Diffusion Hindrance vs. Wood-Induced Catalytic Activation of MUF Adhesive Polycondensation

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SYNOPSIS

The reaction of hardening of melamine–urea–formaldehyde (MUF) adhesive resins in the presence of wood and cellulose was confirmed to have a lower energy of activation than the MUF adhesive alone, both in the presence or absence of ammonium chloride hardener, thus both in mildly acid and mildly alkaline environments. DSC exotherms showed that during hardening of melamine to melamine, melamine to urea, and urea to urea crosslinks through methylene bridges occur. Only the earliest reaction, mainly melamine to melamine crosslinking, presents a decrease in energy of activation which can be assigned to catalytic activation by the cellulosic substrate. The other types of crosslinking reactions (i) appear not to occur due to the more favorable and rapid melamine to melamine reaction which precedes them at lower temperature or (ii) do not present catalytic activation by the substrate but rather hindrance by it or (iii) variation of their energy of activation appears to be due to increased diffusion hindrance by the substrate caused by the increasing molecular weight of the resin while hardening. This because the Kissinger equation plots of the resin alone are in the main linear, for all the exotherms, indicating that in hardening of the resin alone diffusion problems appear to be limited. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

An understanding of the phenomenon of adhesion of resins to a lignocellulosic substrate is fundamental to the evaluation of bond strength development in wood products. The influence the substrate exercises on the kinetic and curing behavior of the resin, and the reasons for such an influence, are not immediately obvious. Recent studies on the substrate-induced autocondensation of phenol–formaldehyde (PF) resins[1] and on the autocondensation of polyflavonoid tannins[2,3] without formaldehyde have, however, pointed out that a cellulosic-induced catalytic activation effect on reactions of autocondensation and hardening of the adhesive resins exists. Such results are confirmed on the application side by (i) phenolic adhesives hardening in wood particleboard application in 60–180 s at 100–110°C while their gel time without lignocellulosics being present

is 25–40 min[4] and (ii) polyflavonoid tannins being able to give, by substrate-catalyzed autocondensation, boards of elevated strength while without the substrate they are not capable of hardening.[2,5] The former of these studies[1] was aimed at establishing the existence of such an effect in relation to the existence or not of interfacial resin–substrate covalent bonds under wood adhesive application conditions. This study confirmed what had been repeatedly established before,[6–18] namely that the energy of activation of the reaction of polycondensation of PF and other formaldehyde-based resins in presence of wood is considerably lowered. The existence of a catalytic effect was established and attributed mainly to cellulose; the formation of covalent bonds at the interface was also confirmed, but found to be minimal under wood adhesives application conditions. It also became evident, however, that the extent of the decrease in apparent energy of activation is also influenced by diffusion effects.[1] In short, if diffusion constraints within the resin itself or of the resin within the substrate become important during hardening, this results in a

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lowering of the apparent energy of activation too. This is a well-known phenomenon in heterogeneous catalysis.[19] Furthermore, an interesting and recent study on cure reactions of paper-phenolic composites[20,21] indicated with good reason that the cure reactions of the PF resin can be described best by homogeneous reaction models and by three-dimensional diffusion models; while homogeneous reaction models described very well the reaction in the 0–95% degree of conversion range, three-dimensional diffusion models described equally well and sometime slightly better the 30–95% degree of conversion range.[20]

Melamine–urea–formaldehyde (MUF) resins have attracted attention as a very feasible alternative to the use of melamine–formaldehyde (MF) resins on account of the lower cost of the former.[3] They have been used for the present study because they are an attractive resin system to study substrate-induced catalytic activation effects as (i) they can harden in acid (as for industrial use)[3] and in mildly alkaline environment,[3,22] and (ii) on hardening they are likely to present melamine to melamine, melamine to urea, and urea to urea crosslinking reactions through methylene bridges.[23] These two characteristics might render possible some extrapolation of the results to other formaldehyde-based adhesive systems (UF, MF, and PF). A MUF formulation in which urea and melamine were already effectively copolymerized in the liquid resin before hardening was used.[3,24]

EXPERIMENTAL

Resin Preparation[3,24]

To 113 parts by weight of formurea (a formaldehyde concentrate stabilized by urea of mass content of 57% formaldehyde and 23% urea) are added 13 parts urea and 30 parts 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 1 h 30 min to 1 h 35 min to a value of 5.2 (the pH must never fall below 5). To bring the pH to 9.5 or higher, 22% NaOH was added, then 41 parts of melamine premixed with 19 parts of water. One part of dimethylformamide and 2 parts of diethylene glycol are then added to the reaction mixture, maintaining a temperature of 93°C. The water tolerance point[1,32] is checked every 10 min while the pH is allowed to fall by itself. When the water tolerance reached is

180–200% (this was reached after 35–40 min, and the pH reached is 7.2), 6.5 parts by mass of second 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 9.5 again, and the reaction mixture cooled and stored. Resins produced using this procedure have a solids content of 58–65%; a density of 1.260–1.280 at 20°C, a viscosity of 70–150 cP, free formaldehyde of 0.32 g/100 g, and gel times with 3% ammonium chloride of 51–57 s at 100°C. As the molar ratio of the MUF resin was M : U : F = 1 : 2.3 : 6.6, hence (M + U) : F = 1 : 2, the control MF and UF resins were prepared according to procedures and formulations already reported[25,26] maintaining the same molar ratio.

^{13}C-NMR Characterisation of MUF Resin

The MUF resin above was characterized by ^{13}C-NMR. ^{13}C-NMR of the liquid resin was obtained on a Bruker AC200 FT-NMR spectrometer at frequency of 50.5 MHz with the sample spectra at 35 Hz. Chemical shifts were calculated relative to trimethylpropyl silane sodium sulfonate for NMR control, which was dissolved in deuterated water and then run to set the four signal shifts. About 1 mL of liquid resin at 50% resin solids concentration was placed in an NMR tube and diluted with 0.4 mL of deuterated water added directly to the sample. The spectrum was run overnight. Aquisition time was 1.8 s with number of transients at 10,000. The spectrum was run with relaxation delay of 5 s and was accurate to 1 ppm. The spectra were run with nOe enhancement, spectral width was 15000 Hz, and digital resolution 0.825. Typical spin lattice relaxation times were not measured but standard values shown in the literature for this type of system were used.[27–30]

Differential Scanning Calorimetry (DSC) of Resins

The MUF resin was tested alone and premixed to a resin solids–substrate ratio of 1 : 1 weight to weight, with filter paper (Whatman Number 1 filter paper), with softwood lignin powder, and with fine 200 mesh pine (Pinus radiata) wood flour according to procedures already described.[1] In the resins containing ammonium chloride the latter was added as a 25% solution to the resin in the proportion of 2% ammonium chloride solids on resin solids.

The sample resins or resin mixes were tested by placing a small amount into a sample crucible. The

Table I   Apparent Activation Energies of Exotherms of MUF Resins Polycondensation and Curing by DSC and Kissinger Equation[a]

	Activation Energy (kcal/mol)				
MF	32.2 ±0.7	17.1 ±1.4	b	b	55.7 ±1.1
UF	b	b	b	10.9 ±0.5	b
MUF	30.0 ±0.6	50.4 ±2.0	12.0 ±0.6	10.6 ±0.5	12.6 ±0.5
MUF + cellulose	12.7 ±0.5 (spans cols 1–2)		b	10.8 ±0.5	b
MUF + lignin	23.6 ±0.8	62.5 ±0.5	16.1 ±0.7	13.4 ±0.8	10.6 ±0.6
MUF + wood	9.0 ±0.7 (spans cols 1–2)		19.1 ±1.1	56.2 ±1.2	82.0 ±0.6
MUF + NH4Cl	32.0 ±0.5	19.9 ±0.4	9.4 ±0.6	b	b
MUF + NH4Cl + cellulose	8.5 ±0.8 (spans cols 1–2)		92.1 ±1.7	b	b
MUF + NH4Cl + lignin	b	13.4 ±0.7	c	b	41.0 ±1.0
MUF + NH4Cl + wood	1.8 ±0.8 (spans cols 1–2)		64.7[d] ±0.4	108.5 ±0.8	37.2 ±1.3
Peak max temperature (range °C)	83–102 ±0.5	89–109 ±0.5	113–150 ±0.5	123–168 ±0.5	168–204 ±0.5
Crosslink type	MM[e]	MM[e]	MU[e]	UU[e]	MM[e]

[a] Results enclosed in boxes are those where linearity of correlation exists (no diffusion hindrance present).
[b] Peak does not exist or it is not noticeable.
[c] Peak exists but energy not calculable.
[d] Not enough data for a reliable result.
[e] MM = melamine-to-melamine methylene crosslinks; MU = melamine-to-urea methylene crosslinks; UU = urea-to-urea methylene crosslinks.
From Ref. 31.

sample crucibles were then heated in a Dupont DSC calorimeter at different heating rates, namely 5, 10, 15, and 20 K per minute until a maximum of 573 K. The activation energy of the curing reaction of the MUF resin alone, or of the MUF resin on different substrates, was calculated on the basis of the variation of the temperature of the maximum of each exotherm (T_{max}) of the DSC scan as a function of the temperature rate increase of the DSC scan, using the Kissinger equation.[31] Thus, the ln [rate of temperature increase/(T_{max})2] was graphed as a function of $1/T_{max}$, and from the Kissinger equation the energy of activation corresponding to each identified exotherm was obtained. All the scans were conducted in nitrogen atmosphere.

DISCUSSION

In Table I are presented the apparent energies of activation of the hardening exotherms of a MUF copolymer resin alone and in presence of cellulose, lignin, and wood, when an acid catalyst is not present (hence in alkaline environment) as well as the same in the presence of 2% ammonium chloride, thus in acid environment. The exotherms' apparent energies of activation of a MF and a UF resin, prepared as similarly as possible to the MUF resin, are also presented as controls. The MUF resin when alone presents four main exotherms in common to the MF and UF resin (Table I) and one exotherm characteristic of melamine to urea crosslinking

through methylene bridges. The last, considering the relative reactivities of melamine and urea with formaldehyde[22,26] is most likely to describe the reaction of a methylol group on urea with a melamine amino group rather than vice versa. The DSC traces of pure MF and pure UF sometimes also present a few small exotherms at lower temperature (UF) and at higher temperature (MF) then the five main peaks observed and followable in the MUF copolymer. The MUF resin also presents one and sometime two other exotherms in the temperature range 240–280°C (Figs. 1 and 2), but these are not reported as they have been shown to belong only to transformations of the lignocellulosic substrate and are not present in the resin alone.

The MUF resin used has already been shown to be a true copolymer of urea and melamine.[22,25] In the Figure 3 ^{13}C-NMR spectrum this can be observed from the region between 40 and 60 ppm. In this the sharp bands at 55.4 and 47 ppm belong to methylene bridges connecting two urea amide groups; the sharp band at 49.8 ppm belongs to methylene bridges connecting two melamines and the bands at 53–54, 50.8, and 46 ppm to methylene bridges connecting urea to melamine.

Crosslinking and hardening of a MUF copolymer resin can occur by formation of methylene bridges

between two melamine groups, two urea groups, and between a melamine group and a urea group: The relative temperature ranges in MF and UF exotherms allow one to assign to which of these three crosslinking reactions the different exotherms of a MUF resin belong (Table I). Thus, the first two exotherms, at the lower temperatures, correspond to melamine to melamine methylene bridge formation, the third exotherm to melamine to urea methylene bridge formation, the fourth to urea to urea methylene bridge, and the fifth again to melamine to melamine methylene bridge crosslinking. The first observation of interest is that in MUFs to which ammonium chloride hardener has not been added, hence tested in mildly alkaline environment, the same very evident decrease in the apparent energy of activation of hardening is noticeable when the resin is tested on a cellulosic (paper) or a wood substrate. Such a decrease is quite marked in the melamine to melamine crosslinking exotherms and does not appear to be present in the other types of exotherms. The decrease in energies of activation does not present itself in urea to urea and in urea to melamine crosslinks. This might be due to the rate of condensation under mild alkaline conditions between two melamine groups being considerably greater than between two urea groups or a urea and
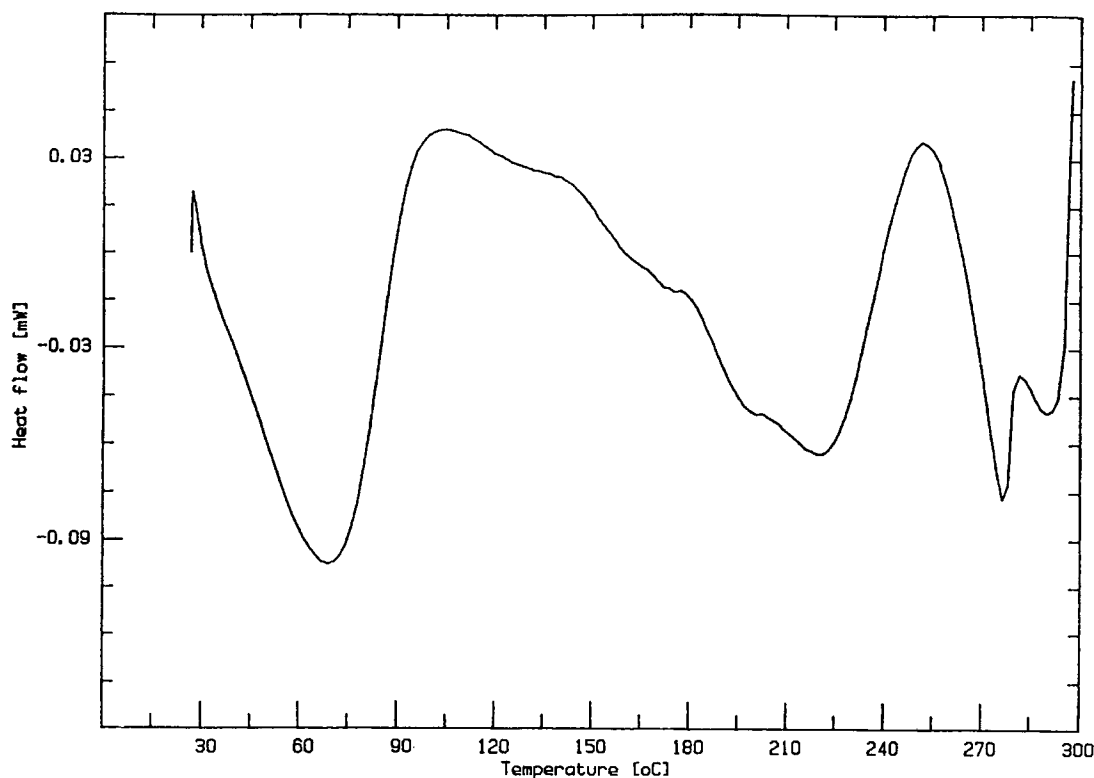

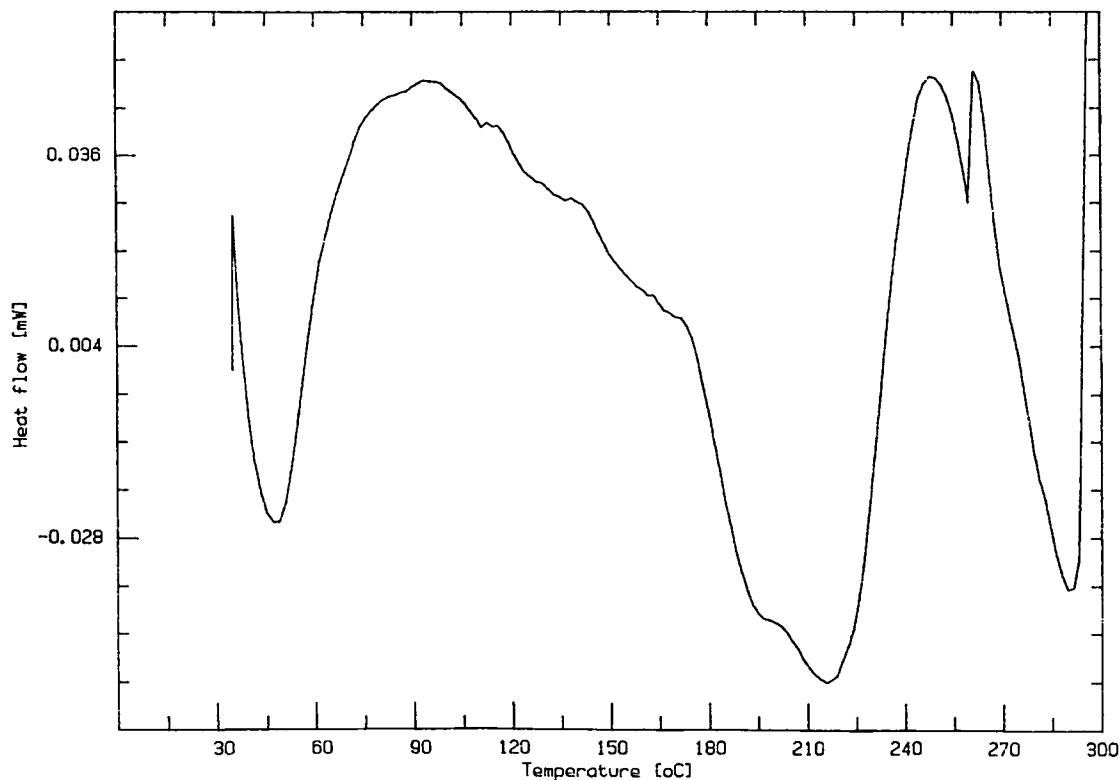**Figure 1**   DSC trace at 10 K/min of MUF resin in the presence of cellulose.

Figure 2   DSC trace at 10 K/min of MUF resin in the presence of wood flour.

a melamine.[32,33] Thus, the melamine to melamine reaction occurring earlier, at the beginning of resin condensation, then the other two reactions: by the time the network has started to form very little of

the other two reactions is likely to occur. Of interest also is the increase in energy of activation of most of the exotherms for the reaction on lignin, indicating clear interference by lignin with the process
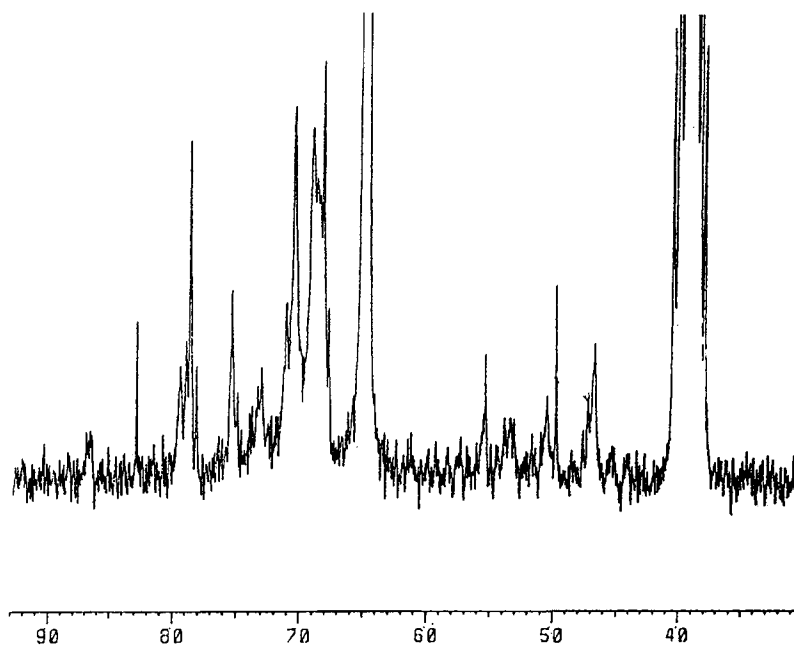

Figure 3   Detail of the ^{13}C-NMR spectrum of liquid MUF resin.

of resin curing.[1] This might be the consequence of some covalent bonds being formed, as well as other causes.

When 2% ammonium chloride is added to a MUF resin alone, invariate or a slightly lower apparent energy of activation is observed, as would be expected. However, the urea to urea exotherm disappears: this is also expected because as the pH is lowered by ammonium chloride addition, the reactivity of melamine in relation to that of urea also increases, favoring even more melamine to melamine crosslinking and decreasing the probability of urea to urea crosslinking. The melamine to urea crosslinking exotherm is still present but it is much less intense.

The apparent energy of activation of the ammonium chloride-induced hardening of the MUF resin under acid conditions also decreases when the resin system is in the presence of cellulose and wood. The decrease is as evident as that observed under alkaline conditions and is again even more strictly limited to the first two exotherms (melamine to melamine). The evident increase in apparent energy of activation of the subsequent three exotherms, and often their complete disappearance, in the ammonium chloride-hardened resins is an indication that the importance of melamine to melamine crosslinking has increased to such an extent to deny, or to render considerably more difficult, any of the three other crosslinking reactions which follow. This does not mean to say that a decrease in the apparent energy of activation of UF resins in presence of cellulose and wood does not occur, as it has already been shown that it does.[8] It only means that in MUF systems the melamine reactivity is such that a decrease is only observed for the melamine groups, strongly depressing any effect on other groups crosslinking.

It is important to discuss to what extent the decrease in apparent energy of activation is due to the catalytic effect of the substrate surface or rather to a diffusion hindrance effect. It is well known in heterogeneous catalysis that the correlation of $\ln \beta/T^2$ vs. $1/T$ (where β is the rate of temperature increase) from the Kissinger equation[19,31] shows a marked deviation from linearity when either diffusion hindrance on the catalyst surface or the occurrence of a low degree of surface covering exist.[19] The situation of a low degree of surface covering does not present itself under the conditions used. As a consequence, any deviation from linearity of the correlation would indicate a diffusion hindrance effect. In Table I all the apparent energies of activation in which the data give strictly linear results are marked by a rectangular window. From these it can be seen that in the

initial crosslinking reactions of the resin, those between melamine and melamine groups, the decrease in energy of activation is mostly due to a substrate-induced catalytic effect and not to diffusion hindrance.

That diffusion hindrance becomes important in the subsequent reactions, due possibly to the considerable increase in molecular mass of the resin, confirms the deductions of other authors.[20,21] That the diffusion hindrance which is important is that exercised by the substrate onto the growing, networking resin can be seen by the fact that the Kissinger equation plots of the resin alone (or even with just ammonium chloride) are linear for all the exotherms, indicating that in the hardening of the resin alone diffusion problems can only occur at the very end of the reaction. The result instead that linearity of the plots is lost at a much earlier stage in the reaction when the resin is cured in the presence of the substrate indicates that it is mainly the resin–substrate hindrance rather than resin–resin hindrance which is the main contributor. This also confirms what was found for paper–phenolic resins composites by other authors[20,21] in which diffusion appears to play an important role only at the higher degrees of resin conversion. It also shows that within-resin diffusion does not appear to play a role, as in MF, UF, and MUF resins in the absence of the substrate the correlations are all linear. This has also been found for PF resins where the decrease in apparent energy of activation has been attributed $\frac{1}{3}$ to diffusion and $\frac{2}{3}$ to substrate-induced catalysis for the main hardening exotherm of the resin.[1]

It is also of interest to discuss what could be the mechanism of the diffusion hindrance. The effect in the experiments is observed under more favorable conditions than what occurs on solid wood surfaces eliminating possible wood anatomical interferences (if any), because a fine powder (200 mesh) wood flour had to be used as the substrate. The effect then might result from both portions of large and growing resin molecules chemically absorbed on the lignocellulosic substrate surface, as well as the polymeric high-molecular-weight constituents of the substrate hindering relative molecular movement and consequently hindering and slowing down contact between resin reactive sites.

As for the case of phenolic resins, another question of interest is: Do interfacial resin to substrate covalent bonds exist in MUF resins on lignocellulosics? Contrary to PF systems, in MUF systems the answer is a definite no. No exotherms belonging to a substrate–resin condensation are observed. This is to be expected if it is considered that the rate of

reaction of melamine with formaldehyde in mild acid and neutral and mild alkaline conditions is much greater than PF resins in the same pH range.[1] This does not exclude their formation outside the ranges of pH investigated.

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