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Multifunctional β-amino alcohols as bio-based amine curing agents for the isocyanate- and phosgene-free synthesis of 100 % bio-based polyhydroxyurethane thermosets

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The aminolysis of bio-based glycidylethers and limonene dioxide with aqueous ammonia represents a versatile one-step synthesis of multifunctional bio-based amine curing agents and does not require either organic solvents besides bioethanol or tedious purification. Moreover, the identical bio-based glycidylether serves as the raw material for both the amine curing agent and the polyfunctional cyclic carbonate, both of which are key intermediates in non-isocyanate polyhydroxyurethane (NIPU) production. This study elucidates the influences of molecular architecture and amine content of multifunctional β-amino alcohol (AA) curing agents, as determined by means of ^{13}C-NMR spectroscopy, and the type of polyfunctional cyclic carbonates on the thermal and mechanical NIPU properties, NIPU degradation and NIPU solvent swelling. Preferably, owing to their rather high viscosities, polyfunctional AAs are blended together with hexamethylene diamine (HMDA) to enable facile NIPU cure at ambient temperatures. As compared to HMDA, the addition of the less reactive polyfunctional AAs increases gel time, as measured by oscillatory rheological experiments, and simultaneously improves NIPU stiffness, as determined by the Young's modulus (+200 %).

Introduction

Among polymeric materials, 68 years after the pioneering advances of Otto Bayer[1], polyurethanes (PUs) are well known for their outstanding versatility, as reflected by their broad range of commercial applications varying from flexible and rigid foams to rubbers, coatings and adhesives. Stimulated by strict government regulations like REACH and the quest for sustainable development, there exists a growing demand for greener processes reducing potential hazards for humans and environment and exploiting renewable resources. Hence, PU development aims at the development of bio-based, isocyanate- and phosgene-free PUs with properties comparable to PUs based on fossil resources and favorable economics. The *2015 Presidential Green Chemistry Challenge Award* by the *U.S. Environmental Protection Agency* in cooperation with the *American Chemical Society* was presented to Hybrid Coatings Technology Company for their development of green, non-isocyanate polyhydroxyurethanes (NIPUs).[2, 3]

Typically, NIPUs are produced by curing polyfunctional cyclic carbonates with polyfunctional amines. The absence of toxic and hydrolytically sensitive isocyanate resins in NIPU synthesis greatly facilitates safety and handling procedures with respect to conventional isocyanate-based PUs. Several recent reviews have addressed NIPU formation and applications.[4-6] Albeit six- and seven-membered cyclic carbonates are more reactive with respect to five-membered carbonates[7-9], the focus of NIPU development has been placed on five membered cyclic carbonates which are readily available from epoxy resins by chemical fixation of carbon dioxide.[10,11] During recent years, various bio-based epoxy feed stocks have been employed in NIPU syntheses. Besides the oxidation of unsaturated compounds like plant oils and terpene derivatives, the glycidylization of polyols with epichlorohydrin, derived from glycerol (a by-product of the bio diesel production), represents a promising route to bio-based epoxy resins.[12, 13, 14] Suitable polyols like trimethylolpropane or pentaerythritol are synthesized by aldol addition and subsequent Cannizzaro reaction of formaldehyde with *n*-butyraldehyde or acetaldehyde, respectively.[15, 16] These aldehydes can be derived from bio-based raw materials through the acetone butanol-ethanol fermentation process (ABE process) of lignocellulosic biomass or through the catalytic dehydration of biomass.[17-21] These epoxy resins can further be converted with carbon dioxide into cyclic carbonates. The carbonation of epoxy resins is accelerated by catalysts such as tetrabutylammonium bromide (TBAB) and LiBr which exhibit the best balance of performance, cost efficiency and facile handling.[22-24] More reactive systems like salen complexes of Al^{III}, Cr^{III} and Co^{III}, accompanied with various co-catalysts[25], and the use of ionic liquids[26, 27] are less viable in commercial production of green cyclic carbonates and fail to meet the demands of green chemistry. Typically, the carbonation of

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epoxy resins occurs at 120-140 °C in the presence of 1-4 wt.-% TBAB, and requires 20-40 bar CO_2 pressure and reaction times of a few hours.[23, 24, 28]

Several strategies have been introduced to produce 100 % bio-based NIPUs by polyaddition of bio-based polyfunctional cyclic carbonates with bio-based amines. 100 % bio-based NIPU thermoplastics were obtained by polyaddition of difunctional bio-based cyclic carbonates with difunctional bio-based amines.[24, 29, 30] Bio-based NIPU thermosets were reported by Javni et al. who cured soy bean oil based polyfunctional cyclic carbonates with bio-based diamines such as ethylene, butylene and hexamethylene diamine (HMDA).[23] However, the resulting highly flexible bio-based NIPUs exhibited low glass transition temperatures (T_g) around 38-40 °C.[23] According to Bähr et al. the higher carbonate functionality of linseed oil based cyclic carbonate afforded higher T_g values.[31] In 2012, Bähr and Mülhaupt reported on bio-based NIPU thermosets prepared by curing limonene dicarbonate with multifunctional amines like *tris*(*N*-2-aminoethyl)amine, hyperbranched polyethylene imines and citric acid amino amides, derived by reacting triethyl citrate with HMDA or 1,12-dodecamethylene diamine.[24]

Bio-based NIPU thermosets with a broad spectrum of tailor-made mechanical and thermal properties were derived from polyfunctional carbonates exploiting bio-based epoxy resins as raw materials. Typically, glycerol- (GGC), trimethylolpropane- (TMPGC) and pentaerythritol-polyglycidylether based cyclic carbonates (PGC) were produced by chemical fixation of CO_2 (30 bar) at 120 °C and reaction time of 10 h.[28] A detailed analysis of the products obtained by the glycidylization of these polyols is given by Camara et al.[32] On curing them with HMDA and also with mixtures of HMDA and citric acid amino amides, NIPUs exhibiting Young's moduli of 7-2500 MPa and elongation at break of 3-310 % became available. It was shown, that 1,4-diazabicyclo[2.2.2]octan (DABCO) catalyzed the NIPU formation at room temperature. More reactive catalysts include triazabicyclodecene (TBD) and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU).[33] As compared to the sterically hindered limonene dicarbonate, polyfunctional carbonates prepared by carbonation of glycidyl ethers are much more reactive, owing to the presence of the electron withdrawing ether groups. [24] Boyer et al. further investigated the differences of the reactivity of terminal and internal cyclic carbonate groups in fatty acid diesters.[34] Moreover, the NIPU cure rate decreases with increasing molar mass and steric hindrance of the amine curing agent, whereas electron donating groups adjacent to the amine group enhance the nucleophilicity, thus accelerating NIPU cure rate.[35] Hence, primary amines react with cyclic carbonates at room temperature, albeit higher cure temperature around 70 °C is preferred for achieving full cure, especially in the case of NIPUs with high glass transition temperatures. In contrast, NIPU cure with secondary amines requires much higher cure temperatures varying between 90 and 200 °C.[32] At very high cure temperatures, however, decarboxylation and alkylation are encountered as side reactions. Therefore, it is an important objective in NIPU synthesis to tailor bio-based multifunctional primary amine curing agents in order to improve NIPU properties without impairing cure at ambient temperature.

Several attempts have been made to develop polyfunctional amine curing agents for NIPUs. For example, multifunctional amines were prepared by the addition of excess triethylenetetramine to difunctional cyclic carbonates.[36, 37] However, as far as we know, the resulting polyamines were used to cure epoxy resins but not for NIPU preparation. Figovsky et al. claimed the use of polyfunctional siloxane amines prepared by the hydrolysis of commercially available γ-aminopropyltriethoxy silane.[38] Croda introduced 100 % bio-based flexible di- and trifunctional amine curing agents, commercially available under the trade name Priamine™, prepared by di- or trimerization of fatty acids and subsequent conversion of the carboxylic acid end groups into amines.[39]

Herein, we report on tailoring multifunctional β-amino alcohols (AAs) as versatile bio-based amine curing agents for designing 100 % bio-based NIPU thermosets with improved thermal and mechanical properties. Both polyfunctional cyclic carbonates and multifunctional AA curing agents were derived from the same bio-based polyglycidylethers (see **Scheme 1**). While the chemical conversion of polyglycidylethers with carbon dioxide affords polyfunctional carbonates, ring-opening of polyglycidylethers with ammonia in water and bioethanol yields the corresponding polyfunctional AAs in essentially quantitative yields. This facile aminolysis is a one-step process and does not require tedious purification in separate steps. A similar strategy to synthesize monofunctional AAs was introduced by Kaburagi et al. who investigated regioisomer formation and the influence of catalyst types.[40] In contrast to AA synthesis, many other polyamine syntheses such as Gabriel synthesis, Curtius reaction, Hofmann rearrangement or direct catalytic conversions of alcohols with ammonia, pioneered by Milstein et al.,[41, 42] fail to meet the demands of green chemistry, as they require special purification to remove catalyst residues and by-products. In this study, AA structures and AA amine functionalities, obtained by ring-opening of multifunctional bio-based epoxy resins with ammonia, were determined by ^{13}C-NMR spectroscopy. The role of HMDA as reactive diluent was examined in order to control resin viscosity, gel time and pot life, as determined by rheological measurements. An important objective was to elucidate the basic structure/property correlations of the resulting 100 % bio-based NIPU, especially with respect to the structures of NIPU components such as polyfunctional cyclic carbonates and multifunctional AA curing agents.

Experimental

Materials

Glycerol polyglycidyl ether (ipox CL 12, epoxy eq. 159 g eq^{-1}), trimethylolpropane polyglycidyl ether (ipox RD 20, epoxy eq. 136 g eq^{-1}) and pentaerythritol polyglycidyl ether (ipox CL 16, 167 g eq^{-1}) were kindly provided by ipox chemicals GmbH. Limonene dioxide was supplied by Rheinmetall Nitrochemie.

Aqueous ammonia solution (28 wt.-%) and hexamethylene diamine were obtained from Alfa Aesar. Ethanol, tetrabutyl ammonium bromide (TBAB) and phenol were purchased by Sigma Aldrich. Carbon dioxide grade N45 was obtained by Air Liquide.

Characterization

The FTIR measurements were performed on a Bruker FTIR Vector 2200 spectrometer with a Goldengate unit by using the attenuated total reflectance (ATR) technique (30 scans per one recording, 4 cm^{-1} resolution).

All ^{1}H- (299.87 MHz) and ^{13}C-NMR spectra (75.40 MHz) were recorded on a Bruker Avance II spectrometer. As internal standard the signals of the deuterated solvents were used. For the determination of epoxide (EC), carbonate (CC) and primary amine content (AC), phenol was used as internal reference during ^{1}H- and ^{13}C-NMR experiments. [32] In case of decoupled inverse-gated ^{13}C-NMR spectra, $Cr(acac)_3$ was added to reduce the relaxation times. The average integrals of the five aromatic, non-phenolic carbon atoms of phenol have been used for further calculations. The carbonate content could also be calculated directly from the determined epoxide content (EC) assuming 100 % conversion to cyclic carbonates, yielding identical results compared to NMR experiments. Following equations (s. Eq. 1-3) were used for calculations:

$$EC = \frac{m_{phenol} \times I_{epoxide}}{M_{phenol} \times I_{phenol} \times m_{epoxide}} \times 1000 \quad (1)$$

$$CC = \frac{EC}{1 + \frac{EC}{1000} \times 44.01} \quad (2)$$

$$AC = \frac{m_{phenol} \times I_{amine}}{M_{phenol} \times I_{phenol} \times m_{amíne}} \times 1000 \quad (3)$$

The viscosities, pot and gelation times were measured using an Anton Paar Physica MCR 301 rheometer with plate-plate geometry with a diameter of 25 mm. Viscosities were measured by a frequency sweep from 100 to 0.1 rad s^{-1} with 5 % deformation at 20, 50, 80 and 100 °C. Pot times were determined by the time reaching a viscosity of 10 Pa s. Gelation times were analyzed by the crossover of storage (G') and loss modulus (G'') during an oscillatory experiment with 10 rad s^{-1} and 5 % deformation at 80 °C. Melting points were obtained by a Büchi Melting Point B-540 with a heating rate of 2 K min^{-1}. Glass transition temperature (T_g) measurements were conducted on Netzsch DSC 204 F1 Phoenix with a heating and cooling rate of 10 K min^{-1} from -50 to 200 °C. T_g values were determined by the second heating step. Glass transition temperatures of NIPU samples were obtained by the tanδ method by dynamic mechanical analysis performed on a DMA Q800 by TA Instruments. All measurements were conducted with 1 Hz and 0.1 % deformation between -50-100 °C with a heating rate of 3 K min^{-1} with a preceding equilibrium step at -50 °C for 5 min^{-1} The mechanical properties of NIPU materials were determined by using a Zwick Z005 (Ulm, Germany, ISO/DP 527) according to DIN-EN-ISO527. Mechanical properties (Young's modulus, tensile strength and elongation at break) were measured at 23 °C by taking the statistical average of at least five specimens. Thermogravimetric analysis was performed on a TGA 4000 by PerkinElmer with a heating rate of 10 K min^{-1} from 50 to 650 °C under air. Additionally, swelling tests of NIPU materials were carried out in water and toluene over a period of 14 days. The degree of swelling was calculated from the percentage of weight increase.

General procedure of the syntheses of multifunctional β-amino alcohols

Pentaerythritol polyglycidyl ether (ipox CL 16, 167 g eq^{-1}, 6.02 mmol g^{-1}, 20.7 g, 0.125 mol) was dissolved in ethanol (100 mL) and placed together with an aqueous ammonia solution (28 %, 500 mL, 140 g, 8.22 mol, 66.0 eq) in a 2 L stainless steel reactor. The mixture was stirred at 100 °C for 15 h and then cooled to room temperature. The reactor was depressurized by conducting excess gaseous ammonia through two gas-washing bottles filled with diluted sulfuric acid. Ethanol and water were removed under reduced pressure (1 mbar, rotary vane pump) and recycled. The pentaerythritol polyglycidyl ether based amino alcohol (PG-AA, 21.97 g, 96 %) was obtained as a highly viscous yellow substance after drying under high vacuum.

Glycerol- (GG-AA, 8.63 g, 97 %) and trimethylolpropane polyglycidyl ether based amino alcohols (TMPG-AA, 7.82 g, 83 %) were also obtained as yellow, highly viscous liquids. Limonene amino alcohol (L-AA, 9.35 g, 97 %) was obtained as a brown solid.

Glycerol glycidylether based amino alcohol (GG-AA, 1):

Amine content: 5.13 mmol g^{-1}

^{1}H-NMR (299.87 MHz, MeOD-d_4): δ/ppm = 2.76-3.15 (1/1'-CH_2-NH_2), 3.54 (3-CH_2), 3.61 (4-CH_2), 3.69 (2/2'-C*H*-OH), 3.89 (5-CH).

^{13}C-NMR (75.40 MHz, MeOD-d_4): δ/ppm = 42.80 (1/1'-CH_2-NH_2), 44.30 (1/1'-CH_2-NH_2), 69.28 (2/2'-CH-OH), 72.26 (3-CH_2), 73.73 (3'-CH_2), 74.03 (3'-CH_2), 74.72 (4-CH_2), 79.02 (5-CH), 79.79 (5-CH).

ν_{max}/cm^{-1} = 3272 (ν_{O-H}, ν_{N-H}), 2870 (ν_{CH2}), 1602 (δ_{NH2}), 1507, 1454 (δ_{CH2}), 1336 (δ_{O-H}, ν_{C-N}), 1082 (ν_{C-O}).

Trimethylolpropane glycidylether based amino alcohol (TMPG-AA, 2):

Amine content: 6.41 mmol g^{-1}

^{1}H-NMR (299.87 MHz, MeOD-d_4): δ/ppm = 0.87 (7-CH_3), 1.40 (6-CH_2), 2.80 (1-CH_2-NH_2), 3.37 (3-CH_2), 3.40-4.05 ppm (2-C*H*-OH, 4-CH_2).

^{13}C-NMR (75.40 MHz, MeOD-d_4): δ/ppm = 7.98 (7-CH_3), 23.63 (6-CH_2), 24.09 (6-CH_2), 43.63 (5-C), 44.32-45.26 (1-CH_2-NH_2), 53.88 (1'-CH_2-NH-1'-CH_2, Dimer), 66.05 (2'-CH-OH, Dimer), 70.08 (2-CH-OH), 73.16 (3-CH_2), 74.93 (4-CH_2), 77.41 (4-CH_2).

ν_{max}/cm^{-1} = 3280 (ν_{O-H}, ν_{N-H}), 2864 (ν_{CH2}), 1598 (δ_{NH2}), 146((δ_{CH2}), 1380-1287 (δ_{O-H}, ν_{C-N}), 1099 (ν_{C-O}).

Pentaerythritol glycidylether based amino alcohol (PG-AA, 3):

Amine content: 5.29 mmol g^{-1}

^{1}H-NMR (299.87 MHz, MeOD-d_4): δ/ppm = 2.80-3.18 (1-C*H*$_2$-NH$_2$), 3.50 (3-CH$_2$), 3.56-3.85 (4-CH$_2$), 3.87-4.06 (2-C*H*-OH).

^{13}C-NMR (75.40 MHz, MeOD-d_4): δ/ppm = 42.54 (5-C), 44.14 (1-CH$_2$-NH$_2$), 45.66 (1-CH$_2$-NH$_2$), 46.42 (1-CH$_2$-NH$_2$), 52.07 (1'-CH$_2$-NH-1'-CH$_2$, Dimer), 54.12 (1'-CH$_2$-NH-1'-CH$_2$, Dimer), 65.34 (2'-CH-OH, Dimer), 65.64 (2'-CH-OH, Dimer), 68.62 (2-CH-OH), 72.01 (3-CH$_2$), 74.91 (4-CH$_2$), 76.91 (4-CH$_2$).

ν_{max}/cm^{-1} = 3283 (ν_{O-H}, ν_{N-H}), 2872 (ν_{CH2}), 1606 (δ_{NH2}), 1457 (δ_{CH2}), 1361-1260 (δ_{O-H}, ν_{C-N}), 1090 (ν_{C-O}).

Limonene amino alcohol (L-AA, 4):

Amine content: 6.28 mmol g^{-1}

^{1}H-NMR (299.87 MHz, MeOD-d_4): δ/ppm = 1.05-1.37 (1/10-CH$_3$), 1.43-2.28, (5-CH, 4/6/7-CH$_2$), 2.55-2.72 (3-C*H*-NH$_2$, 9-C*H*$_2$-NH$_2$), 2.76-2.90 (3-C*H*-NH$_2$, 9-C*H*$_2$-NH$_2$), 2.95-3.10 (3-C*H*-NH$_2$, 9-C*H*$_2$-NH$_2$).

^{13}C-NMR (75.40 MHz, MeOD-d_4): δ/ppm = 22.27 (1-CH$_3$), 23.37 (6-CH$_2$), 24.57 (6-CH$_2$), 26.67 (4-CH$_2$), 28.02 (10-CH$_3$), 28.61 (4-CH$_2$), 28.76 (10-CH$_3$), 29.06 (10-CH$_3$), 29.26 (10-CH$_3$), 29.76 (7-CH$_2$), 30.81 (7-CH$_2$), 33.91 (7-CH$_2$), 35.50 (7-CH$_2$), 35.90 (7-CH$_2$), 39.20 (5-CH), 39.55 (5-CH), 52.08 (9'-CH$_2$-NH-R, Dimer), 53.28 (9-CH$_2$-NH$_2$), 53.43 (9-CH$_2$-NH$_2$), 56.22-57.22 (3-CH-NH$_2$), 71.05 (2-C-OH), 71.30 (8-C-OH), 71.70-72.65 (8-C-OH).

ν_{max}/cm^{-1} = 3357 (ν_{O-H}, ν_{N-H}), 2933 (ν_{CH2}), 1596 (δ_{NH2}), 1455 (δ_{CH2}), 1404 (δ_{CH3}), 1372 (δ_{CH3}, δ_{O-H}, ν_{C-N}), 1125 (ν_{C-O}).

After recrystallization of crude L-AA (**4**) from acetonitrile (2-amino-4-(2-amino-1-hydroxy-1-methylethyl)-1-methylcyclo-hexanol):

Melting temperature: 80 °C

^{1}H-NMR (299.87 MHz, MeOD-d_4): δ/ppm = 1.14 (10-CH$_3$), 1.26 (1-CH$_3$), 1.57-2.19, (5-CH, 4/6/7-CH$_2$), 2.60 (3-C*H*-NH$_2$, 9-C*H*$_2$-NH$_2$), 2.65 (9-C*H*$_2$-NH$_2$), 2.96 (9-C*H*$_2$-NH$_2$), 3.00 (3-C*H*-NH$_2$, 9-C*H*$_2$-NH$_2$).

^{13}C-NMR (75.40 MHz, MeOD-d_4): δ/ppm = 24.54 (6-CH$_2$), 26.63 (4-CH$_2$, 1-CH$_3$), 29.04 (10-CH$_3$), 35.48 (7-CH$_2$), 39.20 (5-CH), 53.26 (9-CH$_2$-NH$_2$), 56.98 (3-CH-NH$_2$), 71.07 (2-C-OH), 73.23 (8-C-OH).

MS (dir. HR pos. APCI): m/z 203.1756 ([M+H]$^+$, 3 %), 186.1489 ([M+H-OH]$^{+\cdot}$, 100 %).

General procedure of the syntheses of cyclic carbonates

Glycerol-, trimethylolpropane- and pentaerythritol polyglycidyl ether based cyclic carbonates were synthesized according to Fleischer et al.[28] For example, trimethylolpropane polyglycidyl ether (992.2 g, 7.084 mol) was placed in a 2 L stainless steel reactor. Then TBAB (1.0 g, 1.0 wt.-%) and carbon dioxide (30 bar pressure) were added. The reaction mixture was stirred and heated at 100 °C until no epoxy groups were detected by ^{1}H-NMR spectroscopy. At full conversion, a nearly colorless viscous liquid was obtained in quantitative yield.

After cooling to room temperature and degassing under reduced pressure, all cyclic carbonates were obtained in high yields and were used without further purification. Glycerol-(GGC, carbonate content 4.9 mmol g^{-1}), trimethylolpropane-(TMPGC, carbonate content 5.6 mmol g^{-1}) and pentaerythritol polyglycidyl ether based cyclic carbonate (PGC, carbonate content 4.8 mmol g^{-1}) were obtained as viscous liquids. A detailed structural analysis of these cyclic carbonates is given by Fleischer et al.[28]

Glycerol glycidylether based cyclic carbonate (GGC, 5):

Carbonate content: 4.9 mmol g^{-1}

^{1}H-NMR (299.87 MHz, $CDCl_3$): δ/ppm = 3.44-4.0 (3/4-C*H*$_2$, 5-CH), 4.39 (1-C*H*$_2$), 4.50 (1'-C*H*$_2$), 4.83 (2-C*H*).

ν_{max}/cm^{-1} = 2960 (ν_{CH2}), 2916 (ν_{CH2}), 2874 (ν_{CH2}), 1785 ($\nu_{C=O}$), 1480 (δ_{CH2}), 1396 (δ_{O-H}), 1363, 1338, 1308, 1172, 1132, 1103, 1082, 1043 (ν_{C-O}).

Trimethylolpropane glycidylether based cyclic carbonate (TMPGC, 6):

Carbonate content: 5.6 mmol g^{-1}

^{1}H-NMR (299.87 MHz, $CDCl_3$): δ/ppm = 0.82 (7-C*H*$_3$), 1.36 (6-C*H*$_2$), 3.25-4.0 (3/4-C*H*$_2$), 4.38 (1-C*H*$_2$), 4.49 (1'-C*H*$_2$), 4.82 (2-C*H*).

ν_{max}/cm^{-1} = 2969 (ν_{CH2}), 2920 (ν_{CH2}), 2880 (ν_{CH2}), 1782 ($\nu_{C=O}$), 1482 (δ_{CH2}), 1386 (δ_{O-H}), 1360, 1335, 1305, 1168, 1132, 1103, 1043 (ν_{C-O}).

Pentaerythritol glycidylether based cyclic carbonate (PGC, 7):

Carbonate content: 4.8 mmol g^{-1}

^{1}H-NMR (299.87 MHz, $CDCl_3$): δ/ppm = 3.33-4.0 (3/4-C*H*$_2$), 4.41 (1-C*H*$_2$), 4.50 (1'-C*H*$_2$), 4.83 (2-C*H*).

ν_{max}/cm^{-1} = 2960 (ν_{CH2}), 2918 (ν_{CH2}), 2873 (ν_{CH2}), 1785 ($\nu_{C=O}$), 1480 (δ_{CH2}), 1396 (δ_{O-H}), 1363, 1338, 1309, 1254, 1171, 1132, 1103, 1084, 1051 (ν_{C-O}).

General procedure of NIPU formation

All NIPU samples were prepared according to the following procedure: The AAs were mixed with HMDA at 100-130 °C, varying the AA content (0, 25 and 50 wt.-% AA). After homogenization by mechanical stirring, the resulting blend was cooled to 80 °C and mixed with equimolar amounts of cyclic carbonate. After mechanical stirring for 20 s, the mixture was poured into a mold and heated at 80 °C for 14 h and for additional 4 h at 100 °C.

Results and discussion

Preparation and characterization of multifunctional amino alcohols by the aminolysis of glycidyl ethers with aqueous ammonia

Bio-based multifunctional amino alcohols (AAs) were derived by aminolysis of polyglycidylethers of glycerol (GG-AA, **1**), trimethylolpropane (TMPG-AA, **2**), and pentaerythritol (PG-AA **3**) or from limonene dioxide (L-AA, **4**), respectively. Typically, the aminolysis using aqueous ammonia was performed in a

stainless steel reactor at 100 °C for the duration of 15 h. All aminolysis reactions gave full epoxy conversion and high AA yields (83-97 %). While most AAs were highly viscous liquids, limonene-based AA was obtained as a solid substance with a melting point of 80 °C. Both the AAs as well as the corresponding cyclic carbonates were derived from the same polyglycidylethers (s. **Scheme 2**). Hence, they contain the same molecular architectures as well as structural defects resulting from the well-known side reactions occurring during glycidylization of polyols with epichlorohydrin, as analyzed by Camara et al.[32]

To obtain primary amines as the main product of the epoxy ring opening reaction with ammonia, the aqueous ammonia solution was used in large excess in order to suppress the formation of secondary amines as side reaction involving the reaction of the AA amine group with epoxy groups. A detailed analysis by ^{1}H-NMR spectroscopy was not possible, owing to the nearly identical chemical shifts of methylene groups adjacent to primary and secondary amine functions. Yet, the formation of primary amines was determined by IR, monitoring the appearance of the distinctive absorption band at 1600 cm^{-1}, and by means of ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectrum of TMPG-AA (**2**), as a representative example of a glycidylether based AA, is shown in **Fig. 1**. All NMR spectra showed rather broad signals typical for oligomers and side products of the glycidylization reaction. In case of the glycidylether based AAs, the carbon atoms adjacent to the primary amine groups exhibited a chemical shift of 44 ppm, whereas the secondary amines, formed by reaction of the primary amine with additional glycidylether, accounted for a shift of the corresponding carbon atom signals to approximately 53 ppm. During the aminolysis reaction, 100 % regioselectivity with respect to terminal, primary amine formation was achieved, as verified by HSQC experiments. As determined by quantitative, decoupled inverse-gated ^{13}C-NMR spectroscopy, the amount of secondary amines, formed by the reaction of amino alcohols with epoxy resins, was calculated to 6.8-8.2 mol-% (s. **Tab. 1**). The diverse architecture of limonene accounts for different chemical shifts, as compared to the characteristically signals of GG-AA (**1**), TMPG-AA (**2**) or PG-AA (**3**). Similar to limonene dioxide and limonene dicarbonate, limonene-AA contained different stereoisomers.[34] Hence, the spectrum of L-AA (**4**) is rather complex. After recrystallization of the crude product from acetonitrile, however, a complete assignment was achieved (s. **Fig. 2**). The carbon atoms adjacent to the primary amine groups correspond to the signals at 53 and 57 ppm, whereas the signals at 52 ppm were assigned to the dimer containing a secondary amine group. According to mass spectroscopy, L-AA was free of secondary amines after recrystallization, whereas the secondary amine content of crude L-AA was 1.4 mol-%. The amine values of all synthesized AAs were determined by quantitative, decoupled inverse-gated ^{13}C-NMR experiments with phenol as internal standard and matched within the margin of error to the expected values calculated by the epoxy content. A summary of all determined properties is given in **Tab. 1**.

The viscosities of the glycidylether based AAs were characterized by oscillatory frequency sweep experiments at different temperatures. As shown in **Tab. 1**, all AAs were highly viscous liquids. PG-AA had the highest viscosity in this series with 18.9 Pa s at 100 °C and 188.5 Pa s at 80 °C. Owing to the presence of the ethyl side chain in the trimethylolpropane based AA, the viscosity of TMPG-AA was lower than that of GG-AA and PG-AA. A similar trend was reported for the corresponding cyclic carbonates by Fleischer et al.[28] TMPG-AA exhibited a very high viscosity at room temperature of 819 000 Pa s. With decreasing temperature, the glycerol and pentaerythritol based AA showed shear thinning behavior. PG-AA featured this non-Newtonian behavior already at 50 °C and GG-AA at 20 °C. These results correlate with the glass transition temperatures measured by DSC analysis. GG-AA showed a T_g of 23.1 °C, TMPG-AA of 8.4 °C and PG-AA of 51.3 °C (s. **Tab. 1**). Hence, at temperatures above T_g, Newtonian behavior is observed. Crude L-AA exhibited a T_g of 30.3 °C. According to thermogravimetric analysis under air, the glycidylether based amino alcohols decomposed at 304-313 °C and L-AA at 248 °C.

Rheological investigations of pot life and gelation time

To produce NIPU thermosets it is mandatory to understand the cure process of cyclic carbonates with amines. Two key parameters of the curing process are the pot life and gelation time. The pot life, also referred to as working time, corresponds to the time during which the viscosity of the resin remains low enough to permit processing by casting. Preferably, the viscosity of the resin/curing agent mixture falls in the range of 10 Pa s. In contrast to pot life time, the gelation time is the time required for gelation, equivalent to the formation of a polymer network by crosslinking cyclic carbonates with multifunctional amines. According to rheological measurements, the gelation time was determined as the time at which the crossover of storage (G') and loss modulus (G'') took place during cure. Typically, curing was performed in a rheometer with plate-plate geometry at 80 °C with 10 rad s^{-1} and 5 % deformation. Owing to the high AA viscosities, blends with HMDA containing 0, 25 and 50 wt.-% AA were prepared. Above 50 wt.-% AA, the AA/HMDA blends were too viscous and did not permit appropriate mixing prior to gelation. This prevented full cure and was accompanied by phase separation. After blending AAs with HMDA at 100-130 °C, cooling to 80 °C and adding trimethylolpropane glycidylether carbonate (TMPGC), the mixtures were stirred for 30 s at 80 °C and placed in the rheometer. The results of all these rheological measurements are summarized in **Fig. 3.**

Since the pot life time reflects the viscosity build-up, it correlates with the viscosity of the corresponding AA type, the AA content in the HMDA blend and also with the total amine content. The pot life time of the benchmark system, consisting of TMPGC cured with HMDA, was rather short (60 s). Owing to the electron withdrawing effect of the β-hydroxy group adjacent to the amine group (–I inductive effect), the lower amine nucleophilicity slowed down the cure reaction, as

evidenced by the increased pot life time. Typically, the pot life times of the glycidylether based AAs were in the range of 60-108 s. Raising the AA amount from 25 to 50 wt.-% accounted for increased viscosities, paralleled by shorter pot life times. The viscosities of limonene (L)AA/HMDA blends were much lower with respect to the systems presented above. Taking into account that L-AA is difunctional like HMDA, but less reactive due to the steric hindrance of the amine group attached to the cyclohexyl ring, the pot life time of the resin increased with increasing L-AA content of the L-AA/HMDA blend. Since the gelation time only depends on the rate of network formation, all measured gel times prolonged with increasing amount of amino alcohol and decreased with increasing overall functionality of the amine curing agent.

NIPU preparation by curing cyclic carbonates with AA/HMDA blends

Taking into account tailoring pot life and gelation times, NIPU thermoset specimens were prepared by mixing the AAs (0, 25 and 50 wt.-%) together with HMDA at 100-130 °C prior to the addition of the corresponding cyclic carbonates GGC (**5**), TMPGC (**6**) and PGC (**7**). After stirring for about 30 s until the mixtures were rendered homogenous, they were poured into molds and cured at 80 °C for 14 h and post-cured for 4 h at 100 °C. All NIPU samples showed complete conversion of cyclic carbonate groups, as verified by IR spectroscopy. While the urethane band appeared at 1691 cm^{-1}, the cyclic carbonate band at 1791 cm^{-1} and the amine band at 1600 cm^{-1} completely disappeared. Side-reactions as described by Besse et al. like the formation of ureas (1620 cm^{-1}) or 2-oxazolidinones (1745 cm^{-1}) were not observed by means of IR spectroscopy.[43] As compared to the cure using conventional diamines like HMDA, IPDA or Priamine 1074, the use of AA curing agents was more demanding owing to their higher viscosities and their short pot life and gelation times.

Mechanical and thermal NIPU properties

In the first part of this study, all AAs were cured with TMPGC to investigate the influence of the amine functionality and the molecular structure of the AAs (s. **Tab. 2**). The benchmark system TMPGC/HMDA exhibited a Young's modulus of 1600 MPa. By using our bio-based, multifunctional AAs as curing agents (s. **Fig. 4**), the Young's moduli were substantially increased. For 50 wt.-% PG-AA, the Young's modulus raised to 3300 MPa (+200 %). Although L-AA is only difunctional, it was possible to gain similar improvements to 3400 MPa, due to the rigidity of limonene molecular structure. As anticipated, the elongation at break decreased from 2.9 % to 0.5 % with increasing Young's modulus. The tensile strength of the benchmark system TMPGC/HMDA of about 44 MPa was increased to 60-64 MPa for the cure with HMDA/AA blends containing 25 wt.-% AA. Both, elongation at break and tensile strength values decreased with increasing AA content of the HMDA/AA blend. Unlike AA, the choice of the cyclic carbonate greatly affected NIPU glass transition temperatures. For example, GGC-based NIPU thermosets exhibited T_g values of 32-38 °C, TMPGC of 50-56 °C and PGC of 53-56 °C (s. **Tab. 2**). Additionally, the potential of AA curing agents was demonstrated by curing different cyclic carbonates with HMDA/TMPG-AA blends containing 50 wt.-% TMPG-AA. The results are shown in **Fig. 5**. In all cases, massive improvements were achieved. The Young's moduli of GGC/HMDA and PGC/HMDA were increased from 31 MPa to 710 MPa and from 2340 MPa to 3440 MPa, respectively, when HMDA was substituted by the HMDA/TMPG-AA (50/50) blend. For GGC, cured with HMDA/TMPG-AA (50/50) high elongation at break values of 20 % were retained, albeit the Young's modulus of the resulting NIPU was increased to 710 MPa.
According to thermogravimetric analysis under air, all NIPU thermosets decomposed at 253-261 °C.

Solvent swelling of NIPU samples

The solvent swelling was investigated by measuring the weight increase of cubical specimens immersed in water and toluene for the duration of 14 days at room temperature. As shown in **Tab. 2**, all samples showed increased swelling degrees in water with increasing amount of multifunctional amine curing agent, as expected for the higher hydroxy group content and the higher polarity of the resulting network. Typically, swelling falls in the range of 20 to 53 wt.-%. Only for L-AA, water swelling markedly decreased. This was attributed to the incorporation of the non-polar cyclohexyl backbone structure typical for limonene units. In contrast to the water swelling, the rather polar NIPU network structures accounted for extremely low toluene swelling (0-0.6 wt.-%).

Conclusions

Liquid and crystalline multifunctional amino alcohols (AAs) are readily available as bio-based curing agents from limonene dioxide and various bio-based glycidylethers, derived from glycerol, trimethylolpropane and pentaerythritol by aminolysis with ammonia. In contrast to many conventional amine syntheses, this very versatile one-step process affords di- and polyfunctional amine curing agents in essentially quantitative yields and does not require either organic solvents besides bioethanol or tedious purification such as the removal of catalyst residues and other undesirable by-products. In this aminolysis reaction, the excess ammonia is essential to suppress the formation of secondary amine groups as side reaction when a primary AA amine group reacts with an epoxy group. According to decoupled inverse-gated ^{13}C-NMR experiments, the secondary amine content varies between 1.4 and 8.2 mol-%. While most AAs are viscous liquids, the limonene amino alcohol melts at 80 °C and can be recrystallized from acetonitrile. The identical bio-based epoxy raw material is employed to prepare both polyfunctional cyclic carbonates by catalytic conversion with carbon dioxide and the corresponding AA curing agents by aminolysis with ammonia. Hence, it is possible to produce novel families of 100 % bio based non-isocyanate polyhydroxyurethanes (NIPU) from the

same bio feed stock. Neither phosgene, isocyanates or conventional curing agents based on fossil resources are required in this bio-based NIPU synthesis.

Preferably, owing to the rather high AA viscosities, HMDA/AA blends, containing 25 and 50 wt.-% AA, were used as NIPU curing agents. The systematic variation of molecular AA architectures of these curing agents reveals the basic NIPU structure/property correlations. Owing to steric hindrance, limonene AA is much less reactive with respect to AAs derived from glycidyl ethers. Moreover, both pot life and gelation times decrease with increasing amine functionality. Since the electron withdrawing effect of the adjacent hydroxy groups reduces the overall reactivity of the amine groups, gel time increases and pot life decreases with increasing AA content. Hence, in contrast to HMDA as curing agent, HMDA/AA blends afford improved processing and tailoring of NIPU properties. In fact, blending together HMDA with AAs substantially improves the NIPU stiffness, as expressed by the increased Young's moduli. In the case of TMPGC cured with HMDA/AA blend containing 50 wt.-% PG-AA, the NIPU Young's modulus increased from 1600 to 3300 MPa. Although the limonene-based L-AA is only difunctional, the incorporation of L-AA further improved NIPU stiffness. The high polarity of the network structure and the presence of hydroxyl groups account for increased water swelling of NIPU but drastically reduce uptake of less polar solvents such as toluene. Going beyond the scope of NIPU systems, this facile one-step synthetic route to tailored multifunctional β-amino alcohols holds great potential as green curing agents for other thermoset resins such as epoxy resins and conventional polyurethanes.

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Tab. 1 Properties of β–amino alcohols (AA) prepared by aminolysis of glycidylethers and limonene dioxide with aqueous ammonia.

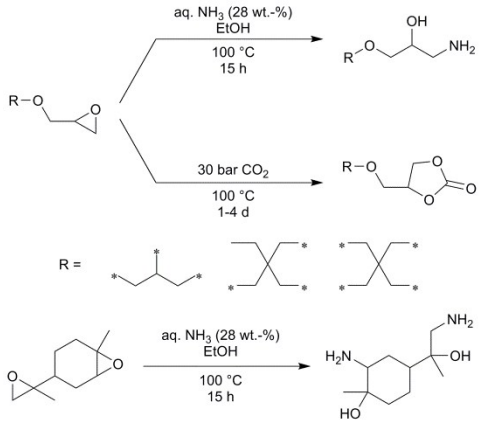
AA	AC[a] / mmol g^{-1}	x_{sec}[a] / mol-%	T_m[b] / °C	T_g[c] / °C	T_d[d] / °C	$\eta^e_{20\,°C}$ / Pa s	$\eta^e_{50\,°C}$ / Pa s	$\eta^e_{80\,°C}$ / Pa s	$\eta^e_{100\,°C}$ / Pa s	yield / %
GG-AA	5.13±0.14	8.0	-	23.1	307	n.m.[c]	7479	107	16.4	97
TMPG-AA	6.41±0.24	6.8	-	8.4	313	819 000	866	24.1	4.9	83
PG-AA	5.29±0.18	8.2	-	51.3	304	n.m.[f]	n.m.[f]	188.5	18.9	96
L-AA	6.28±0.17	1.4	80	30.3	248	-	-	-	-	97

[a] primary (AC) and secondary (x_{sec}) amine content, quantitative ^{13}C-NMR spectroscopy; [b] Büchi Melting Point B-540, 2 K min^{-1}; [c] DSC, 10 K min^{-1}, -50-200 °C, 2nd heating curve; [d] TGA, 10 K min^{-1}, air; [e] Rheology: oscillatory frequency sweep, 100-0.1 rad s^{-1}, 5 points per decade, 5 % deformation; [f] n.m.: not measurable, due to non-Newtonian behavior

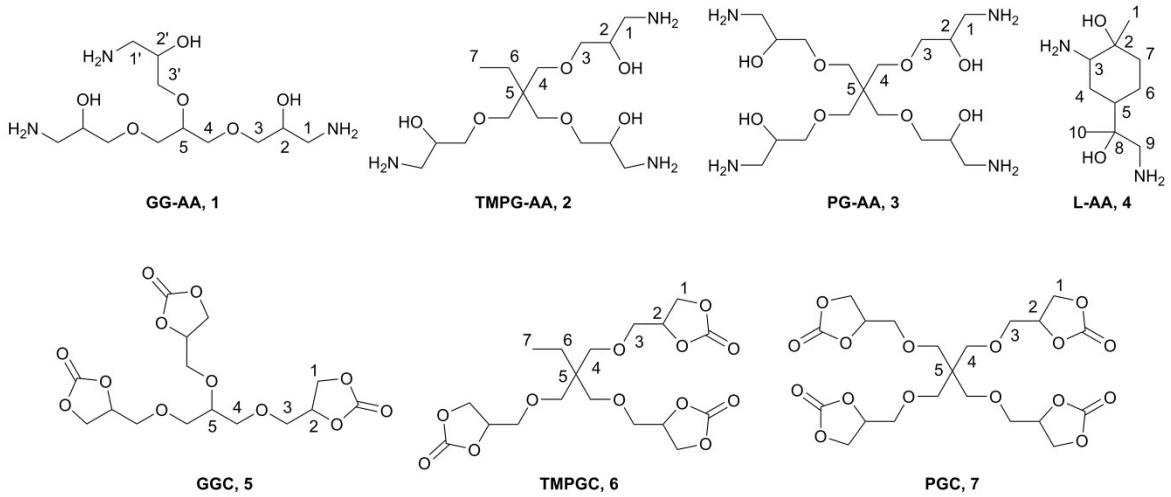
Tab. 2 Mechanical and thermal properties of all prepared NIPU thermosets by blending bio-based AAs with HMDA.

cyclic carbonate	AA	w(AA) / wt.-%	Young's modulus / MPa	tensile strength / MPa^{max}	ε_{break} / %	T_g[a] / °C	T_d[b] / °C	Q_{water}[c] / wt.-%	$Q_{toluene}$[c] / wt.-%
TMPGC	-	0	1600±200	44±11	2,86±0,05	50	261	20	0
TMPGC	GG-AA	25	2400±300	64±10	2,7±0,5	56	n. m.[d]	28	0,1
TMPGC	GG-AA	50	3000±200	18±3	0,55±0,10	51	254	53	0,6
TMPGC	TMPG-AA	25	2500±400	66±8	2,8±0,4	45	n. m.[d]	23	0,2
TMPGC	TMPG-AA	50	2800±130	59±8	2,0±0,3	50	258	32	0,4
TMPGC	PG-AA	25	2850±170	60±20	2,1±1,0	55	n. m.[d]	28	0,3
TMPGC	PG-AA	50	3300±200	17±4	0,48±0,10	52	255	52	0,3
TMPGC	L-AA	25	2400±200	62±11	2,6±0,4	49	n. m.[d]	16	0,1
TMPGC	L-AA	50	3400±120	15.9±1.8	0,43±0,05	55	253	13	0,2
GGC	-	0	31±12	12.5±0.8	99,8±1,8	32	n. m.[d]	27	0,4
GGC	TMPG-AA	50	710±50	31.3±1.1	20±20	38	n. m.[d]	42	0,3
PGC	-	0	2340±130	69±4	3,1±0,7	56	n. m.[d]	28	0
PGC	TMPG-AA	50	3440±80	20±8	0,6±0,3	53	n. m.[d]	34	0,3

[a] DMA, 1 Hz, 0.1 %, -50-100 °C, tan δ method; [b] TGA, 10 K min^{-1}, 50-650 °C, air; [c] degree of swelling after 14 days; [d] n.m.: not measured



Scheme 1 Preparation of multifunctional AA curing agents and cyclic carbonates from the same bio-based glycidylethers or limonene dioxide by aminolysis with ammonia and chemical fixation of CO_2, respectively.



Scheme 2 Structures of the prepared bio-based AAs (above) and cyclic carbonates (below): glycerol- (GG-AA**, 1**), trimethylolpropane- (TMPG-AA, **2**) and pentaerythritol glycidylether-based AAs (PG-AA, **3**), limonene AA (L-AA, **4**), glycerol- (GGC, **5**), trimethylolpropane- (TMPGC, **6**) and pentaerythritol- glycidylether-based carbonate (PGC, **7**).

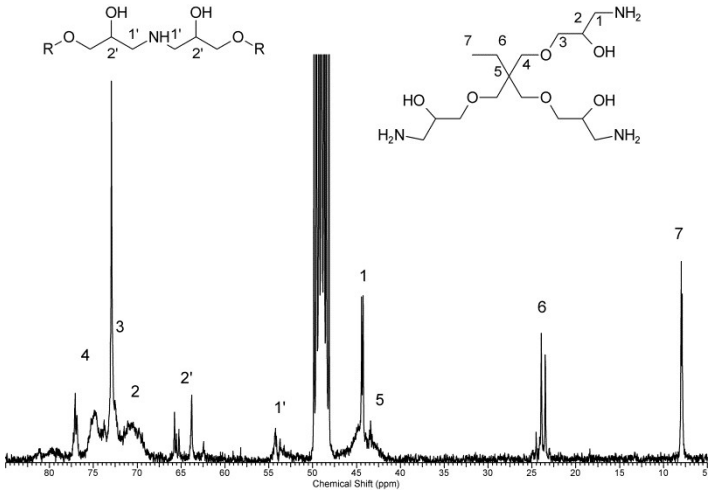


Fig. 1 ^{13}C-NMR spectrum (MeOH-d_4) of TMPG-AA (**2**) as a representative example of glycidylether based β-amino alcohols.

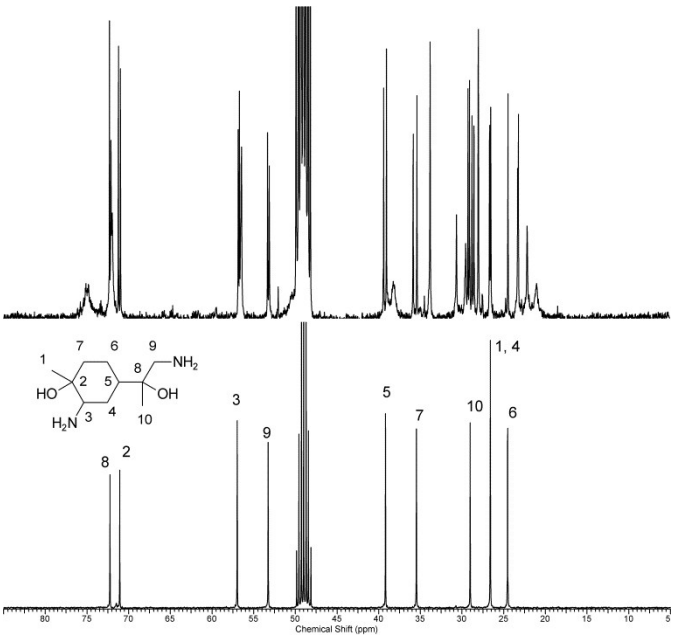


Fig. 2 ^{13}C-NMR spectra (MeOH-d_4) of L-AA (**2**) before (above) and after recrystallization from acetonitrile (bottom).

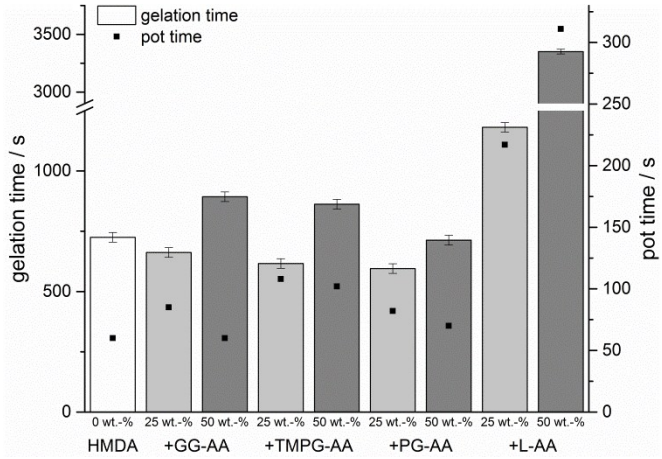


Fig. 3 Gelation (left) and pot life time (right) for curing TMPGC with AA/HMDA blends at 80 °C, as measured by oscillatory rheological experiments (10 rad s^{-1}, 5 %).

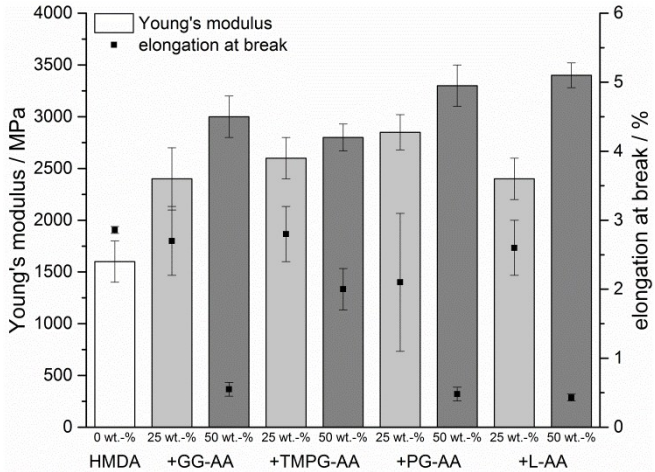


Fig. 4 Young's moduli (left) and elongation at break values (right) for TMPGC cured with HMDA/AA blends containing 25 and 50 wt.-% AA. All NIPUs were cured at 80 °C for 14 h and post-cured 4 h at 100 °C.

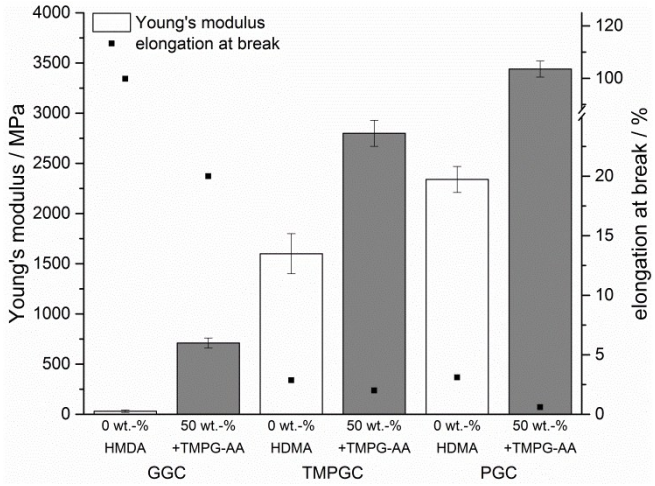
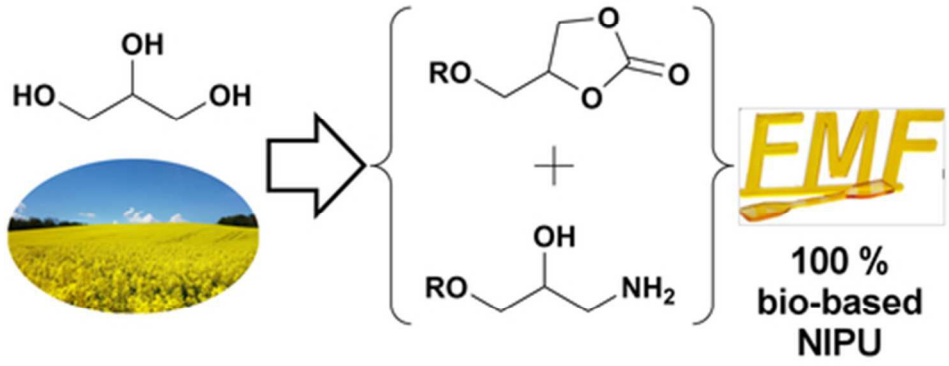


Fig. 5 Young's moduli (left) and elongation at break values (right) of NIPU prepared by curing different cyclic carbonates with HMDA/TMPG-AA (50/50) blends. All NIPUs were cured at 80 °C for 14 h and post-cured 4 h at 100 °C.

Novel 100 % bio-based NIPU thermosets by employing bio-based epoxy resin feedstocks as raw material for both cyclic carbonate and amine curing agent.



39x19mm (300 x 300 DPI)