Determination of the Gel Point of Formaldehyde-Based Wood Adhesives by Using a Multiwave Technique

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ABSTRACT: Determining the instant of gelation of formaldehyde-based wood adhesives as an assessment parameter for their curing rate is important for optimizing the curing behavior. Due to the stoichiometrically imbalanced networks of formaldehyde-based adhesives, the crossover point of storage G' and loss modulus G'' cannot unconditionally be assumed as the gel point in oscillatory time sweeps as the material response is frequency-dependent. This study aims to determine the gel point of selected adhesives by the isothermal multiwave oscillatory shear test. A thorough comparison between the gel and the crossover point of G' and G'' is performed. Rheokinetic analysis showed no significant difference between the activation energies calculated at the gel point determined by a multiwave test and the crossover point obtained by the time sweep test. Hence, for resins with similar curing reactions, a reliable determination of gel point by applying a multiwave test is needed for a comparison of their reactivity.

KEYWORDS: multiwave test, gel point, crossover point, stoichiometrically balanced, kinetics, activation energy
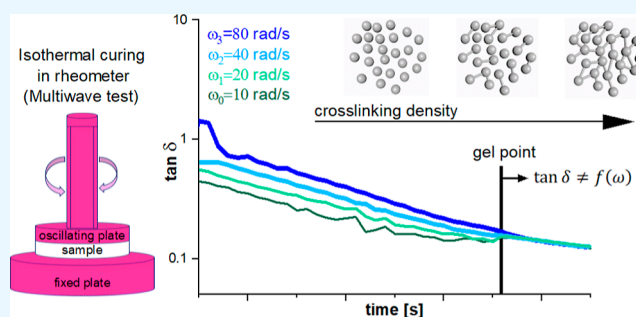
1. INTRODUCTION

The importance of urea formaldehyde (UF) resins as binders with a global annual production of about 11 million tons[1] is well known in the wood processing industry. UF resins are widely used in the production of wood-based panels, such as particle boards or medium density fiber boards for interior applications. Since UF resins typically show poor performance when exposed to moisture, the modification of resin with significantly more expensive compounds such as melamine is required to improve hydrolytic stability.[2] The addition of such compounds may affect the reactivity and, consequently, process-related parameters such as the "press factor". The press factor indicates the rate of curing and refers to the time in seconds required for curing 1 mm of particle board thickness. From an economic point of view, the press factor is an adequate index for estimating the processing costs. Hence, curing of the adhesive is the main cost-driving determinant in the production.[3] The press factor depends on the adhesive system and the processing parameters and is in the range of 3–7 s/mm at hot pressing temperatures of 180–240 °C for an industrial-scale UF resin.[2] However, the temperature in the core layer of the board does not exceed 110–120 °C.[2] This is due to the presence of water vapor both as a byproduct of the polycondensation reaction of UF resin and due to the evaporation of the water content of UF resin (66 wt%) and the moisture content of the wood particles.[2] The curing

temperature significantly affects the curing kinetics of the adhesive. Therefore, a good understanding of the curing process of the adhesive and in particular the curing rate and its temperature dependence can be helpful to optimize the production parameters.

In wood bonding, the gel point (GP) is one of the most important resin parameters for understanding the curing behavior. At the GP, a pronounced deceleration of the curing rate is observed because the reaction rate becomes no longer kinetically but diffusion controlled. Since a three-dimensionally crosslinked solid network is formed, the gelling process of wood adhesives is substantial for developing the strength of the bonded joints.[4] The GP of a UF resin is influenced by various parameters such as the molar ratio of formaldehyde to urea (F/U), the pH value, the solid content, and the type and amount of the catalyst.[5] Aside from resin parameters, GP is also strongly influenced by other factors such as low-molecular-weight extractives from the surrounding wood matrix which may have an accelerating or decelerating effect on curing
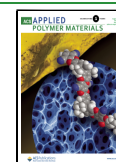
depending on their chemical nature.[6] The fast curing behavior and rapid development of mechanical strength can be directly related to the kinetics and mechanism of the curing reaction.[7] In practice, the kinetics of adhesive cure is often analyzed by determining the activation energy by using the Arrhenius plots at their GP. Reliable determination of the GP therefore is a prerequisite for the valid characterization of adhesive cure.

During the chemical gelation a cross-linked three-dimensional network is formed by covalent bonds. Numerous theories and methodologies exist that define and model the process of polymer network formation.[8,9] Through chemical gelation, the viscosity of resins increases dramatically[10] and the mobility of the resin decreases until the storage (G') and loss modulus (G'') reaches their maximum. In chemically cross-linking thermosets such as formaldehyde-based polycondensation adhesives, the polymer undergoes a transition from liquid (sol state) to solid state (gel state). This means that a transition from a low-viscous liquid to a non-fluid solid material takes place,[11] which leads to an insoluble or gelled product.[12] Winter[13] defined the GP as a point at which the polymer has a steady shear viscosity of infinite value and an equilibrium modulus of zero. Flory[12] defined GP as the point at which the largest molecular cluster approaches infinite size and for the first time extends across the entire reaction vessel. At GP, i.e., at the moment of gel formation, a certain percentage of reagents have reacted and a particular degree of conversion has been reached. The GP has been studied by several research groups to determine the effect of, e.g., different wood extractives,[14] fillers,[15] hardeners,[16,17] and also the storage stability[18] of the wood adhesive on the crosslinking behavior and their kinetics.

The GP of formaldehyde-based polycondensation products such as UF and melamine urea formaldehyde adhesives (mUF), which are equilibrium-controlled reactions, can be determined by a theoretical approach by which the degree of monomer conversion and, hence, of the advancement of polymerization at the GP is calculated.[8,19−22] This can be achieved by applying different mathematical approaches and physicochemical approximations.[23] However, these approaches suffer from several drawbacks. For instance, the gel theory of Carothers[24] assumes that at the GP of a resin mixture, all the monomer units are connected to build an infinite structure. Although this assumption yields a rough estimation of gelation, it overestimates the degree of monomer conversion. On the other hand, Flory[12,25,26] and Stockmayer[27−29] underestimate in their theory the numerical value of GP. These theories are very simple but do not give any detailed insights into what occurs between reaching the GP and obtaining a fully cured network.[23] To overcome these shortcomings, over the years, more elaborated and complex theories have been developed in the field of polycondensation for describing the molecular reality of gelation comprehensively. Among others, the cascade process theory of Gordon[19,20] offers advantages over other methods by incorporating more complex functions. The Miller and Macosko[21] recursive method and the stochastic graph theory of Bruneau[22] are also noteworthy. While the latter is more comprehensive, it is intricate and challenging to implement. However, these theories suffer from being rather difficult to apply and inflexible for daily practice.[17] Pizzi[30] combined theories of Flory[12,25,26] and Stockmayer[31] to a single equation for predicting the GP of polycondensates.

The complex curing reaction of UF resin makes the application of such theoretical studies very difficult. Hence,

network formation and gelation of UF resins have been studied widely using different experimental methods.[5,18,32−35]

In the wood industry, the GP is quickly determined by measuring a hot gelation time, where it is defined as the point at which the adhesive suddenly loses its fluidity and becomes a solid.[36] In this method, the test tube containing UF resin and a well-defined amount of hardener are immersed into boiling water at constant stirring speed throughout the test. The elapsed time until the point when no further stirring is possible is defined as the GP. This method has the advantage of providing information on the speed of cohesive bond generation. Furthermore, no special equipment is needed for performing this test. However, this crude method is operator-dependent as results may vary for each operator.[36] Giraud et al.[37] studied kinetics of the reaction of gelling of formaldehyde-based resins by means of low-resolution impulsional proton NMR. They obtained S-shaped gel curves by studying the relative changes in molecular mobility of solid-phase protons compared to liquid-phase and total protons. The research focused on analyzing the influence of the amount of hardener, temperature, and the presence of lignocellulosic materials on the gelation. Pizzi et al.[30,38] employed thermomechanical analysis as a recognized and conventional approach for characterizing the crosslink network structure of formaldehyde-based resins and forecasting the GP by using several mathematical equations. They presented a direct indication of the average length of polymer segments between crosslinking nodes in the cured adhesive network. This well-established method has demonstrated its practicality and effectiveness, yielding favorable and reliable results.

Another commonly used method for determining the GP is oscillation rheometry. The degree of advancement of polymerization and the point of gel formation while curing are responsible for changes in the polymer network and consequently the rheological behavior of resin. As the curing process of thermosetting resins progresses, the average molecular weight and viscosity increase with increasing crosslinking extent. After a certain reaction time (i.e., gel time), the system reaches a critical point at which a primary macromolecular cluster extends over the entire sample, a certain degree of conversion is achieved, the solubility of the system is lost, and both storage and loss moduli increase logarithmically with advancing reaction.[39] Beyond the GP, both moduli reach a maximum as a result of the increase in crosslinking density and completion of the chemical curing reaction. In the 1980s, different scientists, Tung and Dynes (1982),[40] Adam (1985), and Delsanti and Durand (1987)[41,42] determined the GP as the transition from the viscous liquid to the solid state, i.e., the GP is based on rheological measurements. Tung and Dynes (1982) suggested the crossover point (CP) of G' and G'' as the GP. In the literature, the CP of G' and G'' is generally accepted as the instant of gelation, that is, also as the GP of formaldehyde-based adhesives.[43] However, this criterion is just applicable for stoichiometrically balanced network polymers.[11] Winter and Chambon[13,39,44−46] have defined the point of gelation for stoichiometrically imbalanced networks as the point at which the slopes of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ are parallel to each other, which causes the loss factor (tan $\delta = G''/G'$) to be independent of angular frequency (ω). While a curing system is subjected simultaneously to several multiwave frequencies, tan δ can be determined as a function of the curing time at different frequencies. The onset of

gelation or the GP is where tan δ becomes independent of the applied frequencies. At the GP, both $G'(\omega)$ and $G''(\omega)$ obey power laws as follows

$$G' \sim G'' \sim \omega^n \qquad (0 < n < 1) \tag{1}$$

where ω represents the frequency and n represents the relaxation exponent. For stoichiometrically balanced networks, the onset of gelation is at CP of G' and G'' on the curing curve, where tan $\delta = 1$ and $n = 1/2$.[39] Nevertheless, for stoichiometrically imbalanced networks tan $\delta \neq 1$ at the GP and according to Winter et al.,[11] n has different values. Winter claimed[11] that if the CP occurs before the GP, then $n < 1/2$ and if the CP occurs after the GP, $n > 1/2$.

As stated by IUPAC,[47] a perfect polymer network is composed of chains that are all connected at their two ends with different junction points. A nonlinear polymerization during network formation, nonstoichiometric amounts of reactants, or incomplete reaction may lead to the networks containing loose ends and consequently imperfections. Additionally, if the crosslinking of existing polymer chains is involved to form the network, two loose ends are created per existing polymer chain.[47] Winter and Chambon[39] mentioned that stoichiometrically balanced networks, where tan $\delta = 1$, are the most perfect networks and consequently stoichiometrically imbalanced networks possess some degrees of imperfection. So, the gap between tan δ of the stoichiometrically imbalanced network and tan $\delta = 1$ can be assumed as a criterion to indicate the degree of imperfection of the network.

Thoma et al.[48] showed that for carbohydrate—HMF—amines, the CP coincides with the GP and found the GP by means of multiwave tests (MW tests) at tan $\delta = 1$. Du et al.[49] performed time sweep tests (TS tests) at three different frequencies to determine the GP based on the frequency independence of tan δ for a polythiourethane system. Since the tan δ values did not intersect at a single point at different frequencies, they took the CP of G' and G'' as the GP.

Although UF resins are still the most commonly used wood adhesives for the particle board industry, it has not yet been reported if the GP happens exactly at the CP or just somewhere in its proximity. To the best of the authors' knowledge, there is no published work available on performing the MW test method and applying the Winter—Chambon criterion for determination of the GP of formaldehyde-based adhesive during curing. This study aims at determining the GP by means of an MW test, where multiple frequencies as complex waveforms consisting of a fundamental frequency and harmonics are applied. One objective is to clarify the difference between the GP and the CP of G' and G''. Another objective is to study how the kinetics of the adhesive is affected when determined at the GP or at the CP of G' and G''. Rheokinetic analysis is performed by using the Arrhenius plot. For this study, two examples of industrial UF and one industrial mUF resin, containing a small amount of melamine, are chosen. The resins differ in the molar ratio of formaldehyde to urea and are synthesized by standard processes.

2. MATERIALS AND METHODS

2.1. Materials. The adhesives used in this study are commercially available formaldehyde-based adhesives (Primere, Metadynea GmbH, Krems, Austria), which are widely applied as standard products in the production of particle boards. The adhesives provided by Metadynea GmbH differ primarily in their F/U mol ratio. An overview of the selected adhesives is listed in Table 1. Ammonium nitrate is purchased from Sigma-Aldrich (St. Luis, MO, U.S.A.), and 2.3 wt % is added as a hardener to the resin (solid/solid) as an aqueous solution (15 wt %).

Table 1. Molar Ratio and Solid Content of Formaldehyde-Based Adhesives

resin	UF1	UF2	mUF
molar ratio	F/U = 1.2	F/U = 1.0	F/(NH$_2$)$_2$ = 0.8
solid content	62.9%	66.2%	65.1%

2.2. Methods. *2.2.1. Rheological Characterization.* All oscillatory rheological measurements were performed using an MCR 302 rheometer (Anton Paar GmbH) in a strain-controlled measuring mode. The measurements were performed using a 25 mm parallel plate geometry with a gap size of 1 mm. Measurements were done under ambient air (relative humidity 50% and room temperature 23 °C) using a temperature control unit P-PTD200 (Anton Paar GmbH, Graz, Austria). To keep the temperature stable during the test, the chamber surrounding the plates was closed.

2.2.2. Oscillatory Time Sweeps. Isothermal time sweeps (TS) tests were performed at different temperatures (60, 70, and 80°C) and a constant angular frequency (ω) of 20 rad/s with a constant oscillation amplitude of 0.5% to record the dynamic rheological parameters. As a result, G', G'', and tan δ are plotted as a function of curing time. Isothermal TS tests were performed within the linear viscoelastic regime of all tested adhesives.

2.2.3. Multiwave Test (MW Test). For MW tests, the fundamental frequency was $\omega_0 = 10$ rad/s with an initial strain of 0.5%. The harmonic frequencies were $\omega_1 = 20$ rad/s, $\omega_2 = 40$ rad/s, and $\omega_3 = 80$ rad/s with an amplitude factor of 1. The resulting maximum amplitude was 1.25%. The amplitude and harmonics were chosen to be within the linear viscoelastic regime.

Additionally, the GPs determined by the two isothermal measurements, MW test and TS test, were used to determine the apparent activation energy (E_a) based on the Arrhenius equation, for which the temperature dependence is exponential,[50] according to eq 2

$$\ln(1/t_{gel}) = \ln A - \frac{E_a}{R}\frac{1}{T} \tag{2}$$

where A, R, and T represent the pre-exponential factor of the Arrhenius equation, the universal gas constant ($R = 8.314$ J mol^{-1} K^{-1}), and the absolute temperature (K), respectively. The apparent activation energy is obtained from the slope of the Arrhenius plot. t_{gel} will be replaced by the time required to reach the GP or the time needed to reach CP at which G' and G'' cross each other during the isothermal curing measurements.

3. RESULTS AND DISCUSSION

3.1. Oscillatory Time Sweeps. Isothermal TS tests at 60, 70, and 80°C, using a constant amplitude (0.5%) and a constant angular frequency ($\omega = 20$ rad/s) were performed to monitor the thermal curing behavior of UF2 and mUF resins (see Figure 1A,B). For both resins, the storage and loss moduli have approximately the same initial values. At initial stages of curing, where the viscous behavior dominates as indicated by $G'' > G'$, the moduli slightly decrease due to the initial temperature increase. Afterward, during the curing reaction, the values for G' and G'' increase with time. After a specific time has elapsed, a transition from liquid to solid state occurs. This time can be assumed to mark initiation of gelation (GP) due to the crosslinking of polymer clusters. Beyond the GP, with increasing the average molecular weight and crosslinking density, G' and G'' reach a maximum. When curing of the UF resin is observed with a rheometer, it is important to mention that at the maximum moduli, the resin is not yet chemically fully cured and from this point on still further chemical curing
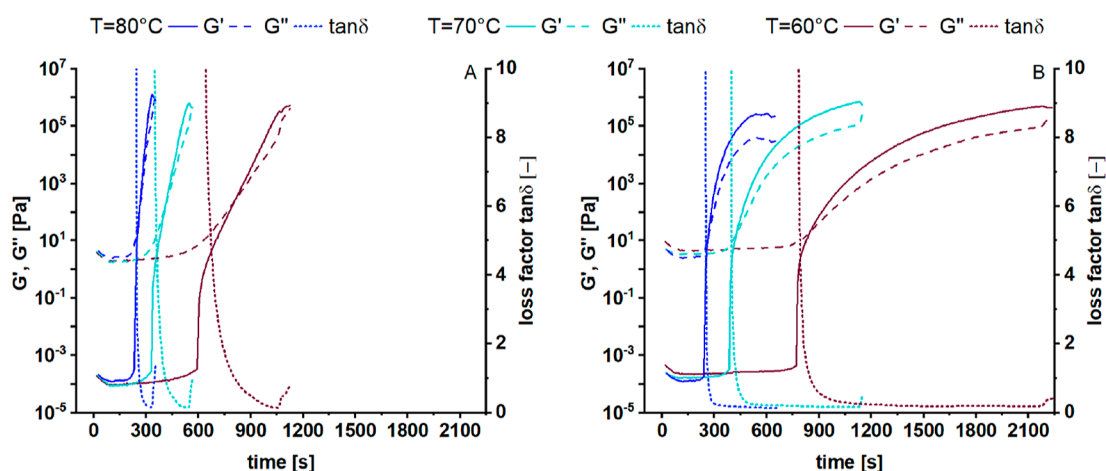
Figure 1. Rheological behavior of UF2 (A) and mUF (B) based on the isothermal measurements in oscillatory mode with an angular frequency of 20 rad/s and an initial strain of 0.5%.

reactions take place. However, due to the force limitations of the rheometer, these further advancements in crosslinking can no longer be measured rheologically. These processes beyond resin gelation are important for developing the strength properties of the composite material and will be studied in a follow-up study using differential scanning calorimetry.

For both resins, the curing rate increases with increasing temperature. This can also be seen by comparing the slope of the curves, where the larger slopes reflect the faster curing rate. The times passed until the CPs of G' and G'' are reached, which are conventionally accepted as the GP, are listed in Table 2.

Table 2. Crossover point time during the isothermal time sweep tests performed at 60, 70, and 80°C and at a constant angular frequency of ω = 20 rad/s

| isothermal time sweep test at	crossover point time [s]	
	UF2	mUF
60°C	784	902
70°C	406	417
80°C	269	260

These results show the pronounced influence of the curing temperature on the time to reach the CP and the cure reaction of the formaldehyde-based systems. It is well-known that the formaldehyde content correlates with the curing rate. However, only at 60°C, the CP of mUF differs significantly from the CP of UF2 and is shifted by 118 s. This is due to the lower formaldehyde content, the presence of melamine, and consequently the buffering capacity of the melamine triazine rings.[36] However, the effect of the higher formaldehyde content of UF2 compared to that of mUF on the CP is not remarkable at higher temperatures.

3.2. Gel Point Determination. As mentioned already, in the literature, the point of gelation is mainly defined as the CP of G' and G'', which is only valid for stoichiometrically balanced polymers. First, the CP of the moduli resulting from the MW tests is evaluated. Figure 2A illustrates the results of the MW tests at 60°C and at four harmonic frequencies (10, 20, 40, and 80 rad/s) for UF2. Due to the severe fluctuations at ω = 80 rad/s up to 780 s, the corresponding curves are not shown in this diagram. The uncured thermosetting resin, which consists of a mixture of monomers and oligomers, is a Newtonian liquid.[51] Minor elastic shares probably originate from the surface tension of the resin, inducing a measurement artifact at the edge of the plate–plate geometry. As a result, significant fluctuations of the signal were generated at the beginning of the measurements (up to 600 s in Figure 2A). As the curing proceeded, the signal from the bulk material stabilized and the apparent feedback vibration from the
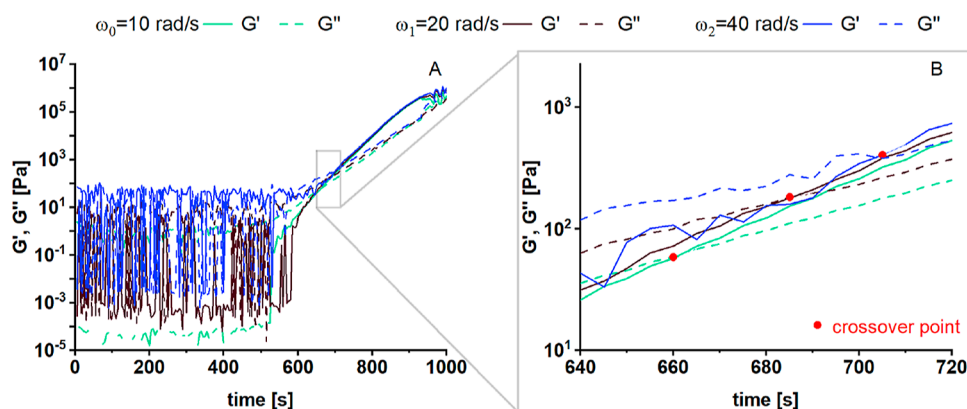
Figure 2. (A) Multiwave test of UF2 measured isothermally at 60°C at three different frequencies (10, 20, and 40 rad/s) and (B) image section of crossover points.
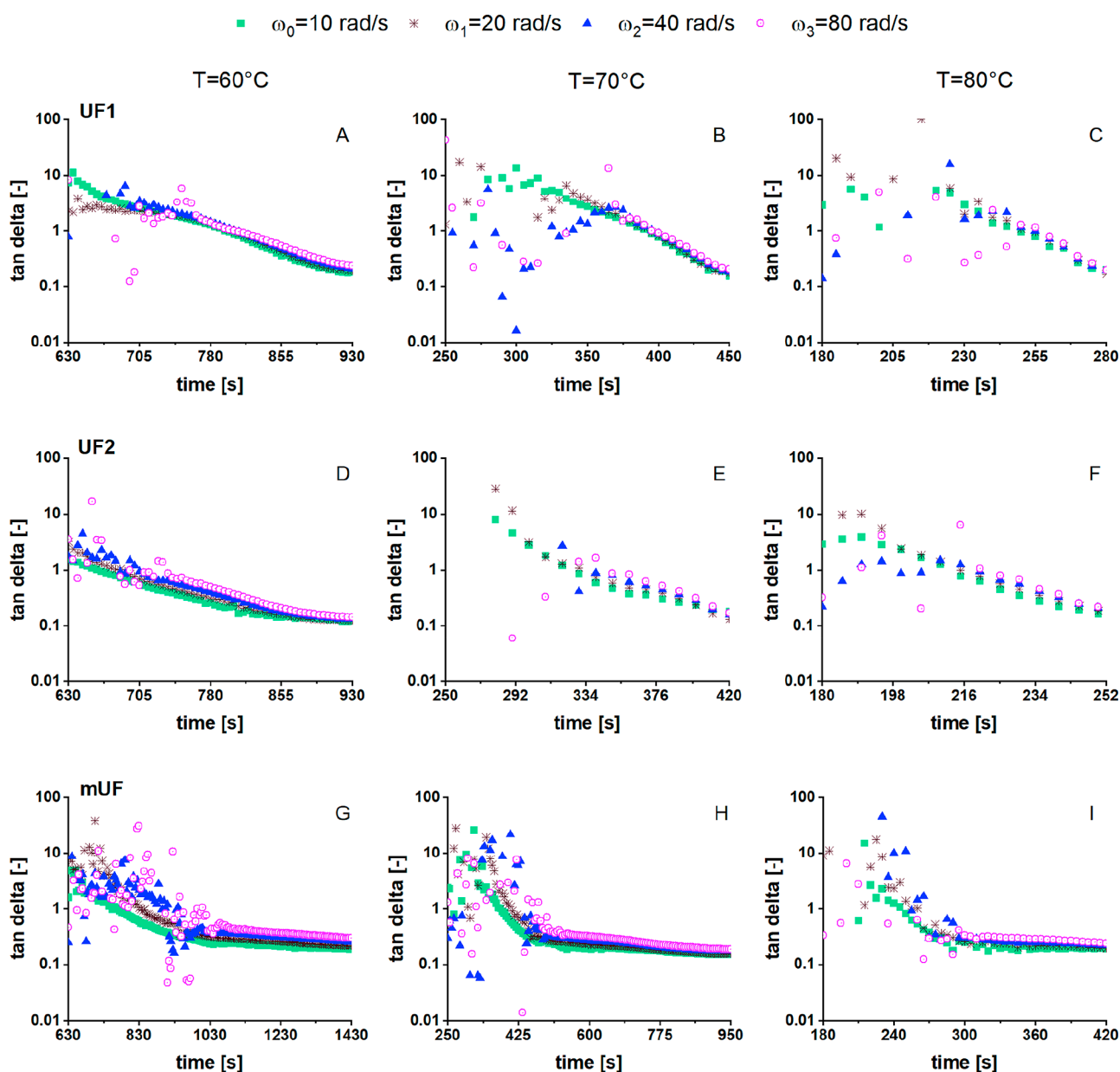
Figure 3. Multiwave tests of UF1 (A−C), UF2 (D−F), and mUF (G−I) measured isothermally at three different temperatures (60, 70, and 80°C) and at four different frequencies (10, 20, 40, and 80 rad/s) for each adhesive.

interface no longer affected the result, so that the increase of both G' and G'' with increasing molecular weight was properly measured. It can be seen in Figure 2B that G' and G'' shift slightly to higher values at increased frequency. Increasing frequency has a similar effect on the rheological behavior of the sample as a decrease of the temperature has. Both factor variations result in a higher G' and G'' value. This effect was also observed by Dörr et al. (2020)[52] for the gelation of chemically modified polyamide 12 by means of the MW test. However, in contrast to Dörr et al. (2020),[52] the CP of G' and G'' with higher frequency is shifted to greater times (see Figure 2B). Based on the Winter−Chambon criteria, the frequency-dependent CP can thus not be considered as the GP.

In contrast to CP, as can also be seen in Figure 2A, the maximum values of G' and G'' in the gel state are not significantly affected by the frequency. A cured network with a higher crosslinking density and, consequently, a higher

network stability may have a higher resistance to frequency changes compared to the critical region close to the GP where rather fragile network structures are expected to prevail which can easily be broken up by the rheological measurement.[9] In this paper, the GP from rheology is determined by employing the Winter−Chambon criterion (i.e., G', $G'' \sim \omega^n$ or $\tan \delta \equiv G''/G' =$ constant).[13,53]

Figure 3 shows the plots of $\tan \delta$ as a function of curing time at all four frequencies (10, 20, 40, and 80 rad/s) for each resin. The $\tan \delta$ values vary depending on frequency until a point, at which the material response becomes independent of frequency. The results show that all three resins follow the Winter−Chambon criterion since all the $\tan \delta$ curves become frequency-independent from a specific point on, which is, hence, considered to be the GP.

As shown in Figure 4, for all three resins, the gelation time determined by the MW test, i.e., the time at which $\tan \delta$
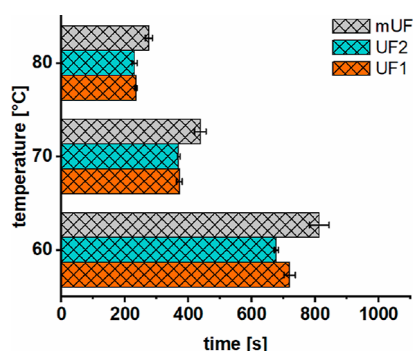
Figure 4. Comparison between the gel times determined by the multiwave test for all three adhesives.

becomes independent of frequency, decreases as the temperature increases. Although UF1 has a higher molar ratio than UF2, the impact of the higher formaldehyde content on curing speed is not clearly detectable at 70 and 80°C and its gel time is even lower than that of UF2 at 60°C. However, the low-molar-ratio partly melamine-substituted mUF has a significant longer gelation time. The error bars in Figure 4 correspond to the standard deviation of the corresponding measurement with three replicates for each sample at each temperature.

For all three resins, the corresponding tan δ values at the GPs as determined by the MW test and the tan δ value of the CPs of G' and G'' which by definition is equaling to one are depicted in Figure 5. As mentioned above, stoichiometrically balanced networks, where tan $\delta = 1$, are the most perfect networks and consequently stoichiometrically imbalanced networks possess some degrees of imperfection.[39] Accordingly, the gap between tan δ of a stoichiometrically imbalanced network and tan $\delta = 1$ is taken as a criterion to indicate the degree of imperfection of the network. As shown in Figure 5A, for UF1 with a molar ratio F/U of 1.2, the tan δ values of GP are greater than one at all testing temperatures, i.e., gelation occurs actually earlier than that indicated by the CP. As the temperature increases, the tan δ values become smaller and the deviations from tan $\delta = 1$ become less pronounced. An overall trend for the dependence of tan δ on temperature cannot be found for UF2.

The curing of UF resins is a nonlinear polymerization since it leads to the formation of an infinite network structure.[54] The deviation from a perfect network can be attributed to the

existence of "loose", that is, nonreacted ends within the network. Unlike UF1, where the discrepancies of the tan δ values from 1 become smaller with increasing temperature, the deviations from 1 of the tan δ values at its GP become larger with higher curing temperatures in the case of the mUF resin, which corresponds to an increasingly less-perfect network structure as well. In addition to the presence of loose ends, which cause network imperfections, ring structures that are usually present in mUF networks may also contribute to these imperfections.[47]

A comparison between the gel times determined by MW tests and the times at which G' and G'' coincide (CP) during the isothermal TS test at $\omega = 20$ rad/s for UF2 and mUF are presented in Figure 6A,B, respectively. As mentioned earlier, for a stoichiometrically balanced network, the onset of gelation is at the CP of G' and G'' on the curing curve, where tan $\delta = 1$ and $n = 1/2$. However, for stoichiometrically imbalanced networks, tan $\delta \neq 1$ at the GP and according to Winter et al.,[11] n has a different value than 1/2.

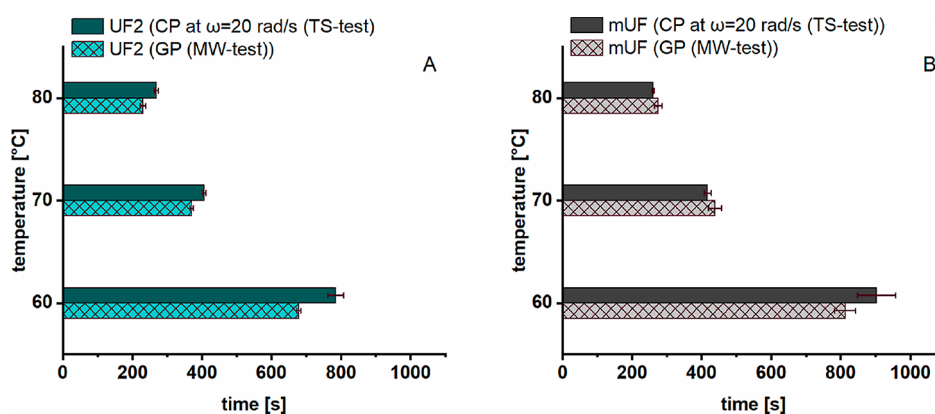The calculated relaxation exponent (n) values for all resins are listed in Table 3. Accordingly, the relaxation exponents of UF1 with a molar ratio F/U of 1.2 are greater than 1/2. However, the relaxation exponents of both UF2 (F/U = 1) and mUF (F/(NH$_2$)$_2$ = 0.8) are less than or equal to 1/2, although in the case of UF2 the CP from the TS test occurs after the GP from the MW test at all testing temperatures. This is in contrast to Winter[11] statement which said that for stoichiometrically imbalanced gels, if the CP occurs before the GP, then $n < 1/2$ and if it occurs after the GP, $n > 1/2$.

The difference between the GP time and the CP time is more pronounced for UF2 than for mUF, but these differences become smaller with increasing temperature for both resins. It can be concluded that raising the temperature compensates for the differences between the GP and CP. This could be due to the possibility of the occurrence of different types of reactions at higher temperatures.

3.3. Rheokinetics Analysis of Gelation. Kinetics provides information on the rate at which a chemical reaction happens and links the reaction rate to macroscopic process parameters such as concentration.[50] Upon applying an isoconversional model-free method, the Arrhenius equation can be used to determine the temperature dependence of the curing reaction at the GP and CP, which are determined by the MW test and at the CP of G' and G'' resulting from the
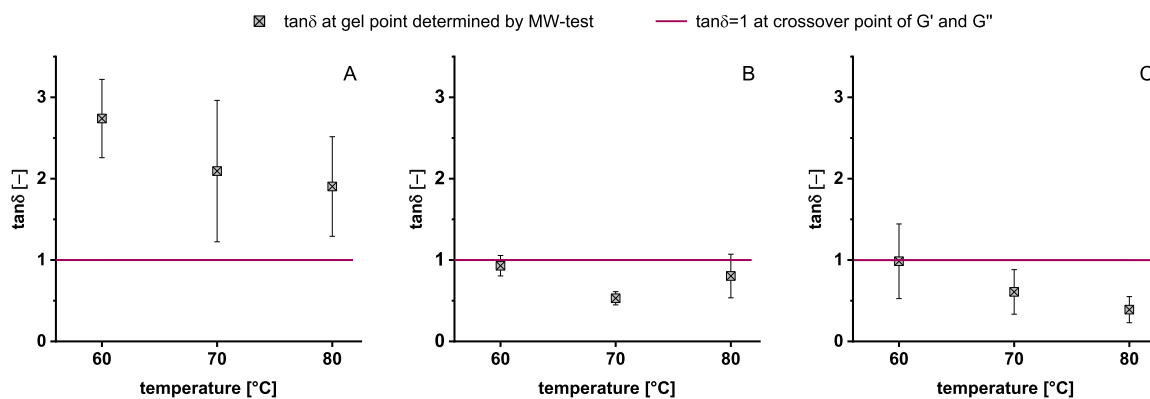
Figure 5. Comparison between loss factor (tan δ) values of gel points determined by the multiwave test (MW test) (squares) and tan δ value of stoichiometrically balanced networks (tan $\delta = 1$) (solid line) as a function of temperature for UF1 (A), UF2 (B), and mUF (C). Three replicate measurements at four different frequencies were made for each adhesive. Error bars depict the standard deviation of tan δ of the combined data.

Figure 6. Comparison between the determined gel point (GP) by the multiwave test (MW test) (hatched bars) and crossover point (CP) of G' and G'' at ω = 20 rad/s (solid bars) at three different temperatures for UF2 (A) and mUF (B).

Table 3. Calculated relaxation exponent (n) values.

testing temperature \ resin	relaxation exponent (n)		
	UF1	UF2	mUF
60°C	0.8	0.5	0.5
70°C	0.7	0.3	0.3
80°C	0.7	0.4	0.2

Table 4. Activation Energy (E_a) of UF1, UF2, and mUF calculated for the time required to reach the GP (determined by the MW test) or the CP (determined by the TS test)[a]

activation energy E_a \ resin	UF1	UF2	mUF
E_a (GP) [kJ/mol] (MW test)	55	53	53
E_a (CP) [kJ/mol] (MW test)	58	54	57
E_a (CP) [kJ/mol] (TS test)		52	58

[a]GP—gel point, CP—crossover point, MW test—multiwave test, and TS test—time sweep test.

performed TS tests. From the slope of the linearly fitted curves in the Arrhenius plot, the effective activation energies, E_a, of curing at the GP or CP (determined by the MW test) and at the CP (determined by the TS test) are calculated (Figure 7). The E_a values calculated for the time required to reach the GP or CP for UF1, UF2, and mUF are given in Table 4.

To statistically test the difference in the collected samples, a two-sample *t*-test was applied on the calculated activation energies by using the MATLAB function "ttest2". The result of this testing showed that there was no significant difference between any of the groups at a confidence level of 5%.

The apparent activation energy depends on the number of reactive sites. The fact that the activation energies at a specific point (GP or CP) are alike implies that similar curing reactions are taking place in the case of all three resins. Since the ratios between the numerous curing reactions of formaldehyde-based resins are unknown, the reaction order and the concentration of the reaction components cannot be given.

The calculated activation energies at GP or CP refer exclusively to the similar rate constant of the reaction steps among the tested resins in or close to the gelation stage. This similarity provides no information on the concentration of reactive components and is not the sole criterium for comparing the reactivity of different resins. Therefore, a precise definition of the GP is of extreme importance.

4. CONCLUSIONS

In this study, the Winter−Chambon criterion is applied for accurately determining the GP of selected aminoplastic resins from rheological data. An MW test was applied to UF1, UF2, and mUF to determine a frequency-independent GP. It was found that all resins follow the Winter−Chambon criterion since all the tan δ curves become frequency-independent from
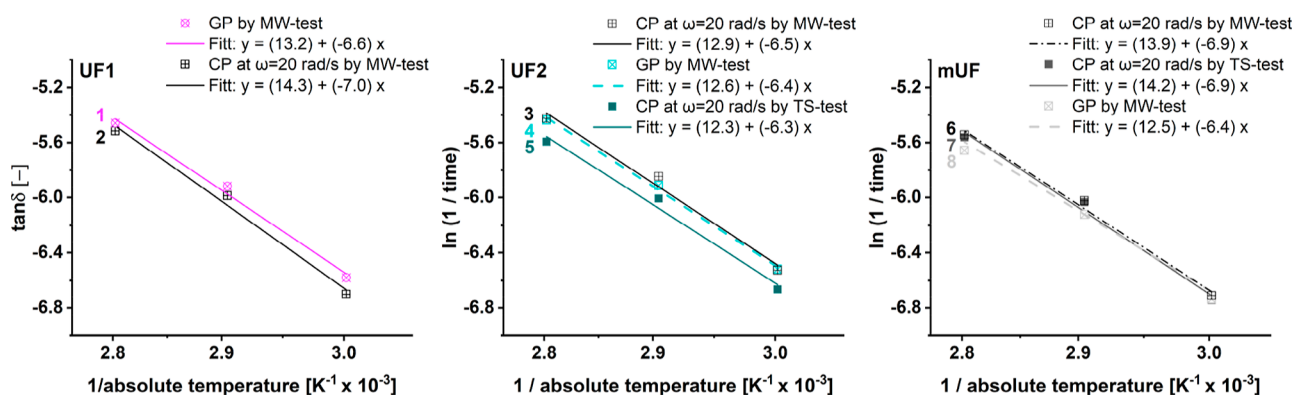
Figure 7. Arrhenius plot of the logarithmic inverse gel or crossover time as a function of the reciprocal absolute curing temperature for UF1 (left), UF2 (middle), and mUF (right) as measure for the curing rate at 60, 70, and 80°C. The correlation coefficients R^2 obtained with linearization of the Arrhenius dependence are (1) 0.992, (2) 0.989, (3) 0.986, (4) 0.997 (5) 0.987, (6) 0.993, (7) 0.990, and (8) 0.996.

a specific point which is recognized as the GP. In addition, for all three resins, the gelation times decrease as the temperature increases. The frequency-dependence is more pronounced close to the GP region.

The comparison of the difference between tan δ at GP of a stoichiometrically imbalanced network and tan $\delta = 1$ showed that for UF1, as the temperature increases, the tan δ value converges to tan $\delta = 1$, i.e., its network approaches a stoichiometrically balanced network. Unlike UF1, at higher curing temperatures, the tan δ value of mUF at its GP deviates more strongly from tan $\delta = 1$, indicating formation of a network structure with some degrees of imperfections.

Gel times determined by MW tests and the times at which G' and G'' coincide (CP) during the isothermal TS test are compared. In the case of UF2, at all isothermal temperatures and for mUF at 60°C, the CP occurs after the GP at later times. It can be concluded that increasing the temperature compensates for the difference between the GP and CP. In the case of UF2 with a molar ratio equal to 1, the tan δ values at 60 and 80°C are equal to one within their standard deviations, as shown in Figure 5B. Therefore, based on the MW test, the GP is very close (if not) at tan $\delta = 1$, which is CP. It hints at a network which is close to a stoichiometrically balanced state. However, for the analyzed resin with a molar ratio and subsequently a tan δ value other than one, the CP cannot be adopted as the GP. Hence, using the Winter–Chambon criterion and applying an MW test is required for a reliable determination of the GP as compared to the method measuring rheological parameters at a single oscillation frequency. Rheokinetic analysis was performed by using an Arrhenius plot. The results showed that for all resins apart from their molar ratios, no significant difference was found when the apparent activation energies were calculated for the times required to reach the GP (determined by the MW test) or the CP (determined by the TS test). The similar activation energies refer to the analogous rate constant of the reaction steps of all tested resins. This result implies the importance of the GP for the comparison between formaldehyde-based resins with similar reactions during curing but various molar ratios.

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Notes

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■ ABBREVIATIONS

UF, urea formaldehyde
mUF, melamine urea formaldehyde
GP, gel point
CP, crossover point
G', storage modulus
G'', loss modulus
tan δ, loss factor
T, temperature [°C]
MW, multiwave
TS, time sweep
ω, angular frequency
n, relaxation exponent
wt %, weight percent

E_a, activation energy [kJ/mol]

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