

DEVELOPMENT OF COMPOSITES FROM EPOXY RESINS AND BIOPOLYMERS

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Keywords: Epoxy resins, lignin, cellulose, starch

Abstract

Epoxy resin-biopolymer formulations (biopolymer = lignin, cellulose or starch) were prepared employing a DGEBA resin, an epoxy novolac and mixtures of these two resins. High biopolymer loadings around 100 phr were adjusted and curing was accomplished with isophorone diamine as hardener. Curing processes were investigated by DSC and viscosity measurements. The resulting materials were characterized by TGA and glass transition temperatures were determined. Thermal stability of the materials remained high, even at high biopolymer loadings, and glass transition temperatures remained in the same range as those of the reference systems without biopolymer. Some epoxy resin-lignin formulations could be cured without any additional hardener, indicating that lignin was involved in the curing reaction.

1. Introduction

Within the broad class of thermosetting resins, epoxy resins certainly play a key role and applications are manifold, e.g. in the fields of coatings, composites, electrical laminates or adhesives [1]. Epoxy resins can be cured by various strategies and the properties of the resulting materials can be influenced to a large extent by choice of the hardeners [2]. Thus, imidazoles, carboxylic acid anhydrides or amines can be employed and the obtainable materials are, from a chemical point of view, polyethers, polyesters and polyamines, respectively [3]. Material properties also largely depend on processing parameters such as curing temperature and time, post-cure treatment or the mixing ratio of the components.

Further strategies to optimize the materials are the use of specialty resins and the use of extra components, e.g. additives, fillers or fibers [4,5]. Typical additives are flame-retardant compounds or additives to improve toughness, thermal resistance or mechanical strength. Regarding fibers, high-performance materials can be manufactured such as carbon fiber-reinforced systems for light-weight construction. To reduce material and processing costs, it is desirable to reach maximum performance with minimal amounts of high-cost components or, vice versa, maximum amounts of low-cost components. Another objective is that more than one benefit can be realized by employing one and the same additive. In the case of two and more additives, these should not only exhibit maximum compatibility but also interact in a synergistic manner. Regarding sustainability criteria, development of new materials or at least material components from renewable feedstocks is highly desirable and extensive research is currently dedicated to this approach [6,7].

Within this work, materials based on commercially available epoxy resins and biopolymers, e.g. lignin, cellulose and starch, are described. Very different biopolymer contents typically from 10 to around 100 phr were employed and thus the continuous transition from conventional epoxy resin systems, simply modified by bio-additives, to genuine epoxy resin-biopolymer composites with new properties was systematically investigated. Within one class of biopolymers the available materials can differ remarkably, depending on the raw materials and the production process. Especially in the case of lignin various types are available, which exhibit clear differences and therefore a series of lignin types was investigated and compared. Regarding curing, this work concentrates on the use of isophorone diamine (IPDA), which is an exemplary representative of the broad class of amine curing agents. The possibility of curing epoxy resin-lignin formulations without any additional hardener was also investigated.

2. Experimental

Two epoxy resins, namely Epilox A 18-00 from LEUNA-Harze GmbH and DEN 431 from Dow, were employed. The former is based on the diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight of 175-185 g/eq (viscosity at 25 °C: 8000-10000 mPa·s) and the latter is an epoxy novolac with an epoxy equivalent weight of 172-179 g/eq (viscosity at 52 °C: 1100-1700 mPa·s). Different types of lignin, i.e. lignin alkali (Lignin 1, $M_n \approx 5000 \text{ gmol}^{-1}$, $M_w \approx 28000 \text{ gmol}^{-1}$), lignin alkali with a low sulfonate content (Lignin 2, $M_n \approx 10000 \text{ gmol}^{-1}$, $M_w \approx 60000 \text{ gmol}^{-1}$) and a desulfonated lignosulfonic acid sodium salt (Lignin 3, $M_n \approx 5000 \text{ gmol}^{-1}$, $M_w \approx 12000 \text{ gmol}^{-1}$) were purchased from Aldrich. The lignins were pulverized by milling and powders with particle sizes below 80 μm were employed. Cellulose powder (Cotton-Linters, Type 20, 20 μm) was obtained from Sigma-Aldrich and starch (conventional starch from potatoes) was obtained from Carl Roth GmbH + Co. KG. All biopolymers were dried for several hours at 100 °C before use. Isophorone diamine (IPDA) was purchased from BASF SE.

The resin formulations were prepared by mixing the components in a SpeedMixerTM DAC 150 FVZ (Dual Asymmetric Centrifuge) from Hauschild & Co. KG or a laboratory dissolver DISPERMAT[®] CA60-1 from VMA-Getzmann GmbH. In the curing reactions with IPDA, stoichiometric amounts of the amine relating to the resin were used. Biopolymer contents in terms of parts per hundred (phr) refer to the epoxy resin, without hardener. Curing of the resin systems was investigated by Differential Scanning Calorimetry (DSC) using a Mettler Toledo DSC822[°] 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 reaction 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. Thermogravimetric analyses (TGA) were carried out employing a Mettler Toledo TGA/SDTA851[°] thermobalance. The heating rate was 10 °Cmin⁻¹ and nitrogen was used as inert gas.

3. Results and discussion

As already mentioned above, very different hardeners can be employed for the curing of epoxy resins. Formerly, we reported on the curing of epoxy resin-biopolymer formulations employing imidazoles and imidazolium salts, methylhexahydrophthalic anhydride and tris-(3-aminopropyl)amine [8]. For the work described here IPDA was chosen, which usually leads to materials with beneficial thermal and mechanical properties.

3.1. Curing of epoxy resin-lignin formulations with IPDA

Curing of DGEBA-based epoxy resin systems with IPDA was investigated and different lignins (see experimental part) as well as lignin contents were employed (Figure 1). DSC measurements showed that glass transition temperatures T_g and peak maxima T_p were only slightly influenced by the lignin type and the values remained constant or decreased weakly with increasing lignin content. T_g values remained remarkably high and T_g 's at around 155 °C were reached, even with high lignin loadings. Regarding the curing rate, measurements of relative viscosity at 80 °C with a lignin content of 60 phr revealed an accelerating effect of the lignins (Figure 2). This effect varies and depends on the lignin.

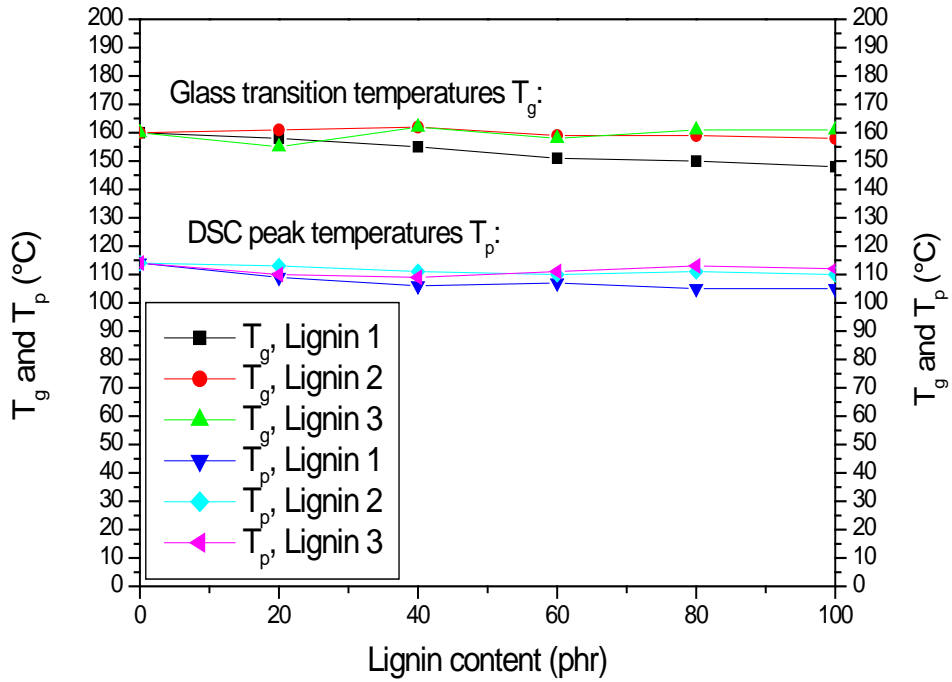


Figure 1. Curing of DGEBA-lignin formulations with IPDA: Influence of lignin type and content on T_g and T_p (curing temperatures before T_g determination: 16 h at room temperature, 0.5 h at 40 °C, 0.5 h at 60 °C, 0.5 h at 80 °C, 0.5 h at 100 °C, 0.5 h at 120 °C and 2 h at 140 °C).

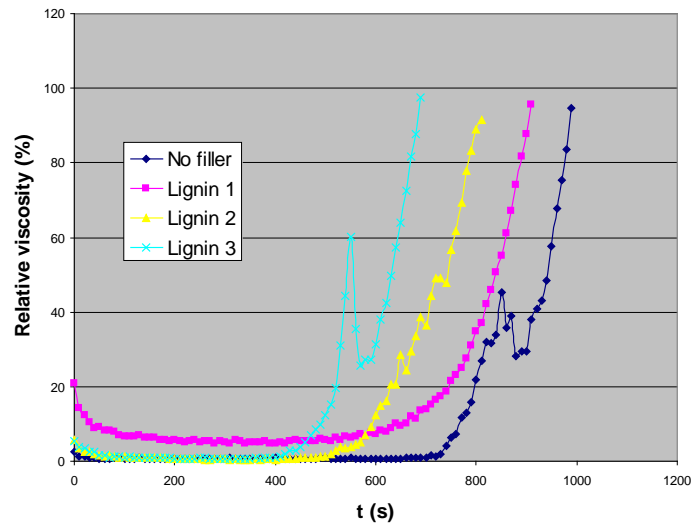


Figure 2. Curing of DGEBA-lignin formulations with IPDA: Time dependence of relative viscosity at 80 °C and 60 phr lignin loading.

Regarding thermal stability of the cured materials, TGA measurements with Lignin 1 showed that there is almost no difference between 40 and 80 phr lignin loading (Figure 3). Thus, thermal stability is not significantly reduced with increasing lignin content. Compared to the reference system without lignin, weight loss of the DGEBA-Lignin 1 systems is in the same range.

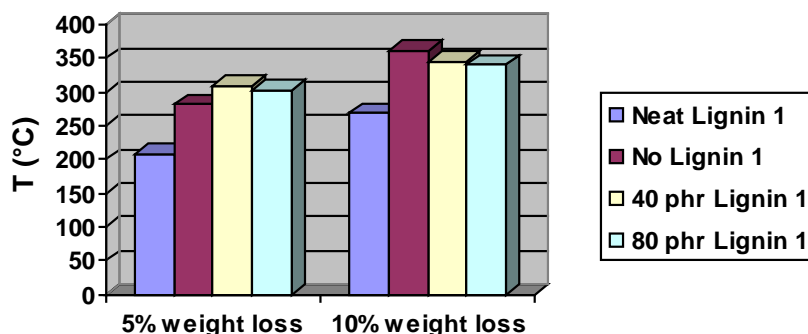


Figure 3. Curing of DGEBA-Lignin 1 formulations with IPDA: Thermal stability of the resulting materials according to TGA measurements (curing temperatures: see Figure 1).

In this context resin formulations comprising only DGEBA and Lignin 1, without any hardener, were also investigated. Variable contents of Lignin 1 up to 100 phr were employed and the curing of the formulations was studied by DSC (Table 1). Lignin contents below 30 phr did not lead to significant curing but from 30 phr on distinctive peaks and reaction enthalpies were observed. Up to a lignin loading of 70 phr three peaks were detected indicating a multistep curing process. In the range from 80 to 100 phr only two peaks occur. In all cases, the peak at around 148 °C is comparatively weak and the following peaks are dominating. It is remarkable that the main reaction peak is shifting from 266 (30 phr of Lignin 1) to 184 °C (90 phr of Lignin 1) indicating an enhanced curing rate. The increase of T_p from 184 (90 phr of Lignin 1) to 207 °C (100 phr of Lignin 1) is probably due to the low resin content in the overall formulation and this assumption is supported by the distinctive decrease of ΔH from 230 to 199 Jg⁻¹. Regarding ΔH values at lower lignin contents, an increase up to 267 °C is observed (50 phr of Lignin 1) followed by a significant decrease. T_g 's increase remarkably from 95 (30 phr of Lignin 1) to 141 °C (90 phr of Lignin 1) and finally decrease to 135 °C (100 phr of Lignin 1). It is worth mentioning that no comparable curing was observed employing Lignin 2 and Lignin 3.

Entry	Lignin 1 content (phr)	DSC data			
		T_o (°C)	T_p (°C)	ΔH (Jg ⁻¹)	T_g (°C)
1	30	125	147, 224, 266	254	95
2	40	121	146, 218, 261	259	106
3	50	121	149, 215, 260	267	117
4	60	120	146, 212 , 257	237	121
5	70	128	149, 197 , 260	221	125
6	80	130	149, 185	223	138
7	90	128	147, 184	230	141
8	100	120	142, 207	199	135

Table 1. DSC data for the curing of DGEBA-Lignin 1 formulations without additional hardener (curing temperatures before T_g determination: 20 min at 80 °C, 20 min at 120 °C, 1 h at 140 °C and 4 h at 160 °C; values in bold: main reaction peaks).

3.2. Curing of epoxy resin-cellulose formulations with IPDA

In addition to epoxy resin-lignin formulations, analogous formulations with cellulose were studied. Different resins, namely DGEBA, an epoxy novolac and mixtures of both resins were employed (Figure 4). T_g 's do not vary strongly and are typically around 155 °C. Reactivity of the formulations in terms of T_p 's decrease in the order novolac > DGEBA > novolac/DGEBA. It is remarkable that T_p 's of the resin mixture are the highest, especially since one would expect values between those of the epoxy novolac and DGEBA. Regarding TGA data, values for a weight loss of 10% do not differ distinctly from the reference system without cellulose (Figure 5). Furthermore, a remarkable improvement of fracture toughness was observed and the K_{Ic} value increased from 0.55 (reference system without cellulose) to 1.23 MPa·m^{1/2} for the system with 50 phr cellulose loading. The E-modulus increased from 2570 (reference system) to 3750 MPa (system with 50 phr cellulose).

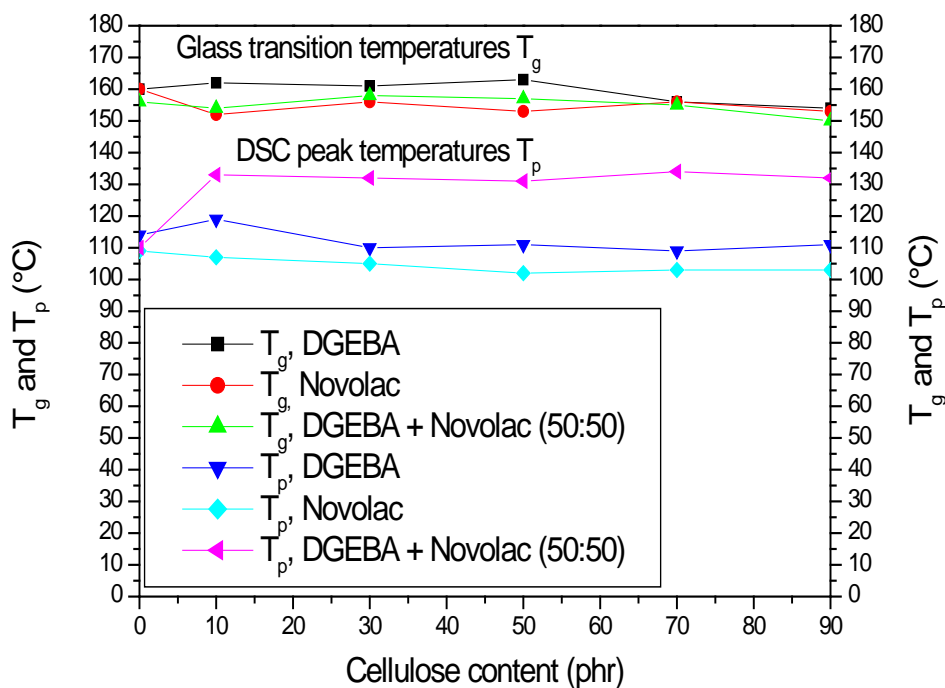


Figure 4. Curing of epoxy resin-cellulose formulations with IPDA: Influence of cellulose content on T_g and T_p (curing temperatures before T_g determination: 2 h at room temperature, 0.5 h at 40 °C, 0.5 h at 60 °C, 0.5 h at 80 °C, 0.5 h at 100 °C, 0.5 h at 120 °C and 2 h at 140 °C).

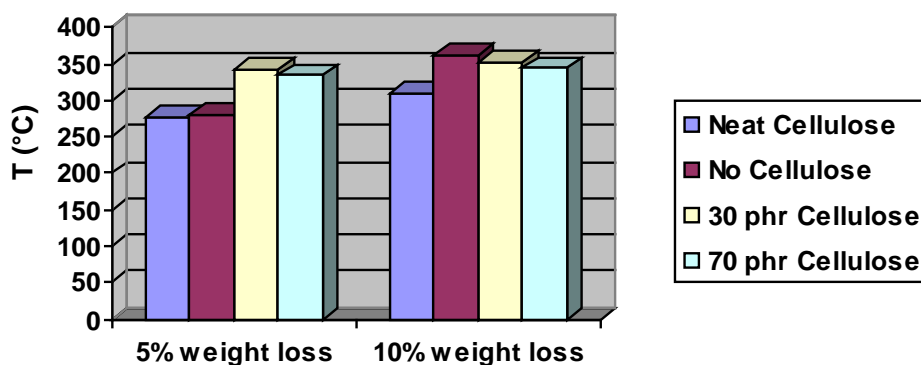


Figure 5. Curing of DGEBA-cellulose formulations with IPDA: Thermal stability of the resulting materials according to TGA measurements (curing temperatures: see Figure 4).

3.3. Curing of epoxy resin-starch formulations with IPDA

Due to the good miscibility of starch with several epoxy resins, a series of epoxy resin-starch formulations with starch contents up to 150 phr was investigated. Like in the case of cellulose three resins were employed (DGEBA, epoxy novolac and mixtures of these two epoxy resins; Figure 6). T_g 's are not affected by starch, even at high contents, and reactivity in terms of T_p decreases in the order novolac > novolac/DGEBA > DGEBA. Regarding material properties, TGA measurements revealed that thermal stability is significantly lower than in the case of the reference system without starch (Figure 7). However, the difference between 50 and 100 phr loading is low. In contrast to the epoxy resin-cellulose systems described above, no increase of K_{ic} and E-modulus was observed by adding 50 phr of starch to the DGEBA-IPDA system. Thus, epoxy resin-cellulose materials seem to be superior compared to analogous epoxy resin-starch materials, at least with respect to the investigated parameters.

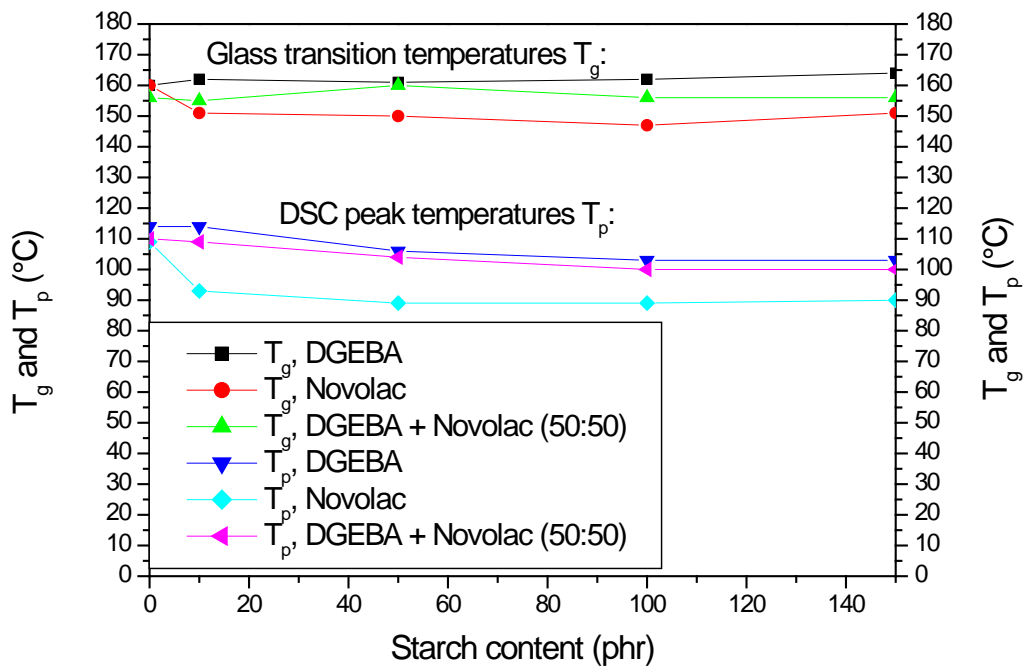


Figure 6. Curing of epoxy resin-starch formulations with IPDA: Influence of starch content on T_g and T_p (curing temperatures before T_g determination: 2 h at room temperature, 0.5 h at 40 °C, 0.5 h at 60 °C, 0.5 h at 80 °C, 0.5 h at 100 °C, 0.5 h at 120 °C and 2 h at 140 °C).

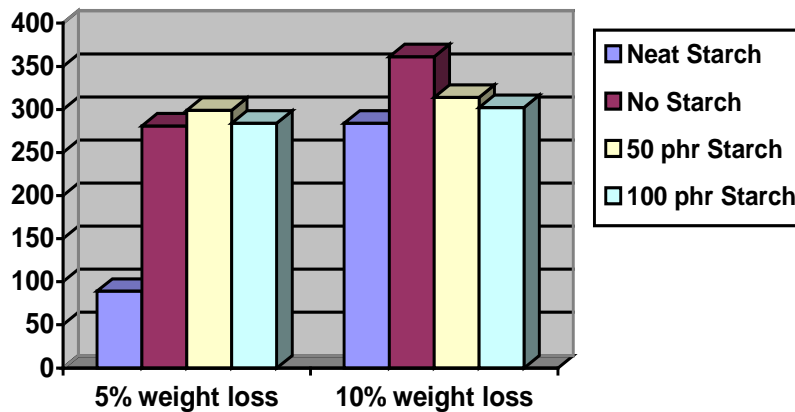


Figure 7. Curing of DGEBA-starch formulations with IPDA: Thermal stability of the resulting materials according to TGA measurements (curing temperatures: see Figure 6).

4. Conclusions

A systematic study on the curing of epoxy resin-biopolymer formulations was carried out. Two epoxy resins, a DGEBA resin and an epoxy novolac, were employed and IPDA was chosen as curing agent. These resin systems were combined with three different lignins, cellulose powder and starch, respectively. In the case of the epoxy resin-lignin formulations, curing reactions were slightly accelerated by lignin and T_g 's of the resulting materials remained in the range of the reference system without lignin, even at high lignin contents up to 100 phr. Thermal stability of the materials was not significantly affected by lignin.

In this context, epoxy resin-lignin systems were identified, which could be cured without any additional hardener. Hence, lignin itself was involved in the crosslinking reaction. The observed reaction enthalpies indicate high crosslinking and T_g 's increase remarkably with increasing lignin content in the formulation.

Regarding epoxy resin-cellulose materials, T_g 's and TGA results did not differ significantly from the reference system without cellulose. The corresponding values remained in the same range up to a cellulose content of 90 phr. However, material properties such as fracture toughness and E-modulus could be remarkably improved. In contrast, analogous materials containing starch did not exhibit similar characteristics. Due to the good miscibility of the employed starch with epoxy resins very high starch contents up to 150 phr could be realized and T_g 's remained in the range of the reference system without starch. Current work concentrates on a deeper characterization of such materials and the chemical modification of biopolymers. Furthermore, materials are developed, which are stemming exclusively from renewable resources.

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