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Development of Biobased Epoxy Matrices for the Preparation of Green Composite Materials for Civil Engineering Applications

*Amandine Viretto and Jocelyne Galy**

Epoxy matrices are successfully used for structural strengthening in civil engineering applications by means of carbon fiber reinforced polymers (CFRPs). In the context of sustainable development, the aim of this study is to develop biobased epoxy matrices as an alternative to the traditional petroleum-based epoxy matrices used in CFRPs. This study focuses on two biobased epoxy monomers: a diglycidyl ether of bisphenol A (DGEBA) and a sorbitol polyglycidyl ether (SPGE). These monomers are reacted with a biobased curing agent, a phenalkamine (PhA), derived from cardanol. After in-depth characterization of the chemical structures of the three monomers, the reactivity of both systems, DGEBA-PhA and SPGE-PhA, is studied using differential scanning calorimetry and rheology. The properties of the networks are characterized via dynamic mechanical analysis and water uptake measurements for polymers with partial or full conversion of epoxy groups, which are obtained by crosslinking at room temperature or at high temperature, respectively. The results reveal that the two systems are good candidates for the preparation of green composite materials as they meet the requirements necessary for manufacturing composites in civil engineering applications.

1. Introduction

Composite materials based on carbon fibers and epoxy matrices are used in civil/structural engineering applications including the repair of structurally deficient piping, structural rehabilitation, and the reinforcement of new infrastructures.[1–4] These high-performance materials present unique properties that make them especially attractive for civil engineering applications—quick cure time, good mechanical strength, and ease of processing. Current research mainly focuses on the ageing process, and prediction of the lifetime and durability of the repaired structures.[5–7] However, recent years have witnessed an increasing demand for natural products for use in industrial applications because of environmental issues, waste disposal problems, and the depletion of nonrenewable resources. Therefore, another avenue of research is to look for biobased composite materials as an alternative to the classical systems which are currently used for the rehabilitation of concrete structures. Properties and costs of such biobased materials must rival to those of standard composites made with synthetic constituents. To our knowledge the use of natural fibers to replace glass or carbon fibers in composite materials, as well as the use of biobased matrices, for this specific application is new and barely considered in the literature.[8–11] The work presented in this paper focuses on epoxy matrices, but is part of a much larger research study to develop biobased composite systems, where the use of flax fibers as reinforcing fibers is investigated.[12]

Regarding epoxy matrices, almost 90% of the world production is based on the reaction between Bisphenol A (2,2-bis(4′-hydroxyphenyl)propane) and epichlorhydrin, yielding the diglycidyl ether of bisphenol A (DGEBA). Epichlorhydrin is a key raw material for the production of epoxide resins. Formerly, it was produced from propylene, a raw material obtained from crude oil. The industrial production of biobased epichlorhydrin from glycerine, a renewable raw material resource, has been possible for a few years,[13,14] using residual glycerine by-product from biofuel production. This new technology opened the way to the synthesis of partially biobased DGEBA—green epoxies—that are now commercially available. A low-risk first route to obtain a biobased epoxy matrix is to replace the traditional DGEBA with a biobased one.[15–17] The main drawback of this method is the use of bisphenol A which is known to be extremely toxic.[18]

There are numerous alternatives to this method to produce epoxy monomers. One of these alternatives for obtaining epoxy precursors is via the epoxidation of double bonds. Investigations have been conducted into the development of biobased epoxy prepolymers from vegetable oils.[19,20] Plant oils mainly consist of triglyceride molecules, i.e., esters derived from glycerol and fatty acids. Most common plant oils contain fatty acid groups that vary in carbon chain length and in the number of double bonds per chain. Epoxidized soybean oil and epoxidized

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linseed oil are the only biorenewable epoxies that have achieved industrial scale production, and they are mainly used as plasticizers and stabilizers in poly(vinyl chloride) synthesis. However, the reactivity and the network properties obtained are far from what is required for a matrix for use in structural composite materials. Other alternatives have been reported based on potential platform monomers, such as cardanol, rosin, lignin, glycerol, sorbitol, isosorbide, gallic acid, succinic acid, and furan, obtained from biomass and use as the starting materials for the synthesis of epoxy resins. This has been the subject of many research studies summarized in different reviews.[21–25] Natural saccharide such as sorbitol can be converted into sorbitol polyglycidyl ether (SPGE) which are commercial multifunctional epoxy monomers mainly used in paint, adhesives, fiber, and paper processing.

In order to improve the biobased carbon content of the whole epoxy matrix, it is necessary to add a biobased curing agent to the system.[26] Amines are generally used in civil engineering applications, but only few biobased diamines are commercially available. An interesting diamine family is the one based on cardanol, an unsaturated meta-alkylphenol obtained by distilling cashew nutshell liquid, a by-product of the cashew industry.[27–30] Phenalkamines are prepared by the Mannich reaction occurring between cardanol, formaldehyde, and appropriate diamines. A variety of phenalkamines (PhA) are available, with different reactivities and viscosities, depending on the targeted application.[31]

In the field of civil engineering the external reinforcement of a damaged structure is typically conducted using wet hand layup, in which the fibers are saturated with an epoxy reactive system and applied directly to the surface of the concrete; or by using an epoxy adhesive to fix a precured carbon–epoxy laminate to the surface.[1] The whole process is performed under ambient conditions of temperature and humidity, i.e., not under controlled conditions. Therefore, the epoxy formulation must fulfill strict requirements: the viscosity must be compatible with a hand lay-up process and as well as the reactivity (often expressed in terms of pot-life defined in technical datasheets); curing at room temperature in a reasonable time must lead to glassy networks, with a high modulus and low water absorption. In addition, the system must be robust enough to withstand severe conditions of outdoor processing. An example of a typical epoxy formulation commonly used for infrastructure repair is a two-component system:[32] part A (resin) is mainly composed of a mixture of DGEBA, epoxy novolac, reactive epoxy diluent, and calcium carbonate as filler, and part B (hardener) is mainly composed of polyetheramine, triethylenediamine, and mixture of catalysts. This blend has a Brookfield viscosity of 18 Pa s and a pot-life of 1 h at 25 °C. The maximum cure is obtained after 2–3 d at this temperature. The resulting network has a Young modulus of 2.3 GPa and a glass transition temperature close to 50 °C, a typical value for epoxy networks cured at room temperature.[33] The development of a biobased epoxy formulation with this target range of properties could be achieved by the appropriate choice of both the epoxy resin and the curing agent.

In this paper, two biobased epoxy formulations were selected, one formulated from a biobased DGEBA and PhA, the other from SPGE and the same PhA. Indeed our previous work on the characterization of networks based on sorbitol polyglycidyl ether (SPGE), led us think that this epoxy prepolymer may have potential for the preparation of biobased composites.[34,35] The present study involves the in-depth characterization of the monomer structures, the kinetics of the crosslinking reaction, and the characterization of the networks in terms of their thermomechanical properties and hygrothermal ageing. The objective is to determine if these biobased formulations are good candidates for civil engineering applications.

2. Experimental Section

2.1. Materials and Sample Preparation

Biobased DGEBA was obtained from Spolchemie with the reference CHS-G530. Its viscosity at 25 °C is 9000 mPa s and the equivalent epoxy weight (EEW) is 184 g eq^{-1}. SPGE was obtained from Nagase Chemtex with the reference Denacol EX-622; its EEW is 181 g eq^{-1}, its viscosity at 25 °C is 11 800 mPa s. This grade was selected following previous studies which showed that this monomer led to more hydrophobic networks.[34,35] A biobased phenalkamine curing agent derived from cardanol, with the reference NX5619 was supplied by Cardolite. Its amino hydrogen equivalent weight is 104 g eq^{-1}, and its viscosity at 25 °C is 425 mPa s. The simplified chemical structure of the reagents is shown in **Figure 1**.

All compounds used in this work were viscous liquids at room temperature. The epoxy prepolymer was mixed with the curing agent using a high-speed mixer (IGT Testing Systems). The stoichiometric ratio of amino hydrogen to epoxy, a/e, was 1. Afterward, the mixture was degassed under vacuum and transferred into a polytetrafluoroethylene (PTFE)-coated aluminum mould. The networks were either partially cured at room temperature for 7 d, or fully cured for 24 h at room temperature followed by a postcure treatment of 2 h at 120 °C; these two curing cycles were named as RTa and RTaHT, respectively.

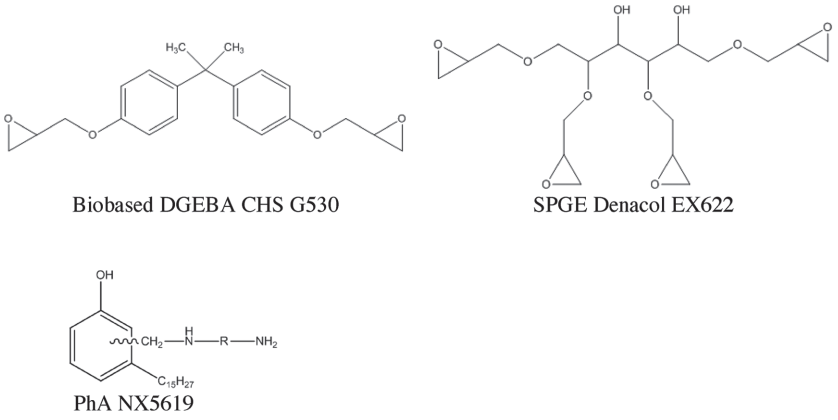

Figure 1. Simplified chemical structures of the epoxy monomers and the PhA NX5619 curing agent.

2.2. Monomer Characterization

Size exclusion chromatography (SEC) was used to measure the molar mass distribution of the monomers, by means of a Shimadzu instrument. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}. The solution concentrations were ≈5 mg mL^{-1}. The separation was performed using a series of three columns (Waters HR0.5, HR1, and HR2), with peak detection based on the signal of a refractive index detector (Shimadzu RID-10A). Column calibration was performed using a set of polystyrene standards, in the range of 100–50000 g mol^{-1}.

Fourier-transform-infrared (FT-IR) spectra were recorded on a Nicolet iS10 instrument from Thermoscientific, in attenuated total reflectance mode. Monomers were in direct contact with the diamond. Spectra were acquired using 32 scans, with a resolution of 4 cm^{-1}.

^{1}H and ^{13}C NMR spectra were recorded at frequencies of 400 and 100.6 MHz, respectively, using a Bruker Avance 400 NMR spectrometer. Deuterated dimethyl sulfoxide was used as a solvent and tetra methyl silane as an internal standard.

2.3. Network Formation and Characterization

Differential scanning calorimetry (DSC) was used to monitor the non-isothermal curing reaction. A Q10 instrument (TA Instruments) operating under an inert atmosphere (nitrogen) and with a heating rate of 10 °C min^{-1} from –70 to 250 °C was used. The samples were weighted (5–10 mg) into hermetically sealed aluminum pans. The glass transition temperature of the unreacted system, T_{g0}, the enthalpy of reaction, ΔH_r, and the temperature at the peak maximum were measured. DSC was also used to measure the glass transition temperature of the cured networks, T_{gx} and $T_{g\infty}$, after the two different curing cycles, RTa and RTaHT, respectively; the onset point was considered. The values of T_{gx} were used to calculate the epoxy conversion, x, through the DiBenedetto empirical model modified by Pascault and Williams[36]

$$\frac{T_{g_x} - T_{g_0}}{T_{g_\infty} - T_{g_0}} = \frac{\lambda x}{1-(1-\lambda)x} \tag{1}$$

where T_{g0} and $T_{g\infty}$ are the glass transition temperatures of the unreacted initial system and of the fully cured network, respectively; λ is the ratio of the change in specific heat capacity ΔCp at the glass transition temperature, for the fully cured and uncured states

$$\lambda = \frac{\Delta Cp_\infty}{\Delta Cp_0} \tag{2}$$

All these values were taken from DSC runs.

Rheological properties were measured using an Ares G2 Rheometer from TA Instruments, at 40 °C. The reactive mixture was placed between parallel plates with a 25 mm diameter and a gap of ≈1 mm. Multifrequency sweeps were performed and the complex viscosity, the storage modulus (G'), and the loss modulus (G'') were recorded. The gel time was determined according to the Winter–Chambon criterion that implies the independence of the loss factor, $\tan\delta = G''/G'$, as a function of frequency.[37]

Dynamic mechanical analysis in tension mode was carried out using a Mettler Toledo DMA/STDA 861e instrument, in order to determine the storage (E') and loss (E'') moduli, as well as $\tan\delta$ as a function of temperature. Samples (10.5 × 5 × 1 mm^3) were heated from –20 to 150 °C at a heating rate of 3 °C min^{-1}. The frequency was 1 Hz and the static force was equal to 3 N. Experiments were performed in duplicate and showed excellent reproducibility.

Water uptake experiments were performed by first taking initial mass of the sample, W_0, prior to immersion in a distilled water bath at room temperature. The samples were removed and weighed at periodic intervals, W_t, and then replaced in the water bath. The relative water uptake, M_t, was calculated according to

$$M_t = \frac{W_t - W_0}{W_0} * 100(\%) \tag{3}$$

The sample dimensions were 1 × 5 × 30 mm^3. Three samples of each type of epoxy network were aged. The results given were averaged over the three measurements.

3. Results and Discussion

3.1. Characterization of Monomers

The structural elucidation of the monomers was carried out using chromatography, FT-IR, ^{1}H NMR, and^{13}C NMR spectroscopy. To obtain information on the molar mass distribution, the two epoxy prepolymers and the PhA curing agent were analyzed by SEC. The chromatograms of the three compounds are presented in **Figure 2**. The chromatogram of the biobased DGEBA is identical to that of a typical DGEBA of similar EEW;[34] the main peak at an elution volume of 24.8 mL is due to the pure monomer (n = 0) with a molar mass of 340 g mol^{-1}, two other small peaks at 22.13 and 20.9 mL are due to some oligomers (n = 1 and n = 2, respectively) of higher molar mass, and the peak at 23.6 mL corresponds to the presence of different terminal groups such as primary and secondary alcohols.[38,39] The SPGE chromatogram is very different; it shows a broad peak centered at 21.56 mL and a few small peaks at higher elution volumes. Average molar masses M_n and M_w, determined via a polystyrene calibration, are equal to 700 and 100 g mol^{-1}, respectively. As published in previous works, the chemical structure of SPGE is complex, with many oligomers containing chlorine atoms attached to the molecule.[34,35] This structure is well-known and is explained by the synthesis pathway. The sorbitol polyglycidyl ether and the glycerol polyglycidyl ether are obtained by the reaction of epichlorhydrin with sorbitol or glycerol. These natural aliphatic polyols contain primary alcohol groups at chain ends and secondary alcohol groups in the chain. The reaction generates new alcohol groups, which are also reactive toward epichlorhydrin. Hydroxyl groups resulting from the reaction between the polyols and epichlorhydrin present similar reactivity to the starting polyols. This mechanism implies multiple additions of epichlorhydrin onto the same alcohol, which therefore it is not able to undergo cyclization into epoxide form, thus explaining the high chlorine content.[22]

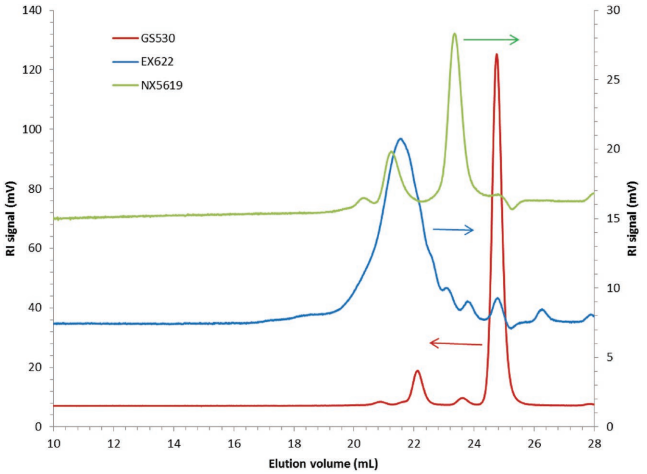

Figure 2. SEC chromatograms of DGEBA (red), SPGE (blue), and PhA (green): refractive index signal (mV) as a function of retention volume (mL).

The chromatogram of PhA NX5619 shows three well-defined peaks of different magnitudes, at 20.31, 21.24, and 23.35 mL. The molar masses, calculated via calibration with polystyrene standards, are 1360, 950, and 500 g mol^{-1}, respectively. The PhA curing agent is clearly a mixture. The datasheet supplied by Cardolite indicates the presence of m-xylenediamine (MXDA). The chemical structure of the main component (eluted at 23.35 mL) is plotted in Figure 1, where R is $-(CH_2)-C_6H_4-(CH_2)-$, derived from MXDA.

IR and NMR analyses of the three compounds give some indications about their chemical structure. The IR spectra of DGEBA and SPGE are not presented here (see the Supporting Information). The biobased DGEBA has all of the typical features expected, confirming that there is no perceptible difference between a biobased and a petrobased DGEBA. The IR spectrum of SPGE shows three broad peaks: one in the region 3100–3600 cm^{-1}, which indicates the presence of −OH groups due to the incomplete epoxidation of sorbitol; one between 2800 and 3100 cm^{-1} due to aliphatic C−H stretching; and one at 1100 cm^{-1} due to the C−O aliphatic ether bonds. The presence of epoxy groups is characterized by the typical bands at 915 and 830 cm^{-1}. Finally, the peak at 750 cm^{-1} is attributed to C−Cl bonds. In the ^{1}H NMR spectra (shown in the Supporting Information), the peaks at 3.1, 2.75, and 2.55 ppm are assigned to the protons in epoxy groups; the peak at 3.3 ppm is due to the proton in α position of Cl. The broad and overlapping peaks between 3.4 and 3.9 ppm are attributed to protons in the α position of O (ether linkage) and are difficult to assign more precisely. In ^{13}C NMR spectra, chemical shifts at 43.5 and 50.5 ppm belong to epoxy groups. The peaks between 69 and 80 ppm correspond to C in α position of oxygen. The chemical shift of C−Cl appears at 44.4 ppm.

In order to further identify the structure of PhA NX5619 the IR, ^{1}H, and ^{13} C NMR spectra were analyzed. The IR spectrum of PhA is shown in the SI and is similar to spectra reported in the literature.[40,41] Characteristic absorption bands are observed at 3370 cm^{-1}, assigned to −OH stretching; 3297 cm^{-1}, assigned to N−H stretching; 3013 cm^{-1}, attributed to aromatic C−H stretching; 2925 and 2851 cm^{-1}, due to alkyl C−H stretching; 1610 and 1581 cm^{-1}, due to aromatic C=C stretching; 1460 cm^{-1}, due to $-CH_2$ scissoring; 1274 cm^{-1}, due to −OH bending; 1156 cm^{-1}, due to C−O stretching; and 1114 cm^{-1}, attributed to aliphatic C−N stretching. In the ^{1}H NMR spectrum of PhA (**Figure 3**), all signals due to cardanol protons can be observed: unsaturated protons (g, h, and i) between 4.8 and 5.9 ppm, the protons of the aliphatic chain

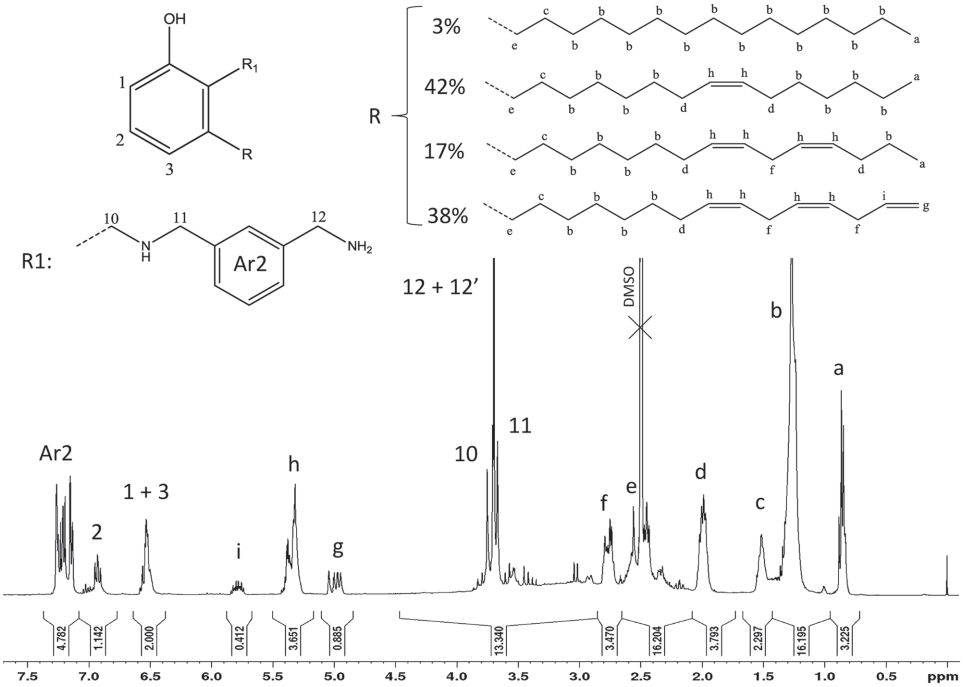

Figure 3. The ^{1}H NMR spectrum of PhA NX5619.

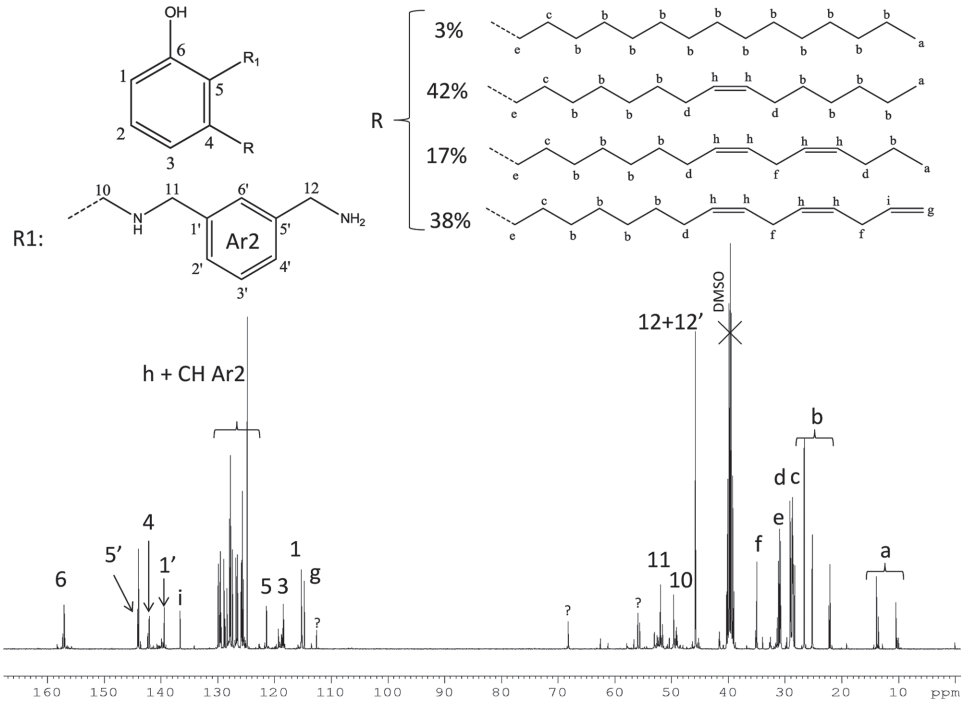

Figure 4. The ^{13}C NMR spectrum of PhA NX5619.

(a, b, c, d, e, and f) between 0.8 and 2.9 ppm, and the aromatic protons (1, 2, and 3) between 6.4 and 7.1 ppm.[42] In the aromatic area, other peaks are observed; they are identified as aromatic protons (Ar2) between 7.1 and 7.4 ppm, from the MXDA. The observed peaks (10, 11, and 12) between 3.5 and 4.0 ppm are characteristic of the chemical shift of the methylene linkages (Ph—CH_2—N) in the Mannich structures.[40–44] The ^{13}C NMR spectrum is presented in **Figure 4**, showing the characteristic peaks of cardanol, and new peaks due to the R1 chain as a result of the reaction with MXDA, with signals in the aliphatic area (10, 11, 12) and in the aromatic area (1′, 2′, 3′, 4′, 5′, 6′). The amino groups in the phenalkamine NX5619 are aliphatic, thus a high reactivity is expected. Indeed, it is known that aliphatic amines are more reactive with epoxy groups than cycloaliphatic and aromatic amines.

3.2. Curing Behavior

Matrix viscosity is an important parameter that is directly and relevantly associated to the process of making the composite material. In civil engineering applications, wet hand lay-up is one of the preferred processes. It is therefore important to investigate the rheological behavior of biobased epoxy systems to determine if they can be adapted to the process. The variation of the viscosity of the biobased epoxy systems as a function of the reaction time at 40 °C is plotted in **Figure 5**. It can be seen that the initial viscosity is around 2–3 Pa s for both systems. This low viscosity is compatible with hand lay-up processes. The systems show no significant increase in viscosity over 90 min for the DGEBA-PhA and 55 min for the SPGE-PhA, at 40 °C. The gel times at 40 °C were determined from multifrequency experiments. The DGEBA-PhA formulation has a longer gel time than the SPGE-PhA formulation—140 and 57 min, respectively (**Table 1**). The shorter gel time of the SPGE-PhA system is due to the functionality of the SPGE prepolymer, which is greater than two;[45] and also to the presence of numerous hydroxyl groups which catalyze the epoxy–amine reaction.[34,35] At 40 °C the pot-life is long enough to allow the manufacture of composites. This temperature represents somehow extreme temperature conditions that may nonetheless be experienced during infrastructure repair.

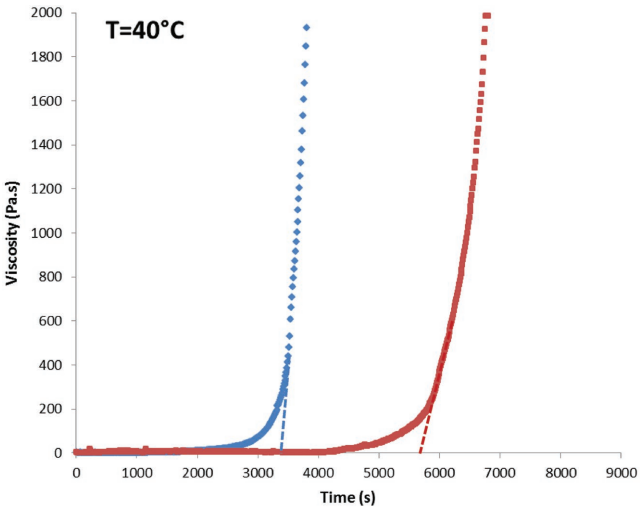

Figure 5. Viscosity as a function of time at 40 °C, measured at 5 Hz between parallel plates: ■: DGEBA-PhA, ◆: SPGE-PhA.

Table 1. Curing behavior results for the two biobased epoxy systems: pot-life at 40 °C (time after which viscosity started to increase), gel times at 40 °C, and DSC results.

	Pot-life [min]	Gel time [min]	T_{g0} [°C]	ΔCp_0 [J g^{-1} °C]	T_{max} [°C]	ΔH_r [J g^{-1}]	T_{gx} [°C]	$T_{g\infty}$ [°C]	ΔCp_∞ [J g^{-1} °C]
DGEBA + PhA	90	140	−42	0.52	119	320	56	70	0.39
SPGE + PhA	55	57	−41	0.40	107	250	39	43	0.35

The two biobased systems were analyzed using non-isothermal DSC, and the obtained thermograms are shown in **Figure 6**. Table 1 shows the glass transition temperatures of the unreacted systems (T_{g0}), the peak maximum temperatures (T_{max}), and the total heat of reaction (ΔH_r). The initial glass transition temperatures, T_{g0}, and the beginning of the reaction are almost the same for both systems. SPGE-PhA showed a lower temperature peak compared with the DGEBA-PhA system; this is an indication that the SPGE-PhA system has a slightly higher reactivity, assigned to the catalyst effect of hydroxyl groups.[34] The enthalpy of reaction of the SPGE-PhA system is significantly lower than that of the DGEBA-PhA system, while the EEW values for the two epoxy prepolymers are similar. A similar result has also been observed by Chrysanthos using isophorone diamine as the curing agent.[35] This previous study also placed in evidence the unusual behavior of the system, i.e., the maximum T_g was not observed at a stoichiometric ratio a/e equal to 1, unlike all other epoxy–amine networks.[46] In fact, T_g increased as the a/e ratio increased 0.75 to 2. This behavior, not clearly understood, was related to the presence of chlorohydrine ($-CH_2-Cl$) and its involvement in reactions with amino groups. Our current experiments with PhA do not allow us to conclude whether or not the behavior is the same in the present system. However, the lower enthalpy of the reaction is an indication that the epoxy–amine reaction is not complete, and some oxirane functionalities are very likely hindered.

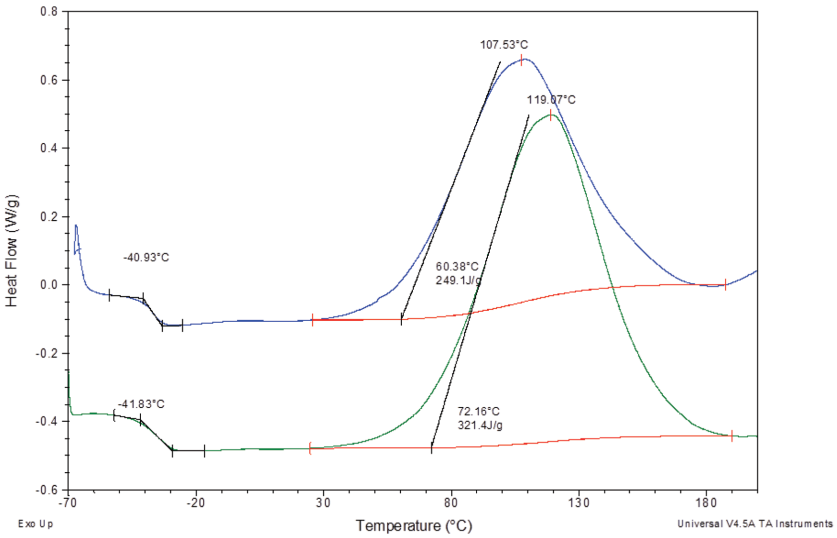

Figure 6. DSC Thermograms of biobased DGEBA-PhA (green curve) and SPGE-PhA (blue curve) reactive systems.

3.3. Network Properties

The one-to-one nonlinear relationship between T_g and epoxy conversion, x, expressed by the empirical DiBenedetto equation (Equation (1)), was used to evaluate the epoxy conversion of the biobased networks after the curing cycle at room temperature (RTa). T_{gx} obtained by DSC are equal to 56 and 39 °C for DGEBA-PhA and SPGE-PhA networks, respectively, which means that at room temperature both networks are in the glassy state. The data needed to calculate the corresponding conversion are T_{g0}, ΔCp_0, $T_{g\infty}$, and ΔCp_∞ which were obtained through DSC runs on unreacted system and fully cured network (their values are given in Table 1). A conversion rate of 90% was obtained for both room temperature cured networks. These similar values of conversion obtained are a coincidence. One can note that a small increase in conversion, from 90% to 100%, leads to significant increase in T_g for DGEBA-PhA networks, while this increase is reduced for SPGE-PhA networks. This can be explained by the fact that the T_g versus x curve for DGEBA-PhA network presents a higher slope at high conversion compared to the SPGE-PhA network, since $T_{g\infty}$ values are very different.

The thermomechanical properties of the materials were evaluated by means of dynamic mechanical analysis. **Figures 7** and 8 show the temperature dependence of E' and tanδ for the two biobased networks either partially cured at room temperature (RTa) or fully cured after a postcuring cycle at 120 °C. **Table 2** summarizes the main parameters calculated from these curves. The two networks cured at room temperature have a similar modulus, ≈3 GPa, at low temperature (−10 °C). However, the decrease in the modulus in the glassy state until the glass transition is more pronounced for the SPGE-PhA network compared with the modulus of the DGEBA-PhA network which is nearly constant. After the glass transition in the rubbery state, the modulus of the SPGE-based network is significantly higher than the rubbery modulus of the DGEBA-based network, with values of 25 and 8.8 MPa at Tα + 30 °C, respectively. Given that the degree of cure is the same for both networks (x = 90%), the difference in the rubbery modulus between the two room temperature cured networks is due to differences in epoxy prepolymers structure. This should be especially related to the structure functionality, which has consequences on the number of crosslinking points, while the chemical structure between crosslinking points has consequences on the flexibility and the length of the chains between crosslinks.[47] It is also observed that the rubbery modulus for the DGEBA-PhA network increases significantly and continuously as the temperature is increased, while it remains almost constant for the SPGE-based network. This means that the DGEBA-PhA network undergoes a postcure process during the DMA experiment, as expected for a partially cured network. According to the rubber elasticity theory, the average molar mass of the segment between crosslinking

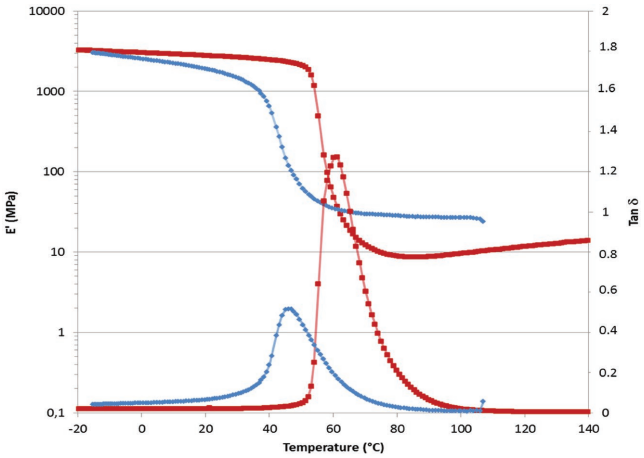

Figure 7. Temperature dependence of E' and tanδ of the two biobased networks cured at room temperature:■: DGEBA-PhA, ◆: SPGE-PhA.

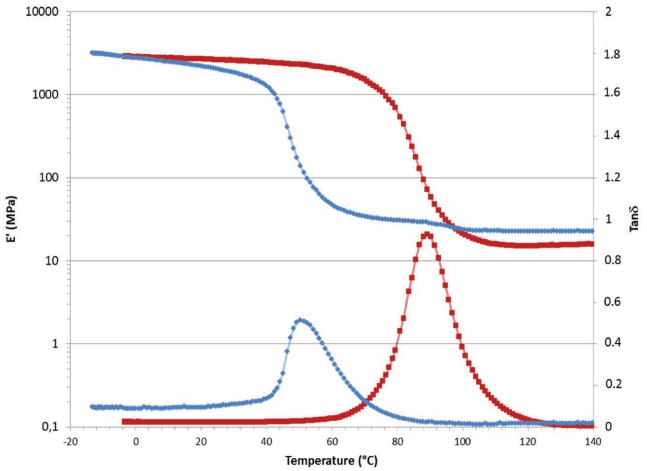

Figure 8. Temperature dependence of E' and tanδ for the two biobased networks after postcure:■: DGEBA-PhA, ◆: SPGE-PhA.

points (Mc) and the crosslinking density (ν_e) can be calculated using the following equation

$$E' = 3dRT/\text{Mc or } E' = 3\nu_e RT \quad (4)$$

where E', d, R, and T are the storage modulus (MPa) at Tα + 30 °C, the density of the network (g cm^{-3}, measured by Archimedes' method in water), the gas constant (8.314 J mol^{-1} K), and the temperature (K), respectively. The calculated values of Mc are presented in Table 2 .The smallest value of Mc is obtained for the network based on SPGE, which has a functionality higher than two, leading to a higher density of crosslinking points in the cured network.

Obviously, the main transition, α, is higher for the DGEBA-based network with Tα = 61 °C compared with Tα = 46 °C for the SPGE-based network. This difference, also noticed by DSC, is explained by the epoxy monomer structures: DGEBA has an aromatic structure and SPGE has an aliphatic structure. DGEBA leads to rigid segments in the network while SPGE leads to more flexible segments having an improved mobility.

A postcuring cycle of 2 h at 120 °C causes some changes in the networks, which are especially marked for the DGEBA-based network (**Figure 8**). The temperature at the maximum of tanδ is increased to 89 °C and the rubbery modulus becomes 15.12 MPa at Tα + 30°C. The rubbery modulus increases only slightly with increasing temperature, in agreement with the rubber elasticity theory assuming that ν_e is now constant, unlike the case of the room temperature cured network. Therefore, it is the evidence that the network is fully cured as expected. The molar mass between crosslinking points after the postcuring cycle is 740 g mol^{-1}. For the SPGE-PhA network, the changes are less significant: T_{max} is increased to 50 °C, the rubbery modulus becomes 31 MPa at Tα + 30 °C and Mc is 347 g mol^{-1}. These changes confirm that the SPGE-PhA network was not fully cured at room temperature, and the postcuring cycle allowed some of the residual epoxy and amine functions to react.

The two fully cured networks exhibit distinct features: the DGEBA-PhA network has a higher glass transition temperature than the SPGE-PhA network, but a lower crosslink density.

The percentage of water absorbed, at equilibrium by the four networks after immersion in distilled water at room temperature is reported in Table 2. Equilibrium was obtained after 14 d of immersion in water at 23–24 °C. Very low values of water uptake were obtained for the DGEBA-based networks, less than 1 wt%. The water absorption at equilibrium is independent of the curing cycle: the postcured and room temperature cured networks show similar values, lower than 1 wt%. This is a very positive result from the perspective of the materials durability. To our knowledge such values are exceptional in epoxy networks synthesized from DGEBA and diamine curing agents. Studies on hygrothermal ageing have evidenced the presence of many factors influencing the diffusion kinetics and the amount of absorbed water at equilibrium in epoxy-based resins, as for example the free volume hole size, the fractional free volume, the chemical structure of the curing agent, and the resulting polarity. In general, the use of aliphatic amines leads to networks which present lower water absorption compared to networks obtained from cycloaliphatic or aromatic diamines.[48,49] The hydrophobic behavior of our DGEBA-based networks is due to the structure of the PhA curing agent, which has a long aliphatic side chain on the aromatic ring. A very different behavior is observed for the SPGE-based networks. Higher values of water absorption are reached at equilibrium, 4.80 and 4.51 wt%, for the room temperature and postcured samples respectively. Such high values are explained by the polarity of

Table 2. Thermomechanical properties, density (d, measured by Archimedes method), and equilibrium water uptake at 25 °C (Mm) for the biobased networks.

Network/curing cycle	Tα [°C]	E' (20 °C) [GPa]	E' Tα + 30 °C) [MPa]	d [g cm^3]	Mc [g mol^{-1}]	Mm [wt%]
DGEBA+PhA/RTa	61	2.78	8.8	1.14	1176	0.88
DGEBA+PhA/RTaHT	89	2.70	15.12	1.14	740	0.89
SPGE+PhA/RTa	46	1.88	25	1.22	425	4.80
SPGE+PhA/RTaHT	50	2.2	31	1.22	347	4.51

the epoxy prepolymer. As mentioned previously SPGE has a large number of hydroxyl groups which makes the compound more hydrophilic than DGEBA. Even if the PhA curing agent introduces hydrophobicity to the system, it is not sufficient to compensate for the hydrophilic character of the SPGE. Nevertheless, water absorption in the range of 5 wt% is not unusual in epoxy networks, especially when aromatic curing agents are used.

4. Conclusions

In this paper, two biobased epoxy precursors (DGEBA and SPGE) and a biobased curing agent (PhA), all commercially available, were selected with the aim of developing reactive formulations for the processing of composite materials that could be used for structural strengthening of concrete structures. The initial biobased components used in their synthesis were epichlorhydrin, sorbitol, and cardanol, respectively. A first focus was on the deep analytical characterization of the three monomers. Next, a study of the reactivity of the two systems, DGEBA-PhA and SPGE-PhA, showed that the first system is less reactive than the second, but both are compatible in terms of viscosity, pot-life, and gel time with the processing conditions in wet hand lay-up. The behavior of the system based on SPGE is linked to the presence of numerous hydroxyl groups and to the high epoxy functionality of this monomer. Comparison of Tα and the modulus of the fully cured networks show that the networks based on SPGE have a lower glass transition temperature, 46 °C, but a higher rubbery modulus, 25 MPa, than the networks based on DGEBA. The high functionality of SPGE leads to a higher crosslinking density and thus a higher rubbery modulus, but the flexible aliphatic chains between crosslinking points lead to a lower glass transition temperature. Crosslinking reaction performed at room temperature leads to a partially cured network, with an epoxy conversion close to 90%. The Tα values measured after curing at room temperature are in the range of the expected values for the DGEBA-PhA network, for the applications targeted but need to be increased of a few degrees for the SPGE-PhA network. It was also noted that the glass transition temperature of DGEBA-based network increased up to 89 °C, and the rubbery modulus up to 15.12 MPa after a postcure cycle at 120 °C, while in the case of the network based on SPGE smaller changes in these properties were observed. Water uptake is a very important property for these materials, and the DGEBA-PhA network has exceptionally low water absorption, less than 1 wt%. This is very positive for the targeted applications in which the involved materials will be exposed to outdoor environmental conditions, including humidity, water from rain, saline water, etc. The SPGE-PhA network showed a higher water uptake; nevertheless, it was in the range of values found for traditional epoxy–amine networks.

It can therefore be concluded from the results obtained in this study that the two biobased epoxy matrices developed can meet the requirements for the manufacture of composite materials under ambient conditions, via a wet hand lay-up process, with preference given to the DGEBA-PhA formulation. They may thus be used for different applications in the field of civil engineering, for example in the strengthening of deteriorating concrete structures or in infrastructure rehabilitation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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