MANUFACTURE OF COMPOSITES BASED ON THERMOSETS AND RENEWABLES

M. Döring[1], L. Zang[2], U. Arnold[2*]

[1]Deutsches Kunststoff-Institut, Schloßgartenstraße 6, 64289 Darmstadt, Germany
[2]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
*ulrich.arnold@kit.edu

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Abstract
Composite materials based on epoxy resins and renewables, e.g. different lignins, cellulose and starch, were prepared and the corresponding curing reactions were investigated, mainly by DSC measurements. Some of the most important curing methods were employed, i.e. polymerization or polyaddition with carboxylic acid anhydrides and amines. A systematic study was carried out focusing on high contents of renewables and compatibility of the biopolymers with other components in the formulations. Several other important parameters such as different polymerization initiators, hardeners and accelerators, curing conditions and highly variable compositions of the materials were also investigated.

1 Introduction

Considering the shortage of fossil resources coming along with steadily increasing commodity prices, fabrication of polymeric materials from renewable resources is very attractive and numerous research activities are currently dedicated to this seminal topic [1]. Further advantages of this strategy are reduced climate impact and the possibility to obtain biodegradable materials. Regarding biopolymers, one has to distinguish between man-made polymers produced from biomass-derived monomers and naturally occurring polymers, also denoted as biological polymers [2]. The former class can be divided into conventional polymers such as polyethylene, polyurethane or polyamide, and currently expanding developments such as polylactic acid or polyhydroxybutyrate. Prominent examples for the latter class are lignin, cellulose and starch in various types. In principal, all biopolymers can be further modified by various processing steps thus offering an enormous potential for the development of new materials.

Within this work, composite materials comprising epoxy resins and renewables, e.g. different types of lignin, cellulose and starch, were investigated. Various curing agents such as imidazoles, carboxylic acid anhydrides and amines were employed [3]. Depending on the curing agent, very different materials were obtained. Thus, curing by anionic polymerization using small amounts of polymerization initiators yielded polyethers, whereas curing by polyaddition employing stoichiometric amounts of carboxylic acid anhydrides and amines yielded highly cross-linked polyesters and polyamines, respectively. A comprehensive study was carried out, covering different curing strategies, different biopolymers and a series of parameters, e.g. biopolymer contents, curing accelerators and curing conditions.

2 Experimental

Two epoxy resins, namely Epilox A 19-00 from LEUNA-Harze GmbH and Baxxores TM ER 2200 from BASF, were employed. The resins are based on the diglycidyl ether of bisphenol A (DGEBA) with epoxy equivalent weights around 182 g/eq. Different types of lignin, i.e. lignin alkali (Lignin 1), lignin alkali with a low sulfonate content (Lignin 2) and a desulfonated lignosulfonic acid sodium salt (Lignin 3) were purchased from Aldrich. Cellulose powder type 20 and conventional starch from potatoes were obtained from Sigma-Aldrich and Roth, respectively. N-methylimidazole (NMI) was obtained from FLUKA and methylhexahydrophthalic anhydride (MHHPA, EPODUR C609) was obtained from DUROPLAST-CHEMIE. 1-Ethyl-3-methyl-imidazolium-thiocyanate (EMIM-Thiocyanate) and tris-(3-aminopropyl)amine (TAPA) were obtained from BASF and zinc-2-ethylhexanoate was purchased from ABCR. API-Adipate was prepared by reacting N-(3-aminopropyl)-imidazole (API) with adipic acid in an equimolar ratio.

The resin formulations were prepared by mixing the components in a SpeedMixer^{TM} DAC 150 FVZ (Dual Asymmetric Centrifuge) from Hauschild & Co. KG or a laboratory dissolver DISPERMAT$^{®}$ CA60-1 from VMA-Getzmann GmbH. Curing of the resin systems was investigated by Differential Scanning Calorimetry (DSC) using a Mettler Toledo DSC822^{e} device. Measurements were carried out under nitrogen using typically 3-10 mg resin samples with a heating rate of 10 °Cmin^{-1} and onset temperatures of the exothermic processes T_o (tangent onset), peak maxima T_p and polymerization enthalpies ΔH were recorded. Glass transition temperatures T_g were also determined by DSC according to DIN 53765. Relative resin viscosities were measured using a GELNORM$^{®}$-RVN device from Gel Instrumente AG.

3 Results and discussion

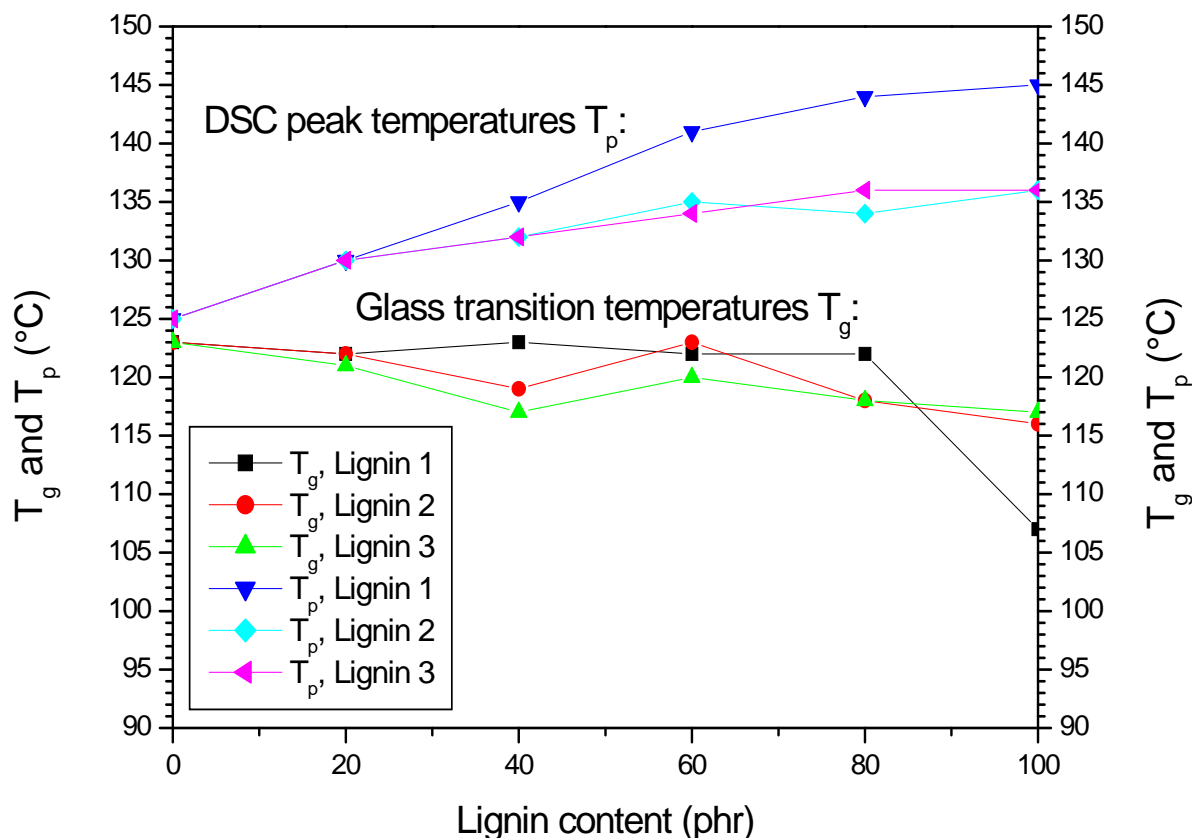### 3.1 Curing of DGEBA-Lignin formulations by anionic polymerization

Three different polymerization initiators were tested in the curing of DGEBA and DGEBA-Lignin mixtures with a lignin content of 40 phr (Table 1). DSC data were recorded and most promising results concerning reactivity and T_g were obtained employing NMI as initiator (Table 1, entries 1, 4, 7 and 10).

No.	Filler (40 phr)	Initiator (5 phr)	DSC data			
			T_o (°C)	T_p (°C)	ΔH (Jg^{-1})	T_g (°C)
1	–	NMI	109	125	661	123
2	–	API-Adipate	132	139	552	141
3	–	EMIM-Thiocyanate	93	123	533	127
4	Lignin 1	NMI	115	135	447	123
5	Lignin 1	API-Adipate	129	153	349	87
6	Lignin 1	EMIM-Thiocyanate	140	162	406	116
7	Lignin 2	NMI	112	132	457	119
8	Lignin 2	API-Adipate	129	151	330	98
9	Lignin 2	EMIM-Thiocyanate	104	126, 151, 192	298	107
10	Lignin 3	NMI	113	132	466	117
11	Lignin 3	API-Adipate	132	157, 220	387	106
12	Lignin 3	EMIM-Thiocyanate	103	127, 148	385	91

Table 1. Curing of DGEBA-Lignin formulations employing different polymerization initiators (Typical curing conditions before T_g determination: 0.5 h at 40, 60, 80, 100, 120 and 140 °C).

Further experiments with NMI as initiator and variable contents of lignin in the resin formulations were carried out (Fig. 1). Obviously, curing is significantly influenced by the

lignin type. Reactivity of the formulations in terms of T_p decreases remarkably with increasing lignin content, especially in the case of Lignin 1. Using this lignin, T_g's do not vary significantly up to a lignin content of 80 phr while in the case of Lignin 2 and 3 T_g's decrease approximately 10 °C up to a lignin content of 100 phr.
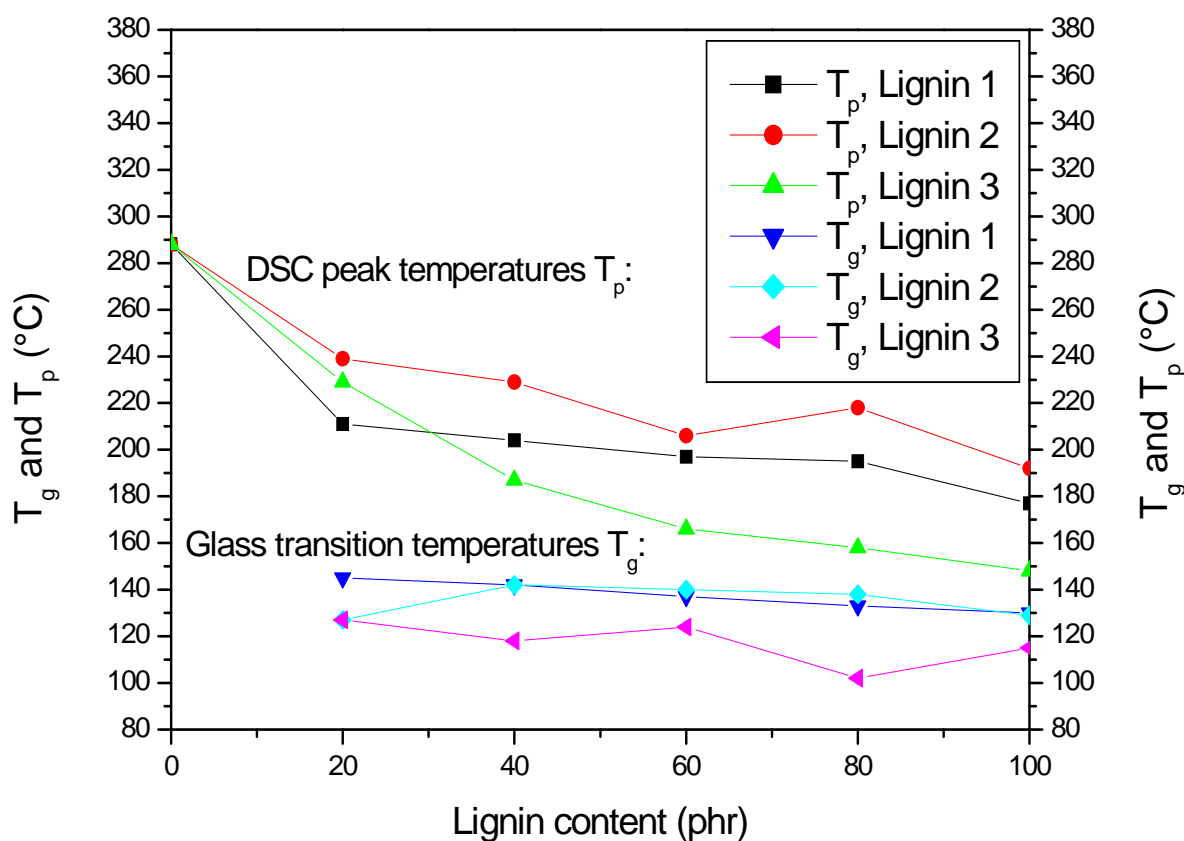

Figure 1. Curing of DGEBA-Lignin formulations employing NMI as polymerization initiator (5 phr of NMI; Typical curing conditions before T_g determination: 0.5 h at 40, 60, 80, 100, 120 and 140 °C).

3.2 Curing of DGEBA formulations with variable amounts of lignin, cellulose and starch by polyaddition with MHHPA

Curing of DGEBA-Lignin mixtures with stoichiometric amounts of MHHPA was investigated with a focus on the influence of lignin type and content on T_p and T_g (Table 2 and Fig. 2). Usually, the use of accelerators is necessary to support the curing reaction (see entries 1 and 2 in Table 2). In the presence of lignin no additional accelerator is necessary (Table 2, entries 3, 5 and 7) indicating that lignin is involved in the curing reaction. Employing a common accelerator such as zinc-2-ethylhexanoate, no accelerating effect was observed in the case of Lignin 2 and 3 (Table 2, entries 6 and 8) and in the case of Lignin 1 and 2, T_g's decrease significantly if an accelerator is employed (Table 2, entries 4 and 6). Comparing the systems without accelerator (Table 2, entries 3, 5 and 7 and Fig. 2), only T_g's of resins containing Lignin 3 are affected. In contrast to the polymerizing systems described above, the resins get more reactive with increasing lignin content (Fig. 2).

No.	Filler (40 phr)	Accelerator (1 phr)	DSC data			
			T_o (°C)	T_p (°C)	ΔH (Jg^{-1})	T_g (°C)
1	–	No	266	288	No sufficient curing	
2	–	Yes	147	169, 228	339	138
3	Lignin 1	No	169	204	394	142
4	Lignin 1	Yes	143	190	357	123
5	Lignin 2	No	182	229	254	142
6	Lignin 2	Yes	203	240	267	130
7	Lignin 3	No	124	187	356	118
8	Lignin 3	Yes	119	193	284	122

Table 2. Curing of DGEBA-Lignin formulations with MHHPA in the absence and presence of zinc-2-ethyl-hexanoate as accelerator (Curing conditions before T_g determination: 3 h at 100 °C and 2 h at 150 °C).
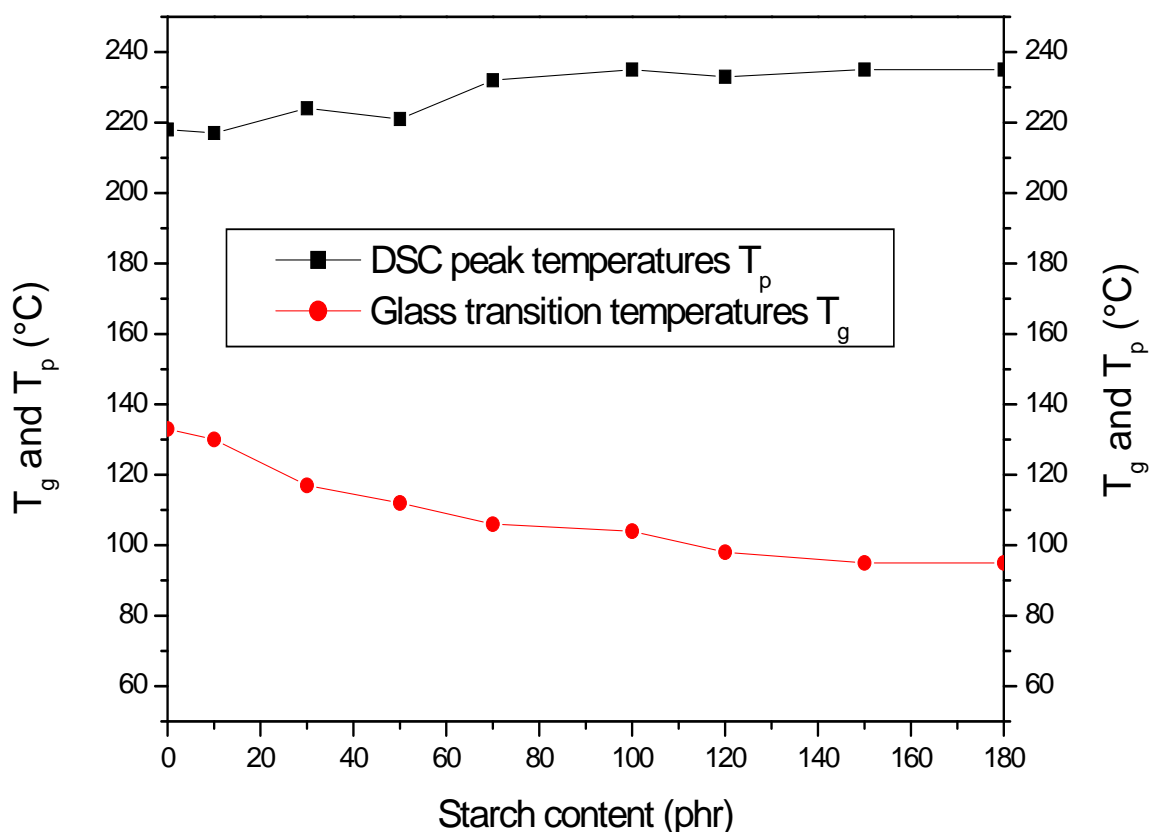

Figure 2. Curing of DGEBA-Lignin formulations employing MHHPA without accelerator (Typical curing conditions before T_g determination: 3 h at 100 °C and 2 h at 150 °C).

Analogous work was carried out employing cellulose instead of lignin (Table 3). Since curing was not efficient without accelerator, zinc-2-ethylhexanoate was added. T_p's are not influenced even up to a cellulose content of 90 phr while T_g's decrease significantly with increasing cellulose loading. However, the resulting materials are very brittle and it can be stated that the employed cellulose is not compatible with such resin systems under the chosen reaction conditions.

No.	Cellulose content	DSC data			
	(phr)	T_o (°C)	T_p (°C)	ΔH (Jg^{-1})	T_g (°C)
1	–	147	169, 228	339	138
2	10	145	164, 219	311	Not detected
3	30	142	180, 227	282	135
4	50	135	229	248	Not detected
5	70	130	234	265	119
6	90	125	229	264	120

Table 3. Curing of DGEBA-Cellulose formulations with MHHPA employing 1 phr of zinc-2-ethylhexanoate as accelerator (Typical curing conditions before T_g determination: 3 h at 100 °C and 2 h at 150 °C).

Curing of DGEBA with MHHPA in the presence of starch was also investigated with high starch loadings up to 180 phr (Fig. 3). Initial experiments revealed that, like in the case of DGEBA-Cellulose mixtures, an accelerator has to be used to improve the curing reactions. T_p's slightly increase with increasing starch content while T_g's decrease significantly. Similar to the analogous systems containing cellulose, the resulting materials are very brittle and thus, applicability of such systems is, without further modification, limited.
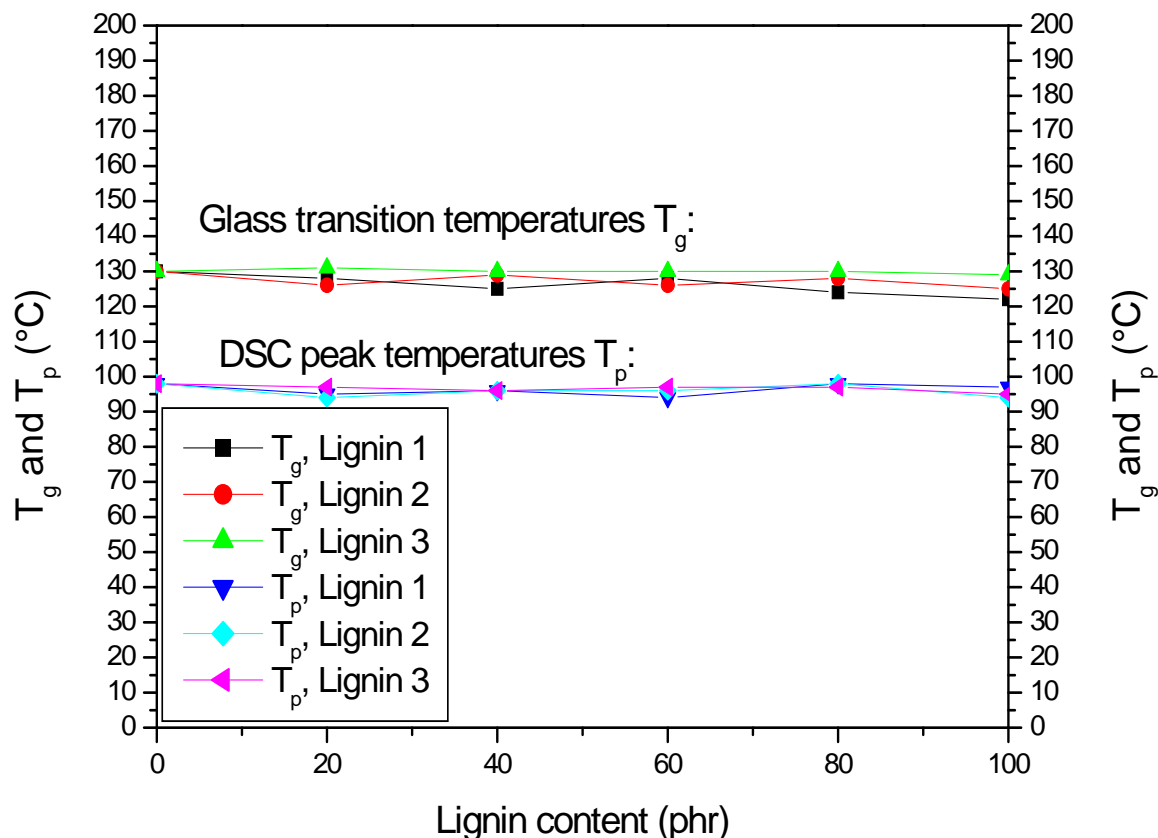

Figure 3. Curing of DGEBA-Starch formulations with MHHPA employing 1 phr of zinc-2-ethylhexanoate as accelerator (Typical curing conditions before T_g determination: 3 h at 100 °C and 2 h at 150 °C).
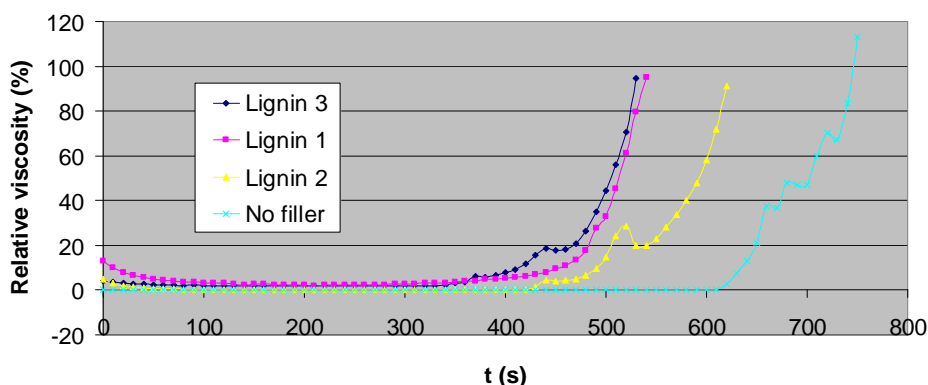
3.3 Curing of DGEBA-Lignin formulations by polyaddition with TAPA
Besides polymerization and anhydride curing, polyaddition with amines is another important strategy for the hardening of epoxy resins. A wide variety of amines is available and processing as well as material properties can be tuned to a large extent by choice of

appropriate amine hardeners. Within this work, TAPA was chosen as hardener due to its good performance in several applications. The influence of lignin type and content on curing and T_g's was investigated and the lignin content in the formulations was successively increased up to 100 phr (Fig. 4). Almost no influence of the lignin type was observed and T_g's as well as T_p's remain in the same range. Differences between the reference formulation without lignin and the formulations containing lignin are also narrow. It can be seen from relative viscosities that the curing reactions are slightly accelerated in the presence of lignin (Fig. 5).

Figure 4. Curing of DGEBA-Lignin formulations with TAPA (Typical curing conditions before T_g determination: 0.5 h at 40, 60, 80 and 100 °C and 1.5 h at 120 °C).

Figure 5. Relative viscosities in the curing reactions of DGEBA-Lignin formulations with TAPA.

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Conclusion

The results showed that, on the one hand, the limited miscibility of biopolymers with other components in the formulations, their reduced thermal stability as well as their distinct hygroscopicity can be drawbacks. This is especially pronounced in the case of high bio-polymer loadings. On the other hand, promising material properties were observed and these could be realized using comparatively low-cost components. For instance, in many cases glass transition temperatures were almost not affected even at high biopolymer contents and fracture toughness could be remarkably enhanced. Ongoing work focuses on a detailed characterization of the composite materials, lower contents of renewables in the formulations, investigations on the influence of particle sizes, chemically modified biopolymers and the development of fibre-reinforced composites based on such modified resin matrices.

References

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