



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Full paper/Mémoire

Design and synthesis of biobased epoxy thermosets from biorenewable resources

Camille François ^a, Sylvie Pourchet ^{a, **}, Gilles Boni ^a, Sari Rautiainen ^b, Joseph Samec ^b, Lucie Fournier ^c, Carine Robert ^c, Christophe M. Thomas ^c, Stéphane Fontaine ^d, Yves Gaillard ^e, Vincent Placet ^e, Laurent Plasseraud ^{a, *}

^a ICMUB UMR6302, CNRS, Université Bourgogne Franche-Comté, 21000 Dijon, France

^b Department of Organic Chemistry, Stockholm University, 106 91 Stockholm, Sweden

^c Chimie ParisTech, PSL Research University, CNRS, Institut de recherche de Chimie Paris, 75005 Paris, France

^d DRIVE EA1859, Université Bourgogne Franche-Comté, 58000 Nevers, France

^e Université de Bourgogne Franche-Comté, FEMTO-ST Institute, CNRS-UFC–ENSMM–UTBM, Department of Applied Mechanics, 25000 Besançon, France

ARTICLE INFO

Article history:

Received 7 September 2017

Accepted 19 October 2017

Available online xxxx

Keywords:

Biobased resins

DEGEB alternative

Epoxy-anhydride thermosets

Curing process

Nanoindentation

ABSTRACT

Biobased diepoxy synthons derived from isoeugenol, eugenol or resorcinol (DGE-isoEu, DGE-Eu and DGER, respectively) have been used as epoxy monomers in replacement of the diglycidyl ether of bisphenol A (DGEBA). Their curing with six different biobased anhydride hardeners leads to fully biobased epoxy thermosets. These materials exhibit interesting thermal and mechanical properties comparable to those obtained with conventional petrosourced DGEBA-based epoxy resins cured in similar conditions. In particular, a high T_g in the range of 90–130 °C and instantaneous moduli higher than 4.3 GPa have been recorded. These good performances are very encouraging, making these new fully biobased epoxy thermosets compatible with the usual structural application of epoxy materials.

© 2017 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Thermoset epoxy resins are used in a wide variety of applications, for example, composites, aeronautic and automotive components [1]. Indeed, they have high performances among the available commercial resins. They exhibit excellent adhesion and mechanical properties as well as chemical, electrical and heat resistance. Currently, most of the epoxy resins and hardeners used are derived from oil resources leading to the harmful environmental impact. Moreover, bisphenol A is widely used as a basic

building block for the preparation of these epoxy resins, in particular, the well-known diglycidyl ether of bisphenol A (DGEBA). However, bisphenol A was recently proved to be an endocrine-disrupting chemical [2,3] and a water contaminant [4]. Therefore, its substitution with biobased building blocks is strongly encouraged, which would also reduce the petrochemical contribution [5].

During the last decades, many studies were devoted to develop a wide variety of molecules for the preparation of sustainable epoxy resins [6,7]. A part of this work concerns the replacement of DGEBA in epoxy resins. The authors were obviously interested in synthesizing diepoxy components containing rigid aromatic rings to obtain polymers with high modulus and high glass transition temperatures. For this purpose, Auvergne et al. [8] and also Ding and Matharu [9] reviewed the potential of polyphenols and

* Corresponding author.

** Corresponding author.

E-mail addresses: sylvie.pourchet@u-bourgogne.fr (S. Pourchet), laurent.plasseraud@u-bourgogne.fr (L. Plasseraud).

<https://doi.org/10.1016/j.crci.2017.10.005>

1631-0748/© 2017 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article in press as: C. François, et al., Design and synthesis of biobased epoxy thermosets from biorenewable resources, *Comptes Rendus Chimie* (2017), <https://doi.org/10.1016/j.crci.2017.10.005>

tannins. More recently, Aouf et al. [10,11], Yang et al. [12] and Shibata and Ohkita [13] reported biobased diepoxy resins obtained, respectively, from functionalization of gallic and vanillic acids, plant-based phenolic acids or vanillin derivatives. An alternative way to produce eugenol-based epoxy resins was proposed by Qin et al. [14] and Wan et al. [15,16]. Other appropriate candidates are molecules extracted from lignin, which are very competitive to DGEBA-based thermosets as reviewed by Llevot et al. [17] and Ferdosian et al. [18]. Recently, such a lignin-based epoxy resin was reported for potential application in epoxy asphalt [19]. Thus, lignin-based epoxy resins are currently the subject of innovative and intense investigations [20].

In this context, we recently described a suitable lignin synthon for epoxy thermoset applications, 2-[3-methoxy-4-(2-oxiranymethoxy)phenyl]-3-methyloxirane, named DGE-isoEu [21]. This new biobased monomer was prepared according to a two-step procedure, from isoeugenol, catalytically fragmented from lignin. Diepoxy derivative of isoeugenol (DGE-isoEu) was cured satisfactorily with acid derivative hardeners to obtain thermosetting epoxy polymer having high T_g and promising mechanical properties. Continuing our approach and with the aim to develop fully biobased epoxy thermoset materials, the curing of the DGE-isoEu with biobased anhydride hardeners is studied in this article. Compared with the classical diamine hardeners, these curing agents present several major advantages. First, they avoid the use of toxic aliphatic diamine. Moreover, as reported by Paramarta and Webster [22], anhydride hardeners are preferred to diamines for their higher reactivity, especially in the case of internal DGE-isoEu epoxide that is less reactive as compared to terminal epoxide. Furthermore, to reduce the environmental impacts of the epoxy thermosets, the curing agents used in this study are synthesized with high yield from biorenewable and inexpensive dicarboxylic acid agents [23]. Recently an innovative route to renewable anhydrides from biobased furanics has also been described by Thiagarajan et al. [24]. It is worth noting that recently much attention has also been paid to biobased amine hardeners as reviewed by Froidevaux et al. [25] and Fache et al. [26]. It is also noticeable that, after curing, some of the tested hardeners still contain a rigid cycle: this is anticipated to produce epoxy thermosets with high glass temperature and high modulus.

In this article, DGE-isoEu or diepoxy derivative of eugenol (DGE-Eu) was successively cured with six biobased anhydride hardeners: the resulting materials were analysed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and nanoindentation. These results were compared with those obtained by curing commercially available epoxy resins (DGEBA and the biobased diglycidyl ether resorcinol [DGER] resin) with six anhydride hardeners.

2. Experimental section

2.1. Materials

DGE-isoEu was prepared from biobased isoeugenol [27] and biobased epichlorohydrin [28] according to our

previously published procedure [21]. DGE-Eu was obtained as recently reported by Qin et al. [14]. XRD single-crystal analysis of DGE-Eu was recently resolved by some of us [29]. DGEBA and DGER were purchased from Sigma–Aldrich.

Six anhydride curing agents were synthesized according to Ref. [23]: diphenic anhydride (DPA), glutaric anhydride (GA), phthalic anhydride (PA), camphoric anhydride (CA), succinic anhydride (SA) and itaconic anhydride (IA). Anhydrides were used after the purification step (separation from $MgCl_2$ by sublimation). 1,2-Dimethylimidazole (DMID, 95% purity) was purchased from Sigma–Aldrich and was used without any further purification.

Molecular representations of reagents used in the resin manufacturing process are presented in Figs. 1 and 2.

2.2. General methods and instrumentation

2.2.1. Fourier transform infrared spectroscopy

FT-IR spectra were recorded using a Bruker Vector 22 fitted with a specac MKII Golden Gate Diamond Attenuated Total Reflectance device equipped with ZnSe lenses in the 4000–500 cm^{-1} wavenumber range (12 scans at spectral resolution of 4 cm^{-1}).

2.2.2. Differential scanning calorimetry

DSC analyses were carried out using TA MDSC 2920 under nitrogen flow (60 $mL\ min^{-1}$) with a sample mass of 10 ± 3 mg. To study curing reaction, samples were heated from -20 to 180 °C at a heating rate of 5 °C min^{-1} . To determine glass transition temperature (T_g), the cured resin was heated from -20 to 180 °C at a heating rate of 20 °C min^{-1} .

2.2.3. Thermogravimetric analyses

Thermogravimetric analyses were performed using a TA Instruments TGA Q600 thermoanalyser using aluminium pans. Samples (5–10 mg) were heated from room temperature to 800 °C at a rate of 20 °C min^{-1} under air flow (100 $mL\ min^{-1}$). Weight loss percentages were determined using the TA Universal Analysis 2000 software accompanying the instrument.

2.2.4. Nanoindentation mechanical property analyses

Nanoindentation experiments were performed using an ultra nanoindenter from Anton Paar. A Berkovich indenter was used. The area function was calibrated by indenting in a fused silica sample with a known Young's modulus and Poisson's ratio. Before carrying out the tests, the samples were polished with SiC paper, alumina particles until 0.03 mm and then colloidal silica. The instantaneous indentation modulus E_I and hardness H at different indentation depths, the relaxed indentation modulus E_R and finally the strain rate sensitivity m were determined from multicycle indentations, indentation at different constant strain rate \dot{h}/h (where h is the indentation depth) and trapezoidal holding force tests with linear loading and unloading segments. The indentation protocols were the same as used previously [21].

2.2.5. Epoxy resin curing protocol

A comparable protocol as described in our previous work [21] was carried out for each sample of this study. Epoxy

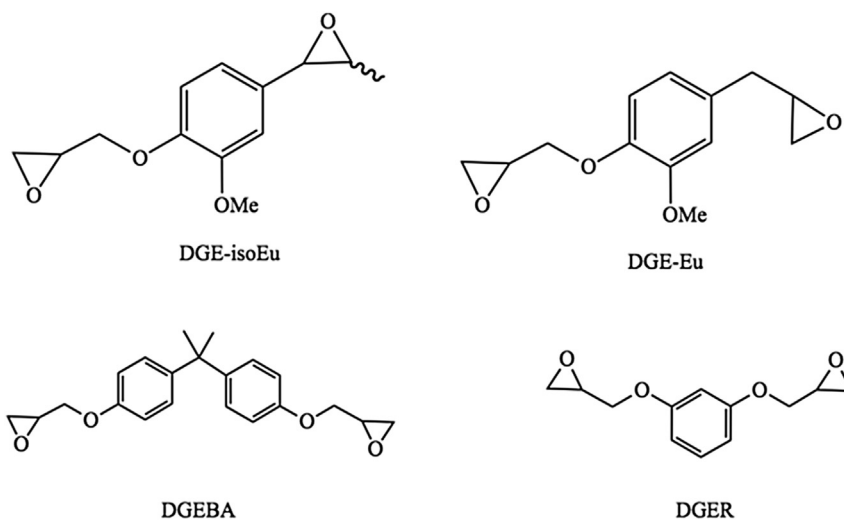


Fig. 1. Molecular representations of reagents used in the resin manufacturing process. Epoxy monomers: diepoxy derivative of isoeugenol (DGE-isoEu), diepoxy derivative of eugenol (DGE-Eu), diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of resorcinol (DGER).

monomers and anhydride hardeners in a 1:1.2 molar ratio were ground in a mortar at room temperature to obtain a homogeneous mixture. DMID catalyst (molar ratio 0.05 with respect to epoxy monomer) was added and intimately

mixed. Polymerization reaction was studied using DSC. A few milligrams of this mixture was heated from room temperature to 180 °C at a heating rate of 5 °C min⁻¹. The remaining mixture was cured in an oven at 150 °C for 1 h.

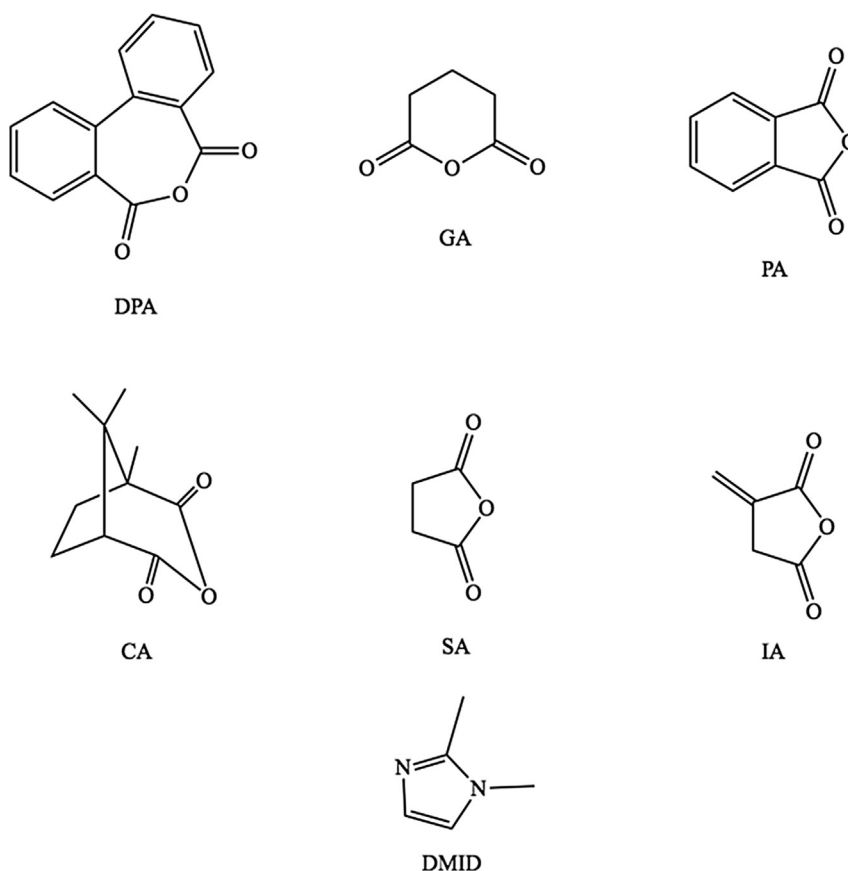


Fig. 2. Molecular representations of reagents used in the resin manufacturing process. Anhydride hardeners: diphenic anhydride (DPA), glutaric anhydride (GA), phthalic anhydride (PA), camphoric anhydride (CA), succinic anhydride (SA), itaconic anhydride (IA). Catalyst: 1,2-dimethylimidazole (DMID).

3. Results and discussion

3.1. Optimization of curing protocol by FTIR analysis

The optimization of the epoxy monomer/anhydride hardener molar ratio was carried out on the DGEBA/PA mixture. On the basis of the equal molar functional groups, 1 mol of epoxy monomer is needed for 2 mol of anhydride hardener giving rise to a ring opening polymerization reaction (because the epoxy monomer is tetrafunctional in the absence of labile proton whereas the anhydride hardener is bifunctional) [12,22]. Nevertheless, because of the potential presence of water molecule it can be assumed that the presence of labile protons could reduce the functionality of the epoxy group. Moreover, as mentioned by Dusek [30] and Paramarta and Webster [22], secondary reactions involving only epoxy groups leading to polyetherification also occur. This hypothesis was confirmed here by curing DGEBA only in the presence of DMID catalyst using the protocol mentioned in Section 2. The exothermic peak at 134 °C observed in DSC evidences the polyetherification reaction occurring during the first heating of this mixture. No exothermic peak is recovered during the second heating cycle indicating that there is no more polymerization reaction during the second heating (see Fig. 3). Consequently, it can be assumed that less than 2 mol of anhydride hardener is needed to react with 1 mol of the epoxy monomer.

To optimize the epoxy monomer/anhydride hardener molar ratio (formally equal to 1:2), several mixtures varying from 1:1.5 to 1:0.8 (epoxy monomer/anhydride hardener molar ratio) were polymerized. Results are reported in Table 1. The best molar ratio is determined on the basis of both FT-IR analysis and T_g values. Indeed the FT-IR spectra

are indicative of the curing reaction. As previously reported [21], the polymerization reaction is highlighted by the appearance of the C=O ester stretching band at about 1723 cm^{-1} . Concomitantly, the epoxy band at 915 cm^{-1} (CeO oxirane group stretching) present in the DGEBA spectrum and the anhydride elongation bands at 1774 and 1850 cm^{-1} (C=O) and at 895 cm^{-1} (CeO) present in the PA spectrum disappear. With the epoxy monomer/anhydride hardener molar ratio of 1:0.8, IR spectrum indicates an epoxy excess ($\nu_{\text{CeO}} 915\text{ cm}^{-1}$), whereas an excess of anhydride remains when using the epoxy monomer/anhydride hardener molar ratio of 1:1.5 ($\nu_{\text{C=O}} 1774$ and 1850 cm^{-1} , $\nu_{\text{CeO}} 895\text{ cm}^{-1}$). With the epoxy monomer/anhydride hardener molar ratio of 1:1.2, the FT-IR spectrum only shows the ester band at 1723 cm^{-1} (see Fig. 4). Moreover, this molar ratio leads to a high T_g value of 110 °C compatible with further applications of the final material. Thus, the best epoxy monomer/anhydride hardener/catalyst molar ratio of 1:1.2:0.05 is used for further work.

3.2. Curing of epoxy monomers with the biosourced anhydride hardeners and DMID catalyst in the molar ratio of 1:1.2:0.05

The curing of epoxy monomers and anhydride hardeners was carried out by heating the mixture of epoxy monomer/anhydride hardener/DMID catalyst. With the aim of application in the composite field, the consistency of the initial mixture has to be taken into account. Depending on the nature of both the epoxy monomer and the anhydride hardener, the initial mixture could be in the solid form or in the form of a waxy paste (WP) or cohesive powder (CP) more or less viscous at room temperature as reported in Table 2. Most of the time, the mixture is in form

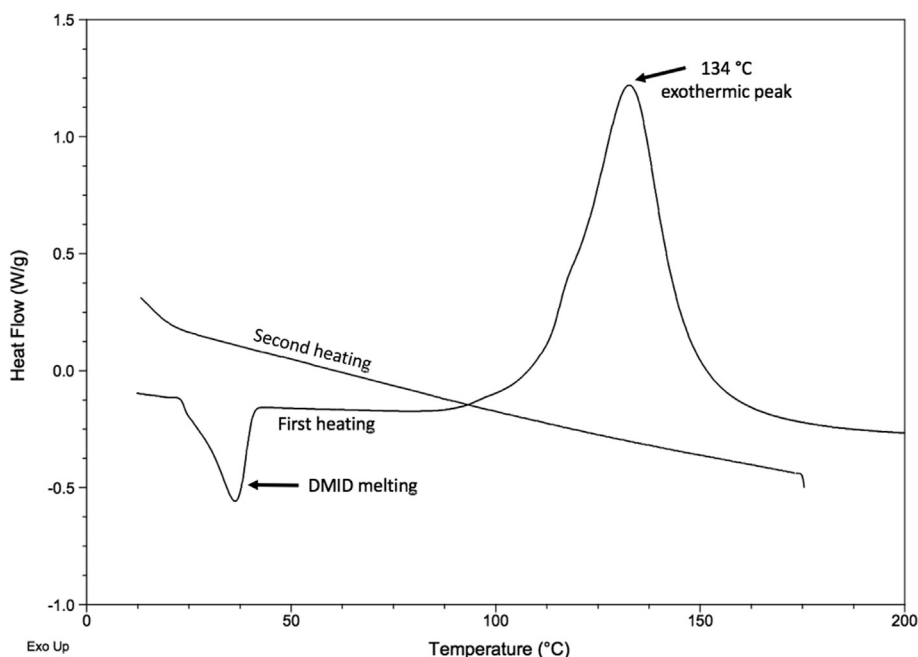


Fig. 3. DSC curves of the curing reaction of DGEBA in the presence of the catalytic amount of DMID.

Table 1FT-IR analysis and T_g values for several epoxy monomer/anhydride hardener/catalyst molar ratios.

Molar ratio of monomer/hardener/catalyst	FT-IR	T_g (°C)
1:0.8:0.05	Presence of remaining epoxy (915 cm^{-1}) and resulting ester (1723 cm^{-1})	90
1:1.2:0.05	Only the presence of the resulting ester (1723 cm^{-1})	110
1:1.5:0.05	Presence of remaining anhydride ($895, 1774$ and 1850 cm^{-1}) and resulting ester (1723 cm^{-1})	135

of WP at room temperature except for the DGE-isoEu for which a CP is often obtained. It is noticeable that all the mixtures become liquid at 60 °C before the polymerization starts. Furthermore, we verified experimentally by TGA that no physical phenomena inherent to the reactants involved (in particular potential sublimation of acid anhydrides) interfere with the curing process. Namely, no weight losses were recorded in the range of polymerization temperatures. Therefore, all of these experimental data are well compatible with usual composite processing.

Immediately after mixing and for each formulation, polymerization reaction was followed by DSC (heating from 0 to 250 °C at a rate of 5 °C min^{-1}). Most of the time one broad exothermic peak is recorded between 60 and $150\text{--}190\text{ °C}$. However, in some cases, two distinct exothermic peaks are observed. For example, polymerization of DGE-isoEu and IA leads to two peaks starting at

room temperature and ending at 175 °C . This phenomenon has previously been attributed to possible parallel curing reactions [14,21]. Furthermore, it is worth noting that the exothermic peak can overlap with the end of the endothermic fusion peak of the epoxy monomer or the anhydride hardener compound. In such case, the calculation of the experimental polymerization enthalpy is impossible.

With the final aim of biocomposite manufacturing, attention must be paid to both temperatures: (1) temperature at the beginning of the polymerization and (2) temperature(s) corresponding to the maximum of the polymerization peak(s). Indeed, the polymerization must be avoided during the step of fibre impregnation. Moreover, to prevent damage of fibres, reticulation reaction has to be carried out at less than 160 °C . Consequently, considering DGE-isoEu monomer, IA hardener is not a good candidate

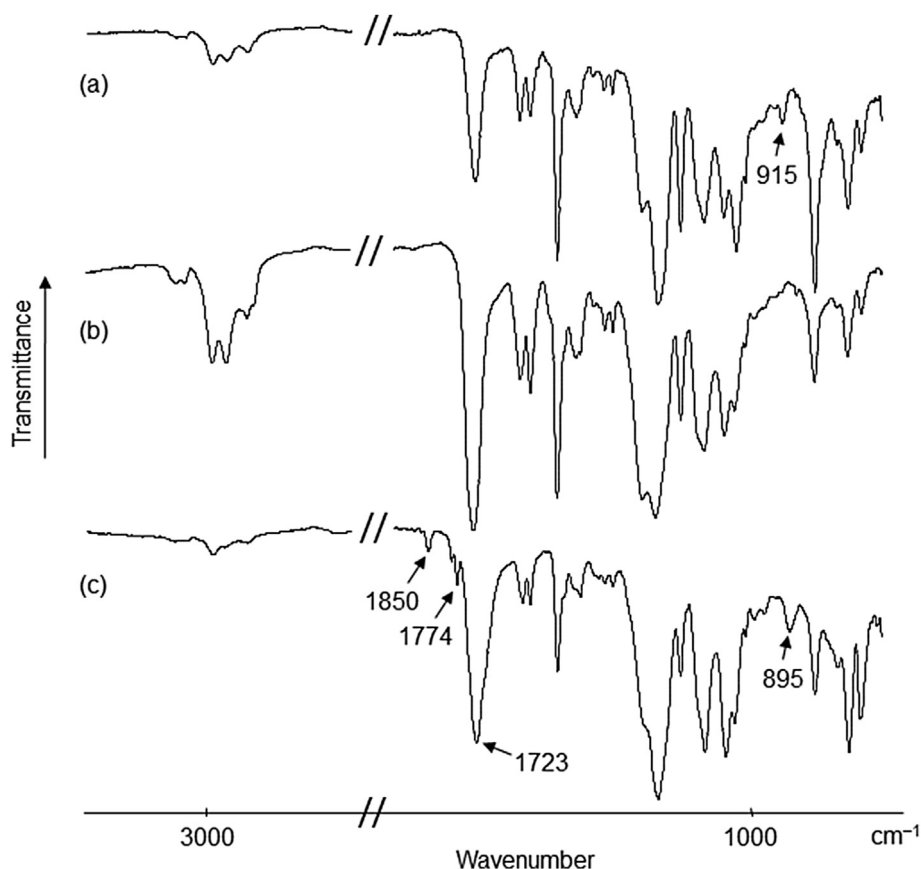


Fig. 4. Infrared spectra attenuated total reflectance of the resulting materials in the epoxy monomer/anhydride hardener/catalyst molar ratio: (a) 1:0.8:0.05, (b) 1:1.2:0.05, (c) 1:1.5:0.05.

Table 2

Values of the polymerization enthalpy/temperature and consistency of the different mixtures before polymerization.

	DPA	GA	PA	CA	SA	IA
DGE-isoEu/anhydride hardeners						
Mixture consistency	CP	WP	CP	CP	CP	WP
<i>Polymerization</i>						
Start–end T ($^{\circ}\text{C}$)	60–150	60–160	60–190	100–190	65–150	25–175
Peak T ($^{\circ}\text{C}$)	108	103	91	129	98	41; 136
Enthalpy ^a (kJ mol^{-1})	/	/	/	157	/	/
DGE-Eu/anhydride hardeners						
Mixture consistency	CP	WP	WP	WP	WP	WP
<i>Polymerization</i>						
Start–end T ($^{\circ}\text{C}$)	50–160	60–150	70–160	80–190	75–210	50–180
Peak T ($^{\circ}\text{C}$)	105; 119	132	122	137	125	116; 151
Enthalpy ^a (kJ mol^{-1})	/	/	156	131	214	/
DGER/anhydride hardeners						
Mixture consistency	CP	WP	WP	WP	WP	Liquid
<i>Polymerization</i>						
Start–end T ($^{\circ}\text{C}$)	50–170	50–170	60–180	70–180	70–170	60–170
Peak T ($^{\circ}\text{C}$)	106; 116	116; 131	112	126	120	109; 122
Enthalpy ^a (kJ mol^{-1})	/	/	/	/	/	/
DGEBA/anhydride hardeners						
Mixture consistency	CP	WP	WP	WP	WP	WP
<i>Polymerization</i>						
Start–end T ($^{\circ}\text{C}$)	60–170	50–210	60–180	80–200	80–150	80–160
Peak T ($^{\circ}\text{C}$)	121	127	118	133	131	124
Enthalpy ^a (kJ mol^{-1})	/	/	/	/	/	/

^a The calculation of the exothermic polymerization enthalpy (in kJ mol^{-1} of the epoxide group) was not always possible because the exothermic peak is not well dissociated from the endothermic fusion peak of the epoxy monomer/anhydride hardener/DMID catalyst mixture.

because it already reacts at room temperature, whereas CA hardener is the most suitable curing agent. When comparing the polymerization temperatures (T ($^{\circ}\text{C}$) of the maximum of the peak), DGE-isoEu monomer appears to be the epoxy resin reacting at the lowest temperature

whatever the hardener. Thus, DGE-isoEu monomer is a well appropriate resin for manufacturing biocomposite reinforced by natural fibres. A typical DSC curve recorded during the curing of DGE-isoEu monomer and CA hardener is reported in Fig. 5.

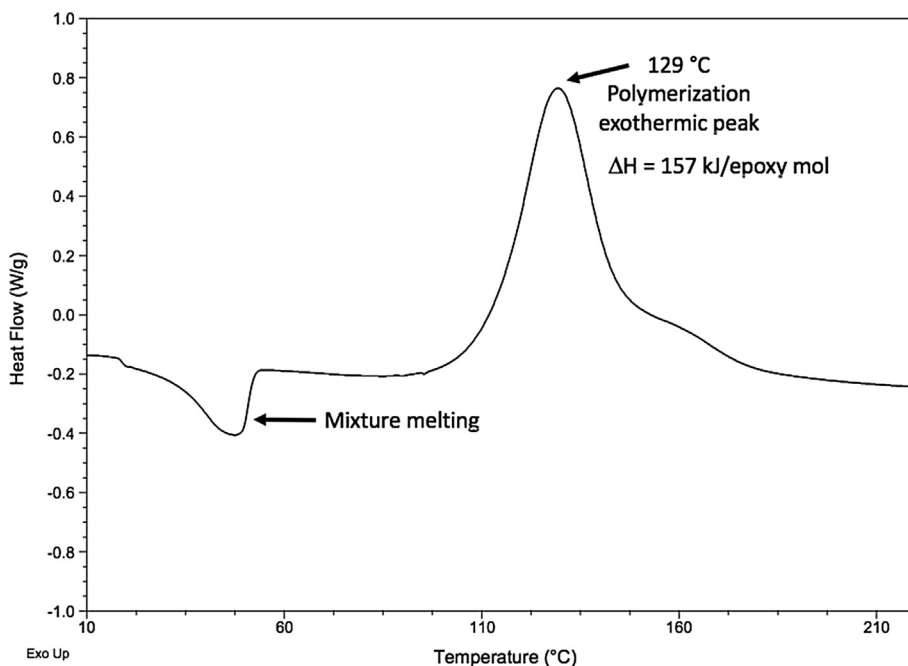


Fig. 5. Typical DSC curve registered during the curing of epoxy monomer with the anhydride hardener according to the procedure described in Section 2 (DGE-isoEu/CA/DMID).

Table 3

T_g values of the different epoxy thermosetting polymers determined by DSC.

Composition of the cured samples	Glass transition temperature (T_g , °C)					
	DPA	GA	PA	CA	SA	IA
DGE-isoEu/hardener	123	78	115	121	94	76
DGE-Eu/hardener	126	65	109	112	79	85
DGER/hardener	149	64	124	153	83	74
DGEBA/hardener	152	90	125	162	101	81

3.3. Characterization of epoxy thermosets

3.3.1. Glass transition temperatures

Glass transition temperatures of the cured samples, determined by DSC, are reported in Table 3. A typical DSC curve showing the T_g value is reported in Fig. 6 (here, DGE-isoEu/CA/DMID). For all the studied epoxy polymers, no additional exotherms are observed in DSC after the curing schedule indicating that the systems are well cured. The high T_g values are close to those of the commercial petrosourced epoxy materials. For instance, T_g of 100–150 °C are usually obtained when using DGEBA and polyamines [12]. Furthermore, it is notable that these values are very higher than those of the commercial biosourced epoxy materials (Epobiox Sandtech $T_g = 80$ °C or Greenpoxy Sicomin $T_g = 85$ °C [31]). Thus, these first results are very encouraging for a biocomposite structural application.

T_g reflects both the chemical structure of the polymer chain and the architecture of the polymer as the length and the cross-linking degree of the chain. Thus, as expected, materials obtained using GA, SA or IA hardeners exhibit lower glass transition temperatures. Namely, when these

anhydride cycles are opened during the curing, these hardeners lead to flexible linear carbon chain. Conversely, when anhydride functions of DPA, PA and CA react, bulky and rigid side groups' cycle still remain, leading to materials with higher glass transition temperatures.

Not surprisingly as the chemical structures of DGE-isoEu and DGE-Eu are similar, the glass temperatures of their corresponding materials are close. Therefore, the difference of the epoxide group position (internal position for DGE-isoEu, terminal position for the DGE-Eu) generally inducing a difference in reactivity is not highlighted in this case.

3.3.2. Thermal degradation by TGA

Degradation temperatures of each epoxy thermoset corresponding to 5%, 50% weight loss and maximum degradation rate are labelled as $T_{5\%}$, $T_{50\%}$ and T_{max} and reported in Table 4. The polymers have a fairly good thermal stability because they are stable till about 300 °C except when IA is used. In this case $T_{5\%}$ is recorded at about 270–280 °C.

3.3.3. Nanoindentation measurements

All the samples were submitted successfully to nanoindentation tests except eight materials (DGE-isoEu/DPA, DGE-isoEu/IA, DGE-Eu/DPA, DGE-Eu/GA, DGE-Eu/SA, DGE-Eu/IA, DGER/DPA, and DGEBA/DPA). The heterogeneity and/or porosity of these last materials after polymerization were too high to ensure appropriate and relevant measurements using nanoindentation. It is possible to note that all the materials obtained using the GA hardener were unsatisfactory (Table 5).

An example of the results obtained for each type of indentation tests performed on the DGE-isoEu/SA can be

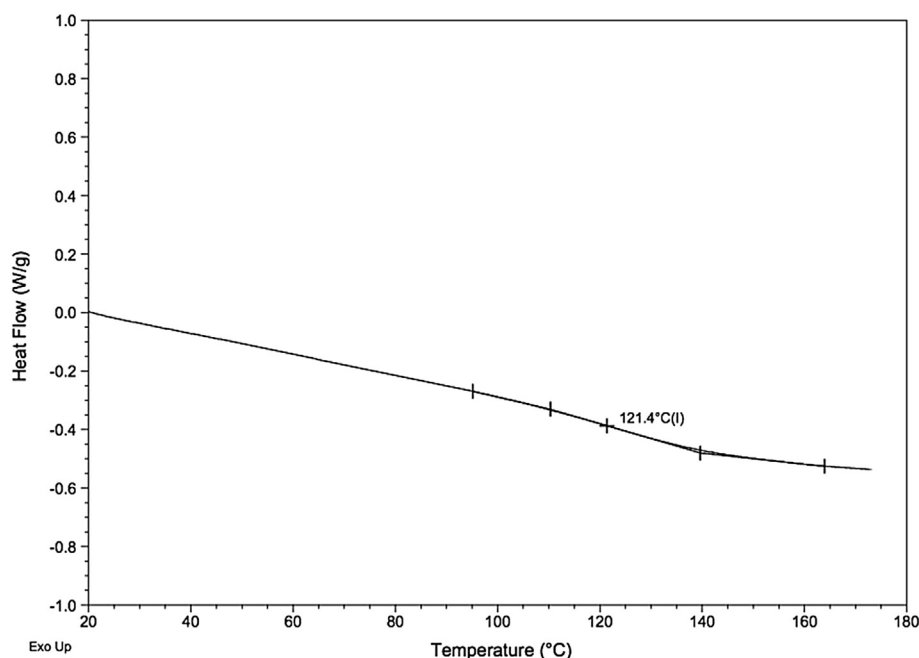


Fig. 6. Determination of the T_g value (DGE-isoEu/CA/DMID) by DSC according to the procedure described in Section 2.

Table 4

Temperatures of thermal degradation ($T_{5\%}$, $T_{50\%}$ and T_{\max}) of the materials resulting from epoxy monomers cured with the different anhydride hardeners.

Thermoset	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{\max} (°C)
DGE-isoEu/DPA	332	415	416
DGE-isoEu/GA	328	412	411
DGE-isoEu/PA	298	376	379
DGE-isoEu/CA	328	414	426
DGE-isoEu/SA	297	408	409
DGE-isoEu/IA	272	408	410
DGE-Eu/DPA	335	420	420
DGE-Eu/GA	355	440	431
DGE-Eu/PA	331	395	366
DGE-Eu/CA	358	419	414
DGE-Eu/SA	331	434	430
DGE-Eu/IA	300	427	421
DGER/DPA	346	421	420
DGER/GA	365	440	433
DGER/PA	321	409	449
DGER/CA	355	417	417
DGER/SA	332	430	429
DGER/IA	272	411	420
DGEBA/DPA	373	441	429
DGEBA/GA	373	446	441
DGEBA/PA	351	407	395
DGEBA/CA	369	435	426
DGEBA/SA	308	437	433
DGEBA/IA	287	421	428

found in Figs. 7–9. The reproducibility can be appreciated in Fig. 9 where three indentation curves are presented and appear almost superimposed. All the figures illustrate the viscous behaviour of the sample. In fact, the response of the sample depends clearly on the values of the constant strain rate \dot{h}/h (see Fig. 7). Furthermore, the multicyle

indentation curve, shown in Fig. 8, exhibits also open hysteresis on the unloading–reloading segments that are generally characteristic of phase transformation, reversible kink bands or time-dependent behaviour. Finally, the holding time of 1200 s leads to a large amount of material creep, as observed in Fig. 9.

This type of behaviour is observed in all the samples. The strain rate sensitivity calculated assuming a G'Sell and Jonas [32] law allows us to compare the different samples; however, viscoelasticity or viscoplasticity cannot be distinguished.

Table 5 presents the mechanical properties determined using the nanoindentation tests. The materials synthesized from the DGEBA have an instantaneous modulus comprised between 3.36 and 4.73 GPa, a relaxed modulus between 3.02 and 4.24 GPa and a hardness between 183 and 289 MPa. All the materials synthesized from the bio-based polymers have equal or superior properties with an instantaneous modulus comprised between 4.31 and 6.10 GPa, a relaxed modulus between 3.41 and 4.94 GPa and a hardness between 188 and 367 MPa.

The time-dependency is also generally slightly higher for materials synthesized from biobased monomers with a strain rate sensitivity comprised between 0.025 and 0.046 (when compared to 0.026 obtained with DGEBA).

4. Conclusions

DGE-Eu and DGE-isoEu monomers were successfully cured with several biosourced anhydride hardeners affording fully biobased materials. These hardeners have also been tested with the commercial biobased DGER and with the well-known petrosourced DGEBA.

Table 5

Properties measured with nanoindentation technique: relaxed (E_R) and instantaneous (E_I) moduli, hardness (H) and strain rate sensitivity (m).

Nanoindentation					
Monomer	Hardener	E_R (GPa) average standard deviation	E_I (GPa) average standard deviation	H (MPa) average standard deviation	m (θ) average standard deviation
DGE-isoEu	DPA	/	/	/	/
	GA	3.42 ± 0.05	4.26 ± 0.19	234 ± 7	0.032 ± 0.008
	PA	4.07 ± 0.01	4.39 ± 0.065	355 ± 5	0.032 ± 0.008
	CA	4.06 ± 0.05	4.77 ± 0.12	297 ± 6	0.027 ± 0.003
	SA	4.18 ± 0.02	4.95 ± 0.12	285 ± 8	0.046 ± 0.007
	IA	/	/	/	/
DGE-Eu	DPA	/	/	/	/
	GA	/	/	/	/
	PA	4.67 ± 0.006	5.31 ± 0.104	367 ± 5	0.025 ± 0.006
	CA	4.05 ± 0.012	4.68 ± 0.098	301 ± 4	0.025 ± 0.009
	SA	/	/	/	/
	IA	/	/	/	/
DGER	DPA	/	/	/	/
	GA	3.41 ± 0.11	4.43 ± 0.20	188 ± 12	0.042 ± 0.025
	PA	4.91 ± 0.03	5.45 ± 0.14	361 ± 11	0.030 ± 0.007
	CA	3.70 ± 0.05	4.31 ± 0.14	238 ± 14	0.029 ± 0.008
	SA	4.43 ± 0.00	5.65 ± 0.22	253 ± 7	0.042 ± 0.011
	IA	4.94 ± 0.01	6.10 ± 0.18	296 ± 5	0.040 ± 0.009
DGEBA	DPA	/	/	/	/
	GA	3.02 ± 0.03	3.36 ± 0.12	183 ± 10	0.030 ± 0.032
	PA	4.24 ± 0.09	4.73 ± 0.16	278 ± 18	0.026 ± 0.014
	CA	3.42 ± 0.02	3.50 ± 0.09	220 ± 17	0.026 ± 0.010
	SA	3.65 ± 0.01	4.14 ± 0.13	223 ± 10	0.026 ± 0.010
	IA	4.21 ± 0.10	4.45 ± 0.09	289 ± 12	0.027 ± 0.013

The quality of the sample surface did not allow satisfactory measurements.

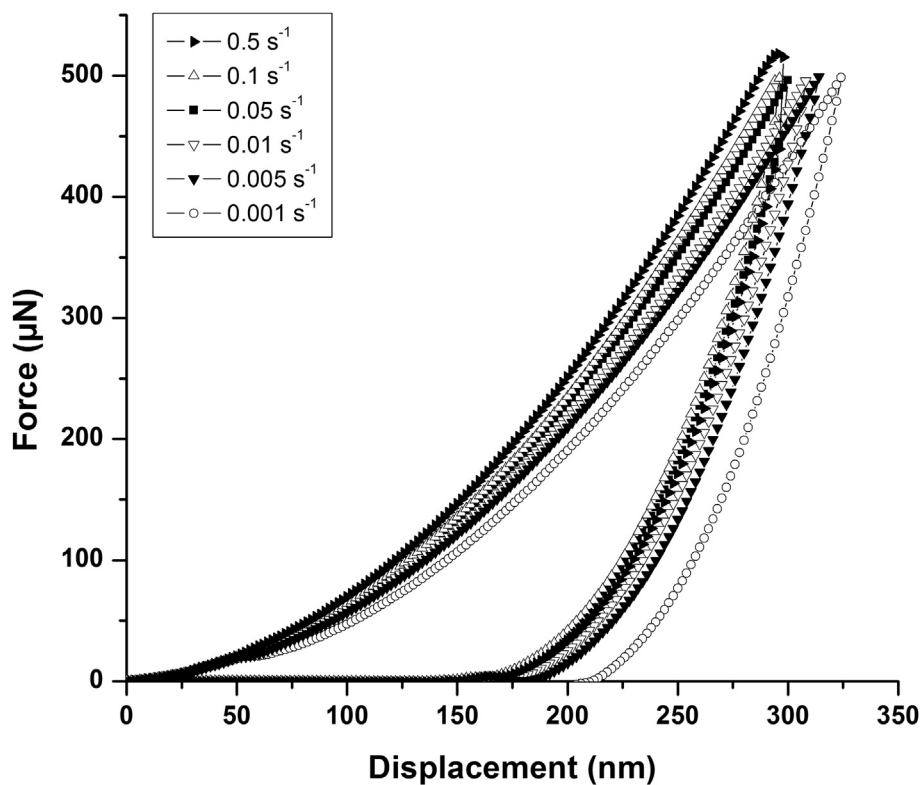


Fig. 7. Load–displacement responses of the DGE-isoEu/SA material obtained at different constant strain rates.

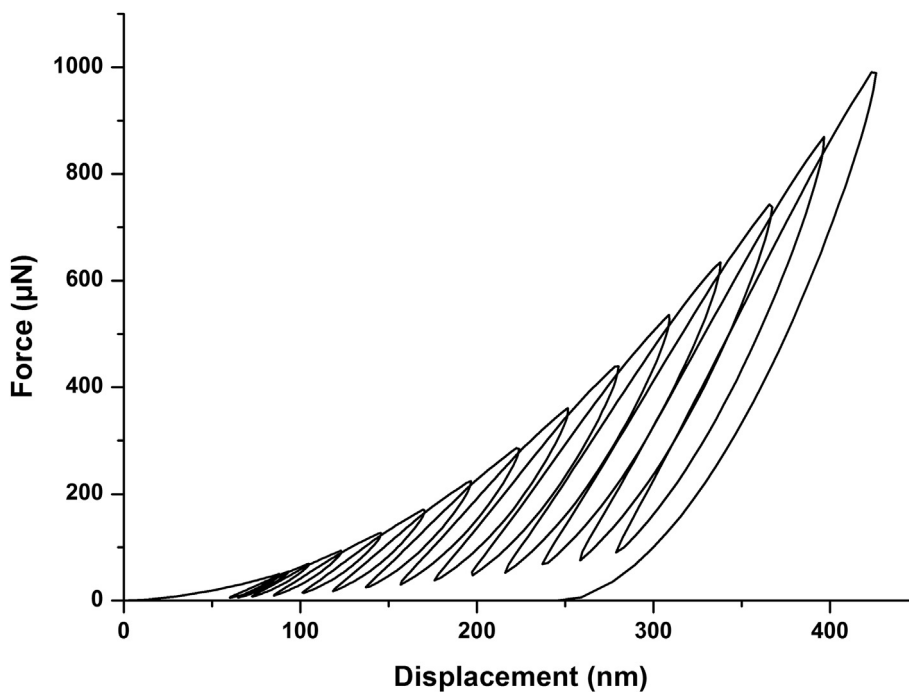


Fig. 8. Load–displacement responses of the DGE-isoEu/SA material during repeated linear load–time indentation ramps with the same rising time (20 s), but different increasing peak loads.

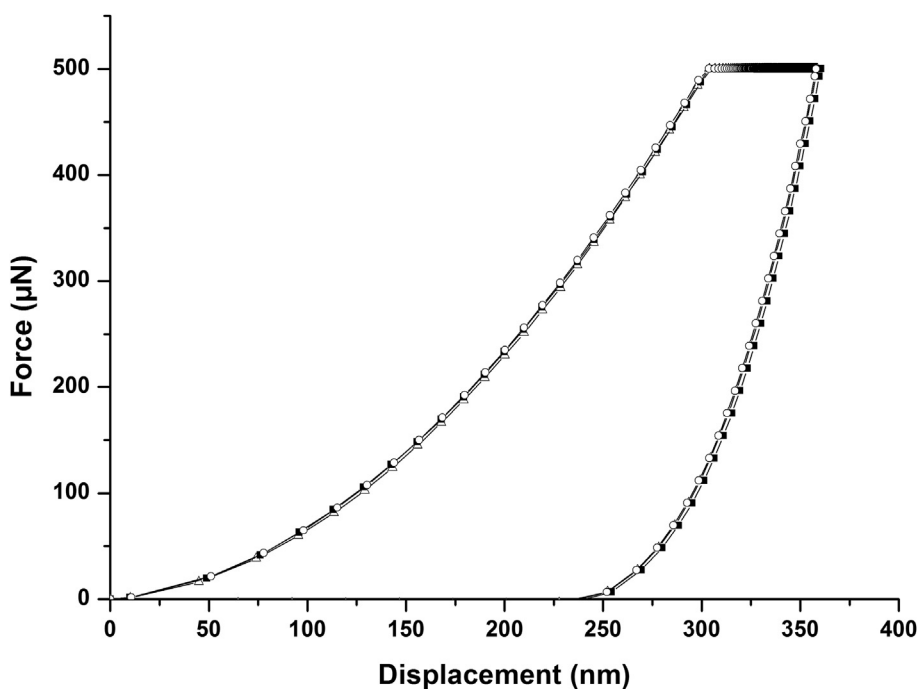


Fig. 9. Load–displacement response obtained under the indenting DGE-isoEu/SA material. A hold period of 1200 s at constant load is applied before unloading.

The biobased thermosetting polymers exhibit satisfactory thermomechanical properties, with T_g higher than 100 °C and instantaneous modulus ranged from 4 to 6 GPa. Their performances are very close to those of the commercial petrosourced epoxy materials and better than those obtained with the commercial partially biobased epoxy thermosets. The curing of DGE-Eu or DGE-isoEU monomers with DPA, PA, CA hardeners, respectively, leads to the most promising epoxy thermosets.

Polymerization occurs in the range of 90–130 °C. These temperatures are compatible with usual composite processing including natural fibres. This allows the manufacture of fully biobased composite. The study sets up a framework for the impregnation of natural fibres to manufacture fully biobased composites.

Acknowledgements

The authors would like to acknowledge Rodolphe Henrot for the DSC measurements. The authors are grateful for general and financial support from the Centre National de la Recherche Scientifique (CNRS-France) and the University of Bourgogne Franche-Comté (BQR2014-19 Bourgogne Franche-Comté). C.F. is thankful for a PhD fellowship awarded by the Conseil Régional de Bourgogne (France) in the frame of the “Jeunes Chercheurs Entrepreneurs-2016” program and in partnership with *AgroComposites Entreprises*.

References

- [1] Q. Guo, *Thermosets Structure, Properties and Applications*, 1st ed., Woodhead Publishing Ltd., Cambridge, 2012.
- [2] P. Fenichel, N. Chevalier, F. Brucker-Davis, *Ann. Endocrinol.* 74 (2013) 211–220.
- [3] J. Michalowicz, *Environ. Toxicol. Pharmacol.* 37 (2014) 738–758.
- [4] Y. Onundi, B.A. Drake, R.T. Malecky, M.A. DeNardo, M.R. Mills, S. Kundu, A.D. Ryabov, E.S. Beach, C.P. Horwitz, M.T. Simonich, L. Truong, R.L. Tanguay, L.J. Wright, N. Singhal, T.J. Collins, *Green Chem.* 19 (2017) 4234–4262, <https://doi.org/10.1039/C7GC01415E>.
- [5] S. Ma, T. Li, X. Liu, J. Zhu, *Polym. Int.* 65 (2016) 164–173.
- [6] J.M. Raquez, M. Deléglise, M.-F. Lacrampe, P. Krawczak, *Prog. Polym. Sci.* 35 (2010) 487–509.
- [7] M.A. Meier, J.O. Metzger, U.S. Schubert, *Chem. Soc. Rev.* 36 (2007) 1788–1802.
- [8] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.-P. Pascault, *Chem. Rev.* 114 (2014) 1082–1115.
- [9] C. Ding, A.S. Matharu, *ACS Sustain. Chem. Eng.* 2 (2014) 2217–2236.
- [10] C. Aouf, H. Nouailhes, M. Fache, S. Caillol, B. Boutevin, H. Fulcrand, *Eur. Polym. J.* 49 (2013) 1185–1195.
- [11] C. Aouf, J. Lecomte, P. Villeneuve, E. Dubreucq, H. Fulcrand, *Green Chem.* 14 (2012) 2328–2336.
- [12] G. Yang, B.J. Rohde, H. Tesebay, M.L. Robertson, *ACS Sustain. Chem. Eng.* 4 (2016) 6524–6533.
- [13] M. Shibata, T. Ohkita, *Eur. Polym. J.* 92 (2017) 165–173.
- [14] J. Qin, H. Liu, P. Zhang, M. Wolcott, J. Zhang, *Polym. Int.* 63 (2014) 760–765.
- [15] J. Wan, J. Zhao, B. Gan, C. Li, J. Molina-Aldareguia, Y. Zhao, Y.-T. Pan, D.-Y. Wang, *ACS Sustain. Chem. Eng.* 4 (2016) 2869–2880.
- [16] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, E.N. Kalali, X. Wang, D.-Y. Wang, *Chem. Eng. J.* 284 (2016) 1080–1093.
- [17] A. Llevot, E. Grau, S. Carloti, S. Grelier, H. Cramail, *Macromol. Rapid Commun.* 37 (2016) 9–28.
- [18] F. Ferdosian, Z. Yuan, M. Anderson, C. Xu, *Thermochim. Acta* 618 (2015) 48–55.
- [19] J. Xin, M. Li, R. Li, M.P. Wolcott, J. Zhang, *ACS Sustain. Chem. Eng.* 4 (2016) 2754–2761.
- [20] (a) G. Engelmann, J. Ganster, *Holzforchung* 68 (2014) 1–12; (b) L.C. Over, E. Grau, S. Grelier, M.A.R. Meier, H. Cramail, *Macromol. Chem. Phys.* 218 (2017) 1600411; (c) D.J. van de Pas, K.M. Torr, *Biomacromolecules* 18 (2017) 2640–2648.
- [21] C. François, S. Pourchet, G. Boni, S. Fontaine, Y. Gaillard, V. Placet, M.V. Galkin, A. Orebom, J. Samec, L. Plasseraud, *RSC Adv.* 6 (2016) 68732–68738.

- [22] A. Paramarta, D.C. Webster, *React. Funct. Polym.* 105 (2016) 140–149.
- [23] C. Robert, F. de Montigny, C.M. Thomas, *ACS Catal.* 4 (2014) 3586–3589.
- [24] S. Thiyagarajan, H.C. Genuino, J.C. van der Waal, E. de Jong, B.M. Weckhuysen, J. van Haveren, P.C.A. Bruijninx, D.S. van Es, *Angew. Chem., Int. Ed.* 55 (2016) 1368–1371.
- [25] V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, B. Boutevin, *Chem. Rev.* 116 (2016) 14181–14224.
- [26] M. Fache, C. Monteremal, B. Boutevin, S. Caillol, *Eur. Polym. J.* 73 (2015) 344–362.
- [27] M.V. Galkin, J.S.M. Samec, *ChemSusChem* 7 (2014) 2154–2158.
- [28] B.M. Bell, J.R. Briggs, R.M. Campbell, S.M. Chambers, P.D. Gaarenstroom, J.G. Hippler, B.D. Hook, K. Kearns, J.M. Kenney, W.J. Kruper, D.J. Schreck, C.N. Theriault, C.P. Wolfe, *Clean* 36 (2008) 657–661.
- [29] J. Vigier, C. François, S. Pourchet, G. Boni, L. Plasseraud, V. Placet, S. Fontaine, H. Cattet, *Acta Crystallogr. E* 73 (2017) 694–697.
- [30] K. Dusek, *Adv. Polym. Sci.* 78 (1986) 1–59.
- [31] These values are indicated in the technical datasheets of the respective providers and were experimentally confirmed in the frame of our study.
- [32] C. G'Sell, J. Jonas, *J. Mater. Sci.* 14 (1979) 583–591.