

NOTE

Influence of Preparation Parameters on the CHT Curing Diagrams of MUF Polycondensation Resins

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ABSTRACT: Lignocellulosic substrates such as wood have been found to have a marked modifying influence on both lower-temperature and higher-temperature zones of TTT and CHT diagrams during hardening of formaldehyde-based polycondensates. While the modifying influence of the substrate has been described, the modifying influence of some of the most important manufacturing parameters of the resins on the CHT diagram, not having been previously investigated, are explored here and clear trends are shown. In the case of melamine–urea–formaldehyde (MUF) resins for wood adhesives, the molar ratio (M+U):F appear to be the dominant parameter influencing the relative position of gel and vitrification curves in relation to each other. The ratio of melamine to urea does not appear to have any effect on the relative position of the curve, lacking any clear trend, at least at the higher (M+U) molar ratio of 1:1.9 used for this series of resins. In the case presented for the first time, the influence of resin manufacturing parameters on CHT curing diagrams was studied in combination with the modifications introduced by the substrate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2821–2825, 2001

Key words: curing diagram; CHT diagram; TTT diagram; polycondensation; melamine–urea–formaldehyde resins; resin parameters' influence; quantitative influences; wood adhesives

INTRODUCTION

Temperature–time–transformation (TTT) curing diagrams and continuous heating transformation (CHT) curing diagrams of melamine–urea–formaldehyde (MUF) polycondensation resins, cured on a wood substrate were recently described.¹ While the general trends of these diagrams have been clearly identified and described, what is needed for the CHT diagrams, more technologically significant for wood-adhesive application, is to de-

termine which manufacturing parameters influence the trends and the values of the time and temperature of the diagram. To this effect, CHT diagrams for MUF resins, where the (M+U):F molar ratio and the M:U weight ratio have been changed to be within industrially acceptable limits, would be particularly useful to define what influence these parameters have on the characteristics of the resin, how their variation influences the relative position on the diagram of the gel and vitrification curves, and, ultimately, to quantify clearly the effects of these parameters on the performance of the resin. MUF adhesive resins were used as they are one of the three industrially important polycondensation resins extensively employed for wood adhesive,² for which clear influences in the manufacturing parameters have recently been defined and

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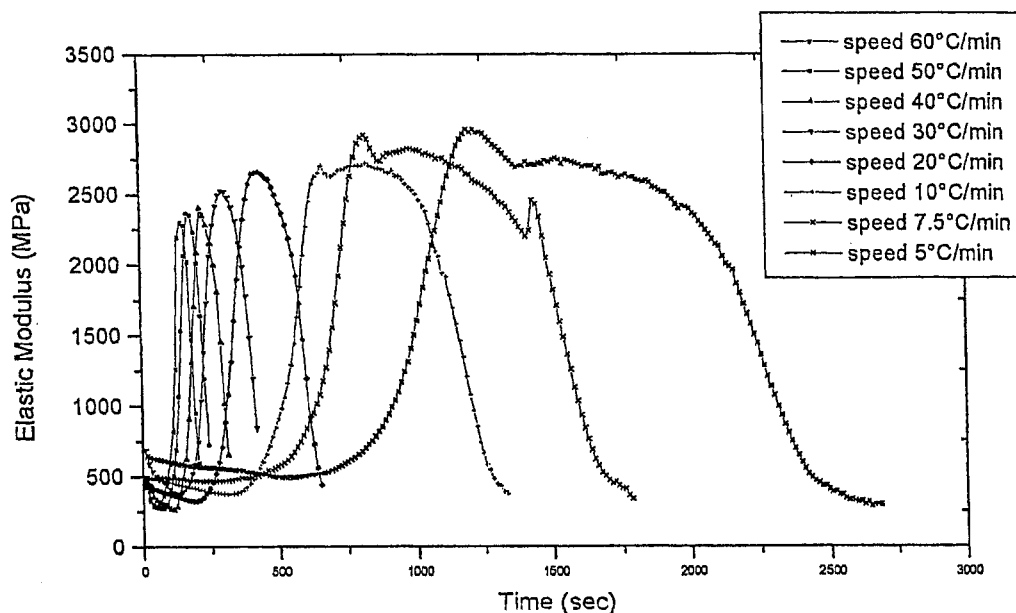


Figure 1 Curves of variation of the elastic modulus as a function of time for a MUF adhesive of an M:U mass ratio of 47:53 and an (M+U):F molar ratio of 1:1.5 hardened at 10°C/min by TMA on a beech joint.

possibly also the more complex case of the thermosetting resins for wood due to the presence in the polymer of two species reactive with formaldehyde, namely, melamine and urea.

EXPERIMENTAL

Thermomechanical Analysis (TMA) Determination of CHT Diagrams as a Function of Resin Composition

Recently, work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood and of polycondensation resins used as wood adhesives has yielded a mathematical relationship.³⁻⁵ This mathematical relationship with a constant k , that is, $f = km/E$, is based on the energy of interaction (E) at the synthetic polymer/wood interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom (m) of the segment of the synthetic polymer between two crosslinking nodes, the coefficient of branching (hence, the functionality of the starting monomer), and the relative deflection (f) obtained by TMA of wood specimens coated or bonded with the adhesive.³⁻⁵ Regression equations³ correlating directly m with E and m with f were derived for hardened phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), melamine-formaldehyde (MF), and tannin-formaldehyde (TF) resins. These relationships were used to calculate m for a series of MUF resins of 60% solids content and (M+U):F molar ratios of 1:1.5, 1:1.7, and

1:1.9 and of M:U weight ratios of 47:53, 40:60, 30:70, 20:80, and 10:90 according to industrial formulations,² all catalyzed with 2% NH_4Cl .

To this purpose, the MUF resins above were tested dynamically by TMA on a Mettler apparatus. The MUF resin was used with the addition of 2% of an ammonium chloride hardener from a 25% aqueous solution. Samples of beechwood alone and of two beechwood plys bonded with each system of liquid polycondensate resins in a layer of 350 μm , for a total samples' dimension of 21 \times 6 \times 1.1 mm, were tested to build the CHT diagrams in a nonisothermal mode. The temperature was varied from 20 to 450°C at heating rates of 3, 5, 7.5, 10, 15, 20, 25, 30, 40, 50, and 60°C/min with a Mettler 40 TMA apparatus using a three-point bending procedure on the specimen on a span of 18 mm exercising a force cycle of 0.1/0.5 N, 12 s each (6/6 s). The resulting modulus curves as a function of both temperature and time were obtained. The classical mechanics relation between the force and deflection $E = [L^3/(4bh^3)][\Delta F/\Delta f]$ allows the calculation of the Young's modulus E for each of the cases tested. As the deflections Δf obtained were proven to be constant and reproducible³⁻⁵ and they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the Young's modulus of two resins can be calculated for the two resins through the relationship $E_1/E_2 = \Delta f_2/\Delta f_1$. The values of the Young's modulus for the resin/substrate systems were then calculated according to already-reported methods based on the equation $f = km/\alpha E$ and connected regression equations.³ The CHT diagrams

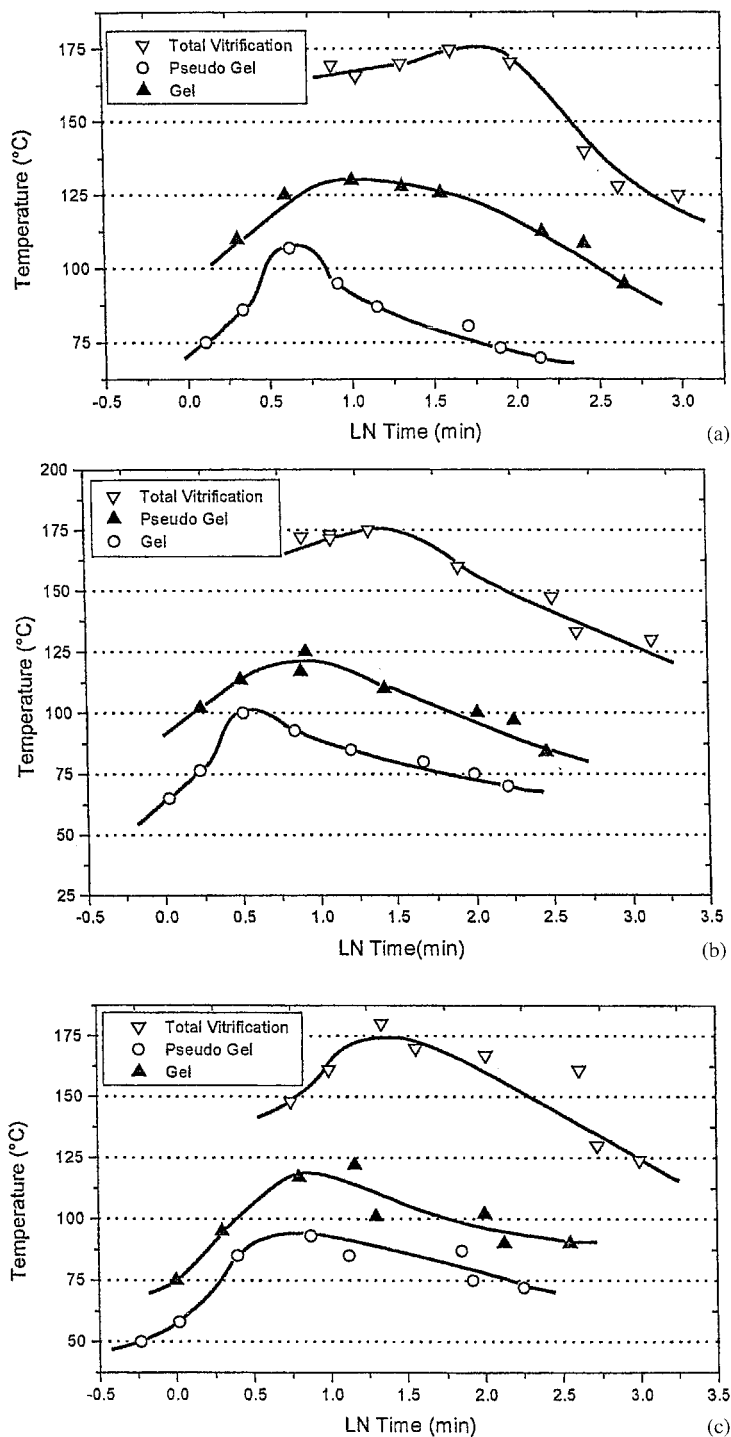


Figure 2 Detail of upper-temperature zone of CHT curing diagrams showing the total vitrification, gel, and pseudogel curves for MUF adhesives of an M:U mass ratio of 47:53 and an (M+U):F molar ratio of (a) 1:1.5, (b) 1:1.7, and (c) 1:1.9.

showing the total vitrification, gel, and pseudogel curves and their variations as a function of the manufacturing parameters were built according to methods already reported.^{6,7}

DISCUSSION

Figure 1 shows the curves of variation of the elastic modulus as a function of time when the MUF adhesive

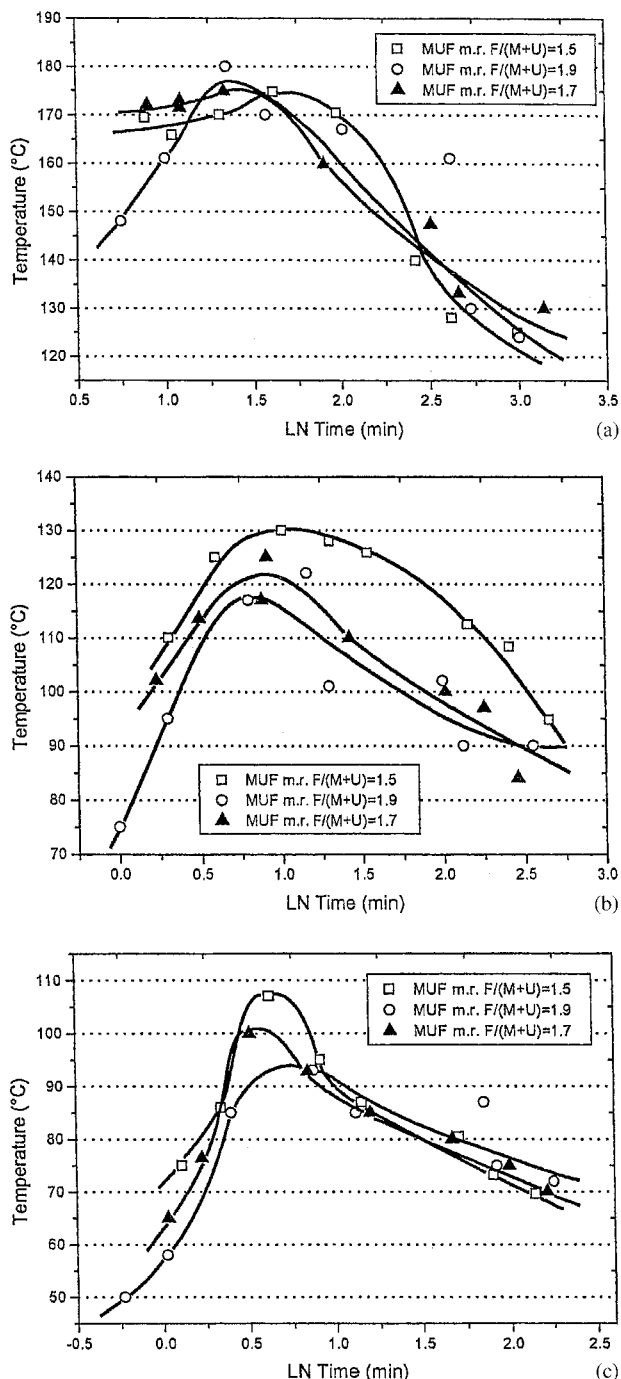


Figure 3 Detail of upper-temperature zone of CHT curing diagrams comparing (a) the total vitrification curves, (b) gel curves, and (c) pseudogel curves for three MUF adhesives of an M:U mass ratio of 47:53 and (M+U):F molar ratios of 1:1.5, 1:1.7, and 1:1.9.

on a beech joint is hardened at different constant heating rates. The trend is the same as noticed for other resins in previously reported work with the max modulus being higher for the slower-cured resin. Although

clearly evident from Figure 1, this trend is clearly less extreme here than that noticed for UF resins alone.⁷ Figure 2(a–c) shows, respectively, the upper-temperature details of the total vitrification curve, gel curve, and pseudogel curve of the CHT diagrams of top of the range MUF resins of an M:U weight ratio of 47:53 and of (M+U):F molar ratios of, respectively, 1:1.5, 1:1.7, and 1:1.9. Furthermore, Figure 3(a–c), respectively, presents all the total vitrification curves, all the gel curves, and all the pseudogel curves for the different molar ratios of the top-of-the-range M:U 47:53 resin. These results indicate that the turning point of the vitrification curves due to inverse of the water movement in the joint⁷ intervenes comparably at the same temperature (between 174 and 177 °C), while the time at which this occurs is longer for the lowest molar ratio considered (1:1.5) at 1.75 ln time in minutes, to almost stabilize at an ln time value of 1.5 and 1.4, respectively, for the 1:1.7 and 1:1.9 molar ratio resins. Other differences are the steeper upward trend of the 1:1.5 curve and the much steeper downward trend of the 1:1.9 curve in relation to the other two. These trends mean that the lower is the molar ratio of the resin the longer is the time at which the inversion of water transfer of the joint occurs, or does start to matter, this being quite clearly dictated by the lower reactivity of MUF resins of a lower molar ratio. This effect becomes less evident as one increases the molar ratio and, hence, increases both the inherent reactivity of the resin and its ultimately possible density of crosslinking. The trends in Figure 3(a) clearly indicate that this effect can become rather more marked for resins of a much lower molar ratio than 1:1.5, meaning that the rate of curing and the reactivity of the resin determines the time at which the max glass transition temperature⁷ of the system is reached and the time at which the reverse flow of the water in the joint is allowed to occur. The slower the rate of the reaction of the resin, for whatever reason, for example, for a lower reactivity of the resin, the slower will be the time to reach its max possible T_g . This appears to indicate an inverse diffusional control of the state in which the resin finds itself in the low time regions of the curve.

Figure 3(a) also indicates that the moisture path direction inversion is much more marked for the highest molar ratio resin but is not very marked for the other two. This leads one to think that moisture-induced degradation is proportionally more marked for the higher molar ratio MUF resin, this being due to the logical and probable increase of the more hydrolysis-sensitive methylene bridges involving urea as the proportion of formaldehyde increases.⁸

The same trend of time dependence, but much less marked (1.05, 0.9, 0.8 as values of ln time) is evident for the gel curves [Fig. 3(b)]. Here, instead, it is the max temperature reached which is more profoundly affected by the different molar ratios of the resins, this passing from 130 °C to 122 and 117 °C as one passes from the 1.5

to the 1.9 molar ratio resin, meaning that, due to the higher reactivity of a resin induced by its higher molar ratio, the crossing of the two effects, hence, of the two curves, changes. This changes also the point of the maximum of the curves, which then occurs earlier and at lower temperature for faster resins. This appears to indicate that a well-defined physicochemical state of the adhesive film corresponds to the turning point in the curve and that the trend observed is not just a mathematical artifact. What this physical state really represents is open to debate.

There is no time dependence for the pseudogel case (the formation of an entanglement network^{6,9}), the \ln time values being in the very narrow range of 0.6–0.7 min with no apparent trend. The temperature trend is the same as for the gel curves passing from 108°C to 101 and 94°C, respectively, for the 1.5, 1.7, and 1.9 molar ratio resins, indicating that both this and the equivalent effect in the gel time curves is a kinetic rather than a structural effect.

Varying the relevant weight proportions of M:U while maintaining the (M+U):F molar ratio constant at 1:1.9, and examining the different resins (M:U = 47:53, 40:60, 30:70, 20:80, 10:90) at the different heating rates, does yield very similar, practically identical CHT diagrams, almost as if one had dealt with the same resin. The likely cause of the lack of curve differentia-

tion in the different M:U resins is due to the (M+U):F molar ratio, which, being relatively high at 1:1.9, tends to eliminate any differences which might be introduced by the less important parameter. It is then the molar ratio which is the most important parameter in determining shifts in the relative position of the CHT curing diagram curves.

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