Received: 29 July 2024 | Revised: 20 September 2024 | Accepted: 5 October 2024

DOI: 10.1002/app.56410

RESEARCH ARTICLE

Journal of Applied Polymer Science WILEY

Curing reactions, reaction kinetics, and latency of epoxy resin cured with L-tryptophan and L-tyrosine

Florian Rothenhäusler[1] | **Daniel Hüser**[2] | **Holger Ruckdaeschel**[1,2]

[1]Department of Polymer Engineering, University of Bayreuth, Bayreuth, Germany

[2]Neue Materialien Bayreuth GmbH, Bayreuth, Germany

Correspondence
Holger Ruckdaeschel, Department of Polymer Engineering, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany.
Email: holger.ruckdaeschel@uni-bayreuth.de

Funding information
Bundesministerium fur Wirtschaft und Klimaschutz, Grant/Award Number: 20E1907A

Abstract

In the research on amino acids as bio-based curing agents for epoxy resins, L-tryptophan and L-tyrosine have emerged as promising alternatives. Understanding the curing reactions and reaction kinetics is crucial for designing an appropriate curing regime to tailor the mechanical properties of thermosets. This study provides a comprehensive analysis of the curing reactions, curing kinetics, and latency of epoxy resin cured with L-tryptophan or L-tyrosine in the presence of urea-based accelerators. L-tryptophan involves three distinct curing reactions, corresponding to its three functional groups, while data on L-tyrosine as a curing agent is less definitive. The degree of cure can be reliably predicted using model-free kinetics for all resin systems studied. Overall, the inclusion of accelerators facilitates rapid curing at elevated temperatures while maintaining adequate processability for up to four weeks of storage at room temperature.

KEYWORDS

amino acid, bio-based, curing kinetics, curing reactions, epoxy resin, latency, sustainability

1 | INTRODUCTION

Amino acids (AAs) have garnered considerable attention as bio-based curing agents for epoxy resins since their initial application nearly two decades ago.[1] In an early study, Li et al.[2] demonstrated that a cyclo-aliphatic epoxy resin could be cured with L-lysine. Building on this pioneering work, they subsequently explored the use of L-tryptophan, which has since been a focal point of various investigations.[3] L-tryptophan is an aromatic α-AA, incorporating an indolyl side chain (see Figure 1). The primary emphasis of studies utilizing L-tryptophan as a curing agent for epoxy resins has centered on the curing reactions and the resulting glass transition temperature (T_g), assessed using Fourier-transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC), respectively.[4–8]

The T_g of DGEBA cured with L-tryptophan ranged from 66 to 101°C if urea-based accelerators were employed.[6,8] In contrast, imidazoles as accelerators yielded T_g between 84 and 104°C.[3,5,6] The broad span of T_g in these studies resulted from the various accelerators added as well as different ratios between the epoxy resin and L-tryptophan. In these investigations, the main focus was on the reaction between the epoxy group and the primary amino group, as well as between the epoxy group and the carboxylic acid group which results in a β-hydroxyester. While the curing reactions and curing kinetics are well studied subjects, the latency of these resin systems has not been researched.

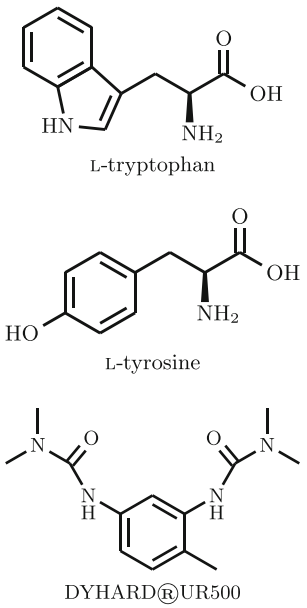

FIGURE 1 Chemical structures of L-tryptophan (top), L-tyrosine (middle), and DYHARD®UR500 (bottom).

Rothenhäusler et al.[9] examined the effects of different AAs as curing agents on the T_g and mechanical properties of thermosets. They introduced AAs such as L-citrulline, γ-amino butyric acid, and L-tyrosine as bio-based alternatives for curing agents. Similar to L-tryptophan, L-tyrosine is also an aromatic α-AA, incorporating a phenyl side chain (see Figure 1). The aromatic AAs L-tryptophan and L-tyrosine pose high steric hindrance due to their indolyl and phenyl side chains once incorporated into the thermoset network. This results in high T_g compared with that of thermosets cured with aliphatic AAs, like γ-amino butyric acid and L-glutamine.[10] This is enabled by their functional groups, that is the secondary amino group and the hydroxyl group, that may react with the epoxy group of the resin.

Other studies have shown that thermosets cured with AAs may exhibit high toughness or tensile strength, depending on the specific AA.[11,12] The high toughness stems from the AA crystals that are embedded into the epoxy matrix. Despite these advances and the frequent use of L-tryptophan and L-tyrosine as curing agents, comprehensive studies on their curing mechanisms, reaction kinetics, and latency are lacking. Understanding the curing reactions and reaction kinetics is crucial for designing an appropriate curing regime, which is essential for tailoring the mechanical properties of thermosets to meet specific application requirements. Additionally, latency is a key consideration for manufacturers, who generally seek a balance between latency which leads to a long shelf-life and high reactivity which allows short curing cycles during production.

This article investigates the curing reactions, reaction kinetics, and latency of diglycidylether of bisphenol A (DGEBA) cured with either L-tryptophan or L-tyrosine. These resin systems are combined with two commercially available urea-based accelerators (DYHARD®URAcc57 and DYHARD®UR500), providing insights into variations in curing kinetics and a range of properties, such as T_g. The curing mechanisms and curing kinetics are examined using FTIR and DSC. Furthermore, the activation energies (E_a) derived from dynamic DSC measurements are employed to model the degree of cure or conversion (α) using model-free kinetics (MFK) and validated through isothermal DSC measurements. Latency is assessed by evaluating changes in the glass transition temperatures of the uncured resin systems (T_{g0}) after different storage periods at room temperature and by analyzing viscosity increases using plate-plate rheometry.

2 | EXPERIMENTAL

2.1 | Materials

The resin system utilizes DGEBA with an epoxide equivalent weight of 187 g mol^{-1}, sourced from Blue Cube Assets GmbH & Co. KG, Olin Epoxy (Stade, Germany). L-tryptophan and L-tyrosine were procured from Buxtrade GmbH in Buxtehude, Germany. DYHARD®UR500 and DYHARD®URAcc57 are supplied by Alzchem Group AG, headquartered in Trostberg, Germany.[13]

2.2 | Resin formulation

The DGEBA and AAs were mixed so that the stoichiometric ratio of active hydrogen atoms to epoxy groups is one. The resin mixtures were prepared following the three-roll milling procedure outlined by Rothenhäusler et al.[11] Afterwards, 1 wt% of accelerators were added, and the resin systems were mixed using a centrifuge speed mixer from Hauschild Engineering (Hamm, Germany) at 3000 min^{-1} for 120 s. Subsequently, any trapped air was removed prior to analysis by degassing the mixtures for 30 min at 10 mbar at 40°C.

2.3 | Material characterization

2.3.1 | Precuring of resins

To investigate the FTIR spectra of the resin systems at specific α, 0.6 g of the resin systems were dispensed into polypropylene cups (10 mL capacity). These cups were

then placed in a Memmert ULE 400 convection oven supplied by Memmert GmbH + Co. KG, located in Schwabach, Germany, and maintained at a temperature of 140°C for various durations ranging from 2 to 25 min. After each specified curing time elapsed, the cups were promptly removed from the oven and immersed in liquid nitrogen (−96°C) for 1 min to halt the curing process completely. Subsequently, FTIR spectra were acquired and used to deduce the curing mechanisms of the resins.

2.3.2 | Differential scanning calorimetry

For investigating the curing reactions, isothermal DSC measurements were conducted from 120 to 120°C, employing a Mettler Toledo DSC 1 instrument from Mettler-Toledo International Inc. (Columbus, Ohio, USA). The heating rate to the respective temperature was 10 K min^{-1}, and the specimens were held at the respective temperature for 2 h. The curing kinetics were investigated using dynamic DSC measurements conducted with heating rates ranging from 1 to 20 K min^{-1}, spanning from 25 to 275°C. The α was calculated using the formula:

$$\alpha = \frac{H_{\text{total}} - H_x}{H_{\text{total}}}, \quad (1)$$

where H_x represents the enthalpy of the partially cured resins, and H_{total} represents the enthalpy of the fully cured resins. H_x and H_{total} were experimentally determined by integrating the area under the thermograms of dynamic DSC measurements. The glass transition temperature of the uncured resins (T_{g0}) was determined using a heating rate of 10 K min^{-1}, ranging from −50 to 100°C. Both T_g and T_{g0} were identified by analyzing the inflection points of the DSC thermograms. During testing, sample masses were maintained at 5 ± 0.5 mg, with a constant nitrogen flow rate of 50 mL min^{-1} within the sample chamber. Each resin system was tested using two specimens to ensure consistency and reliability of results.

2.3.3 | Modeling of curing kinetics

The E_a of the resin systems were determined using commonly employed methods, such as Kissinger and Ozawa, as well as via MFK using the Friedman method,[14] integrated into the "STARe" analysis software of the Mettler Toledo DSC.[15–18] Since the E_a derived from the MFK method depends on α but is nearly constant over a broad range of α,[19] a representative value for E_a is depicted in Figure 6.

2.3.4 | Fourier-transform infrared spectroscopy

FTIR spectroscopy was performed using a Nicolet iS50 FTIR spectrometer manufactured by Thermo Fisher Scientific Inc. (Waltham, Massachusetts, USA). Each sample was subjected to an averaging of 128 scans over a wavenumber range from 600 to 4000 cm^{-1}, utilizing attenuated total reflection mode.

2.3.5 | Plate-plate rheometry

The effect of storage on the viscosity of the uncured resin systems was evaluated using an Anton Paar MCR 302 plate-plate rheometer (Graz, Austria). The rheometer featured plates with a diameter of 25 mm, and the gap between the plates was fixed at 1 mm. A constant heating rate of 3 K min^{-1} was applied, starting from 25 up to 195°C. During measurements, a shear amplitude of 5% and a shear frequency of 1 Hz were maintained.

3 | RESULTS AND DISCUSSION

3.1 | Curing reactions

For a precise analysis of the reactions occurring during the curing of the epoxy resins, it is beneficial to first examine the DSC thermograms obtained from isothermal measurements. The thermograms of L-tryptophan (see Figure 2 top) at various temperatures between 120 and 140°C exhibit three exothermal peaks during the initial stages of curing, suggesting the presence of at least three separate curing reactions. These peaks are not entirely distinct from one another but instead overlap. As expected, increasing the curing temperature reduces the time required for curing to initiate and for a specific curing mechanism to be activated.[20]

To correctly assign the exothermal peaks to specific curing reactions, the FTIR spectra of precured resins are analyzed (see Figure 3). The analysis focuses on the changes in signal intensities over time, without assigning all peaks to specific functional groups in DGEBA, L-tryptophan, and L-tyrosine, as these compounds are well-studied.[21–23]

Figure 3 (top left) demonstrates that the peak corresponding to the epoxy group of DGEBA (915 cm^{-1}) diminishes over the course of the curing process until it becomes indistinguishable from the baseline at about 25 min. This indicates that all epoxy groups are consumed during the curing process, achieving complete conversion within that time frame. Additionally, Figure 3

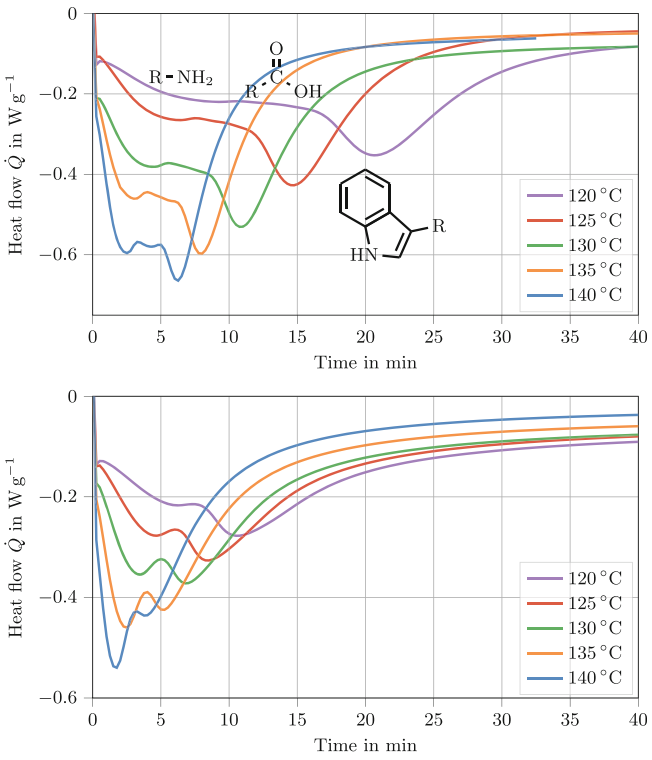

FIGURE 2 Isothermal differential scanning calorimetry measurements of DGEBA cured with either L-tryptophan (top) or L-tyrosine (bottom) with the addition of 1 wt% of DYHARD®URAcc57 at temperatures between $T = 120$ and 140°C. [Color figure can be viewed at wileyonlinelibrary.com]

(bottom left) shows that the peak corresponding to the ammonium zwitter-ion (1665 cm^{-1}) decreases rapidly during the first 4 min.[24] This observation aligns with the period when the first exothermal peak reaches its maximum during the isothermal DSC measurements at 140°C. Previous studies on L-tryptophan as a curing agent for epoxy resins also attribute the peak at 1665 cm^{-1} to the ammonium zwitter-ion formed during the epoxy-amino reaction.[3,25]

Subsequently, the reaction between the epoxy group of DGEBA and the carboxylate group of L-tryptophan forms a β-hydroxyester.[26] This reaction results in an increase in the peak intensity at 1720 cm^{-1}, corresponding to the C═O vibration of the β-hydroxyester after 4 min (see Figure 3 bottom left). Concurrently, the intensity of the peak at 1412 cm^{-1}, attributed to the carboxylate group of L-tryptophan, decreases over time (see Figure 3 top right).

Lastly, the epoxy group of DGEBA reacts with the secondary amino group (3400 cm^{-1}) of the indolyl side chain of L-tryptophan, as indicated by the peak at 3400 cm^{-1} (see Figure 3 bottom right).[27] During the initial minutes of curing, this signal is superimposed by the broad peak of the hydroxyl groups, which appears between 3200 and 3600 cm^{-1}. The intensity of the hydroxyl signal increases throughout the curing process, as hydroxyl groups are formed as a result of all three curing reactions. Eventually, the peak at 3400 cm^{-1} disappears from the FTIR spectra, indicating the consumption of the secondary amino group during the epoxy-amino reaction.

In summary, the first exothermal peak can be attributed to the reaction between the epoxy group and the ammonium zwitter-ion of the α-AA backbone of L-tryptophan (see Figure 4). The second exothermal peak arises from the reaction between the epoxy group and the carboxylate group. Lastly, the third peak stems from the reaction between the epoxy group and the indolyl group.

The sequence of these curing reactions is determined by the E_a of the individual reactions.[29] The ammonium zwitter-ion is significantly more reactive than the carboxylate group of L-tryptophan, which in turn is more reactive than the indolyl group. The lower reactivity of the indolyl group is due to the aromaticity of the indolyl ring and the steric hindrance it imposes on the secondary amino group within it.[30,31]

Based on the previously employed analysis scheme, the curing reactions between L-tyrosine and DGEBA are assessed using isothermal DSC measurements and FTIR spectra of precured resin. Unlike the DSC thermograms of DGEBA cured with L-tryptophan, the isothermal DSC measurements of DGEBA cured with L-tyrosine display only two exothermal peaks (see Figure 2 bottom). These peaks are not distinctly separated but overlap. Given the chemical structure of L-tyrosine, it can be inferred that there are three different types of functional groups in L-tyrosine: the primary amino group, the carboxylic acid group, and the hydroxyl group of the phenyl side chain. The discrepancy between the number of functional groups and the observed exothermal peaks complicates the assignment of these functional groups to specific exothermal peaks. There are two plausible explanations for this discrepancy: first, the reactions of two different functional groups occur simultaneously, making it difficult to distinguish their enthalpies in the DSC thermograms. Second, one of the functional groups in L-tyrosine does not react with the epoxy group, resulting in the absence of a corresponding peak in the DSC thermograms.

While the following conclusions about the curing reactions between L-tyrosine and DGEBA are more speculative than the reaction mechanisms between L-tryptophan and DGEBA, every effort has been made to support these claims using FTIR spectra and available literature. Typically, L-tyrosine forms a face-to-face dimer in which two L-tyrosine molecules align, attracting each other via electrostatic interactions between their respective hydroxyl and carboxylate groups.[32] Due to these

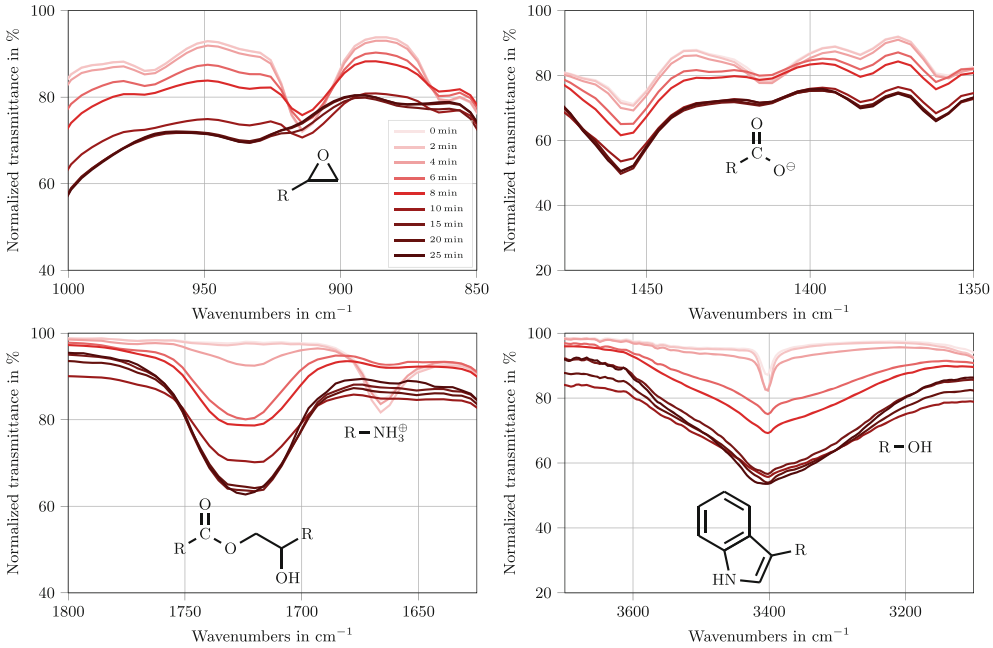

FIGURE 3 Fourier-transform infrared spectra of DGEBA cured with L-tryptophan with the addition of 1 wt% of DYHARD URAcc57 after curing at $T = 140°C$ for different periods. [Color figure can be viewed at wileyonlinelibrary.com]

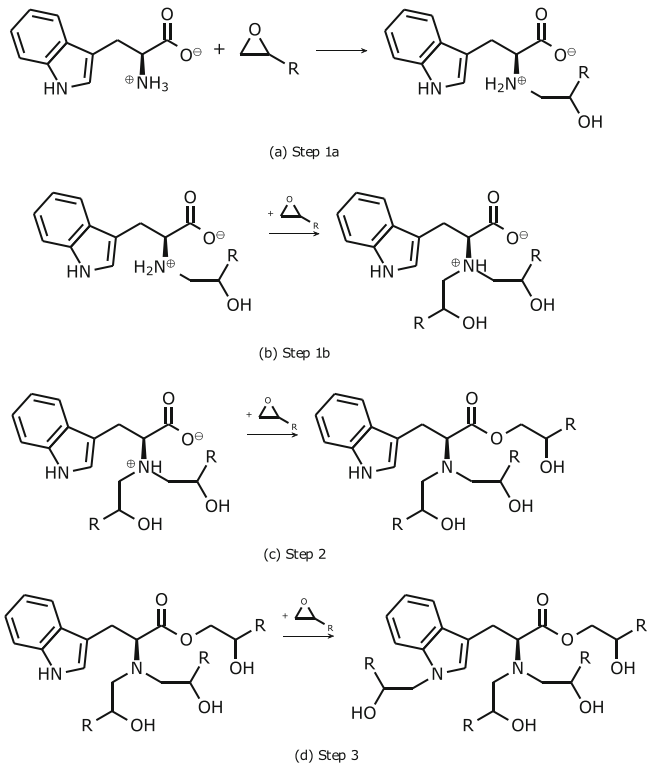

FIGURE 4 Postulated reaction mechanisms of epoxy resin cured with L-tryptophan. Step 1a + b: Reaction of the ammonium zwitter-ion.[28] Step 2: Reaction of the carboxylate group. Step 3: Reaction of the indolyl group.

strong interactions, L-tyrosine crystals, which consist of dimer building blocks, exhibit a considerably higher Young's modulus and decomposition temperature than other AAs.[33] Additionally, L-tyrosine has significantly lower solubility compared with L-tryptophan, resulting in a higher proportion of L-tyrosine crystals in the epoxy matrix.[11,34] This increased presence of crystalline L-tyrosine complicates the analysis of curing reactions via FTIR, as it is more prevalent in the epoxy matrix than L-tryptophan in its crystalline form.

Figure 5 (top left) shows that the intensity of the epoxy group (915 cm^{-1}) decreases only after 6 min. In contrast, the intensities of the hydroxyl group (broad peak between 3200 and 3600 cm^{-1}) and the β-hydroxyester (1730 cm^{-1}) increase significantly as early as 4 min.[25] Over the same period, and continuing until the end of curing, the peak corresponding to the carboxylate group of L-tyrosine at 1412 cm^{-1} remains virtually unchanged (see Figure 5 top right). The formation of a β-hydroxyester without changes in the intensity of the carboxylate group is highly contradictory but is evident from the data, which has been reliably reproduced.

It is possible that reactions between L-tyrosine molecules themselves are responsible for the observed data. Typically, amino acids form peptides or di-cyclic peptides via amide bonds.[27,35] If this were the case, the peak at 1730 cm^{-1} would correspond to the C═O vibration of an amide rather than the C═O vibration of a β-hydroxyester. However, these signals are usually found at wavenumbers lower than 1700 cm^{-1}. Still, such interpretations remain speculative.

In contrast to the FTIR spectra of DGEBA cured with L-tryptophan, there is no peak at 1665 cm^{-1} indicating the presence of an ammonium zwitter-ion for DGEBA cured with L-tyrosine. One possible reason for this absence might be the face-to-face dimerization of L-tyrosine. However, peaks at 1155 and 3000 cm^{-1} can

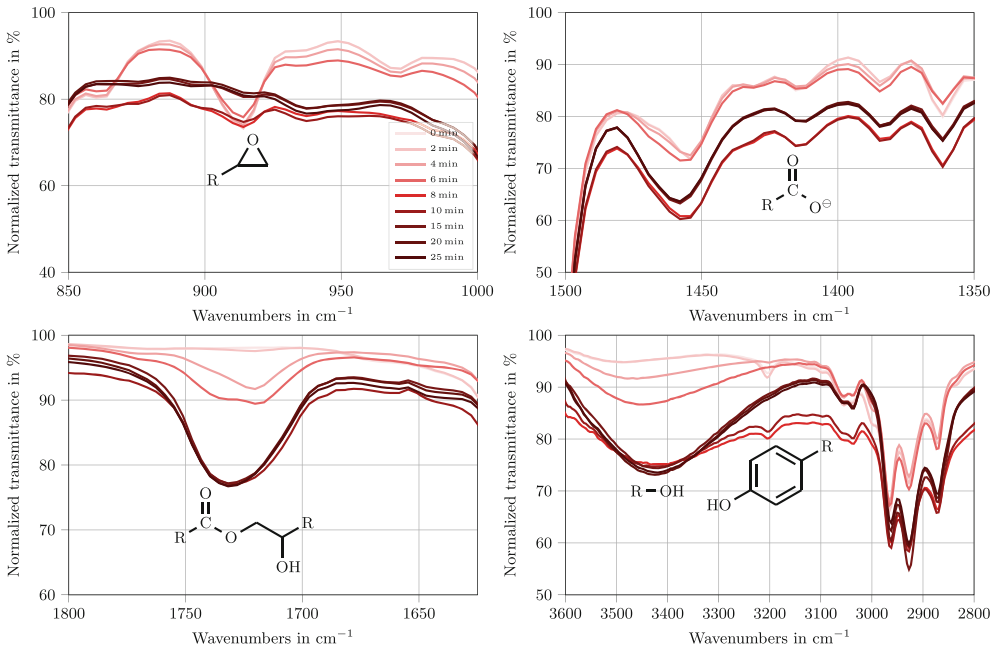

FIGURE 5 Fourier-transform infrared spectra of DGEBA cured with L-tyrosine with the addition of 1 wt% of DYHARD®URAcc57 after curing at $T = 140°C$ for different periods. [Color figure can be viewed at wileyonlinelibrary.com]

be attributed to the primary amino group of the α-AA backbone of L-tyrosine.[36,37] The peak at 1155 cm^{-1} has low intensity, which decreases after a few minutes. The intensity of the peak at 3000 cm^{-1} consistently decreases over time and is indistinguishable from the baseline after 4 min.

In general, the reaction between hydroxyl groups and the epoxy group of DGEBA is challenging to detect for several reasons. First, this reaction results in the formation of a hydroxyl group and an ether bond. Both of these functional groups are present both at the beginning and at the end of the reaction, resulting in no net change in their signals in the FTIR spectra. Nevertheless, the peak of the hydroxyl group of the phenyl side chain shows a distinct peak at 3200 cm^{-1}.[38,39] This peak appears intermittently during certain curing periods but is ultimately absent at the end of the curing reaction, suggesting it is likely consumed by the etherification reaction.

In summary, the curing reactions of L-tyrosine and DGEBA are not fully understood based on the current data. The apparent presence of β-hydroxyester groups without a corresponding change in the intensities of carboxylate groups cannot be explained with certainty at this time. However, it can still be concluded that the primary amino group of L-tyrosine and the hydroxyl group of its side chain participate in the curing reaction.

3.2 | Curing kinetics

Figure 6 illustrates the E_a of DGEBA cured with either L-tryptophan or L-tyrosine, with and without the addition of 1 wt% of DYHARD®UR500 or DYHARD®URAcc57, determined using the Kissinger method, Ozawa method, and MFK. Comparing the effect of different accelerators on the E_a of resin systems provides valuable insights into the performance of individual accelerators for these resin formulations. By analyzing how different accelerators affect the resin systems' E_a alongside their latency properties, manufacturers can select accelerators that offer adequate shelf-life stability (latency) while enabling efficient curing during processing. This dual consideration is crucial for optimizing the performance of epoxy resin systems in various applications.

In general, the E_a determined via the Kissinger method, Ozawa method, and MFK exhibit minimal variation for a specific resin system. When curing DGEBA with L-tryptophan without any accelerator, the E_a is approximately 100 kJ mol^{-1}. The addition of urea-based accelerators reduces the E_a, with DYHARD®UR500 decreasing it to around 79–85 kJ mol^{-1}. DYHARD®URAcc57 further decreases the E_a to approximately 75–78 kJ mol^{-1}, indicating it is a more potent accelerator. This difference in E_a is likely due to reduced steric hindrance associated with functional groups attached to the urea-type groups in DYHARD®URAcc57. Lower steric hindrance typically facilitates faster reaction kinetics, resulting in lower E_a for curing reactions in epoxy resin systems.[40]

For DGEBA cured with L-tyrosine, the E_a values are slightly lower, ranging from 88 to 92 kJ mol^{-1} without the addition of any accelerator (see Figure 6 bottom). This resin system exhibits minimal curing without an

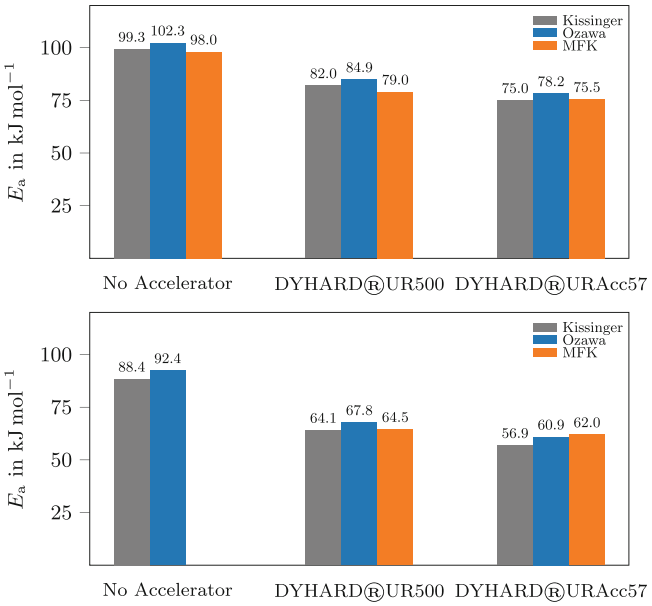

FIGURE 6 E_a of DGEBA cured with either L-tryptophan (top) or L-tyrosine (bottom) without any accelerator or with the addition of 1 wt% of DYHARD®UR500 or DYHARD®URAcc57 derived from dynamic differential scanning calorimetry measurements according to Kissinger (gray), Ozawa (blue), or MFK (orange). [Color figure can be viewed at wileyonlinelibrary.com]

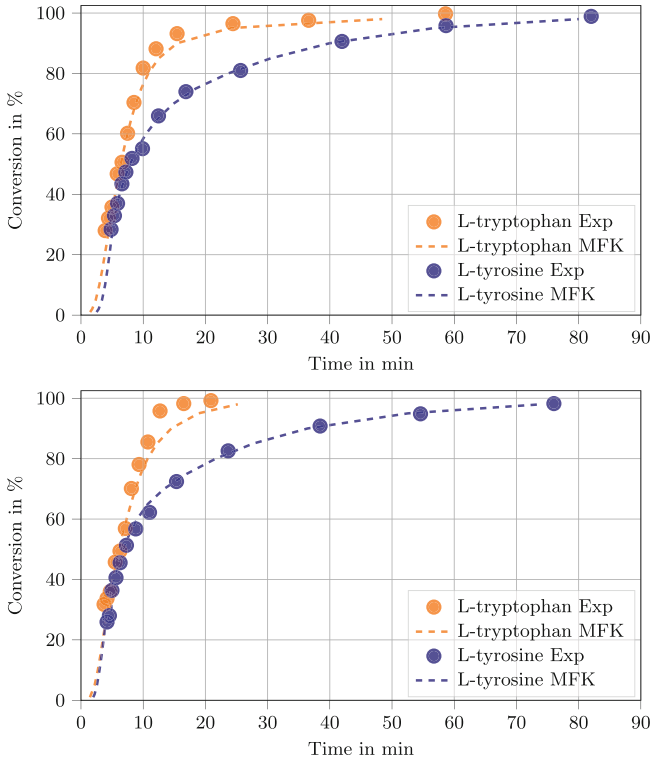

FIGURE 7 α versus time of DGEBA cured with either L-tryptophan (orange) or L-tyrosine (blue) with the addition of 1 wt % of DYHARD®UR500 (top) or DYHARD®URAcc57 (bottom) derived from isothermal differential scanning calorimetry (DSC) measurements at 140°C (points) compared with the prediction of MFK (line) derived from dynamic DSC measurements. [Color figure can be viewed at wileyonlinelibrary.com]

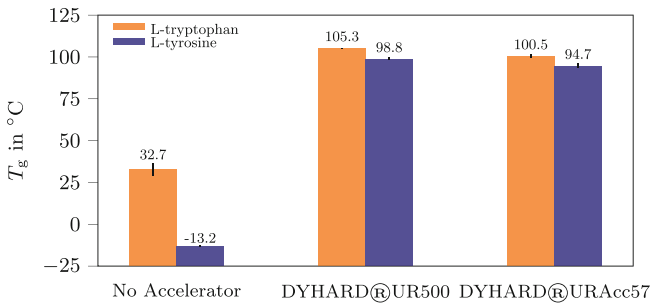

FIGURE 8 T_g of DGEBA cured with either L-tryptophan (orange) or L-tyrosine (blue) without any accelerator or with the addition of 1 wt% of DYHARD®URAcc500 or DYHARD®URAcc57 at $T = 140$°C for 2 h derived from dynamic differential scanning calorimetry measurements. [Color figure can be viewed at wileyonlinelibrary.com]

accelerator, as shown in Figure 8, where the Mettler Toledo "STARe" software's MFK requires complete curing DSC thermograms as input to compute a conversion-dependent E_a.[3] Upon adding DYHARD®UR500 to the resin system, the E_a decreases to approximately 64–68 kJ mol^{-1}. The addition of DYHARD®URAcc57 further lowers the E_a to about 57–62 kJ mol^{-1}. This reduction in activation energies with accelerators indicates their effectiveness in facilitating faster curing kinetics.

In Figure 7, the predictions of MFK for α are compared with the experimental α of DGEBA cured with either L-tryptophan (orange) or L-tyrosine (blue), with the addition of 1 wt% of DYHARD®UR500 (top) or DYHARD®URAcc57 (bottom) at 140°C. To align the experimental α with the predictions from MFK, a time shift of plus 2 min is applied. This accounts for the conversion that occurred during the heat-up phase before reaching 140°C, as well as any curing that took place during the subsequent cooling down to room temperature in the DSC.

In general, MFK reliably predicts the α throughout the curing process. However, for DGEBA cured with L-tryptophan and the addition of 1 wt% of DYHARD®URAcc57, MFK underestimates the degree of cure between 80% and 100%. The time required to achieve nearly complete conversion ($\alpha = 98\%$) differs significantly with different accelerators: with DYHARD®UR500 as accelerator, it takes about 48 min for DGEBA cured with L-tryptophan and approximately 80 min for DGEBA cured with L-tyrosine. In contrast, the addition of DYHARD®URAcc57 as an accelerator reduces the necessary time for 98% conversion to 16 min

for L-tryptophan and 76 min for L-tyrosine, respectively. The more rapid curing with DYHARD®URAcc57 is likely attributed to lower steric hindrance associated with the urea group of this accelerator compared with DYHARD®UR500, making DYHARD®URAcc57 a more potent accelerator for these resin systems.[40]

Notably, the curing of DGEBA with L-tyrosine requires significantly more time compared with curing with L-tryptophan, irrespective of the accelerator used. This observation is intriguing given that the E_a for the curing of DGEBA with L-tryptophan generally exceeds that for DGEBA cured with L-tyrosine (see Figure 6). Still, both the E_a and the preexponential factor in the Arrhenius equation play pivotal roles in governing curing kinetics. The preexponential factor accounts for the frequency of collisions and the likelihood that these collisions result in a reaction. It is influenced by factors, such as molecular geometry, orientation, and steric hindrance.[41]

In summary, these findings demonstrate that MFK can effectively predict the conversion kinetics during the curing of DGEBA using either L-tryptophan or L-tyrosine, under isothermal conditions and with two urea-based accelerators. Moreover, the choice of AA as a curing agent and the type of accelerator exert a substantial influence on the curing time required. Lastly, the time needed to achieve complete conversion in AA-cured epoxy resins is comparable but still slightly longer than that observed for DGEBA cured with dicyandiamide in the presence of DYHARD®UR500.[42]

Figure 8 illustrates the T_g of DGEBA cured with either L-tryptophan (orange) or L-tyrosine (blue) under two conditions: without any accelerator and with the addition of 1 wt% of DYHARD®UR500 or DYHARD®URAcc57, cured at $T = 140°C$ for 2 h, based on dynamic DSC measurements. The T_{g0} of the resin systems, approximately −15°C (see Figure 9), indicates minimal curing at $T = 140°C$. The addition of an accelerator significantly enhances the T_g of the resin systems, particularly those cured with L-tyrosine. For instance, T_g increases from −13.2 to 98.8°C with DYHARD®UR500. Similarly, DGEBA cured with L-tryptophan shows an increase from 32.7 to 105.3°C in T_g. Interestingly, the type of accelerator used systematically affects the T_g of the thermosets. Specifically, compounds incorporating DYHARD®UR500 exhibit T_g values approximately 4.1–4.8°C higher than those using DYHARD®URAcc57.

3.3 | Latency

The latency of resin systems employing different AAs as curing agents and various urea-based accelerators is evaluated based on shifts in T_{g0} and viscosity increase due to curing during storage. Figure 9 presents the glass transition temperatures of uncured resin systems after different storage durations at 23°C.

Consistent with experimental observations and predictions from MFK (refer to Figure 7), resin systems utilizing L-tryptophan as the curing agent exhibit lower latency, indicating higher reactivity compared with those employing L-tyrosine. Furthermore, the incorporation of DYHARD®URAcc57 as an accelerator results in lower latency relative to DYHARD®UR500. This difference in latency between accelerators stems from their distinct molecular structures and consequent variations in steric hindrance at their urea groups.[40] Specifically, over an eight-week period, the T_{g0} of DGEBA cured with L-tryptophan and DYHARD®UR500 increases by approximately 5°C, whereas its counterpart using DYHARD®URAcc57 shows an increase of more than 10°C during the same duration.

Figure 10 displays the norm of the complex viscosity of DGEBA cured with L-tryptophan under two conditions: neat (without any accelerator) and with the addition of 1 wt% of DYHARD®UR500 (top) or DYHARD®URAcc57 (bottom), following various storage

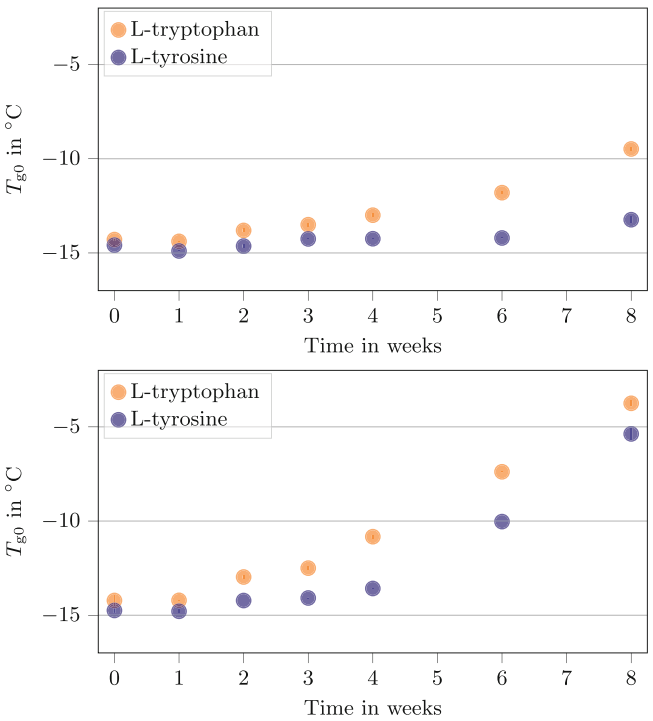

FIGURE 9 T_{g0} of DGEBA cured with either L-tryptophan (orange) or L-tyrosine (blue) with the addition of 1 wt% of DYHARD®UR500 (top) or DYHARD®URACC57 (bottom) after different storage periods at $T = 23°C$ derived from dynamic differential scanning calorimetry measurements. [Color figure can be viewed at wileyonlinelibrary.com]

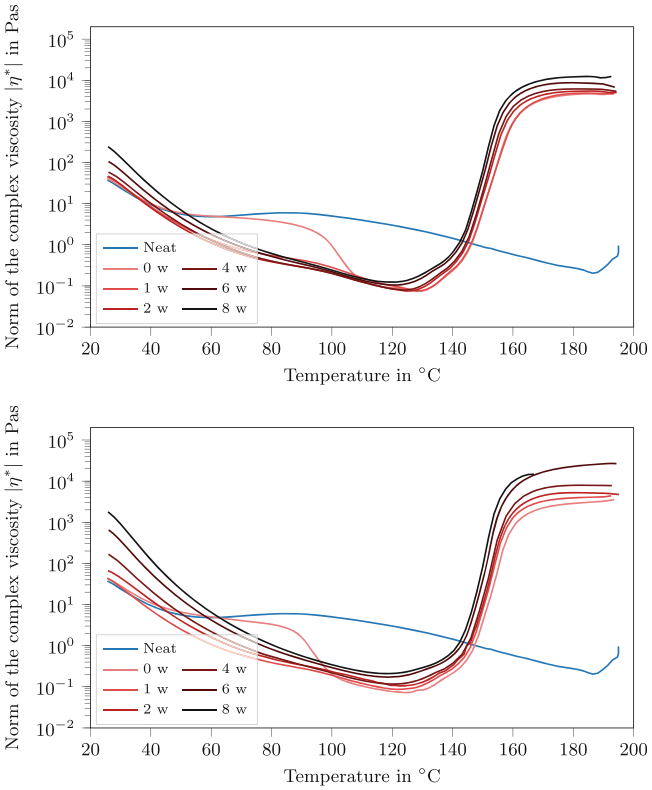

FIGURE 10 Norm of the complex viscosity of DGEBA cured with L-tryptophan without the addition of any accelerator (neat) and with the addition of 1 wt% of DYHARD®UR500 (top) or DYHARD®URAcc57 (bottom) after different storage periods at $T = 23°C$. [Color figure can be viewed at wileyonlinelibrary.com]

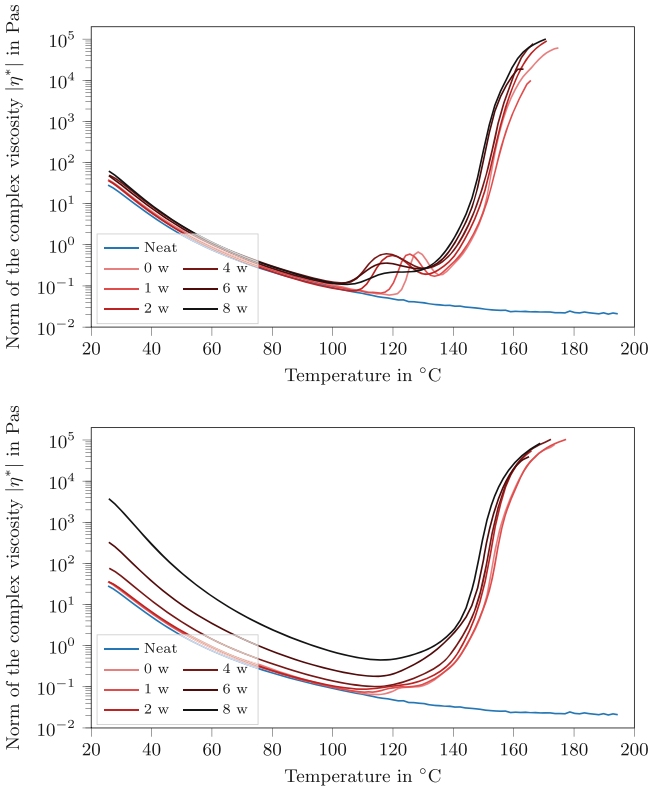

FIGURE 11 Norm of the complex viscosity of DGEBA cured with L-tyrosine without the addition of any accelerator (neat) and with the addition of 1 wt% of DYHARD®UR500 (top) or DYHARD®URAcc57 (bottom) after different storage periods at $T = 23°C$. [Color figure can be viewed at wileyonlinelibrary.com]

periods at $T = 23°C$. Please note that portions of the viscosity functions in Figures 10 and 11 are omitted due to significant noise observed in the data following specimen failure. As expected for a visco-elastic fluid, initially, the viscosity of the neat resin decreases with increasing temperature due to the greater average distance between molecules and reduced friction during relative motion. This viscosity decrease follows an Arrhenius-type behavior, evident from the linear trend observed in the semi-logarithmic plot. However, deviations from this initial trend occur around 40°C, where the viscosity reaches a minimum of approximately 4.8 Pa s. Subsequently, the viscosity increases to about 6 Pa s at 85°C. Similar steps or plateaus in the viscosity function have been observed in epoxy resin cured with L-arginine.[43] Further temperature increase leads to another viscosity decrease, albeit with a shallower slope compared with earlier trends, reaching a minimum around 186°C at 0.2 Pa s. At this point, the viscosity increase due to cross-linking of the neat resin system begins to outweigh the viscosity decrease from temperature effects. Consequently, curing initiates a sharp increase in viscosity, continuing until the end of the measurement at 195°C. This behavior reflects the complex interplay between temperature-dependent viscosity changes and the onset of resin cross-linking during curing.

Interestingly, the addition of the accelerator itself significantly alters the viscosity function. Specifically, incorporating 1 wt% of DYHARD®UR500 reduces the peak height and induces a rapid viscosity decrease thereafter. Consequently, the viscosity minimum occurs at much lower temperatures (128°C) and lower viscosity levels (0.07 Pa s) compared with the neat resin system. Comparing viscosity functions after different storage periods reveals that the peak height, indicating deviation from the expected viscosity decrease, diminishes with longer storage durations. Concurrently, the viscosity at 25°C steadily increases from approximately 40 Pa s at zero weeks to around 240 Pa s at 8 weeks. However, even after the maximum storage period tested, viscosity can still be reduced over an extended time-frame to levels suitable for various epoxy resin manufacturing processes, including prepreg production and curing.[44]

Consistent with the lower E_a (refer to Figure 6), faster curing rates (see Figure 7), and more pronounced shifts in T_{g0} (see Figure 9) observed in resin systems using

DYHARD®URAcc57 compared with DYHARD®UR500, the viscosity of the former increases more significantly over the same storage period (see Figure 10 bottom). Specifically, viscosity at 25°C rises from approximately 40 Pa s at zero weeks to roughly 1800 Pa s at 8 weeks. Even after 8 weeks of storage at room temperature, the viscosity can still be minimized to 0.2 Pa s by increasing the temperature.

Figure 11 illustrates the viscosity functions of the resin systems using L-tyrosine as the curing agent. Interestingly, the neat resin system exhibits a consistent decrease in viscosity as temperature increases up to 195°C. This behavior aligns with its lower reactivity, as evidenced by the slower curing rates and lower T_g observed after curing (see Figures 7 and 8). With the addition of urea-based accelerators, both resin systems containing L-tyrosine as the curing agent show the emergence of a viscosity peak in their respective functions. Over prolonged storage periods, this peak shifts to lower temperatures and diminishes in magnitude. Moreover, the increase in viscosity at 25°C due to storage is more pronounced for resin systems incorporating DYHARD®URAcc57 compared with those with DYHARD®UR500.

4 | CONCLUSION AND OUTLOOK

This study provides a comprehensive analysis of the curing reactions, curing kinetics, and latency of DGEBA cured with either L-tryptophan or L-tyrosine in the presence of commercially available urea-based accelerators. The curing process in resin systems using L-tryptophan as the curing agent involves three distinct curing reactions, corresponding to the primary amino group, the carboxylate group, and the indolyl group of L-tryptophan. A schematic curing mechanism is proposed based on DSC thermograms and FTIR spectra of precured resin. In contrast, there is less definitive data for resin systems using L-tyrosine as the curing agent. DSC thermograms indicate two exothermal peaks, which contrasts with the expected three functional groups: primary amino group, carboxylate group, and phenyl group of L-tyrosine.

The E_a of the resin systems are fairly consistent regardless of the evaluation method used. Overall, the α can be reliably predicted via MFK for all resin systems studied.

In summary, the inclusion of both accelerators facilitates rapid curing at elevated temperatures, while maintaining adequate processability of the resin systems for up to 4 weeks of storage. However, the choice between DYHARD®UR500 and DYHARD®URAcc57 depends on the specific trade-offs deemed most critical: opting for longer storability with slightly extended curing times, or prioritizing shorter production cycles at the cost of a marginally reduced shelf-life. This decision hinges on balancing the requirements of production efficiency and storage stability tailored to the application's needs.

ACKNOWLEDGMENTS

We would like to thank all colleagues of the work group "Resins & Composites" at the Department of Polymer Engineering for their support. Open Access funding enabled and organized by Project DEAL.

FUNDING INFORMATION

Parts of the research documented in this manuscript have been funded by the German Federal Ministry for Economic Affairs and Climate Action (BMWK) within the research projects "EcoPrepregs—Grundlagenforschung zur Klärung der Struktur-Eigenschaftsbeziehungen von Epoxidharzen und Fasern aus nachwachsenden Rohstoffen zur Anwendung in der Sekundärstruktur von Flugzeugen" (grant no. 20E1907A, Germany).

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Florian Rothenhäusler https://orcid.org/0000-0001-9948-3310

Holger Ruckdaeschel https://orcid.org/0000-0001-5985-2628

REFERENCES

[1] C. Ding, A. S. Matharu, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2217.
[2] Y. Li, F. Xiao, K. Moon, C. P. Wong, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *44*, 1020.
[3] Y. Li, F. Xiao, C. P. Wong, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 181.
[4] A. Motahari, A. Omrani, A. A. Rostami, *Comput. Theor. Chem.* **2011**, *977*, 168.
[5] A. Motahari, A. A. Rostami, A. Omrani, M. Ehsani, *J. Macromol. Sci., Part B: Phys.* **2015**, *54*, 517.
[6] L. Mazzocchetti, S. Merighi, T. Benelli, L. Giorgini, *AIP Conf. Proc.* **2018**, *1981*, 020170.
[7] P. Gnanasekar, N. Yan, *Polym. Degrad. Stab.* **2019**, *163*, 110.
[8] S. Merighi, L. Mazzocchetti, T. Benelli, L. Giorgini, *Processes* **2021**, *9*, 42.
[9] F. Rothenhäusler, H. Ruckdaeschel, *Polymer* **2023**, *15*, 385.
[10] R. Q. Albuquerque, F. Rothenhäusler, H. Ruckdaeschel, *MRS Bull.* **2023**, *49*, 59.

[11] F. Rothenhäusler, H. Ruckdäschel, *J. Appl. Polym. Sci.* **2024**, *141*, e55250.
[12] Z. Yu, S. Ma, Z. Tang, Y. Liu, X. Xu, Q. Li, K. Zhang, B. Wang, S. Wang, J. Zhu, *Green Chem.* **2021**, *23*, 6566.
[13] Chemical-suppliers eu. https://www.chemical-suppliers.eu/enp/dyhard-PX501487
[14] H. L. Friedman, *J. Polym. Sci., Part C: Polym. Symp.* **1964**, *6*, 183.
[15] H. E. Kissinger, *J. Res. Natl. Bur. Stand.* **1956**, *57*, 217.
[16] H. E. Kissinger, *Anal. Chem.* **1957**, *29*, 1702.
[17] T. Ozawa, *J. Therm. Anal.* **1976**, *9*, 369.
[18] S. Vyazovkin, C. A. Wight, *Thermochim. Acta* **1999**, *340*, 53.
[19] S. Vyazovkin, *Molecules* **2020**, *25*, 2813.
[20] S. G. Hong, C. S. Wu, *Thermochim. Acta* **1998**, *316*, 167.
[21] M. G. González, J. C. Cabanelas, J. Baselga, *Infrared Spectroscopy—Materials Science, Engineering and Technology*, Vol. 2, IntechOpen, London, United Kingdom **2012**, p. 261.
[22] R. Dojčilović, J. D. Pajović, D. K. Božanić, V. Vodnik, S. Dimitrijević-Branković, A. R. Milosavljević, S. Kaščàkovà, M. Réfrégiers, *Analyst* **2016**, *141*, 1988.
[23] M. Tsuboi, Y. Ezaki, M. Aida, M. Suzuki, A. Yimit, K. Ushizawa, T. Ueda, *Biospectroscopy* **1998**, *4*, 61.
[24] R. J. Koegel, J. P. Greenstein, M. Winitz, S. M. Birnbaum, R. A. McCallum, *J. Am. Chem. Soc.* **1955**, *77*, 5708.
[25] M. Shibata, J. Fujigasaki, M. Enjoji, A. Shibita, N. Teramoto, S. Ifuku, *Eur. Polym. J.* **2018**, *98*, 216.
[26] N. Tudorachi, F. Mustata, *Arab. J. Chem.* **2020**, *13*, 671.
[27] B. B. Ivanova, *Spectrochim. Acta, Part A* **2006**, *64*, 931.
[28] Y. Tanaka, R. S. Bauer, *Epoxy Resins—Chemistry and Technology*, Springer Science+Business Media, Berlin, Germany **1988**, p. 285.
[29] S. Vyazovkin, N. Sbirrazzuoli, *Macromolecules* **1996**, *29*, 1867.
[30] M. Pramanik, E. Fowler, J. Rawlins, *J. Coat. Technol. Res.* **2014**, *3*, 11.
[31] A. S. Mora, R. Tayouo, B. Boutevin, G. David, S. Caillol, *Eur. Polym. J.* **2020**, *123*, 109460.
[32] W. Ji, B. Xue, Z. A. Arnon, H. Yuan, S. Bera, Q. Li, D. Zaguri, N. P. Reynolds, H. Li, Y. Chen, S. Gilead, S. Rencus-Lazar, J. Li, R. Yang, Y. Cao, E. Gazit, *ACS Nano* **2019**, *13*, 14477.
[33] I. Azuri, E. Meirzadeh, D. Ehre, S. R. Cohen, A. M. Rappe, M. Lahav, I. Lubomirsky, L. Kronik, *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 13566.
[34] R. Y. Adhikari, J. J. Pujols, *Nano Select* **2022**, *3*, 1314.
[35] A. B. Hughes, *Amino Acids, Peptides and Proteins in Organic Chemistry, Analysis and Function of Amino Acids and Peptides*, John Wiley & Sons, Hoboken, New Jersey **2013**.
[36] D. G. Babar, S. Sarkar, *Appl. Nanosci.* **2017**, *7*, 101.
[37] S. Chauhan, L. S. B. Upadhyay, *Nanotechnol. Environ. Eng.* **2019**, *4*, 1.
[38] J. Encinar, A. Fernández, M. Molina, A. Molina, J. Poveda, J. Albar, J. López-Barneo, F. Gavilanes, A. V. Ferrer-Montiel, *Biochemistry* **2002**, *41*, 12263.
[39] P. J. Reid, C. Loftus, C. C. Beeson, *Biochemistry* **2003**, *42*, 2441.
[40] X. D. Liu, M. Kimura, A. Sudo, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5298.
[41] S. Vyazovkin, *Molecules* **2021**, *26*, 3077.
[42] Alzchem Group AG, Product Data Sheet DYHARD UR500.
[43] F. Rothenhäusler, H. Ruckdaeschel, *Polymer* **2022**, *14*, 4331.
[44] H. Lengsfeld, J. Lacalle, T. Neumeyer, V. Altstädt, *Faserverbundwerkstoffe: Prepregs und ihre Verarbeitung*, Carl Hanser Verlag GmbH Co KG, Munich, Germany **2020**.

How to cite this article: F. Rothenhäusler, D. Hüser, H. Ruckdaeschel, *J. Appl. Polym. Sci.* **2025**, *142*(4), e56410. https://doi.org/10.1002/app.56410