

# Influence of the Stoichiometric Ratio on the Curing Kinetics and Mechanical Properties of Epoxy Resin Cured with a Rosin-Based Anhydride

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Bio-based alternatives for petroleum-based epoxy resin curing agents, such as maleopimaric acid (MPA), are indispensable for sustainable fiber reinforced polymer composites with thermosetting matrices. However, previous investigations disregarded the importance of choosing the right stoichiometric ratio  $R$  between the anhydride groups in the rosin-based curing agent and the epoxy groups in the resin. Therefore, the influence of  $R$  on the curing kinetics and mechanical properties of an epoxy resin cured with a rosin-based anhydride is studied. Here, Fourier-transform infrared spectroscopy (FT-IR) indicates that for  $R \geq 0.9$  unreacted anhydride groups are present in the thermoset. Consequently, the network density decreases and the glass transition temperature  $T_g$  drops by about 40 °C. On the other hand, the steric hindrance of unreacted functional groups for  $R \geq 0.9$ , increases the flexural modulus and the reduced network density improves fracture toughness. The results indicate that the best  $R$  for overall high mechanical performance and good processability is preferably low ( $R \leq 0.7$ ). Here, a low  $R$  results in a high  $T_g$  and good processability due to a low viscosity. However, the latency of the mixtures is low and therefore, the mixtures are not fit for processing via prepreg technology.

## 1. Introduction

Fiber reinforced composites are important materials for automotive, wind energy generation, and aerospace applications due to their high weight-specific modulus and strength.<sup>[1,2]</sup> Since epoxy resin based thermosets have high moduli and strengths, high glass transition temperatures, and low viscosities

for fiber impregnation, they are among the most important matrix materials.<sup>[3]</sup> However, epoxy resins and their curing agents are derived from petroleum and are therefore not environmentally sustainable. Following the zeitgeist of sustainability in the 21<sup>st</sup> century, researchers have studied various bio-based alternatives for resins and curing agents alike.<sup>[4]</sup>

One possible bio-based feedstock as a basis for curing agents is rosin, which is a mixture of resin acids obtained from pines and conifers.<sup>[5]</sup> The resin acids are diterpenoids, such as abietic acid, neoabietic acid, palustric acid, levopimaric acid, pimaric acid, and isopimaric acid with the exact distribution of the individual components depending on the tree species they originate from and their production location<sup>[6,7]</sup> (see Figure 1). Using rosin as feedstock has many advantages: it is bio-based, cheap, non-toxic, abundant in nature, and there is potential for chemical modification via the resin acids' double bonds or carboxyl group.<sup>[5,8]</sup>

Additionally, the cyclic structure of resin acids is useful for creating a stiff network with high  $T_g$  and modulus.<sup>[9]</sup>


One of the most important compounds derived from rosin is maleopimaric acid (MPA), which is a bio-based anhydride curing agent for epoxy resins. It is synthesized via the Diels-Alder reaction between levopimaric acid and maleic anhydride<sup>[7,10]</sup> (see Figure 2).

Maleopimaric acid has been used in several scientific publications to cure petroleum-based and bio-based epoxy resins.<sup>[10–18]</sup> Liu et al.<sup>[10]</sup> synthesized MPA from rosin and cured a liquid epoxy resin (D.E.R. 332) in a stoichiometric ratio  $R (= n_{\text{anhydride}}/n_{\text{epoxy}})$  of 1.0 in the presence of 1.0 wt.% of 2-ethyl-4-methyl-imidazole. The MPA-cured epoxy resin exhibited similar moduli to that of thermosets cured with petroleum-based anhydrides, while the  $T_g$  of the MPA-cured epoxy resin was 186.1 °C.

Wang et al.<sup>[15]</sup> synthesized MPA from rosin and compared it to diaminodiphenylmethane (DDM). Two solid epoxy resins, DGEBA 1075 and DGEBA 4000, were cured with either of the two curing agents in a stoichiometric ratio of 1.0 in the presence of 0.5 wt.% 2-ethyl-4-methyl-imidazole. Again, curing with the rosin-based curing agent MPA resulted in similar moduli compared to curing with DDM, but resulted in thermosets with higher  $T_g$ . For example, DGEBA 1075 cured with MPA had a  $T_g$

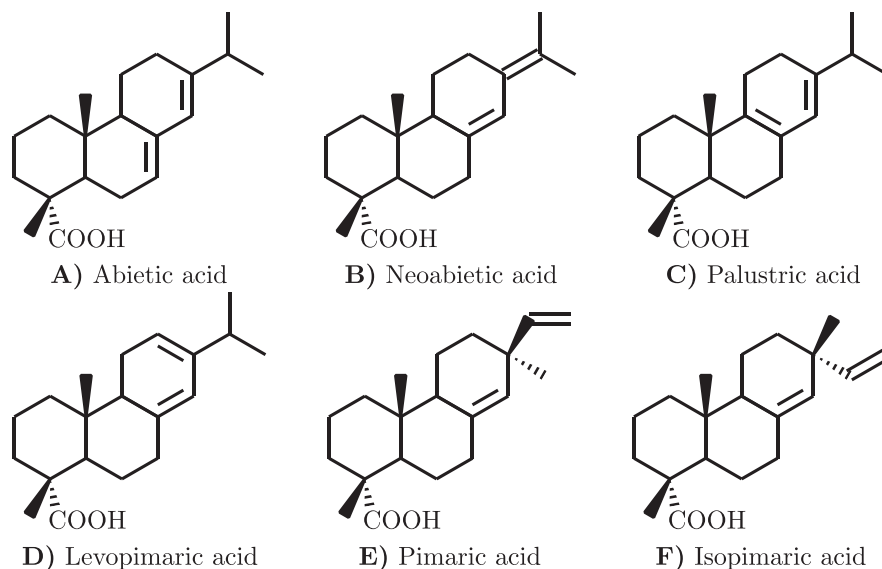
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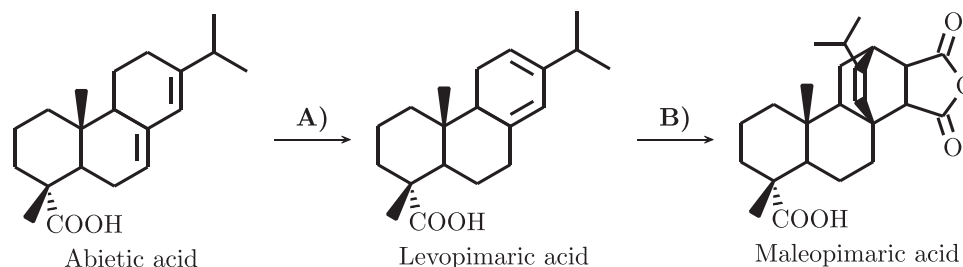
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**Figure 1.** Chemical structures of the most common resin acids found in rosin according to [5].



**Figure 2.** Two-step synthesis of maleopimaric acid according to [10]. A) Isomerization of various resin acids to levopimaric acid. B) Addition of maleic anhydride.

of 114 °C, while the thermoset cured with DDM had a  $T_g$  of only 105 °C. Here, the increased  $T_g$  is attributed to the bulky fused ring structure of MPA, which limits the mobility of network segments.

Liu et al.<sup>[18]</sup> produced a bio-based thermoset using a rosin-based epoxy (triglycidyl ester of MPA) and MPA. They mixed the components in a stoichiometric ratio of 1.0 with 1.0 wt.% of 2-ethyl-4-methyl-imidazole. The thermoset exhibited a  $T_g$  of 164 °C, and a flexural modulus and strength of 2.2 GPa and 70 MPa, respectively.

Chang et al.<sup>[17]</sup> compared the thermo-mechanical properties of isosorbide epoxy resin cured with either MPA or methyl nadic anhydride (MNA). They mixed the resin and hardener in a stoichiometric ratio of 1.0 and used 1.0 wt.% of 1-ethyl-4-methyl-imidazole as a catalyst. Here, the MPA-cured epoxy had a  $T_g$  of 252.9 °C, which is about 120 °C higher than that of the epoxy resin cured with MNA. According to the authors, this can be explained by the higher functionality and rigid structure of MPA. The storage moduli of all thermosets were comparable, ranging from 2.06 GPa to 2.37 GPa.

Qin et al.<sup>[16]</sup> used an eugenol-based epoxy and cured it with either MPA or hexahydrophthalic anhydride (HHPA) in a stoichiometric ratio of 0.8, in combination with 1.0 wt.% of 2-ethyl-4-methyl-imidazole. The rosin-based thermoset showed a  $T_g$  of

155.3 °C, while the system with the commercial curing agent could only achieve a  $T_g$  of 114.2 °C, possibly due to the large rigid structure of the rosin moiety. However, the storage moduli of the MPA- and HHPA-cured thermosets were similar, with values of 2.9 GPa and 2.8 GPa, respectively.

Chen et al.<sup>[11]</sup> cured epoxidized soybean oil (ESO) with different stoichiometric ratios of MPA ( $R = 0.4, 0.5, 0.6, 0.7,$  and  $1.0$ ) in the presence of 2-ethyl-4-methyl-imidazole. Here, the  $T_g$  increased from 11 °C to 70 °C with increasing stoichiometric ratio. For comparison, the ESO was cured with trimellitic anhydride (TMA) and methylhexahydrophthalic anhydride (MHHPA) at  $R = 0.7$ . The MPA system has a lower  $T_g$  than TMA but a higher  $T_g$  than MHHPA ( $53\text{ °C} < 70\text{ °C} < 108\text{ °C}$ ). The authors attributed this result to the fact that the stiffness of MPA with a hydrogenated phenanthrene ring was greater than that of MHHPA with its cycloaliphatic ring, but lower than that of TMA with its aromatic ring. In addition, the same tendency was also demonstrated for the tensile modulus and strength. However, it is important to mention that the calculation of the stoichiometric ratios from the displayed compositions is not comprehensible. Here, calculating the stoichiometric ratios from the given epoxide equivalent weight and molecular weight of the curing agent results in very different values.

Zhang et al.<sup>[13]</sup> used MPA to cure a combination of liquid epoxy resin (E-51) and solid phenolic epoxy resin (weight proportion 60:40) with an imidazole type latent catalyst (two amino imidazole salt complex). To analyze the resin systems, the curing kinetics of MPA and epoxy resin in stoichiometric ratios of 0.38, 0.58, and 0.72 were investigated. Here, the DSC thermograms showed two exothermic peaks. Since MPA has both, carboxyl and anhydride groups, the first exothermic peak is probably related to the reaction between the carboxyl group and the oxirane ring of the resin. The second peak might be the result of the reaction between accelerator and oxirane or between anhydride and oxirane in the presence of the catalyst. With increasing stoichiometric ratio, the peak temperature of the second exothermic peak also increased from 154 °C to 161 °C. Meanwhile, the exothermic peak became broader, while the heat of reaction gradually decreased and the peak temperature of the first peak slightly increased. Zhang et al. concluded that the reactivity of the epoxy system decreases with increasing R.

Xu et al.<sup>[14]</sup> cured a solid epoxy resin (E-12) with MPA at  $R = 0.33$  catalyzed by 1.0 wt.% of 2-methyl-imidazole. Here, the  $T_g$ , storage modulus  $G'$ , Young's modulus  $E$  and tensile strength were 134.5 °C, 1.3 GPa, 1.0 GPa, and 36 MPa, respectively.

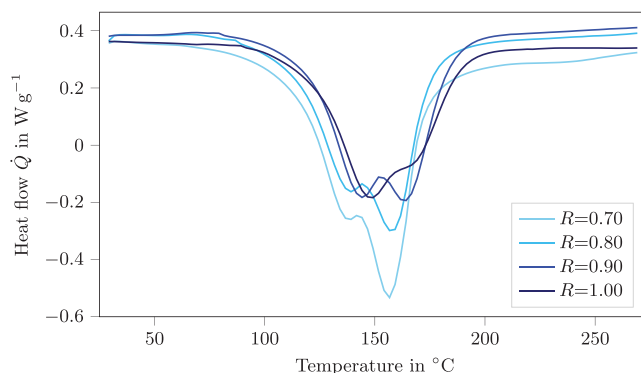
In conclusion, maleopimaric acid was frequently used as a curing agent for a variety of epoxy resins in past investigations. Here, a wide range of stoichiometric ratios were used without justification. Furthermore, there was no systematic study on the influence of the stoichiometric ratio on the mechanical properties of the thermoset. This is especially important for maleopimaric acid as, it contains both a carboxyl and an anhydride group. The carboxyl group might also react with the epoxy and hydroxyl groups of the epoxy resin. This also applies to some works using derivatives of MPA as curing agents for epoxy resin that also contain a carboxyl group.<sup>[19–22]</sup> Thus, for the bio-based curing agent MPA the optimal stoichiometric ratio is not known. For conventional anhydride curing agents, a ratio of  $R = 0.7$  to 0.9 is common in the literature for the full conversion of epoxy and anhydride groups, depending on the anhydride type applied.<sup>[23,24]</sup>

Therefore, the objective of this investigation is to study the influence of the stoichiometric ratio on the curing kinetics, rheology, cross-link density, and glass transition temperature, as well as the flexural, compression, and fracture toughness properties of DGEBA cured with a rosin-based anhydride. Hereby, structure-property relationships between chemical bonds, network structure, and mechanical properties will be established that deepen the understanding of epoxy resins cured with rosin-based anhydrides. The goal is to determine the optimal stoichiometric ratio for a low viscosity, a high  $T_g$ , a high flexural strength and a high bio-content.

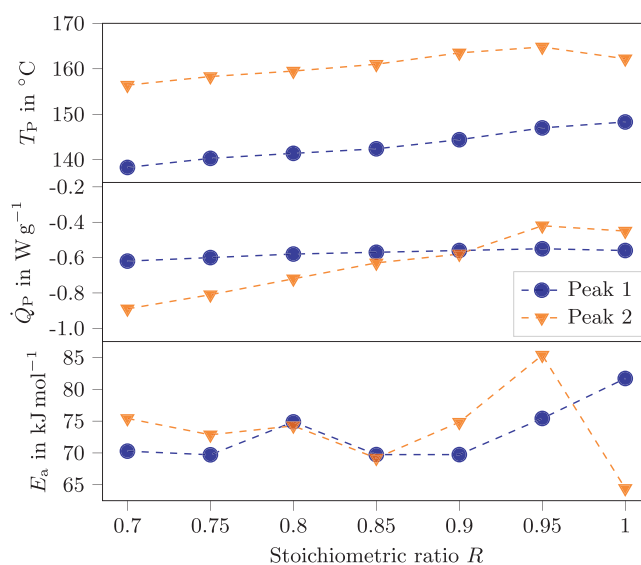
## 2. Results and Discussion

### 2.1. Differential Scanning Calorimetry

Figure 3 shows the DSC thermograms of the first heating run of DGEBA cured with different stoichiometric ratios  $R$  of the rosin-based anhydride with a heating rate of 10 K min<sup>-1</sup>. Here, every thermogram exhibits two exothermic peaks that show a tendency to peak at higher temperatures for increasing  $R$  (see Figure 4). The temperature at which the first exothermic peak reaches its



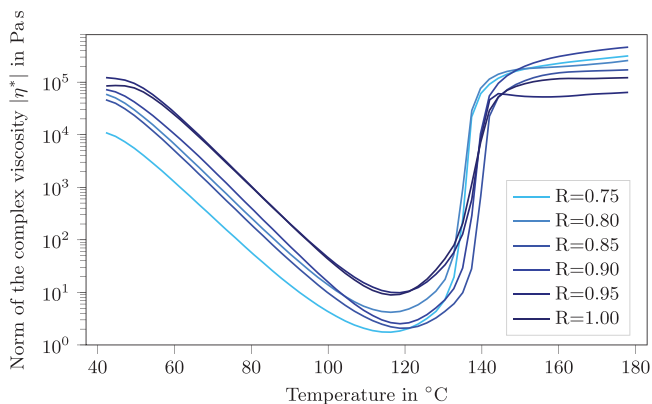
**Figure 3.** DSC thermograms of the first heating run of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.



**Figure 4.** Exothermic peak temperature  $T_p$ , peak heat flow  $\dot{Q}_p$  and activation energy  $E_a$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

maximum shifts from 138.3 °C ( $R_{70}$ ) to 148.3 °C ( $R_{100}$ ), while the second peak shifts from 156.4 °C ( $R_{70}$ ) to 162.2 °C ( $R_{100}$ ). Usually, DSC thermograms of epoxy resin cured with conventional anhydrides show only one exothermic peak.<sup>[25,26]</sup> However, rosin-based anhydrides have a carboxyl group that can also take part in the curing reaction besides the anhydride group (see Figure 1). According to Zhang et al.<sup>[13]</sup> the first of the two peaks can be attributed to the reaction between the carboxyl group of MPA and the epoxy group in the presence of an imidazole-type catalyst. Therefore, the second peak stems either from the reaction between the imidazole and the epoxy group or from the catalyzed reaction between the anhydride and the epoxy group.

Figure 4 shows the temperature at which the exothermic heat flow peaks  $T_p$ , the peak heat flow  $\dot{Q}_p$  and the activation energies of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride. The temperature at which the exothermic heat flow peaks indicates the reactivity of compounds in curing reactions. The lower the peak's temperature, the higher the reactivity. The heat release of the first peak remains relatively stable in



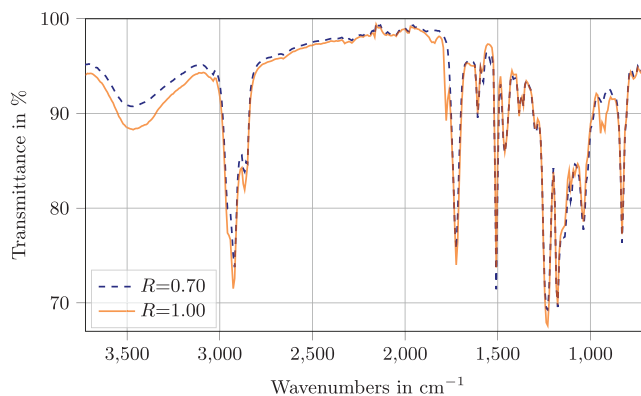
**Figure 5.** Norm of the complex viscosity of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride between 40 °C and 180 °C.

a range of peak heat flow from  $-0.55 \text{ W g}^{-1}$  to  $-0.62 \text{ W g}^{-1}$ . In contrast,  $\dot{Q}_p$  of the second peak decreases steadily and is even lower than that of the first peak for R95 and R100. This could be due to the fact that as  $R$  and thus, the hardener content increases, fewer and fewer epoxy groups are present in the resin-hardener mixture. Thus, fewer epoxy groups remain after the reaction with the carboxyl groups of the rosin-based anhydride, which can react with the anhydride group or the imidazole. As a result, the heat of reaction decreases with increasing  $R$ . Furthermore, the exothermic peaks become broader and both the initial and final temperatures of the reaction increase with increasing  $R$ , showing that the reactivity of the epoxy resin cured with the rosin-based anhydride decreases (see Figure 3).

The activation energies  $E_a$  of the two exothermic peaks were determined with the Kissinger method,<sup>[27,28]</sup> which states that the activation energy can be determined from the peak temperatures during the curing process at different heating rates.<sup>[29]</sup> Here,  $E_a$  of the first peak, which relates to the reaction between the carboxylic acid and the epoxy group is lower or similar to the  $E_a$  of the second peak for a wide range of  $R$ . However, the  $E_a$  of the second peak suddenly drops by about  $20 \text{ kJ mol}^{-1}$  (R100) that causes the reactivity to increase rapidly. Zhang et al.<sup>[13]</sup> investigated the reaction kinetics of an MPA cured epoxy resin system with  $R = 0.38$ . They found that the activation energy of the first peak in the DSC thermograms ( $68.9 \text{ kJ mol}^{-1}$ ) is significantly lower than that of the second peak, which has an  $E_a$  of  $86.5 \text{ kJ mol}^{-1}$  and therefore, the reaction between epoxy and anhydride is significantly less pronounced.

## 2.2. Rheology

Figure 5 shows the norm of the complex viscosity of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride between 40 °C and 180 °C. Here, the viscosity at 40 °C increases significantly with increasing stoichiometric ratio from 13 kPa s (R75) to 123 kPa s (R100). The viscosity is influenced by different factors: first, the rosin-based anhydride consists of a bulky ring structure, a hydrogenated phenanthrene ring, with a molecular weight of  $515 \text{ g mol}^{-1}$ . Second, the electrostatic interaction, caused by the anhydrides' functional groups and thus, the friction



**Figure 6.** FT-IR spectra of DGEBA cured with the rosin-based anhydride at  $R = 0.7$  and  $R = 1.0$ .

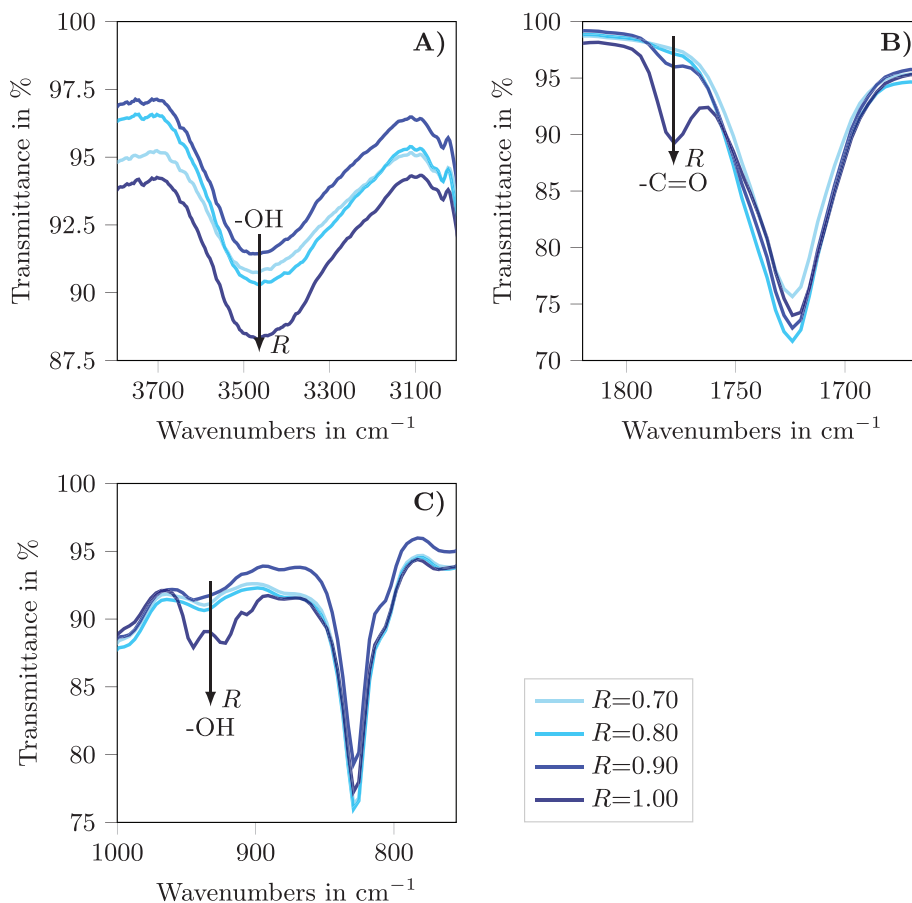
between the molecules is higher. As a result, the molecular mobility is reduced and the viscosity of the resin system increases. Due to the temperature increase during the measurement, the viscosities of the mixtures decrease up to 120 °C. Here, the slope of all the curves is approximately the same, which means that the viscosity decreases at the same rate for all values of  $R$  until a minimum is reached. Similar to the viscosity at 40 °C, the minimum viscosity of the resin-hardener mixtures increases with increasing stoichiometric ratio from about 1.5 Pa s (R75) to 7.5 Pa s (R95). In addition, the viscosity minimum shifts to higher temperatures with increasing  $R$  values, indicating that the curing reaction starts at higher temperatures and therefore, that the mixtures become less reactive. This conclusion is supported by the DSC results (see Section 2.1), which show that the curing reaction shifts to higher temperatures and the reactivity of the mixtures decreases with increasing  $R$ .

Eventually, the viscosity of the resin increases due to curing until it reaches a maximum and the material is converted into an infusible solid at which the viscosity plateaus. Here, the viscosity of the cured thermoset tends to decrease as the stoichiometric ratio increases. This indicates that the cross-link density of the thermoset also decreases, since the viscosity after curing is directly related to the storage modulus in the rubber plateau, which in turn is directly included in the calculation of the cross-link density.<sup>[30]</sup>

As the thermoset is supposed to be a sustainable alternative for thermosetting prepreg matrices, it is essential to be able to lower the viscosity of the resin system down to 1 Pa s to 10 Pa s over a reasonable time-span at higher temperatures.<sup>[3]</sup> However, the interval in which the viscosity drops below 10 Pa s spans only a few minutes. This time span is insufficient for processing via prepreg technology as the resin system first has to be heated to the required temperature.

## 2.3. Fourier-Transform Infrared Spectroscopy

Figure 6 shows the FT-IR spectra of DGEBA cured with the rosin-based anhydride in the stoichiometric ratios of  $R = 0.70$  and  $R = 1.00$ . Here, the differences between the spectra indicate differences in the bond distribution with increasing content of the rosin-based curing agent. The assignments of the absorption



**Figure 7.** Characteristic peaks of the FT-IR spectra in the range of A) 3800  $\text{cm}^{-1}$  to 3000  $\text{cm}^{-1}$ , B) 1825  $\text{cm}^{-1}$  to 1650  $\text{cm}^{-1}$  and C) 1000  $\text{cm}^{-1}$  to 750  $\text{cm}^{-1}$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

features seen in both graphs are as follows: 3478  $\text{cm}^{-1}$  to 3440  $\text{cm}^{-1}$  to hydroxyl groups,<sup>[25]</sup> 2925  $\text{cm}^{-1}$  to 2868  $\text{cm}^{-1}$  to the  $\text{CH}_3$  and  $\text{CH}_2$ ,<sup>[25,31]</sup> 1724  $\text{cm}^{-1}$  and 1607  $\text{cm}^{-1}$  to ester linkages  $\text{C}=\text{O}$ ,<sup>[25,26]</sup> 1508  $\text{cm}^{-1}$  and 1461  $\text{cm}^{-1}$  to combined stretching and vibration of aromatic  $\text{C}=\text{C}$  bonds,<sup>[32]</sup> 1384  $\text{cm}^{-1}$  to symmetric deformation of methyl  $\text{CH}_3$ ,<sup>[32]</sup> 1362  $\text{cm}^{-1}$  to symmetric deformation of  $\text{CH}_3$ ,<sup>[33]</sup> 1296  $\text{cm}^{-1}$  to the asymmetric deformation of  $\text{CH}_2$ ,<sup>[32]</sup> 1234  $\text{cm}^{-1}$  to the aromatic ether  $\phi\text{-O-C}$ ,<sup>[32]</sup> 1179  $\text{cm}^{-1}$ , 1105  $\text{cm}^{-1}$  and 1038  $\text{cm}^{-1}$  to the deformation of aromatic  $\text{CH}$ <sup>[25,32]</sup> and finally 828  $\text{cm}^{-1}$  to the out-of-plane-deformation of aromatic  $\text{CH}$ .<sup>[25]</sup>

**Figure 7** shows three characteristic peaks in the FT-IR spectra of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride. First, the intensity of the peak between 3480  $\text{cm}^{-1}$  and 3440  $\text{cm}^{-1}$  increases significantly for stoichiometric ratios above  $R = 0.9$  (see **Figure 7 A**). This peak is attributed to the O-H bond within the carboxyl group, which is found in the rosin-based anhydride. Next, a new peak emerges in the FT-IR spectrum at 1778  $\text{cm}^{-1}$  above a stoichiometric ratio of  $R = 0.9$  (see **Figure 7 B**). Several previous works<sup>[22,25,33–35]</sup> attribute this peak to the asymmetric stretching of the carbonyl group  $\text{C}=\text{O}$  in the rosin-based anhydride. Last, a double peak can be seen in the spectrum at about 945  $\text{cm}^{-1}$ , which also only occurs at a stoichiometric ratio of  $R > 0.9$  (see **Figure 7 C**). This peak can also

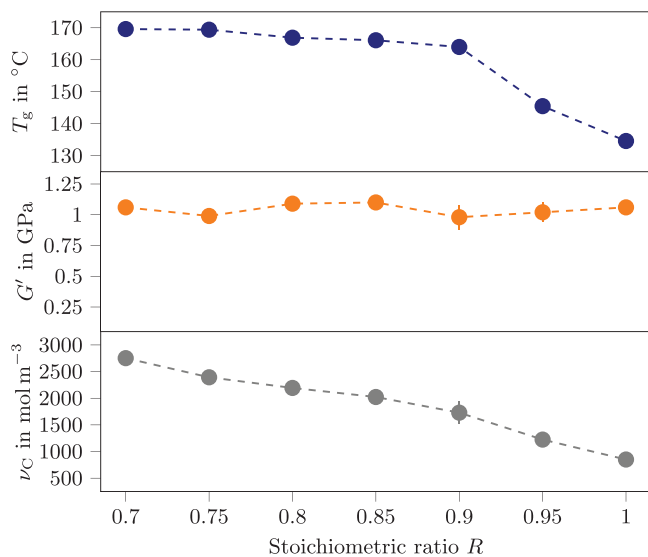
be assigned to the carboxylic acid of the rosin-based anhydride, more specifically to the out-of-plane O–H bend.

These results suggest that above a stoichiometric ratio of  $R = 0.9$ , unreacted anhydride and carboxyl groups are present in the material. This in turn would imply that unreacted rosin-based anhydride groups remain in the cured resin, which contains both anhydride and carboxyl groups. This is also supported by the DSC thermograms: as the content of the curing agent increases, fewer and fewer epoxy groups are present in the material to react with the anhydride and unreacted anhydride and carboxyl groups remain in the cured material. However, the optimal stoichiometric ratio for epoxy resins cured with conventional, petroleum-based anhydrides, like maleic anhydride and trimellitic anhydride, that do not contain a carboxyl group is usually about  $R = 0.8$  to  $0.9$ .<sup>[23,36]</sup> In conclusion, the carboxyl group has a significant effect on the reaction kinetics and therefore on the optimal stoichiometric ratio for epoxy resins cured with rosin-based anhydrides.

#### 2.4. Dynamic Mechanical Analysis

**Figure 8** shows the glass transition temperature  $T_g$ , the storage modulus at  $T = 30$   $^\circ\text{C}$ , and the cross-link density  $\nu_c$  of DGEBA

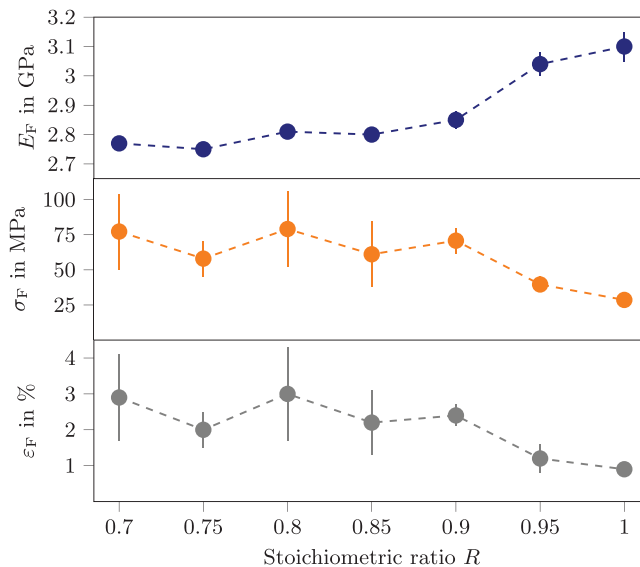




**Figure 8.** Glass transition temperature  $T_g$ , storage modulus  $G'$  at  $T = 30$   $^{\circ}\text{C}$  and cross-link density  $\nu_c$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

cured with different stoichiometric ratios of the rosin-based anhydride. Here,  $T_g$  plateaus between 170.3  $^{\circ}\text{C}$  (R70) to 164.0  $^{\circ}\text{C}$  (R90) with the tendency to slightly decrease with increasing  $R$  values. Above a stoichiometric ratio of  $R = 0.9$ ,  $T_g$  drops to 134.6  $^{\circ}\text{C}$  (R100). The maximum value of  $T_g$  at 170.3  $^{\circ}\text{C}$  is not as high as the  $T_g$  of 186.1  $^{\circ}\text{C}$  at a stoichiometric ratio of  $R = 1.00$  reported by Liu et al. for MPA-cured DGEBA.<sup>[10]</sup> In contrast, Wang et al. reported a  $T_g$  of 114.0  $^{\circ}\text{C}$  for MPA-cured DGEBA at  $R = 1.00$ , which is significantly lower than the  $T_g$  (134.6  $^{\circ}\text{C}$ ) in this study.<sup>[15]</sup> The plateau of  $T_g$  between  $R = 0.70$  and  $R = 0.90$  indicates that in this range, the conversion remains high despite increasing  $R$  and possible excess epoxide. This could be due to different reaction mechanisms that may occur in the Lewis base-catalyzed reaction between the anhydride and epoxy resin, the distribution of which depends on the type of curing agent and accelerator, the ratio of curing agent and accelerator, and the reaction temperature.<sup>[13]</sup> It is known that excess epoxy groups are advantageous to provide sufficient hydroxyl groups for transesterification.<sup>[37]</sup> For this reason, a slight excess of epoxy is preferable to an excess of curing agent in both anhydride-cured and amine-cured epoxy resin systems, as this can lead to a reduction in  $T_g$  and other properties.<sup>[38]</sup> The sudden drop in  $T_g$  above  $R = 0.90$  might be due to unreacted rosin-based anhydride in the network, which exerts a plasticizing effect and forms pendant chains.<sup>[39]</sup>

The storage modulus  $G'$  stays in the range of 0.97 GPa and 1.15 GPa over the entire range of stoichiometric ratios. The fact that the storage modulus  $G'$  remains approximately the same at  $T = 30$   $^{\circ}\text{C}$  might be because the decreasing network density is compensated by the steric hindrance of unreacted groups in the cured material. Here, the storage modulus  $E'$  of non-filled thermosets in the glassy region is about 3 GPa.<sup>[40]</sup> For comparison, Xu et al. cured solid epoxy resin (E-12) with MPA at a stoichiometric ratio of  $R = 0.33$  and measured its storage modulus  $E'$  in single cantilever mode (1.26 GPa).<sup>[14]</sup> The Young's modulus  $E$  is related to the shear modulus  $G$  by multiplying the term  $2(1 + \nu)$ ,<sup>[41]</sup> in



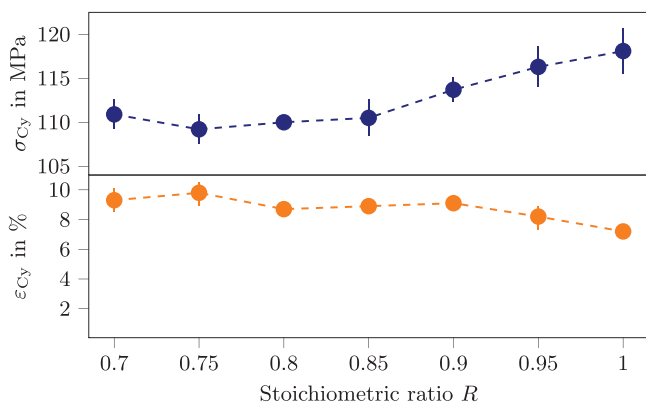
**Figure 9.** Flexural modulus  $E_F$ , flexural strength  $\sigma_F$  and fracture strain  $\epsilon_F$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

which  $\nu$  is the Poisson's ratio (usually about 0.35 in the polymer's glassy state<sup>[42]</sup>). Thus, it is apparent that the storage modulus  $G'$  in this study is considerably higher.

Meanwhile,  $\nu_c$  decreases continuously and almost linearly with increasing  $R$ . This trend in cross-link density was also observed by Chen et al.<sup>[11]</sup> who cured epoxidized soybean oil with MPA at various stoichiometric ratios. Conversely, this also means that as  $R$  increases, the storage modulus in the rubbery state decreases, since it is directly proportional to  $\nu_c$  (see Equation 1). The constant increase in cross-link density with decreasing  $R$  shows that the optimal stoichiometric ratio for high  $\nu_c$  and therefore high  $T_g$  might not be in the range of  $R = 0.7$  to 1.0. As already mentioned in Section 2.3, the optimal  $R$  for epoxy resins cured with conventional anhydrides is about 0.8.<sup>[43,44]</sup> In conclusion, the carboxyl group of the resin acids has a significant influence on the curing kinetics and the resulting network structure. Interestingly,  $T_g$  plateaus despite the constant change in  $\nu_c$ , which indicates that the glass transition temperature is not only influenced by  $\nu_c$  but also by the types of chemical bonds that form and the ratio between the aromatic epoxy resin and the cyclic curing agent.

## 2.5. Three-Point Bending

**Figure 9** shows the flexural modulus  $E_F$ , flexural strength  $\sigma_F$  and fracture strain  $\epsilon_F$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride. Here, the flexural modulus at  $R \leq 0.9$  remains relatively constant, ranging between 2.75 GPa and 2.91 GPa. For higher  $R$ , the flexural modulus increases up to 3.10 GPa (R100) that is slightly lower than that of DGEBA cured with MHPA (3.39 GPa).<sup>[45]</sup> An increase in  $E_F$  with increasing  $R$  was also observed by Chen et al.<sup>[11]</sup> who cured epoxidized soybean oil with MPA. The increase in flexural modulus is attributed to the steric hindrance of unreacted functional groups, showing that



**Figure 10.** Compression yield strength  $\sigma_{Cy}$  and compression yield strain  $\epsilon_{Cy}$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

above  $R = 0.9$  there are unreacted carboxyl and anhydride groups in the thermosets' networks (see Section 2.3).

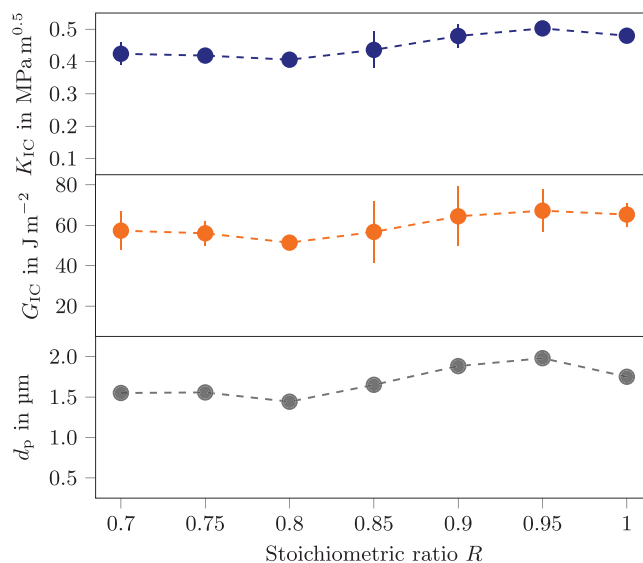
The flexural strength and flexural strain fluctuate between 58 MPa and 79.1 MPa, and 2.0% and 3.0%, respectively for  $R$  between 0.7 to 0.9. Here, R80 possesses the highest  $\sigma_F$  (79.1 MPa) and  $\epsilon_F$  (3.0%). For higher  $R$ ,  $\sigma_F$ , and  $\epsilon_F$  decrease significantly down to 28.6 MPa and 0.9%, respectively. The variations in the flexural strength and flexural strain could result from inclusions and defects in the material. These form due to the low latency of the imidazole-accelerator and the high viscosity of the epoxy-MPA mixtures (see Section 2.2). In contrast, DGEBA cured with MHPA shows a flexural strength and flexural strain of 131.6 MPa and 4.4%, respectively.<sup>[45]</sup>

## 2.6. Compression Tests

**Figure 10** shows the compression yield strength  $\sigma_{Cy}$  and compression yield strain  $\epsilon_{Cy}$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride. Here,  $\sigma_{Cy}$  at  $R \leq 0.85$  is relatively constant at about 110 MPa. This value agrees well with the results of Altuna et al.<sup>[46]</sup> who cured DGEBA with a petroleum-based anhydride. Above  $R = 0.85$ , the strength increases and reaches 118.1 MPa. The steric hindrance of unreacted carboxyl and anhydride functional groups above  $R = 0.85$  increases the stress that is necessary for the onset of plastic deformation. On the other hand,  $\epsilon_{Cy}$  decreases constantly with increasing  $R$ .

## 2.7. Fracture Toughness

**Figure 11** shows the critical stress intensity factor in mode I  $K_{IC}$ , fracture energy  $G_{IC}$  and diameter of the plastic zone  $d_p$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride. Here, the  $K_{IC}$  values initially remain relatively constant at about 0.42 MPa  $m^{0.5}$  and increase from a stoichiometric ratio of  $R = 0.90$  up to 0.50 MPa  $m^{0.5}$  (R95). The changes in  $K_{IC}$  values can be explained by the increase in flexural modulus and the decrease in cross-link density. By decreasing  $v_C$ , the network segments between cross-links become larger. In turn, the network becomes



**Figure 11.** Critical stress intensity factor in mode I  $K_{IC}$ , fracture energy  $G_{IC}$  and diameter of the plastic zone  $d_p$  of DGEBA cured with different stoichiometric ratios of the rosin-based anhydride.

less rigid and the thermoset becomes less brittle.<sup>[47–49]</sup> For a further increase in  $R$  values, the  $K_{IC}$  values drop slightly to 0.48 MPa  $m^{0.5}$ . The reason for this might be the formation of defects as a result of the combined effect of the mixtures' high viscosity and low latency (see Sections 2.1 and 2.2). The  $K_{IC}$  is slightly lower than that of DGEBA cured with MHPA (0.57 MPa  $m^{0.5}$ ).<sup>[50]</sup> The  $G_{IC}$  values follow the trend of the  $K_{IC}$  values, and increase from about 56  $J m^{-2}$  to 67  $J m^{-2}$  at  $R = 0.95$ . Above this stoichiometric ratio, the value decreases again to 65  $J m^{-2}$ . Similar to the  $K_{IC}$  value, the  $d_p$  remains relatively constant for  $R$  in between 0.7 and 0.85, then increases at  $R > 0.85$ , and then decreases again at  $R = 1.00$ . Here, a maximum value of 1.98  $\mu m$  is reached at  $R = 0.95$ .

## 3. Conclusion

In the present study, the influence of the stoichiometric ratio on the curing kinetics and mechanical properties of DGEBA cured with a rosin-based anhydride was examined. The results of DSC and FT-IR analyses, along with the mechanical characterization indicate that above a stoichiometric ratio of 0.9, unreacted anhydride groups are present in the thermoset's network. As a result, the network density decreases and the glass transition temperature drops significantly. On the other hand, the steric hindrance of unreacted functional groups for  $R \geq 0.9$ , increases the flexural modulus, and the reduced network density improves fracture toughness. In conclusion, the carboxyl group of the rosin-based anhydride has a significant influence on the curing kinetics, network structure, and the resulting mechanical properties. Judging from the increase in network density with decreasing  $R$ , the optimal stoichiometric ratio for high  $T_g$  is not in-between 0.7 and 1.0.

The evaluation of the results indicates that the best stoichiometric ratio for overall high mechanical performance and good processability is preferably low ( $R \leq 0.7$ ). Here, a low  $R$  results in a high  $T_g$  and good processability due to a low viscosity. However,

the latency of the mixtures is low, and therefore the mixtures are not fit for processing via prepreg technology. As a consequence of choosing a low stoichiometric ratio, the bio-content of the mixtures is also low (see Table 1).

In conclusion, the rosin-based anhydrides could be used to replace conventional, petroleum-based anhydrides in applications in which high latency is not required and high viscosities are tolerable during processing. The results show that a further in-depth investigation of thermosets with a stoichiometric ratio lower than  $R = 0.7$  is necessary.

## 4. Experimental Section

**Materials:** D.E.R. 331 with an epoxy equivalent weight of  $187 \text{ g mol}^{-1}$  was purchased from Blue Cube Assets GmbH & Co. KG, Olin Epoxy (Stade, Germany). Bre-mar RK 7652 with a molecular weight of  $515 \text{ g mol}^{-1}$  (bio-content 86% by mass) from Robert Kraemer GmbH & Co. KG (Rastede, Germany) served as rosin-based anhydride curing agent. 2-Ethyl-4-methyl-imidazole with a purity of 95% was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

**Resin Formulation:** The rosin-based anhydride Bre-mar RK7652 was mixed with DGEBA according to Table 1 in a 250 mL flask and melted in a silicone oil bath for 60 min under occasional stirring until a homogeneous mixture formed. Afterward, the mixture was poured into a 180 mL speed mixer cup and cooled down to  $90^\circ\text{C}$  in a water bath with  $25^\circ\text{C}$ . The temperature was controlled with an infrared thermometer at two minute time intervals. Then, 1 wt.% of 2-ethyl-4-methyl-imidazole was added to the mass before mixing in a DAC 150.1 FVZ dual asymmetric centrifuge speed mixer from Hauschild Engineering (Hamm, Germany) at  $1500 \text{ min}^{-1}$  for 1 min. For the sake of simplicity, individual mixtures were addressed according to the labels in Table 1.

**Curing Cycle and Sample Preparation:** The mixture of epoxy resin, the rosin-based anhydride and imidazole was poured into aluminum molds that were preheated at  $90^\circ\text{C}$ . Subsequently, the material system was cured for 2 h at  $120^\circ\text{C}$  and 2 h at  $170^\circ\text{C}$  in a Memmert ULE 400 convection oven from Memmert GmbH + Co. KG (Schwabach, Germany). The molds were then cooled to room temperature over 4 h to prevent the build-up of residual stresses. The specimens were prepared from the cured plates according to the ISO standards for each test method with a Mutronic DIADISC5200 diamond plate saw from MUTRONIC Präzisionsgerätebau GmbH & Co. KG (Rieden am Forggensee, Germany).

**Differential Scanning Calorimetry:** The curing kinetics and  $T_g$  were analyzed via dynamic DSC measurements carried out with a Mettler Toledo DSC 1 from Mettler Toledo (Columbus, Ohio, USA) with nitrogen flow set to  $50 \text{ mL min}^{-1}$  and three different heating rates ( $5$ ,  $10$ , and  $20 \text{ K min}^{-1}$ ). The sample mass was  $10 \pm 2 \text{ mg}$ , and two specimens were measured to ensure adequate reproducibility.

**Table 1.** Compositions of mixtures of DGEBA and Bre-mar RK7652 with different stoichiometric ratios ( $R$ ) as well as the resulting bio-content.

Label	$R$	D.E.R. 331 (wt.%)	Bre-mar RK7652 (wt.%)	2E4M-Imidazole (wt.%)	Bio-content (%)
R70	0.70	48.59	50.41	1	41.8
R75	0.75	50.30	48.70	1	43.3
R80	0.80	51.90	47.10	1	44.6
R85	0.85	53.39	45.61	1	45.9
R90	0.90	54.79	44.21	1	47.1
R95	0.95	56.11	42.89	1	48.3
R100	1.00	57.35	41.65	1	49.3

**Rheometry:** The effect of the stoichiometric ratio on the viscosity was measured with an Anton Paar MCR 302 (Graz, Austria) plate–plate rheometer. The plate diameter was 25 mm and the gap between plates was set to 1 mm. A constant heating rate of  $3 \text{ K min}^{-1}$  from  $40^\circ\text{C}$  to  $180^\circ\text{C}$  was used. The shear amplitude was set to 5% with a shear frequency of  $1 \text{ rad s}^{-1}$ .

**Fourier-Transform Infrared Spectroscopy:** FT-IR was performed using a Nicolet iS50 FT-IR spectrometer from Thermo Fisher Scientific Inc. (Waltham, Massachusetts, USA) in a wave-number range from  $500 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  and 32 scans per sample were accumulated in transmission mode.

**Dynamic Mechanical Analysis:** Dynamic mechanical analysis was conducted on a Rheometric Scientific RDA III from TA Instruments Inc. (New Castle, Delaware, USA). Three specimens per stoichiometric ratio with dimensions 50 mm by 10 mm by 2 mm were measured in a temperature range from  $T = 25^\circ\text{C}$  to  $225^\circ\text{C}$  with a constant heating rate of  $3 \text{ K min}^{-1}$ . The shear amplitude was set to 0.1% in combination with a shear frequency of 1 Hz. Here, the glass transition temperature  $T_g$  was chosen as the temperature at which the loss factor  $\tan \delta$  has its peak value. The cross-link density of the thermoset  $\nu_c$  in the rubbery state was calculated as:

$$\nu_c = \frac{G'}{RT} \quad (1)$$

with the storage modulus  $G'$  at  $T = T_g + 50 \text{ K}$  and the universal gas constant  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>[47]</sup>

**Three-Point Bending:** For the three-point bending tests, six specimens with dimensions 80 mm by 10 mm by 4 mm were tested with a cross-head speed of  $2 \text{ mm min}^{-1}$  according to ISO 178. Three-point bending tests were carried out on a ZwickRoell Z2.5 universal testing machine from ZwickRoell GmbH & Co. KG (Ulm, Germany) using a load cell with a capacity of 2.5 kN.

**Compression Tests:** The compression strength was investigated according to EN ISO 604 on specimens with dimensions 10 mm by 10 mm by 4 mm. Ten specimens were tested with a cross-head speed of  $5 \text{ mm min}^{-1}$  on a ZwickRoell Z020 universal testing machine from ZwickRoell GmbH & Co. KG (Ulm, Germany) with a load cell with a capacity of 20 kN.

**Fracture Toughness:** The critical stress intensity factor in mode I  $K_{IC}$  and fracture energy  $G_{IC}$  were determined by testing four compact tension specimens according to ISO 13586 on a ZWICK Z2.5 from ZwickRoell GmbH & Co. KG (Ulm, Germany) equipped with a load cell with a capacity of 2.5 kN. The fracture energy was calculated from  $K_{IC}$  via:

$$G_{IC} = \frac{K_{IC}^2}{E} (1 - \nu^2) \quad (2)$$

with Young's modulus  $E$  taken from three-point bending and Poisson's ratio  $\nu$ , which is about 0.35 in the glassy state of the thermoset.<sup>[42]</sup>

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## Conflict of Interest

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.

## Keywords

bio-based resins, epoxy resins, maleopimaric acid, mechanical properties, rosin, stoichiometric ratios, sustainability

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