Variation of MUF and PMUF Resins Mass Fractions during Preparation

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ABSTRACT: The variation of molecular mass distribution with the progress of the reaction was studied for the following: (i) sequential-type melamine–urea–formaldehyde (MUF) resin formulations in which the sequence of addition of chemicals follows well-defined species reactivity principles; (ii) a nonsequential MUF formulation in which simultaneous melamine and urea competition for formaldehyde yields a MF resin cocondensed with small amounts of urea. This resin became soaked with reacted and unreacted monomeric urea species. (iii) A PMUF resin, namely a MUF resin with a small proportion of phenol (7.8% by weight on melamine and urea) cocondensed with the main MUF fraction. All the formulations used were industrial resins formulations in current use. Development and variation of molecular mass fractions, from which performance and other useful resin parameters depend, have been found to depend on the type of resin formulation used for these type of aminoplastic resins. The two very different MUF resin formulations yielded different variations in molecular mass fractions during the progress of the reaction and during the so-called ambient temperature "maturing" of the resin. The PMUF resin also showed both similar and different fractions present during manufacturing and during short term ageing at ambient temperature. While similarities in recurrent fractions and in trends are common to all the three different formulations, differences between them are also clearly observed. A major proportion of the reaction of some of the aminoplastic resins examined also occurs on ageing (i.e."maturing" of the resin at ambient temperature), this appearing to be an essential phase of the resin preparation process. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4842–4855, 2006

Key words: resins; structures; melamine–urea–formaldehyde; phenol–melamine–urea–formaldehyde; adhesives; mass distribution; GPC

INTRODUCTION

Melamine–urea–formaldehyde (MUF) and phenol–melamine–urea–formaldehyde (PMUF) thermosetting resins are extensively used as exterior-grade adhesives in the wood industry, particularly in the wood panels industry.[1] The wood panels industry relies heavily on the use of these synthetic resins as adhesives, bonded products constituting the majority of the wood products on the market today. Over many years, excellent formulations have been developed for these resins for wood applications. Some trial and error industrial research has been and is still carried out in the field of resin formulations; nonetheless, resin knowledge has progressed to such an extent that scientific principles are used today to develop resins of ever improving performance.

Notwithstanding the considerable tonnage of MUF resins produced yearly, their economic importance, and the trade literature on the subject, the scientific literature on MUF resins is rather limited.[2–5] This has improved in the last few years; however, much remains to be defined in the field of MUF resins. Even more limited is the scientific literature on PMUF resins.[6,7] In both cases, no study appears in the world literature that follows the development of the different mass fractions, and by inference of the average molecular species development, as a function of the type of formulation used. Although a great variety of MUF formulations exist and are used industrially, the greater majority of them reduce to variations on the theme of two basic formulations. These two categories are the so-called (i) "sequential" formulations and (ii) "nonsequential" resins. "Sequential" formulations are those in which the sequence of addition of chemicals follows well-defined species reactivity principles.[2–5] The greater majority of MUF resins falls in this category, as these resins produce real cocondensates of melamine and urea and their performance is good.[3–5] Less used are the "nonsequential" resins in which the still well-defined serial addition of chemicals follows any pattern apparently diverging from the "sequential" formulations. These resins can be excellent too, when the formulation is well-thought out but are more used for some special characteristic or special application.

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The formulation of PMUF resins of good performance are all of the "sequential type," as "nonsequential" types yield much reduced performance and also have some problems.[6,7]

This article deals then with following the distribution of the different mass fractions throughout the preparation of MUF resin formulations for industrial uses, both of the sequential and nonsequential types, and of sequential PMUF resins.

EXPERIMENTAL

Preparation of MUF and PMUF resins

In the sequential MUF resin formulation used, the addition of melamine and urea are done according to their respective reactivities with formaldehyde with a known sequential manufacturing procedure.[2–5] This is done to ensure the maximum extent of copolymerization of melamine and urea. This type of formulation generally gives very strong bonds.

The sequential MUF formulation, of molar ratio (M + U)/F of 1.2 and of M : U weight ratios of 47 : 53, was prepared according to the known sequential manufacturing procedures.[8] Herewith is given the manufacturing procedure for a resin of 1 : 1.2M ratio, M : U of 47 : 53. To 142.2 g of formurea (precondensate of formaldehyde [54%], urea [23%], and water [23%]) are added 16.4 g urea and 30.0–35.0 g of water. The pH is set at 10–10.4 and the temperature brought to 92–93°C under mechanical stirring. The pH is then lowered to 7.8 and the reaction continued at the same temperature, allowing the pH to fall by itself over a period of 1½ h to a pH of 6.5–7 (the pH must never fall below 5). To bring the pH to 9.5 or higher, 30% NaOH solution was added. Then 80 g of Melamine premixed with 42.8 g of Water was added. One to two grams of dimethylformamide is then added to the reaction mixture, maintaining a temperature of 93°C. The percentage water tolerance of the resin is checked every 10 min while the pH is allowed to fall by itself. When the water tolerance (the percentage of water that is possible to add to the liquid resin) reaches a value of 180–200% (the pH reached is around 7.2), 42.8 g of urea is added and the pH is again brought up to 9.5. The reaction is continued until the water tolerance reached is lower than 150% (the pH has reached 7.7 at this stage).

The pH is then corrected to 10.0–10.2 by addition of NaOH solution and the resin cooled and stored

The second was a nonsequential MUF adhesive formulation of the same molar ratio (U + M)/F = 1.2. The manufacturing procedure was as follows: To 390 parts of formurea are added 190 parts water and the pH of the mixture is adjusted to 9 by adding a few drops of 33% NaOH solution. The temperature is brought at 30°C and then 175 parts of melamine powder is added. The reaction is conducted throughout in a glass reactor equipped with reflux condenser and always under mechanical stirring. The temperature of the reaction mixture is brought to 94°C over a period of 1 h and the pH generally goes down to 8.5. The reaction is kept at 94°C for 30 min and the pH decreases to 7.5. The turbidity point, measured at 30°C, is generally reached at this stage. The pH is adjusted to 8.95 by addition of 33% NaOH solution, and then a second amount of 46 parts of melamine is added to the reaction mixture. Small amounts of 33% NaOH solution are added continuously to avoid the pH decreasing too much. The reaction is continued for 15 min and then 155 parts of urea is added. The reaction mix is kept at 74°C for 3–5 min and the pH maintained at 9. The reaction mix is then cooled slowly to reach a temperature of 45°C after ~1 h cooling. The pH is then 9.3. Monoethanolamine (7.7 parts), used as a buffer to maintain the long-time shelf life of the resin, is added and the pH is 9.65. About 15–20 min later, once the resin has cooled down to 30°C, the resin is stored. The MUF obtained has final (M + U) : F molar ratio of 1 : 1.2 and M : U weight ratio of 47 : 53. In reality, if one calculates according to the relative reactivities of melamine and urea with formaldehyde, this is, in reality, a (M + U) : F molar ratio of 1 : 2.15 and M : U weight ratio of 70 : 30, soaked in urea. This is done to reduce the high formaldehyde emission that would be expected by such a high molar ratio resin, when applied to wood panels.[9]

The PMUF resin, of total molar ratio F/(U + M + P) = 1.33, was prepared as follows[6]: To 10.2 g phenol were added 0.8 g methanol, 6 g of paraformadehyde 98% fine powder, and 3.4 g of water. The temperature was maintained at 40°C under continuous mechanical stirring of the reaction mixture. Three amounts of 0.17 g each of 33% NaOH water solution are added to the reaction mixture over a period of 30 min. The temperature is increased to 90°C. After 5 min reaction at this temperature, 19 g of urea is added. The reaction is maintained for 15 min at 90–93°C under continuous mechanical stirring (the pH is of ±9.5) and then 113 g of formurea (HCHO = 64.4 g (57%); urea = 39 g (23%), 13 g urea, and 30 g of water are added. The pH is adjusted to 7.8–8 with formic acid and after 1½ h reaction, the pH is adjusted with 33% NaOH water solution to 9.5 or slightly higher, and then 41 g melamine and 19 g of water are added. When a water tolerance point of 200–220% is reached, 6.5 g urea is added and the pH adjusted with 33% NaOH water solution to 10.2–10.5. The resin is then cooled and stored.

Gel permeation chromatography

Samples of each of the MUF and PMUF resins described earlier were analyzed by gel permeation chro-
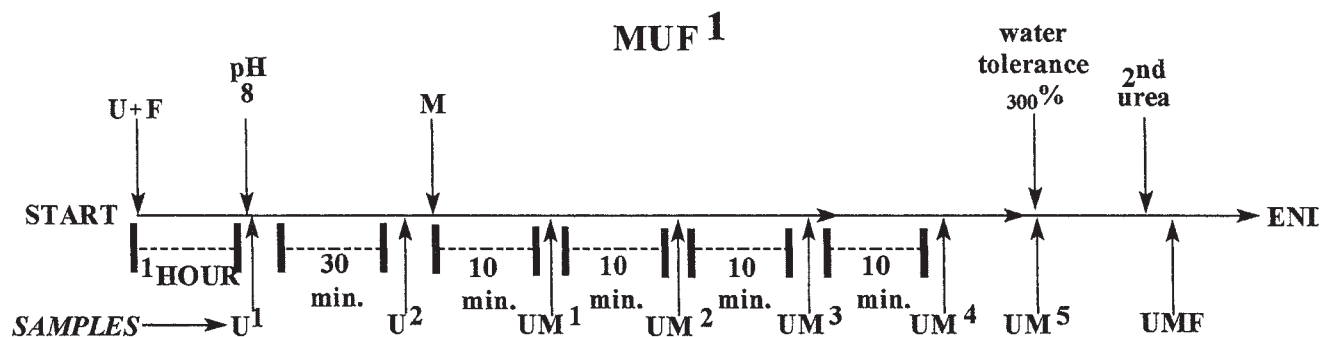
Figure 1 Schematic representation of the preparation procedure of sequential MUF1 resin formulation. Over the line representing the progress of the reaction are indicated the additives added (U = urea, F = formaldehyde, M = melamine). Under the line representing the progress of the reaction are indicated the samples taken, their time relation to the reagents added, and the reaction time intervals.

matography (GPC) at different stages of their preparation. A Waters 515 HPLC pump and GPC system was used and the resins analyzed through a Styragel HR1 column (for determination of M_w between 100 and 5000) at an elution rate of 1 mL/min, after polyethylene glycol (PEG) calibration of the column. The PEG samples used for calibration had M_w of 200, 300, 400, 600, 1000, 2000, 3400, 8000, and 10,000. Each resin sample after having been dissolved in dimethylformamide was tested after having been filtered through a 0.45 μmL filter. A Waters 410 refractometer was used as the detector.

Figures 1 and 2 show at which stage of resin preparation were the samples for GPC and TMA testing taken.

Thermomechanical analysis

The resins above were also tested dynamically, each at different stage of sampling, by thermomechanical analysis (TMA) on a Mettler 40 apparatus. This was done to try to correlate the development of the strength of a cured joint bonded with the resin at that stage with the mass distribution of the resin at the sampling stage. Triplicate samples of beech wood alone, and of two beech wood plys, each 0.6 mm thick bonded with each system, for a total sample dimension of 211.2 mm were tested in a nonisothermal mode between 40 and 220°C at heating rates of 10, 20, and 40°C/min, with a Mettler 40 TMA apparatus in three points, bending on a span of 18 mm, and exercising a force cycle of 0.1/0.5N on the specimens, with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][F/(f)]$ allows the calculation of the Young's modulus E and to follow its rise as function of both temperature and time. The deflections f obtained and the values of E obtained from them were proven to be constant and reproducible.[8,10]

RESULTS AND DISCUSSION

The resin samples were taken at different stages of the manufacturing procedures for both the sequential MUF resin (MUF1) (Fig. 1) and non sequential MUF (MUF2) (Fig. 2) resin formulations.

In the case of MUF1, the GPC series of chromatograms in Figure 3(a–e) shows how the molar masses vary at two different moment of the urea–formaldehyde reaction. The U1 sample [Fig. 3(a)] mainly in the formaldehyde addition phase and the sample U2 [Fig. 3(b)] in the condensation phase form the base UF resin. The GPCs of these two samples show three main peaks at M_n 311–315, 504–510, and 678–688. The species represented by the different peaks are mixtures of different number-average molecular masses. In the case of the peak of number-average molecular mass, M_n is equal to 311–315, of dimers to tetramers. For example, a 309 Mn corresponds to both U—(—U—CH$_2$—)$_3$—OH and to a tetramethylol UF trimer (HOCH$_2$—)$_2$U—CH$_2$—U(—CH$_2$OH)—CH$_2$—U—CH$_2$—OH. The peak centered on M_n = 504–510 being centered on species such as tetramers to octamers, with the average M_n corresponding to species of the type U—(—U—CH$_2$—)$_5$—U—CH$_2^+$(511) and a pentamethylolated pentamer (HOCH$_2$—)—U—CH$_2$—[—U(—CH$_2$OH)—CH$_2$—]$_3$—U—CH$_2$—OH (502), and the 678–688 peak belonging to even higher mass urea–formaldehyde oligomers. These form relatively easy at the very high F/U molar ratio predominant in this initial part of the reaction. The more reacted U2 resin sample shows the same pattern of peaks but a proportional increase with respect to U1 of the relative area and height of the peaks at 688 and 510 in relation to the 311–315 peak, as would be expected from further reaction.

The GPC pattern changes once melamine has been added. This is evident in the UM2 GPC [Figs. 1 and 3(c)] where only two peaks are relatively broader peaks at M_n's 410 and 646 are observed, with the former more marked than the latter. The M_n = 410
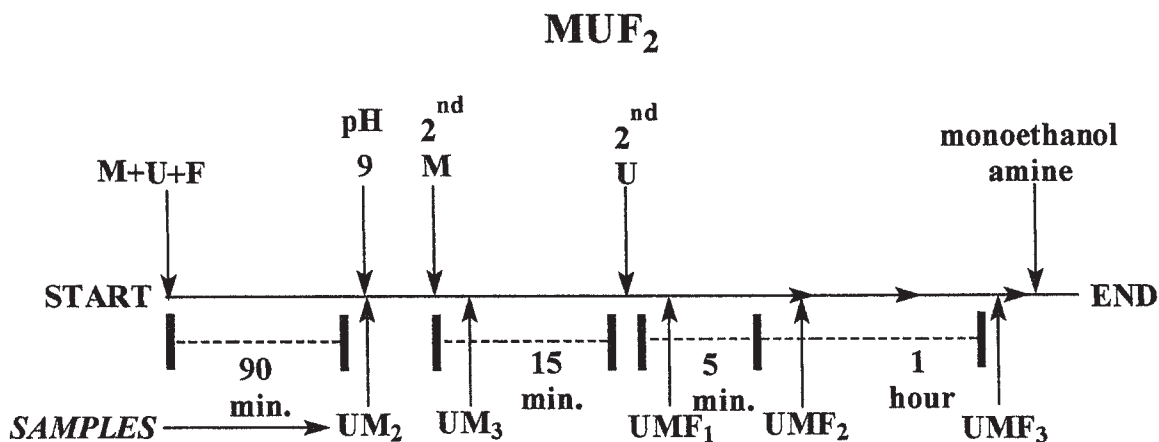
MUF$_2$

Figure 2 Schematic representation of the preparation procedure of nonsequential MUF2 resin formulation. Over the line representing the progress of the reaction are indicated the additives added (U = urea, F = formaldehyde, M = melamine). Under the line representing the progress of the reaction are indicated the samples taken, their time relation to the reagents added, and the reaction time intervals.

peak belongs to melamine oligomers formed rapidly by the more reactive melamine mopping up any free formaldehyde still present at the moment of its addition. Thus, the oligomers obtained are (i) just by reaction of melamine with free formaldehyde,[11] a species of close M_n being a M—CH$_2$—M—CH$_2$—M—CH$_2^+$ (403) and (ii) by reaction of melamine with low molar mass methylolated urea–formaldehyde species M—CH$_2$—(—U—CH$_2$—)$_2$—M (410).[11] The higher M_n peak at 646 represents mainly the same UF species as observed in the U1 and U2 samples. The same pattern of two peaks is observed for the UM5 sample at the end of the reaction [Fig. 3(d)], before addition of the second and final urea. The differences are (i) the number average M_n of the two peaks that has logically shifted to slightly higher values (429 and 707) due to the further advancement of the resin; (ii) the relative growth in area and intensity of the higher M_n peak in relation to the lower M_n one; and (iii) the growth of the even higher molecular mass shoulder of the 707 peak, both reflecting again the greater advancement of the resin. The last sample (UMF) [Fig. 3(e)], of the finished resin, after addition of the last urea, shows a new three peaks pattern. The two higher average M_n peaks at 411 and 675 represent the same species as in Figure 1(c, d). The new lower value average M_n peak at 243 representing species of the type (U—CH$_2$—)$_3$—OH (236) and (U—CH$_2$—)$_3$—U (278) obtained by the last urea mopping up the small amount of free formaldehyde still left. Species of the type (U—CH$_2$—)$_2$—M (271) and U—CH$_2$—M(—CH$_2$OH)(—CH$_2^+$) (241) by reaction on methylolated melamine monomers of the last urea added, or of the UF dimers formed by the last urea mopping up free formaldehyde.

Testing after 1, 10, and 30 days after its preparation, the variation in the molecular mass distribution of the sequential MUF1 resin as a function of its ageing at

ambient temperature also shows some interesting development [(Fig. 4(a–c)]. The most interesting feature appears just 1 day after preparation [Fig. 4(a)] and is mantained 10 days after manufacture [Fig. 4(b)]. Although the three peaks of the finished resin, 1 day earlier [Fig. 3(e)], have remained but with M_n values shifted quite markedly to higher values (from 243 to 322, from 411 to 468, and from 675 to 753), a new peak at M_n = 134–136 appears. This corresponds to U—CH$_2$—U urea dimers and dehydroxylated trimethylol urea ions of the type (HOCH$_2$—)$_2$U—CH$_2^+$ (134). This indicates that "maturing" the resin before use, as is generally done in industrial practice, does indeed change the characteristics of the resin. It indicates clearly that the oligomerisation ⇋ depolymerization equilibrium of urea–formaldehyde resins in solution is present not only in the phase of the formaldehyde addition to urea but also in the condensation phase, even at ambient temperature after the resin has been prepared. These lower molecular mass species have reacted again and been reabsorbed into higher molecular mass oligomers by the time the resin has aged 30 days [Fig. 4(c)]. It is interesting in this respect that the industrial practice of resin "maturing" the resin before using it is generally of 24 h to one week after manufacture, indicating that the resins used industrially are usually of the type showing the molecular mass distribution of Figure 4(a,b). These findings are in line with major work done on ageing of other aminoplastic resins, namely urea–formaldehyde resins, on ageing.[12–17]

TMA of the curing of all these resin samples, shown in Figure 5, allows to correlate the development of the different molecular mass fractions with the variation of resin bonding performance. The modulus of elasticity (MOE) of the resins increase passing from resin sample U1 to U2, to increase further once melamine is
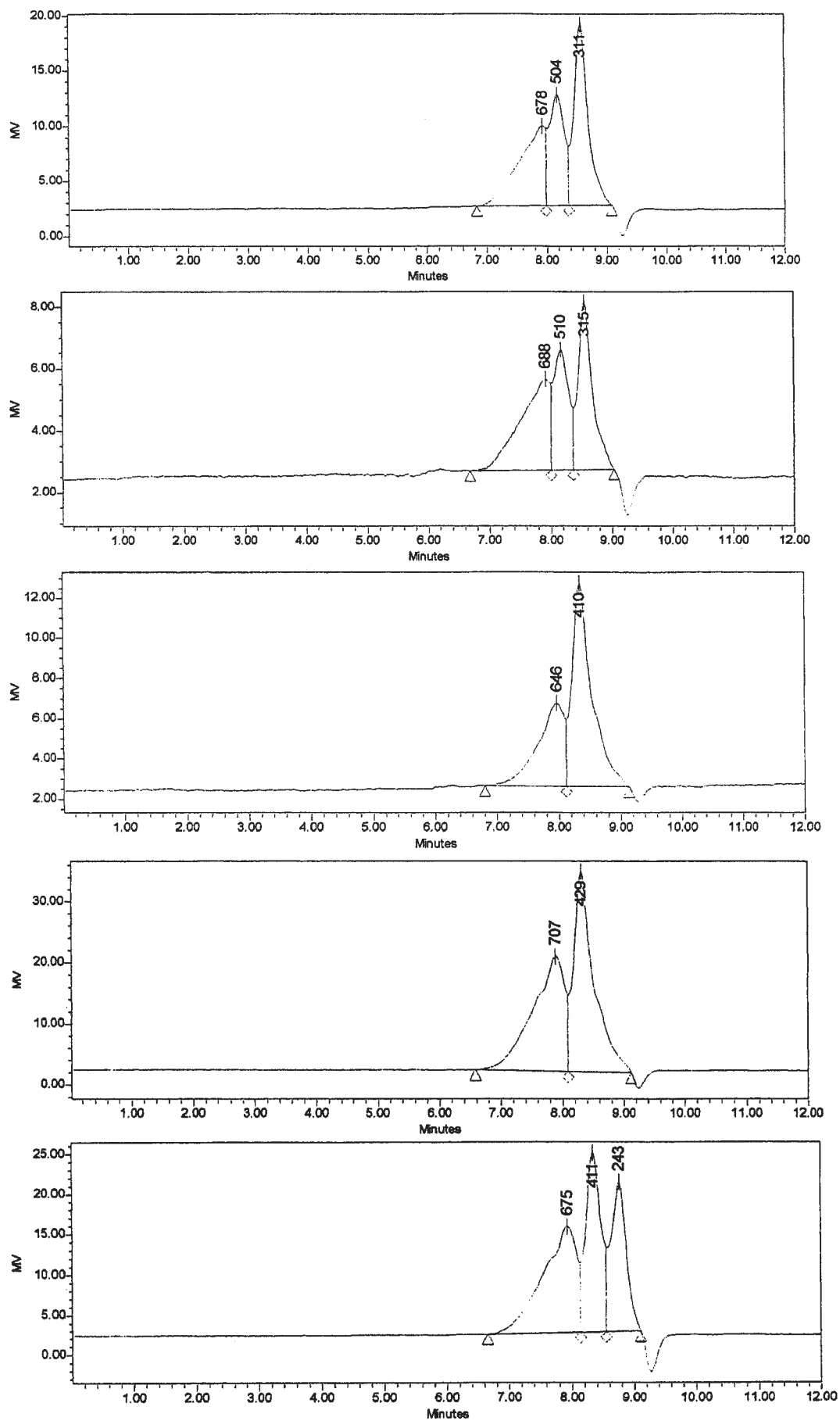
Figure 3 Gel permeation chromatograms of sequential MUF1 resin formulation during preparation: (a) sample U1, (b) sample U2, (c) sample UM2, (d) sample UM5, and (e) sample UMF at reaction end.
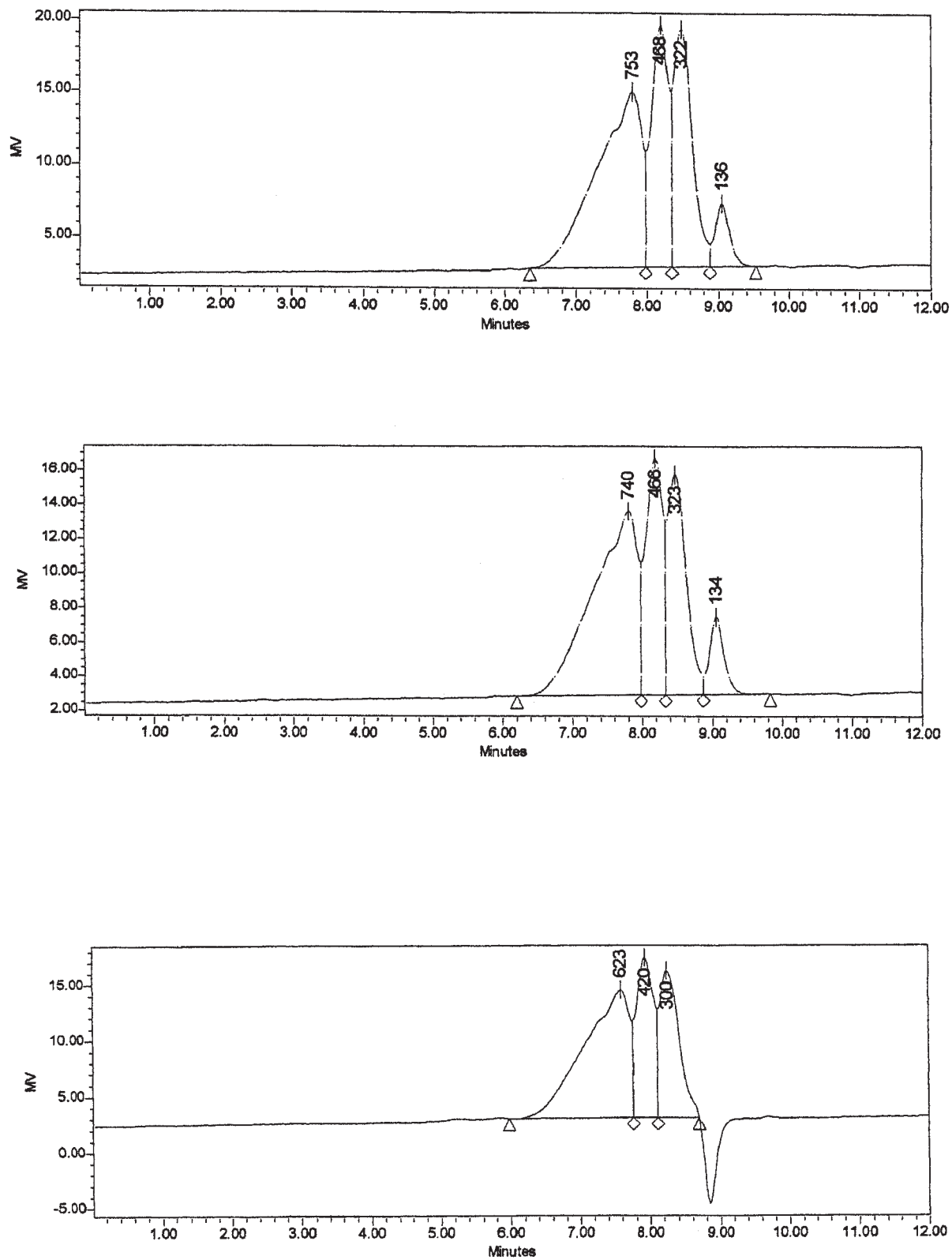
Figure 4 Gel permeation chromatograms of sequential MUF1 resin formulation after preparation, on ageing at ambient temperature (23°C): (a) aged 1 day, (b) aged 10 days, and (c) aged 30 days.
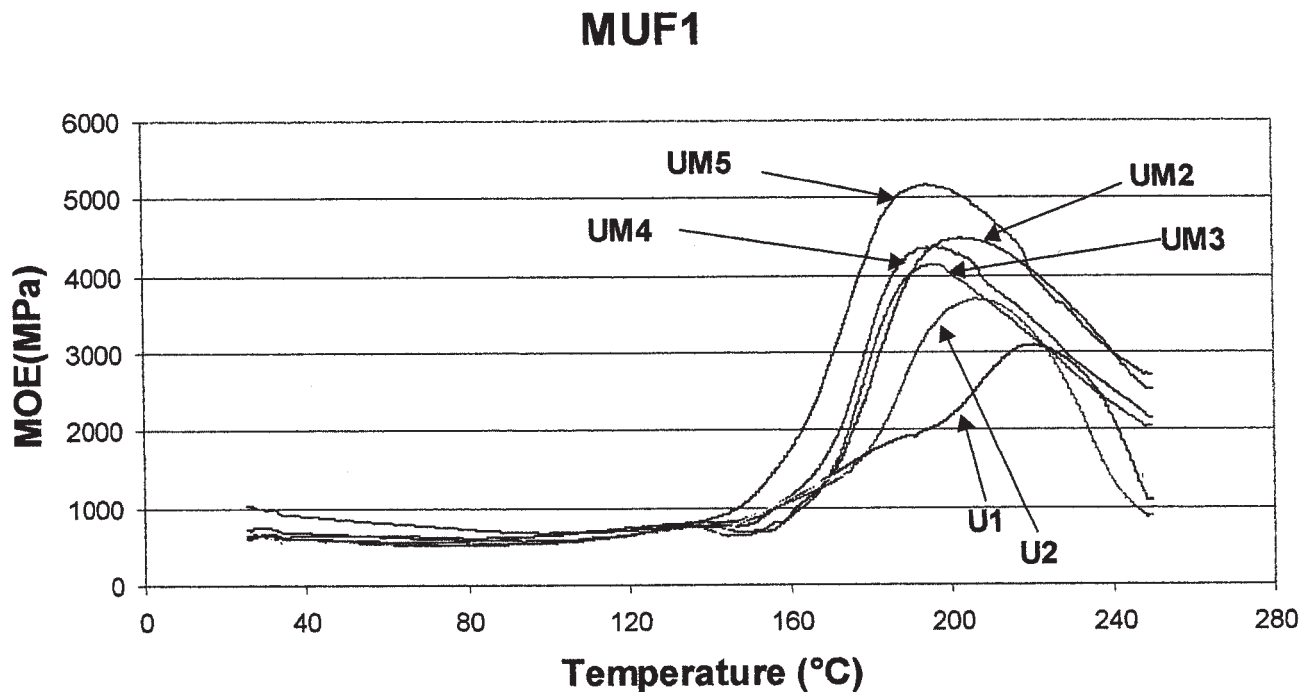
MUF1

Figure 5 Nonisothermal TMA curves of variation of the MOE as a function of temperature of beech wood joints bonded with MUF1 resin samples taken during resin manufacture. Samples tested are U1, U2, UM2, UM3, UM4, and UM5.

added, hence passing to sample UM2 where it stabilizes at comparable values for UM3 and UM4, to further increase in UM5 and remain the same for the UMF final resin. Equally, the rate of curing becomes faster according to the same pattern: faster passing from U1 to U2 and faster again passing to UM2, stabilizing for UM3 and UM4, and getting faster again for UM5 where it finally stabilizes. These observations allow to draw a few conclusions on sequential MUF1-type resins. First, both their curing speed and final cured strength improves with the advancement of the resin during preparation, as it can be expected. Second, both these parameters improve further with the introduction and linking of the more reactive, higher functional groups of melamine to the base UF polymer, as can equally be expected. Third, and of more interest, no apparent resin improvement occurs between UM2 and UM4 which means that the reaction period of the first, higher amount of melamine can be decreased from 40 to 25 min, hence halved, without any performance loss. This is perhaps not much on the total preparation time of a MUF1-type resin but it is nonetheless a 15% saving in reaction time.

The succession of molecular mass distributions as a function of reaction advancement is relatively less complex in the case of the MUF2 resin formulation. In Figure 6 (a–c) are shown the GPC traces of samples UM2, UM3, and UMF1, respectively, (Fig. 2). The GPC chromatogram of samples UMF2 and UMF3 are not reported as they are practically identical to that of UMF1. Figure 6(a) (sample UM2) shows the state of

the resin before the addition of the second melamine. Three peaks at Mn values of 324, 464, and 789, and a peak shoulder at higher molecular mass can be seen in Figure 6(a). The 324 peak mainly corresponds to low molar mass multimethylolated pure melamine–formaldehyde dimers such as $HOCH_2$—M—CH_2—M—CH_2OH (324) due to the reactivity of melamine toward formaldehyde being an order of magnitude higher than urea. The $M_n = 464$ peak corresponds to multimethylolated pure melamine–formaldehyde trimers mainly of the type $HOCH_2$—M—CH_2—M—CH_2—M—CH_2OH (463). The $M_n = 789$ peak corresponds to multimethylolated pure melamine–formaldehyde trimers mainly of the type $HOCH_2$—[—M—CH_2—]$_2$—[—M(—CH_2OH)—CH_2—]$_2$—M—CH_2OH (787). Some urea, but relatively little, possibly just traces, is copolymerized with melamine, but in great minority due to the differences in reactivity. As described previously,[5,18] this formulation can be considered almost as a pure MF resin, soaked in monomeric urea. On addition of the second melamine, the appearance of the GPC chromatograms changes. Two peaks and a shoulder only are present, the peak at 324 M_n having disappeared. This has occurred as the second melamine added to the reaction mixture has reacted with the free formaldehyde to first form a methylolated melamine that instantly reacts with the dimers characteristic of the 324 M_n peak to transform into trimers of the 461–464 peak and higher molecular mass species. The 324 peak subsists only as a small shoulder [Fig. 6(b), UM3]. By this mechanism, a great
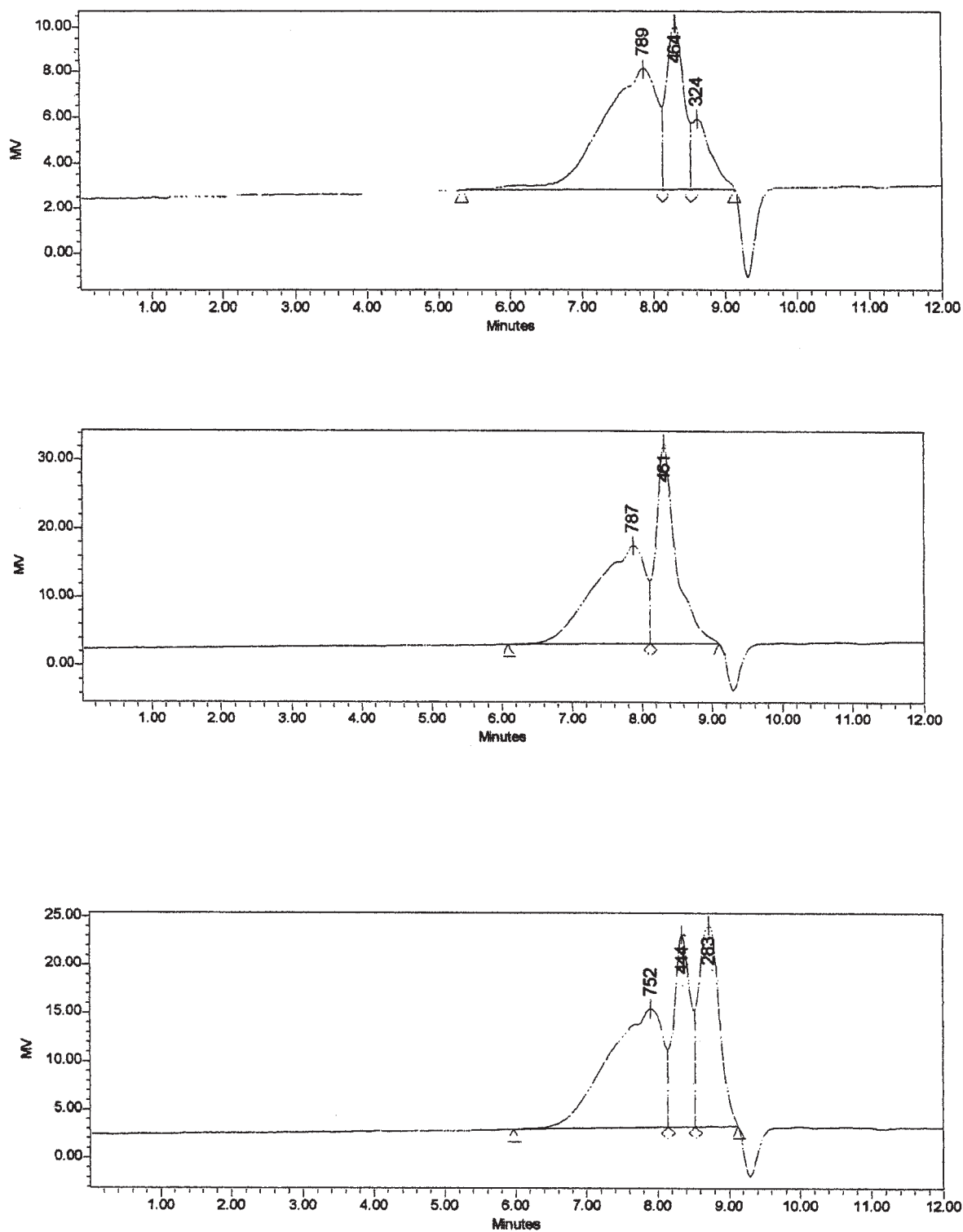
Figure 6   Gel permeation chromatograms of nonsequential MUF2 resin formulation during preparation: (a) sample UM2, (b) sample UM3, and (c) sample UMF1, remaining unaltered up to reaction end.

proportion of free formaldehyde is mopped up by the second melamine and the MF dimers disappear completely from the reaction mix.

The GPC profile of the MUF2 resin changes again, rapidly, after addition of the second urea. The GPC of sample UMF1 in Figure 6(c) shows three peaks but of different M_n than what is seen in Figures 6(a,b). A peak at 283 M_n has appeared: this belongs to pure UF species of the type U—CH$_2$—(—U—CH$_2$—)$_2$—U (278) obtained by further mopping up of what is left of
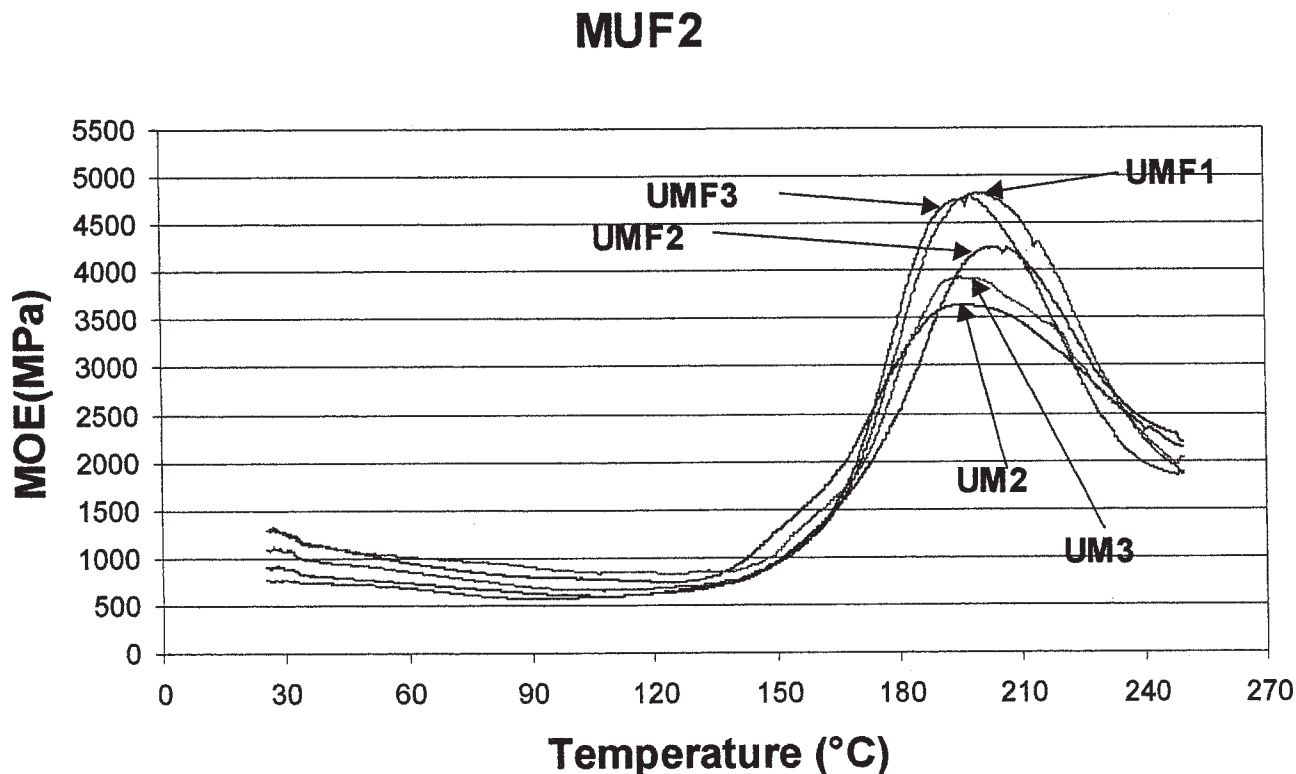
Figure 7 Nonisothermal TMA curves of variation of the MOE as a function of temperature of beech wood joints bonded with MUF2 resin samples taken during resin manufacture. Samples tested are UM2, UM3, UMF1, UMF2, and UM3.

free formaldehyde. Some pure MF dimers of lower methylolation level are still present in the mass distribution of this peak. Thus, M—CH_2—M—CH_2OH (294), M—CH_2—M—CH_2^+ (278) and mixed species of the type U—CH_2—M—CH_2—U— CH_2^+ (284) can well be present in this range of mass. The peaks at 444 and 752 M_n indicate MF oligomers of the same type as in Figures 6(a) and 6(b), with just a small but growing proportion of urea or methylol ureas having been forced to copolymerize in some of them, enough to slightly decrease the average M_n of the two peaks (464 down to 444, and 787 down to 752 M_n). The appearance of the GPC does not change for samples UMF2 and UMF3, taken much later in the reaction (not reported here). This indicates that under the reaction conditions used, further reaction does not really contribute to advance the resin. The reason for this resides in the condensation $\leftrightarrows$ depolymerization equilibrium due to the well known instability of methylene bridges in UF oligomers, and under the conditions used also in MF oligomers (but to a lesser extent). Once equilibrium is reached, no further extension of the reaction time will contribute to advance the resin, or its performance, as indeed is the case here in the MUF2 formulation resin. This is confirmed both by the maintainance of its clear, unclouded appearance for a long time, characteristic of MUF2 type formulations.[4,19] It is also confirmed by the results of TMA experiments

shown in Figure 7. Figure 5 shows that although MOE of the bonded joint improves when passing from the UM stages to the UMF stages after last urea has been added, the improvement is not as marked as between the different stages in MUF1 formulations. Furthermore, the max MOE values of UMF1 and UMF3 are comparable, confirming that no further noteworthy reaction or resin advancement occurs during the last 1 h reaction of MUF2.

Ageing of the MUF2 resin for 4, 15, and 30 days, however, shows some interesting peculiarities [Fig. 8(a–c)]. The same 132–133 peak due to the same condensation $\leftrightarrows$ depolymerization equilibrium is observed as in the maturing stage of MUF1. Here the peak at 133 M_n forms rapidly and decreases slowly in intensity with ageing. Contrary to the MUF1 formulation, this peak is present for much longer for the MUF2 formulation, being still present 30 days after manufacture. The other differences noticed on ageing are the following: (i) the respective lowering in relative intensity of the peaks at 464–480 M_n, although its M_n increases steadily with ageing from 464 to 480; (ii) the relative stability in intensity of the peaks at 729–755 M_n, although its M_n decreases steadily with ageing from 755 to 726 in 30 days ageing; (iii) the relative stability in intensity of the peaks at 309–321 M_n; and (iv) the marked growth of the area of very high molecular mass, 1043 M_n and higher [Fig. 8(c)], at first
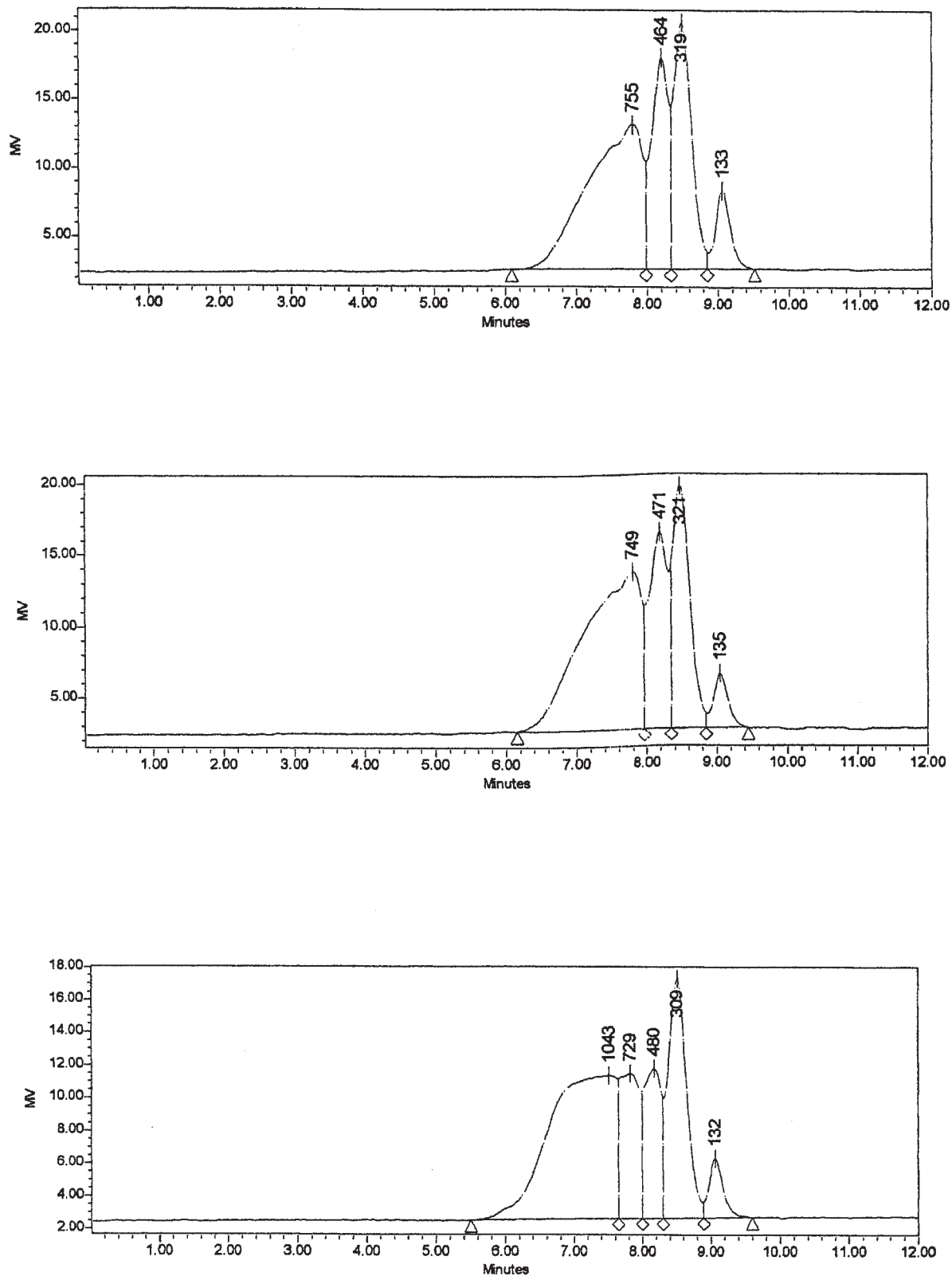
Figure 8 Gel permeation chromatograms of nonsequential MUF2 resin formulation after preparation, on ageing at ambient temperature (23°C): (a) aged 4 days, (b) aged 15 days, and (c) aged 30 days.

appearing as a shoulder [Fig. 8(a,b)] and then assuming equal intensity and much greater area than the 729–755 M_n peak. All these movements show that it is the autocondensation of the 464–480 M_n fraction species, and of their condensation with the higher molecular mass species of the 729–755 M_n range that leads to the much higher oligomers noticed in Figure 8(c). It means that the process is mainly a MF to MF condensation, only a very limited amount of low molar mass methylolated urea species (M_n = 133) contributing, and little, to the further condensation of the MUF2 resin at ambient temperature.

For the PMUF resin, Figure 9(a–d) indicates how the resin molecular weight distribution changes during the progress of the initial PF reaction phase. Initially, in Figure 9(a), after just 5 min of reaction, peaks of average M_n 33, 129, 184, 332, and 521 are present. The average 33 M_n peak includes free formaldehyde (M_n 30) up to formaldehyde in solution in the form of methylene glycol $HOCH_2OH$ (M_n 48). The average 129 M_n peak includes hydroxymethylated phenol, such as monohydroxymethyl phenol $HO—C_6H_4—CH_2OH$ (124) and its ionized forms. The average 184 M_n peak includes trihydroxymethyl phenol $C_6H_2(—CH_2OH)_3$ (184) and its ionized forms. The average 332 M_n peak is the first presenting PF oligomers, such as hydroxymethylated and nonhydroxymethylated PF dimers and trimers such as $HOC_6H_2(—CH_2OH)_2—CH_2—C_6H_2(—OH)(—CH_2OH)_2$ (322), $HOC_6H_4—CH_2—C_6H_4(—OH)—CH_2—C_6H_4OH$ (310), and $HOC_6H_3(—CH_2OH)—CH_2—C_6H_4(—OH)—CH_2—C_6H_4OH$ (340). The average 521 M_n peak represents tetramers, pentamers such as $HOC_6H_4—CH_2—[C_6H_4(—OH)—CH_2]_3—C_6H_4OH$ (526) ,and some higher molecular mass species.

As the reaction progresses, the relative distribution of the different molecular species changes rapidly. Just 10 min after the start of the reaction, the tetramers and pentamers peak has increased considerably in relation to the dimers and trimers peak. Furthermore, these two peaks constitute together a greater proportion of the total reaction mixture. The peaks at 184 and 129 have disappeared and a peak at 201 average M_n has appeared. This peak is centered on an nonhydroxymethylated PF dimer of the type $HOC_6H_4—CH_2—C_6H_4OH$ (M_n = 200). The peak at 33 M_n has also disappeared and in its place a peak of average M_n of 64 has appeared. This includes more complex free formaldehyde species such as $HOCH_2OH$ (48) and hemiformals of the type CH_3OCH_2OH (62) obtained by the reaction of free formaldehyde with the methanol initially added to the reaction mixture. The change trends observed passing from Figure 9(a) to 9(b) continue as the PF resin progresses to 20–25 min [Fig. 9(c)] and 40 min [Fig. 9(d)] of reaction. Thus, the tetramers and pentamers peak originally at 521 decreases its M_n peak down to M_n 502, but the peak becomes the dominant one. All the other peaks of

lower molecular mass, in particular the dimers and trimers peak at M_n 332, decrease proportionally in intensity as the 521 peak increases in intensity. The shoulder at M_n 658 progressively appears and increases in size as the reaction progresses. Also small intensity, higher molecular mass peaks appear. These too have as high a molecular mass to correspond to proper molecular species in PF resins of this type. In other formaldehyde resins, these peaks have been shown to be due to amorphous, labile supramolecular colloidal interactions of the higher oligomers of the resin.[4,19,20]

The second preparation phase of the PMUF resin is similar to the preparation procedure of sequential MUF resins such as MUF1. In Figure 10(a,b) is shown the molecular mass distribution for the PMUF resin at the beginning and at the end of the aminoplastic preparation. A peak at M_n 124 centered on monohydroxymethyl phenol $HO—C_6H_4—CH_2OH$ (124), but also including species such as dimethylol urea $HOCH_2—NHCONH—CH_2OH$ (120), appears. The peaks in the 330 and 530–550 ranges characteristic of the initial PF resin are still present but the 332 peak [Fig. 10(a)] is again by far the dominant peak. This means that introduction of urea has either contributed to increase the 332 peak or to decrease the 530–550 peak of the initial PF resin preparation phase. The appearance of a marked, well visible, broad band at M_n 763 indicates that addition of urea has mainly contributed to the decrease of the 530–550 peak. This occurs as urea reacts faster than phenol itself with the PF resin hydroxymethyl groups,[1,21–23] and it is well known to cause a rapid increase of molecular size of PF resins by linking phenolic oligomers[21–23] as follows

$$—(—P—CH2—)_n—P—CH_2OH + H_2NCONH_2 + HOCH_2—P—(—CH_2—P—)_m— \rightarrow —(—P—CH_2—)_n—P—CH_2—HNCONH—CH_2—P—(—CH_2—P—)_m—$$

At the end of the PMUF resin preparation, all that is left are the bands at M_n 126, 338, 720, and higher, with a single dominant band at M_n 472. This is the 530–550 M_n peak, having shifted due to the considerable decrease in the higher molecular mass oligomers (mainly the pentamers) by reaction with urea as outlined earlier.

Ageing of the resin at ambient temperature, only the 15 days ageing is reported here [Fig. 10(c)], again changes somewhat the molecular mass distribution of the resin. This is in line with major work done on reactions occurring in aminoplastic resins on ageing.[12–17] A peak appears at 34 M_n, indicating the presence of free formaldehyde. This can only have been formed either by hydrolysis of aminoplastic methylene bridges[1,9,12] or by the rearrangement of either aminoplastic or phenolics methylene ether bridges.[1,12,24] The peaks in the 330 and 450–470 ranges have remained but with the 320 one being considerably more marked, as marked than the 450–470 one. The higher
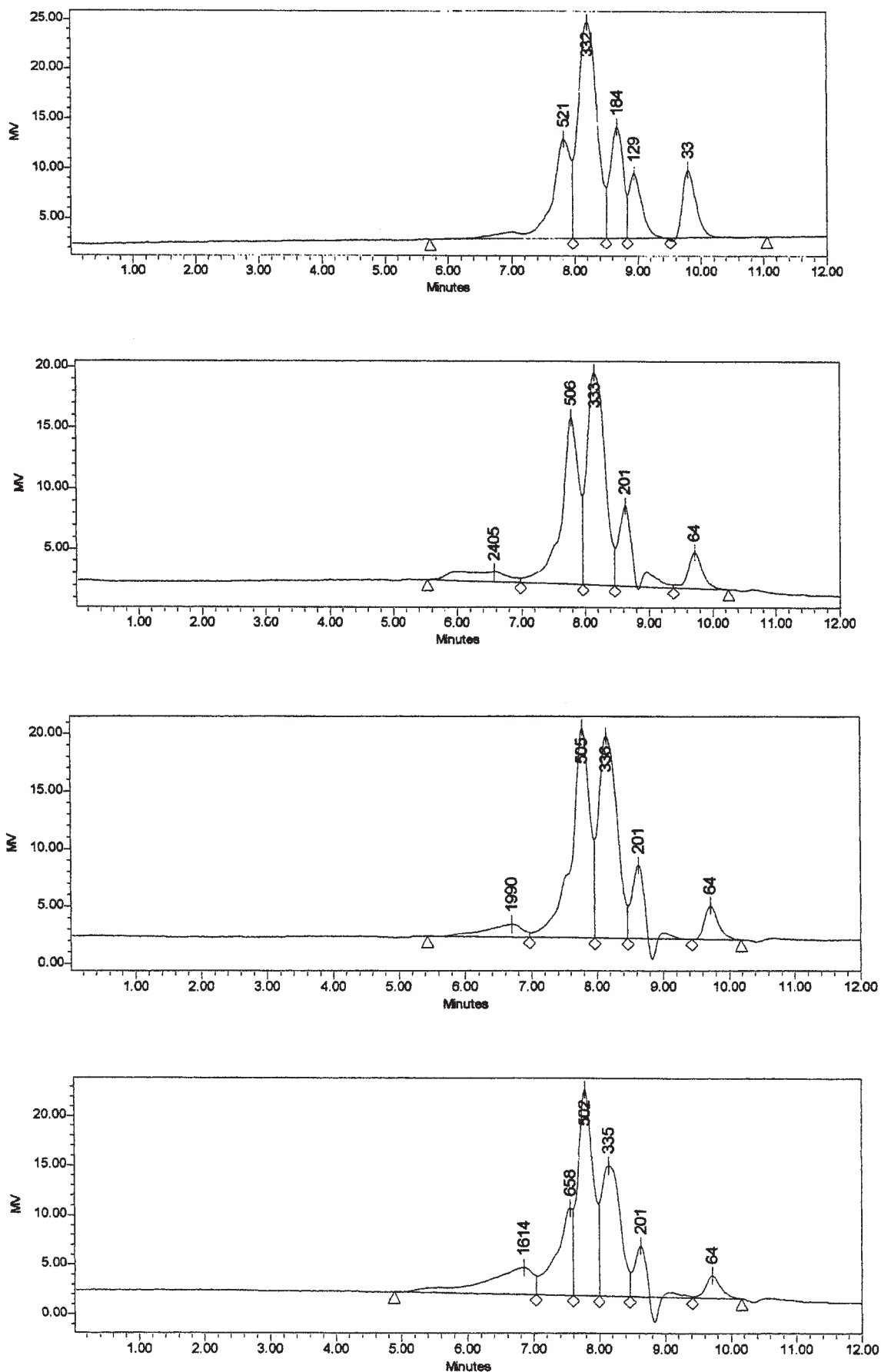
Figure 9 Gel permeation chromatograms of initial PF reaction phase for a sequential PMUF resin formulation during preparation after (a) 5 min reaction at pH 9, (b) 10 min reaction at pH 11, (c) 20 min reaction at pH 11, and (d) 40 min reaction at pH 11.
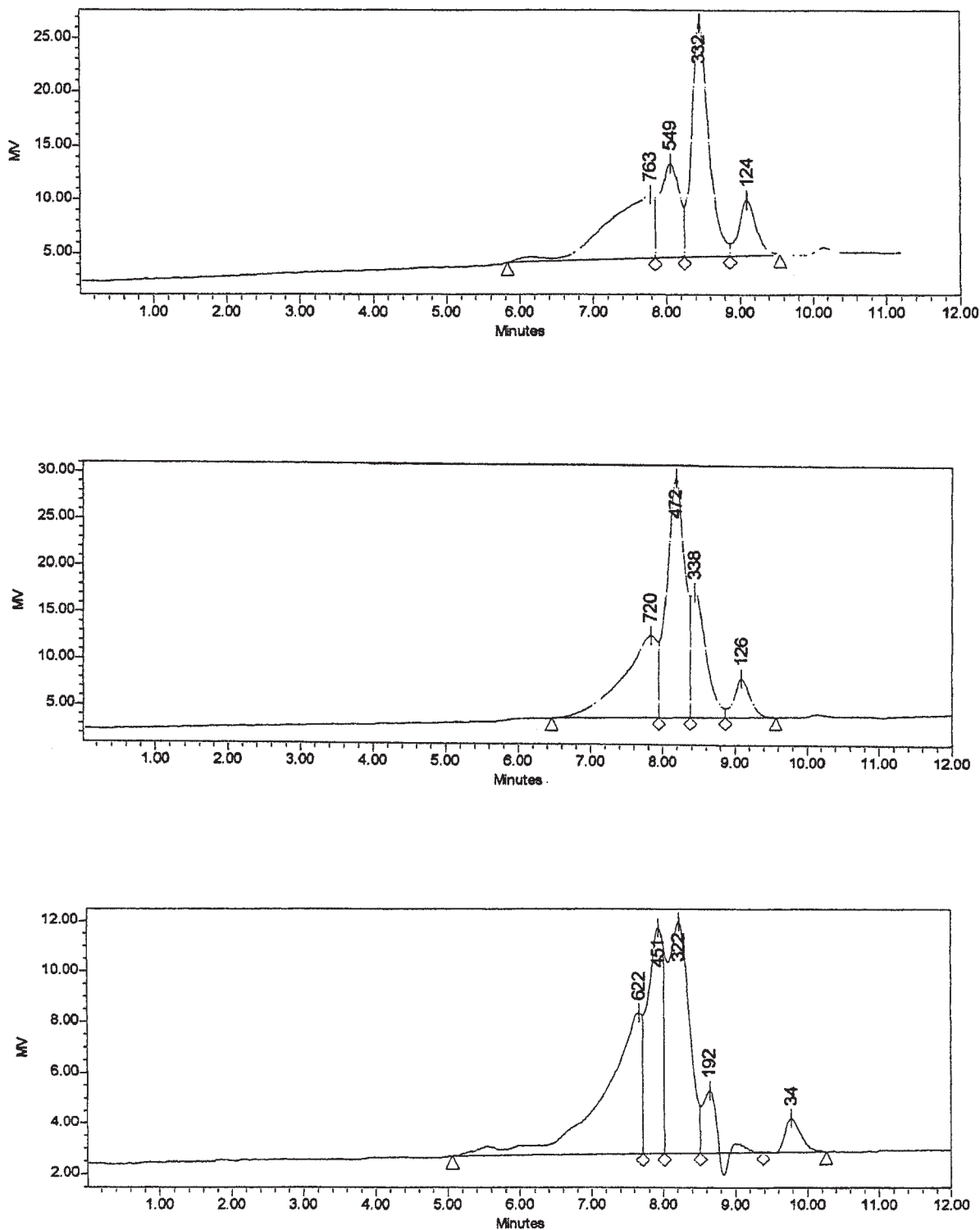
Figure 10 Gel permeation chromatograms of subsequent MUF reaction phase for a sequential PMUF resin formulation during preparation after (a) after halfway of reaction of urea–formaldehyde phase; corresponds to sample U1, Figure 1; (b) at the reaction end after addition of melamine and before second urea addition; corresponds to sample UM5, Figure 1; and (c) aged 15 days at ambient temperature.

molecular weight peak has decreased to M_n 622, indicating a marked contribution in this by higher aminoplastic oligomers, at equal degree of polymerization of lower molecular mass than phenolic oligomers,

hence the downward shift in M_n peak. This indicates that also for PMUF resins, a major proportion of the reaction of some of the aminoplastic portions of the resin occurs on ageing, on what is called "maturing"

of the resin at ambient temperature, this being an essential phase. A M_n 192 peak indicating either presence of trihydroxymethyl phenol $C_6H_2(—CH_2OH)_3$ (184), nonhydroxymethylated PF dimers $HOC_6H_4—CH_2—C_6H_4OH$ ($M_n = 200$), mixed urea/phenol species such as $H_2NCONH—CH_2—C_6H_4(—OH)—CH_2^+$ (181), and $H_2NCONH—CH_2—C_6H_4(—OH)—CH_2OH$ (198) as already shown by NMR analysis[6,22] are indeed present.

CONCLUSIONS

Development and variation of molecular mass fractions, on which performance and other useful resin parameters depend, have been found in MUF and PMUF adhesive resins to depend on the type of resin formulation used. Thus, two rather different MUF resin formulations yielded different variations in molecular mass fractions during the progress of the reaction and during the so-called ambient temperature "maturing" of the resin. A third aminoplastic resin formulation, a PMUF resin, namely a MUF resin with a small proportion of phenol cocondensed with the main MUF fraction also showed both similar and different fractions present during manufacturing and during short term ageing at ambient temperature. Although similarities in recurrent fractions and in trends are common to all the three different formulations, differences between them are also clearly observed. A major proportion of the reaction of some of the aminoplastic resins examined occurs on ageing (i.e.," maturing" of the resin at ambient temperature), this being an essential phase of the resin preparation process.

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