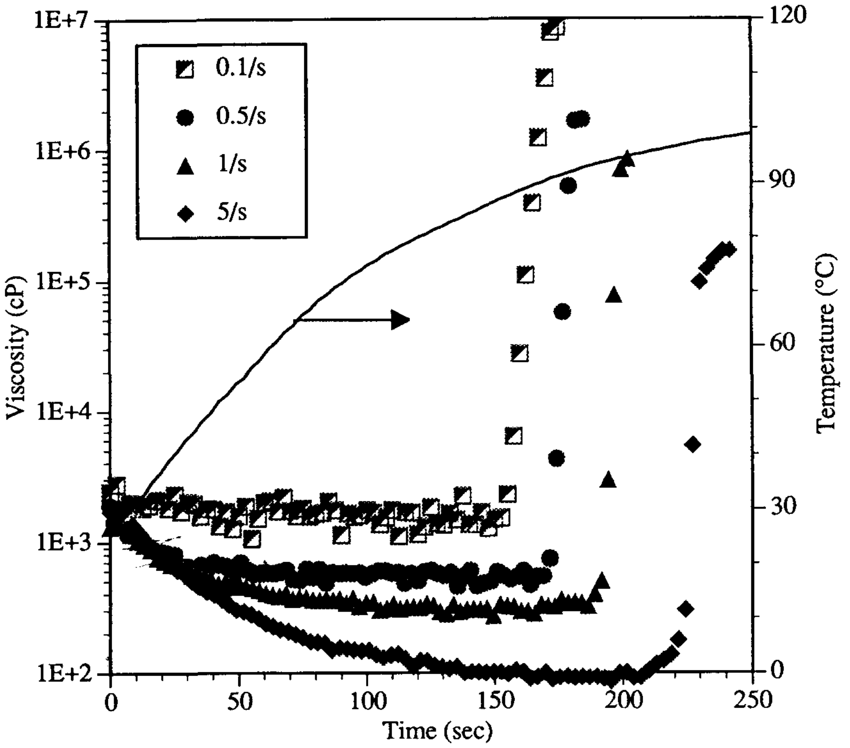


Figure 10 Shear effects on the viscosity changes and gelation time of the unthickened UP system

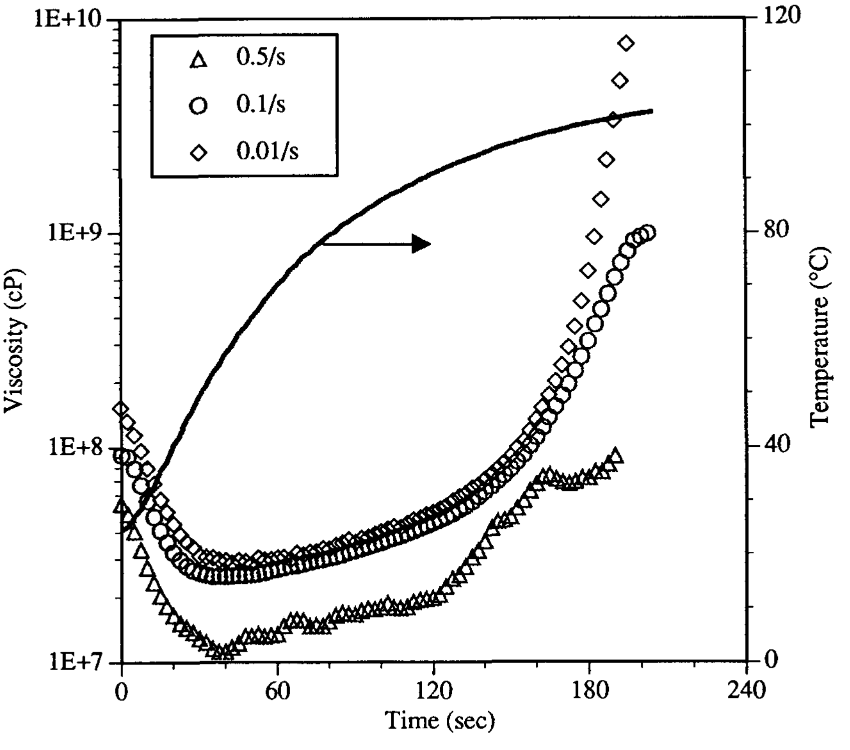


Figure 11 Shear effects on the viscosity changes and gelation time of the MgO-thickened UP system

thickened UP/ST/MgO system (see *Figures 14a* and *14b*). The peak temperatures of these two samples were similar. For the thickened UP/ST/MDI system, *Figure 14c* shows that the major reaction occurred at lower temperatures because of the catalytic effect of the amide groups in the system[12]. A small secondary reaction peak occurred at higher temperatures, probably owing to thermally induced polymerization.

Figure 15 shows the d.s.c. curves for the thickened and unthickened systems with the MUP. In all cases, an endothermic peak occurred before the major reaction peak. A sharp and narrow endothermic peak appeared around 110°C for the unthickened compound (*Figure 15a*), while a broader endothermic peak was found around the same temperature for the MUP thickened with MDI (*Figure 15c*). The reaction peak

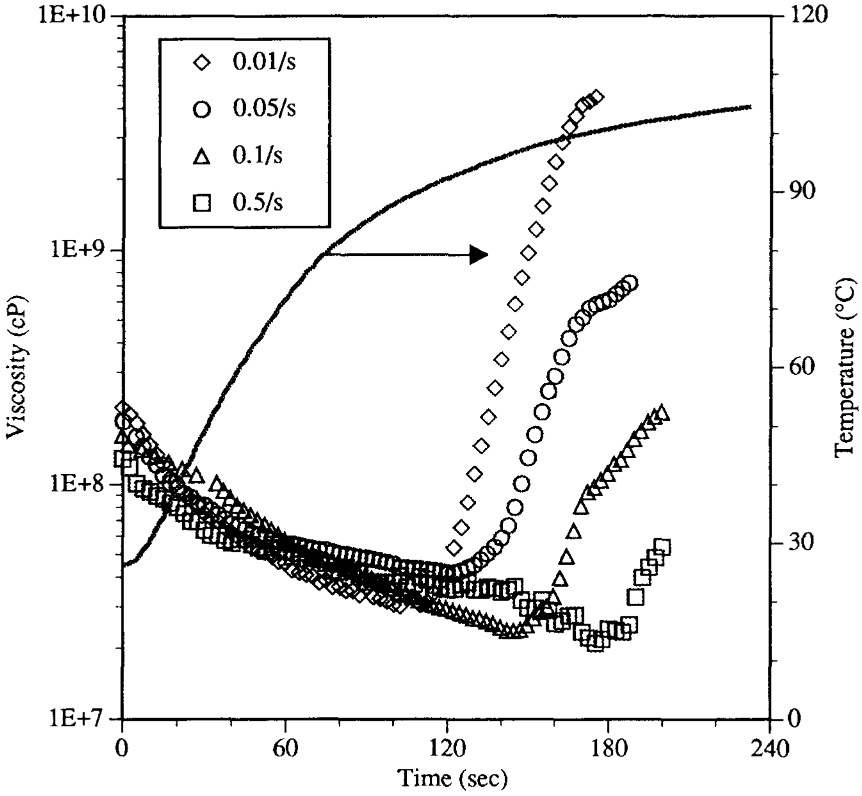


Figure 12 Shear effects on the viscosity changes and gelation time of the MDI-thickened MUP system

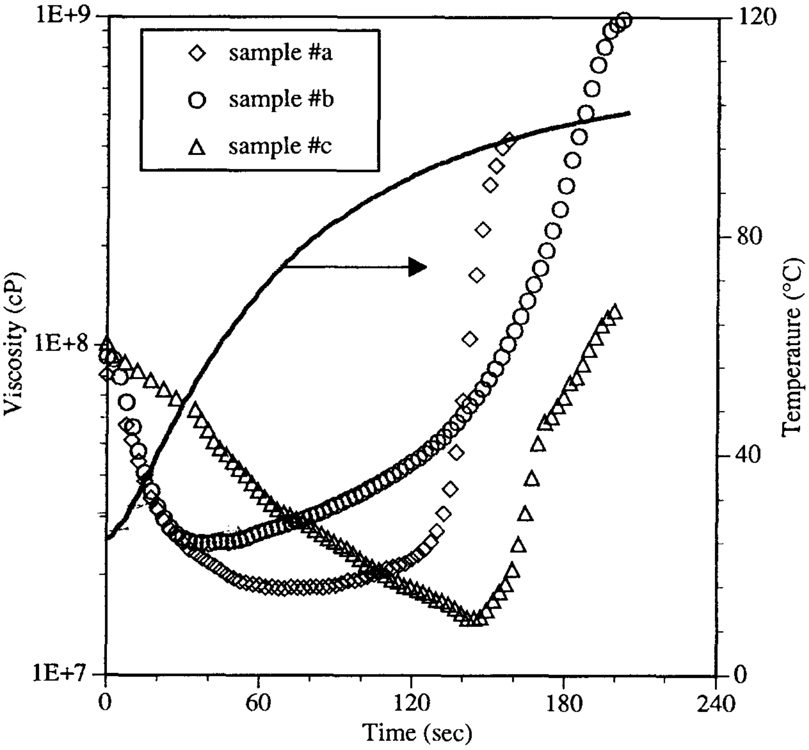


Figure 13 Examples of compound viscosity design: (a) 35% MUP/65% UP/ST/1.5% MgO/1% PDO; (b) 100% UP/ST/1.5% MgO/1% PDO; (c) 100% MUP/ST/3% MDI/1% PDO

occurred at 148°C for the unthickened sample, and was lowered to 135–136°C by the presence of MDI. A shoulder was observed at higher temperatures for the thickened samples. This is similar behaviour to that of samples based on the regular UP resin. In general, the MUP resin tended to react slightly slower than the unmodified resin. Thickening with MDI tended to shift the reaction peak to a lower temperature and resulted in a secondary reaction peak (or shoulder).

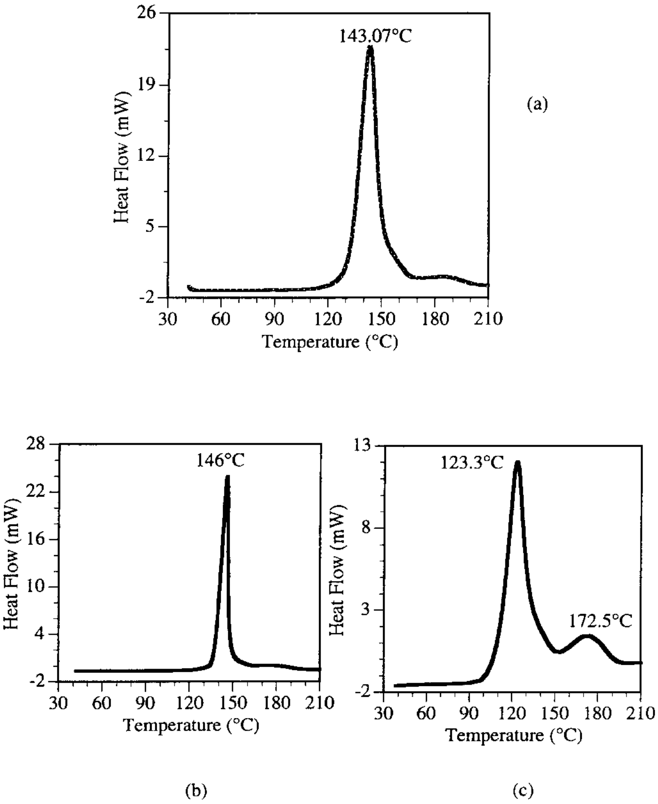


Figure 14 Comparison of d.s.c. reaction curves for unthickened and thickened UP systems: (a) UP/ST/1% TBP; (b) UP/ST/1.5% MgO/1% TBP; (c) UP/ST/8% MDI/1% TBP

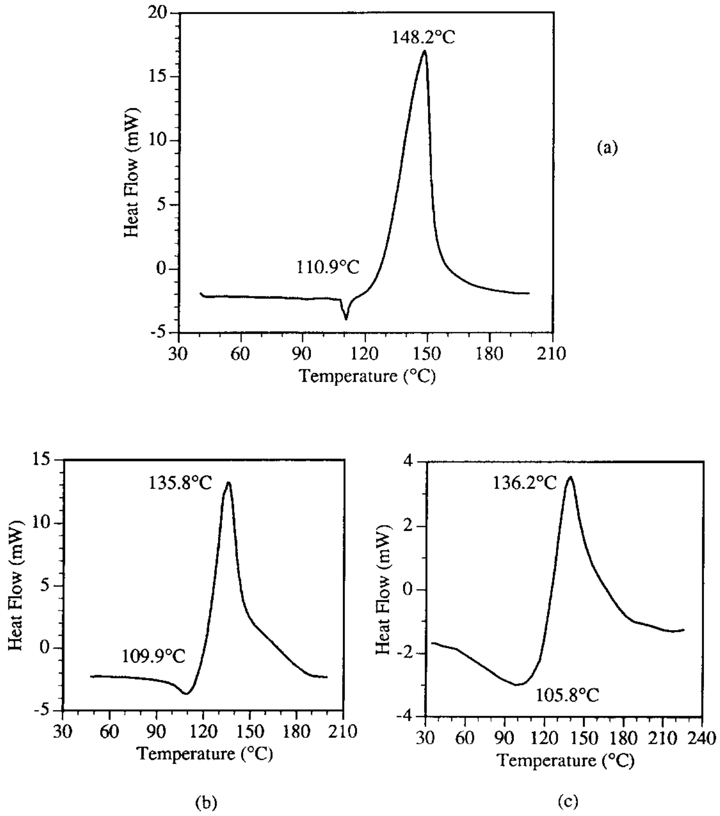


Figure 15 Comparison of d.s.c. reaction curves for unthickened and thickened MUP systems: (a) MUP/ST/1% TBP; (b) 30% MUP/70% UP/ST/6% MDI/1% TBP; (c) MUP/ST/3% MDI/1% TBP

CONCLUSIONS

A modified unsaturated polyester resin was synthesized for the viscosity control of SMCs and BMCs. This modified UP resin contained thermally breakable functional groups (diketo groups and amine salts) which could break at elevated temperatures. When the modified resin was thickened with MDI, it showed a fast viscosity rise during the maturation process and a stable viscosity during room temperature storage. The viscosity of the thickened resin could be reduced significantly upon heating. The resin viscosity and gelation time depended strongly on the shear rate for the unthickened compounds and the thickened compounds based on the modified UP resin. For the regular UP resin thickened by MgO, the resin viscosity was shear rate dependent, but the gelation time remained largely unchanged at various shear rates. The curing behaviour of the unsaturated polyester resin was slightly affected by resin modification, but strongly affected by MDI thickening.

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