Lignocellulosic Substrates Influence on TTT and CHT Curing Diagrams of Polycondensation Resins

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ABSTRACT: Lignocellulosic substrates such as wood were found to have a marked modifying influence on a well-defined region of CHT diagrams during hardening of phenol–formaldehyde (PF) and urea–formaldehyde (UF) polycondensates. This was ascribed to more complex resin phase transitions due to resin/substrate interactions peculiar to these substrates. The chemical and physical mechanisms of the interactions of the resin and substrate causing such CHT diagram modifications are presented and discussed. The Di Benedetto equation describing the glass transition temperature T_g of the system as a function of the resin degree of conversion p has been slightly modified to take into account the modified CHT diagram. The modified CHT diagram can be used to good effect to describe the behavior of polycondensation resins when used as wood adhesives during their curing directly into the wood joint. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 915–925, 1999

Key words: curing diagram; TTT diagram; CHT diagram; polycondensation; phenol–formaldehyde resins; urea–formaldehyde resins; wood adhesives; substrate influence

INTRODUCTION

The concept of the isothermal time–temperature–transformation (TTT) cure diagram in which gelation and vitrification times are plotted versus the isothermal cure temperature is useful for understanding the behavior of thermosetting resins under isothermal cure conditions.[1] In TTT diagrams, the S-shaped vitrification curve and the gelation curve divide the temperature versus time diagram into four distinct states of matter: liquid, gelled rubber, ungelled glass, and gelled glass (Fig. 1).[1] Analogous to the isothermal TTT diagram is the continuous heating transformation (CHT) cure diagram which reports the times and temperatures required to reach similar events during the course of continuous heating at constant heating rates (Fig. 1).[2] The gelation and vitrification curves are the most characteristic features of both TTT and CHT diagrams, the S-shape of the latter in particular defining the region at which the reaction rate is greatly reduced because diffusion control becomes more pronounced in the glass transition region. The quantitative studies of CHT and TTT diagrams reported up to now have mostly been on the curing of epoxy resins on glass fiber braid,[1–3] due to the need of defining the diagrams themselves under conditions of minimum interference between the resin and substrate and with a resin, the curing path of which is well defined and relatively straightforward. The conclusions which have been drawn from them are, consequently, mostly derived from studies on this type of polycondensate and this in the presence of a noninterfering substrate, namely, glass fiber. Notwithstanding this, the conclusions obtained are widely applicable to a variety of polymers and have greatly

Figure 1 Nonmodified, generalized continuous heating transformation (CHT) (and TTT) diagram.[1,2]

contributed to advance knowledge on the polycondensation curing process and of its influence on the variation of the glass transition temperature of resin systems. The concepts exposed in such diagrams are often used and helpful in advancing qualitative deductions on polycondensates other than epoxies.[4]

The most used (by volume) polycondensation resins today are urea–formaldehyde (UF) and phenol–formaldehyde (PF) resins. More than 60% of the UF and PF resins produced today in the world are used for thermosetting wood adhesives.[5] The increase of temperature in the innermost core region of a wood particleboard bonded with such resins, during its hot pressing at constant platen temperature, follows a curve not dissimilar to a constant rate of temperature increase during the majority of its pressing time (it does not change at the onset of pressing, then increases almost linearly from ambient to a value of between 105 and 120°C depending on the moisture content of the panel, and finally stabilizes to a quasi-isothermal mode or with a very slow temperature ramp for a good part of the remaining

press cycle). Thus, a CHT diagram rather than a TTT diagram would be more useful to study the curing behavior of UF and PF resins under conditions which simulate the formation of a thermosetting wood joint such as occurs, for example, in wood particleboard or in plywood glue lines. As the curing behavior of these and other formaldehyde-based resins is furthermore strongly dependent on the substrate on which resin cure takes place,[6–9] namely, wood, to understand their curing behavior as wood adhesives, a standard test wood such as beech wood should be used as a substrate, rather than the more accepted woven glass fiber braid used up to now for epoxy resins.

Thermomechanical analysis (TMA) is a technique which has already been used to build TTT diagrams,[3] again using epoxy resins on woven glass fiber substrates. Recently, an equation, and simpler regressions also, correlating the relative deflections obtained by TMA with the sum of the internal cohesive strength and interfacial energy of the interaction of a synthetic polymer with wood was obtained.[6,10,11] Interesting conclusions on a variety of aspects in UF and PF polyconden-

sation and other networks have already been obtained[6,10,11] by this approach. However, it also appeared that at least in one region of the curing process on wood of formaldehyde-based polycondensates some lack of correspondence might exist with what already has been described from epoxy resins on glass fiber for the generalized form of the CHT (and TTT) diagram itself.[6] As it was not immediately apparent if the difference observed was due to the resin itself or to the substrate alone or to the interaction between the resin and substrate, CHT diagrams for the curing on wood of UF and PF systems were investigated.

Figure 2 Increase of modulus, at heating rates in the range 5–40°C/min, as a function of time for a beech wood joint bonded with a UF resin.

EXPERIMENTAL

TMA Determination of Average Number of Degrees of Freedom of Networks

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[6,10] between 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 through the expression $f = km/\alpha E$, where k is a constant.[6,10] Regression equations[6] correlating directly m with E and m with f have been derived for hardened PF, resorcinol–formaldehyde (RF), melamine–formaldehyde (MF), and tannin–formaldehyde (TF) resins. These relationships were used to calculate m for a commercial PF resin of a molar ratio P : F = 1:2.5, prepared by a multistep reaction procedure, at the delivered resin solids content of 48%, and for a commercial UF resin of 63% solids content, the latter catalyzed with 1.5% NH_4Cl.

To this purpose, the UF and PF resins above were tested dynamically by TMA on a Mettler apparatus. The UF resin used was a plywood one of molar ratio U:F = 1:1.5 and of a resin solids content = 63%. The PF resin was a commercial particleboard resin of a molar ratio of P : F = 1 : 2.5, solids content = 48%, and gel time at 100°C of 24 min. The UF resin was used with the addition of 1.5% on the total resin solids of an ammonium chloride hardener added as a 25%

water solution. The PF resins were used without addition of any other additive. Samples of beech wood alone and of two beech wood plies bonded with each system of liquid polycondensate resins in a layer of 350 μm, for a total sample dimension of 21 × 6 × 1.1 mm, were tested in a nonisothermal mode between 40 and 240°C at heating rates of 5, 7.5, 10, 15, 20, 25, 30, 40, 50, 60, and 70°C/min with a Mettler 40 TMA apparatus in three-point bending on a span of 18 mm, exercising a force cycle of 0.1 N/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s), and the resulting modulus curves as a function of both temperature and time were obtained. The classical mechanics relation between 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 reproducible[6,10] and as they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the Young's modulus can be calculated for the resins through the relationship $E_1/E_2 = \Delta f_2/\Delta f_1$. The values of the Young's modulus for the resins/substrates systems were then calculated according to already-reported methods according to the equation $f = km/\alpha E$ and connected regression equations which also have already been reported.[6]

DISCUSSION

The modulus curves as a function of time and temperature obtained by TMA and shown in Figures 2 and 3 indicate several differences in behavior when the same UF adhesive is hardened at different heating rates. The main features which are noticeable are

Figure 3 Increase of modulus, at heating rates in the range 5–40°C/min, as a function of temperature for a beech wood joint bonded with a UF resin.

1. The maximum value of the modulus which is reached with the same UF adhesive is higher the slower the heating rate. Thus, for example, the maximum value of the modulus obtained at 5°C /min is of almost 4000 MPa, while at 40°C/min, it is of 1550 MPa.

2. The slower the heating rate, the longer the time at which the maximum value of the modulus is reached, which is to be expected, while the temperature at which it is reached is approximately the same.

3. The modulus curves present, in their ascending portion, a discontinuity of slope, namely, a plateau or the beginning of a plateau, in the heating range from 5 to 25°C /min while no plateau is present in the curves obtained at faster heating rates in the range 30–50°C/min.

Points 1 and 3 above are symptomatic of the already-observed[7,12] behavior of polycondensation resins to grow at first linearly and only later to crosslink to form a tridimensional network. The first plateau or shoulder in the modulus curves has been ascribed to the formation of entanglement networks by the linear polycondensates formed. The mechanism of formation of these entanglement networks depends on the relative balance between the linear increase in polymer length in the initial stages of the polycondensation—hence, it is polycondensation advancement-dependent—and the concentration of the linear polymers formed.[8,12] Thus, as the linear length of the polymer increases, the water solvent is also progressively removed from the growing polymer both by sorption by the substrate as well as by evaporation as the temperature increases

during the test.[7,12] Once a certain critical value of the length of the polymer is reached and a certain critical value of concentration is also reached, then entanglement networks will form.[7,12–14]

Figures 2 and 3 show that the slower the heating rate the more evident is the entanglement plateau and the higher its value of the modulus due initially to entanglement. This confirms that linear growth of the polycondensate can be maximized by decreasing the temperature at which polycondensation is carried out (this is likely to be valid both in the reactor during preparation of the UF resin as well as in the resin curing stages on the substrate). Figures 2 and 3 indicate that this effect becomes more marked the slower the rate of heating that is applied. It infers that the polycondensates grow mostly linearly to a higher degree of polymerization, before tridimensional crosslinking starts, the slower the rate of heating. This might depend on the respective reactivities of urea sites with formaldehyde which are in the approximate ratio 9:3:1, respectively, for the first-reacted, second-reacted, and third-reacted urea sites.[5,15,16] The slower heating rates used decrease molecular movement and, therefore, further decrease the chance of the third urea site reacting, hence favoring more linear growth of the polycondensate. Tridimensional covalent networking will still occur, and a tridimensional crosslinked network will still be the final product of the reaction, but will occur later when the polymer has grown to greater lengths.

The considerably higher value of the modulus at slower heating rates must be viewed in this context: It relates to the polymer having time to adjust by better utilization of empty volume spaces, the same reason which gives a lower value of the glass transition temperature T_g the slower the rate of heating. The extent of the effect observed is considerable: The maximum value of the modulus once the resin is tridimensionally crosslinked for the 40°C/min case is lower, due to early tridimensional immobilization of the resin in a less tight tridimensional covalent network than the value of the modulus of just the entanglement network observed for the 15°C /min and slower heating rate curves.

Before building a CHT diagram, a few rules need to be defined: The total modulus curve obtained at constant heating rates can be used to determine the gel point of the system and the start of vitrification according to known techniques[3,17] as well as the peaks of the modulus curve first derivate.[7,12,17] However, while no controversy exists as regards the site representing

the start of vitrification on TMA modulus curves,[3] the real position of the gel point on the modulus curve is still a subject for some debate. For these reasons, the CHT diagrams of the UF adhesive/wood system were then constructed using all the different approaches possible to the gel point to check all the possibilities. What is reported in this article, however, corresponds to taking (i) the gel point of the system as the start of the second upswing of the modulus curve (the start of the real tridimensional crosslinking phase) in the modulus curves cases in which a first, entanglement-derived plateau is also present,[7,12,18] that is, at the crossover point of the elastic and viscous moduli G' and G'' (hence, when tan δ is equal to 1) as already reported[7,18] and taking (ii) the start of the upswing of the first entanglement phase as the pseudo-gel point due to entanglement of the system[7,12] (indicated in Fig. 2). All other approaches (not reported here) led to the same conclusions as discussed later, but with the gel point curve on the CHT diagram shifted to lower or to higher temperatures while presenting exactly the same trend.

From the UF TMA data reported in Figures 2 and 3, a portion of the CHT diagram of this resin system when hardened on a lignocellulosic substrate can be constructed. The first difficulty encountered was that for the higher heating rate curves the increase in modulus occurs as a single step (Fig. 1): Is this single modulus increase step representative of the first or of the second step observed in the curves obtained at slower heating rates? The answer to this question is of importance in determining if the flex points (the incremental log curve peak) of the modulus curves at higher heating rates represent the start of vitrification (as in the second step of the slower heating rate curves) or if they represent the pseudo-gel points of entanglement networks (as in the first step of the slower heating rate curves). In the first case, the data obtained would pertain to the vitrification curve on the CHT diagram, while in the second, to a pseudo-gel point curve.

As such a question could not be answered with the data available for the UF resin, it could not be decided which of the two CHT diagrams obtainable could be the correct one. In both CHT diagrams, however, it was already evident that the shape of the vitrification and gelification curves is different in one diagram region from what was predicted by the classical CHT (and TTT) diagram. To try to solve such a problem, a simpler resin system was used, namely, a PF resin on beech wood. Alkaline PF resol resins for wood do not need a pH-varying catalyst to cure as in the case of UF resins and are slower to cure, rendering observation easier. They also present modulus increase curves in two main steps[7,12,18] and they often present this characteristic also at higher heating rates, resolving the question of the position of the vitrification point, gel point, and pseudogel point at such higher heating rates.

The PF resin used in the experiments was one of a PF molar ratio of 1:2.5. This type of resin does not present any *ortho* and *para* free sites on the phenolic nuclei as they are already all substituted with methylene bridges or methylol groups (—CH_2OH). It is then forced to grow linearly and then crosslink to tridimensional networks through the formation of methylene ether (—CH_2OCH_2—) bridges between the phenolic nuclei. Only later, at higher temperature or longer times, the methylene ether (—CH_2OCH_2—) bridges partly reorganize to methylene bridges (—CH_2—), hence forming a slightly tighter network (this latter step sometime being shown by a third, much smaller, final upswing of the modulus curve) (Fig. 4).[7] The decrease in the max modulus as a function of heating rate is also evident in Figure 5 for PF resins on wood.

The detail of the CHT diagram obtained for the PF resin is shown in Figure 6. It indicates that for the UF resin also the single step for the faster heating rates' modulus curves represent tridimensional crosslinking and vitrification (Fig. 7). From the experimental points of the PF resin (this does not occur for the UF resin), it also appears that while a tendency for the vitrification curve to turn to the right toward an asymptotic value of $T_{g\infty}$ still remains this is soon corrected by a clear swing to the left and a clear decrease in the temperature of the vitrification line. What is the meaning of such a different CHT diagram and why is the diagram different from the accepted general form?[1,2] First of all, at the temperatures used, the behavior of the substrate alone has been found not to interfere.[18,19] Second, the behavior of these polycondensates when cured alone has no reason to be different from the standard CHT diagram shape observed already for epoxy resins. The difference stems then from the resin curing in the presence of the lignocellulosic substrate: This is of importance as 70% of all PF and UF resins are cured on this type of substrate in their use as wood adhesives, and, hence, predictions as to their curing behavior in this context should use the modified form of the CHT diagram.

The modified CHT diagram obtained in Figure 8 indicates that as the temperature increases the

Figure 4 Examples of three-step modulus increase curves as a function of tempera-
ture: (a) 50°C/min; (b) 25°C/min heating rates.

simple phase transition liquid/gelled rubber/
gelled glass domain is indeed more complex once
the substrate is present. At the lower tempera-
ture increase rates at which the effect starts to
occur, the phase change is liquid/nongelled rub-
ber (entanglement network)/gelled rubber/gelled
glass. As a higher temperature increase rate is
used, the system resin/substrate passes from a
gelled rubber state or to a liquid again or to an
entanglement network, then again to a gelled
rubber, and, finally, to a gelled glass phase. At
even higher heating rates, the resin/substrate

system passes from a gelled glass region to a
gelled rubber, with sometime a brief passage
through an entanglement network (nongelled
rubber) followed again by a gelled rubber and,
finally, a gelled glass state. These results are of
some applied interest as they describe the rheol-
ogy and behavior of a thermosetting adhesive
hardening on a wood substrate, *in situ* in a wood
joint, under conditions very similar to those prev-
alent today in the preparation of bonded wood
products. In this context, the specific area of the
wood used as the substrate might well influence

(a)

(b)

Figure 5 Increase of modulus, at heating rates in the range 5–40°C/min, as a function of (a) time and (b) temperature for a beech wood joint bonded with a PF resin.

the relative distances between the different curves but not the general shape of the curves presented in Figures 7 and 8. Equally, the use of faster or slower PF resins or of resins of higher or lower resin solids content (hence, with lower or higher proportions of water in the liquid resin) will definetily influence slightly the relative distances between the different curves but will not influence the general shape of the curves presented in Figures 7 and 8 and this has already been shown experimentally.[7,12,18] The shape of the CHT (and TTT) diagram shown in Figure 8

can be considered then of general applicability as regards fairly standard water-borne polycondensation resins used as wood adhesives when used in the presence of a wood substrate.

What are the causes of the differences in changes of phase remarked on in the cases presented and what is their physical meaning? It is well known that application of a UF or of a PF resin on a wood substrate causes partial separation of the water from the resin and considerable increase of the resin concentration by sorption (and other) on wood. This sorption increases the resin concentration and viscosity. It also greatly increases and accelerates when increasing the temperature of the system to such an extent that curing as measured by the forward proceeding of the polycondensation is already very rapid from the start of the reaction. Molecular movements and reactive site activation are then such that loose tridimensional crosslinking occurs so rapidly that linear growth is stunted, leading to a single step on the modulus increase curve. This will lead the resin to a loosely gelled rubber phase which is indeed what is observed on the CHT diagram, a phase the appearance of which is well known in the manufacture of plywood in the close and open assembly time stage.[5,20] Further water loss at even higher temperature will introduce a loosely gelled glass phase. Both gelled rubber and gelled glass phases obtained in short times at the higher temperature pertain to loose networks.

Given enough heating time at the higher temperatures, three effects pulling in the same direction occur: (i) Some water still trapped in the wood moves again to the glue line and partially reliquifies the sol portion of the resin[5,21] (with sometime concomitant problems of wood overabsorption of the resin and consequent adhesive starvation of the glue line[5,20]), (ii) some resins, such as PF resol networks in which a fair proportion of sol phase is still present, are capable of easily melting, an effect which is already exploited industrially in the use of powdered, dry PF resols in the preparation of oriented strandboard,[5] and (iii) UF loose networks are reversible because the aminoplastic methylene bridge is easily degraded with the emission of formaldehyde, as well as for the easy rearrangement at higher temperatures of the aminomethylene ether bridges ($-CH_2OCH_2-$) to methylene bridges ($-CH_2-$) with liberation of formaldehyde.[22] This step occurs with partial or even total degradation of the aminomethylene ether network, especially if the number of tridimensional crosslinks were only a few. The same rearrangement is also well known for PF resins[23] according to the following scheme:

Figure 6 Detail of the modified zone of the continuous heating transformation (CHT) diagram for a PF resin on a beech wood joint. The experimental points, the curves of the start of vitrification, gelation, and pseudogel and the curves connecting them at the same heating rates are indicated.

It is clear then that on the CHT (and TTT) diagram different locations of the same type of phase indicate different kinds of materials, that is, at shorter times and higher temperatures, a gelled glass and rubber which are obtained by sudden and early immobilization (hence, only partial) of the network present a much lower den-

sity of crosslinks (confirmed by the lower max value of the modulus that the system is capable of reaching; Figs. 2, 3, and 5), while the gelled glass obtained at lower temperatures but at much longer times forms a much tighter and stronger network, presenting a much higher density of crosslinking (shown at lower heating rates by the much higher value of the final modulus; it relates to the polymer having time to adjust by better utilization of empty volume spaces, Figs. 2, 3, and 5). Passage from a loosely gelled rubber to a properly gelled one or even phase transformations of the type of loosely gelled glass/loosely gelled rubber/gelled rubber/gelled glass can then occur with ease, with or without passing through a liquid phase, and similarities between these findings and applied observations are many.[5,20]

The results obtained are then not unexpected from what is partially and qualitatively known of

Figure 7 Detail of the modified zone of the continuous heating transformation (CHT) diagram for a UF resin on a beech wood joint. The experimental points, the curves of the start of vitrification, gelation, pseudogel, total vitrification, devitrification, and degradation and the curves connecting them at the same heating rates are indicated.

the rheology of UF and PF thermosetting adhesive resins curing on wood.[5,20] The CHT diagram approach, however, allows one to define the changes of state of the resin to a much greater extent and to define them quantitatively, rather than by the qualitative, subjective approach which has been taken up to now to the rheology of wood adhesives curing *in situ* for which quantitative data are lacking. The construction of a modified CHT diagram is then a formidable tool to define quantitatively these effects which are es-

sential to understand the behavior of wood adhesives during their application. It must be clearly pointed out here that while a wood substrate such as beech which is widely used for standard tests has been used here, if a different wood of very much different anatomical and physical characteristics is used the trend of the CHT diagram will remain the same but the values of temperature and time are likely to change, even quite markedly. Equally, a marked variation of the type of PF and UF resin may also lead to some variation

Figure 8 Modified, generalized continuous heating transformation (CHT) (and TTT) diagram for UF and PF polycondensates hardening on interacting lignocellulosic substrates.

in the essential values of temperature and time on the diagram while still maintaining fundamentally unaltered the trends described.

A question which needs answering from the above is if the equation of Di Benedetto[24] under the form of Pascault and Williams,[25] describing T_g as a function of the degree of conversion p, namely:

$$(\lambda p)/[1 - (1 - \lambda)p] = (T_g - T_{g0})/(T_{g\infty} - T_{g0})$$

is still usable on polycondensate hardening on wood substrates in which the CHT and TTT diagram differ from their standard model. The discrepancy regards the parameter $T_{g\infty}$. While this parameter can be well determined for the PF and UF polycondensate alone, in absence of the wood substrate, its value would not pertain to the system resin/substrate but to another system, namely, the resin alone. The same parameter appears then to be meaningless when the polycondensate is hardened on a lignocellulosic substrate because no asymptotic approaching to it of the T_g of the system occurs: In short, on a wood substrate, $T_{g\infty}$ or does not exist or

it is likely to be different from its value for the resin alone and cannot be determined (no asymptotic trend of the vitrification curve exists; the devitrification curve on Figure 8, however, appears to tend to an asymptotic value which might still be $T_{g\infty}$, but from the other side indicating a slight relaxation of the maximum tightness network; the data are not sufficient to determine if this trend is true or not). Two main solutions could then be envisaged, namely, (i) to use the equation of Di Benedetto in the form reported above by determining the value of $T_{g\infty}$ of the resin alone and thus assuming the two values to be reasonably near while still being aware of the shortcomings that have been described above. Alternatively, (ii) the $T_{g\infty}$ of a resin alone can be considered in the approximation of $T_g = T_{cure}$ of Enns and Gilham[1] to be the T_g of the resin at its maximum degree of conversion p which is only reached at time equal to infinite to which the vitrification curve tends asymptotically. By maintaining the same approximation of the model of Enns and Gilham as valid also in this case, it is then possible to substitute for $T_{g\infty}$ the maximum value of $T_{cure,max}$

$= T_{g,\text{max}}$ on the modified CHT (and TTT) diagram vitrification curve. The equation of Di Benedetto would then modify to

$$(\lambda p)/[1 - (1 - \lambda)p] = (T_g - T_{g0})/(T_{g\text{max}} - T_{g0})$$

This equation is more appropriate than could be believed at first glance because the coefficient λ in the Di Benedetto equation is really nothing else than a coefficient which blocks the value of (λp) to reach the value of 1, which would be obtained if λ was $= 1$. λ, which was originally defined as the ratio of the mobility of the segments between crosslinking nodes of the cured network at the end and at the start of the crosslinking process is generally obtained experimentally from the degree of conversion p and the three values of $T_{g\infty}$, T_g, and T_{g0}. It has recently been shown, however, that the value of λ can be calculated independently without knowing the three values of T_g or the degree of conversion p by equating its value to the ratio $m_{\text{end}}/m_{\text{start}}$ of the average number of degrees of freedom m of segments between the network crosslinking nodes at the end and at the start of crosslinking.[6] The only experimental data needed to calculate λ in this manner is the deflection in μm obtained by TMA for a given network on wood at its different relevant stages of advancement which is readily obtainable by methods already reported.[6,10,11] This means that substituting $T_{g\text{max}}$ for $T_{g\infty}$ will adjust the value of m_{end} to $T_{g\text{max}}$ and accordingly adjust the value of λ, validating the alternative DiBenedetto equation based on $T_{g\text{max}}$.

To conclude, it must be clearly pointed out that what is outlined above and the modified CHT diagram only applies to formaldehyde-based polycondensates, such as UF and PF resins, used for wood adhesives and this exclusively on lignocellulosic substrates. If what is outlined above may be applicable to other resins on wood or on other types of interacting substrates cannot be determined with the data available. It must be equally pointed out, however, that the powerful tool that is the CHT (and the TTT) diagram in its nonmodified form cannot be used lightly or qualitatively to describe the behavior of a resin in the presence of an interacting substrate but needs, instead, to be adapted and possibly modified, when and if

needed, according to the substrate on which the resin is applied.

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