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Debondable Epoxy-Acrylate Adhesives using β-Amino Ester Chemistry

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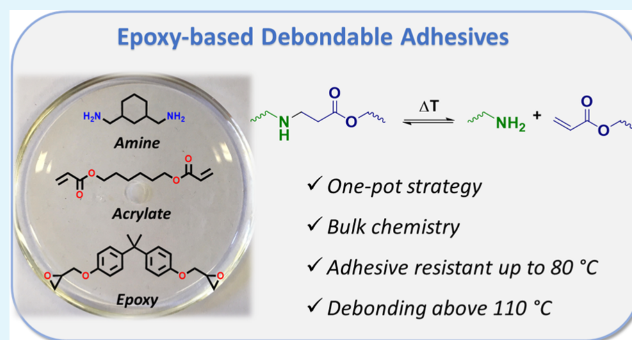
ABSTRACT: The reuse of multilayered materials, which are held together by structural epoxy adhesives, is a major challenge since the bonded substrates cannot be easily separated for recycling. In this research, we explore a one-pot strategy based on β-amino ester chemistry for the development of modified epoxy adhesives with on-demand debonding potential. For this, a formulation of commercially available acrylate, epoxy and amine compounds is used. The research starts with a systematic study, demonstrating the influence of the different compounds on the thermal and adhesive properties of the materials. Subsequently, the potential for debonding is demonstrated using rheological measurements and tensile tests. The fast, catalyst-free Aza-Michael reaction enables the straightforward preparation of such epoxy-based adhesives, while the reverse reaction allows for debonding at 120 °C. In general, a chemical design is demonstrated for producing an industrially attractive generation of debondable epoxy-based adhesives.



KEYWORDS: *debondable adhesives, covalent adaptable networks, epoxy, acrylic structural adhesives, β-amino ester chemistry*

INTRODUCTION

Many daily life products are made up of multiple layers of materials, often combining different substrates that are held together by structural adhesives.[1] While these adhesives facilitate assembly, they also pose a significant challenge for recycling, as the bonded layers are difficult to separate, hindering the effective recovery of individual materials.[2,3] Therefore, new technologies for debonding those structures without damaging the individual parts are needed.

In recent years, many debonding technologies have been reported in publications, reviews and patents.[4−12] These include, for instance, thermally expandable particles and solvent-based detachment.[13,14] However, developing debondable adhesives that are functional, industrially relevant and allow for fast debonding upon application of a suitable trigger are very challenging, as observed from the slow debonding time scale achieved with some technologies.[15−19] The major structural adhesives are made of polyurethane, polyacrylate and epoxy resins.[20] Therefore, these matrices have already been explored for the formation of debondable adhesives.[10,21−23] Epoxy resins, in particular, have been studied much by us and other groups in the area of covalent adaptable networks (CANs) by first preparing cross-linkers wherein a chosen dynamic chemistry is incorporated and subsequently, using them to cure the resins through the ring opening of the epoxides.[10,21,22]

In this context, multiple dynamic chemistries have been proposed for on-demand debondable adhesives such as Diels−Alder chemistry (Figure 1A), amide-imide (Figure 1B) and transesterification (Figure 1C). As expected, the choice of the chemistry platform has a significant impact on the application of the final materials.[10,21,22] For example, the Diels−Alder reaction between furans and maleimides has been well reported in the field of CANs in different matrices because this platform allows for significant debonding above 100 °C and even liquefication of the materials above 120 °C.[9,22,24] However, the (re)formed furan and maleimide groups show poor thermal stability above 150 °C ascribed to side reactions such as maleimide homopolymerization.[22] In addition, for certain applications (e.g., in the automotive industry), higher debonding temperatures are desirable.

When a more thermally stable epoxy adhesive with additional debonding functionality is needed, dynamic chemistries such as amide-imide or transesterification are considered to be more suitable. The first one can be used for designing novel polyamide cross-linkers that can undergo

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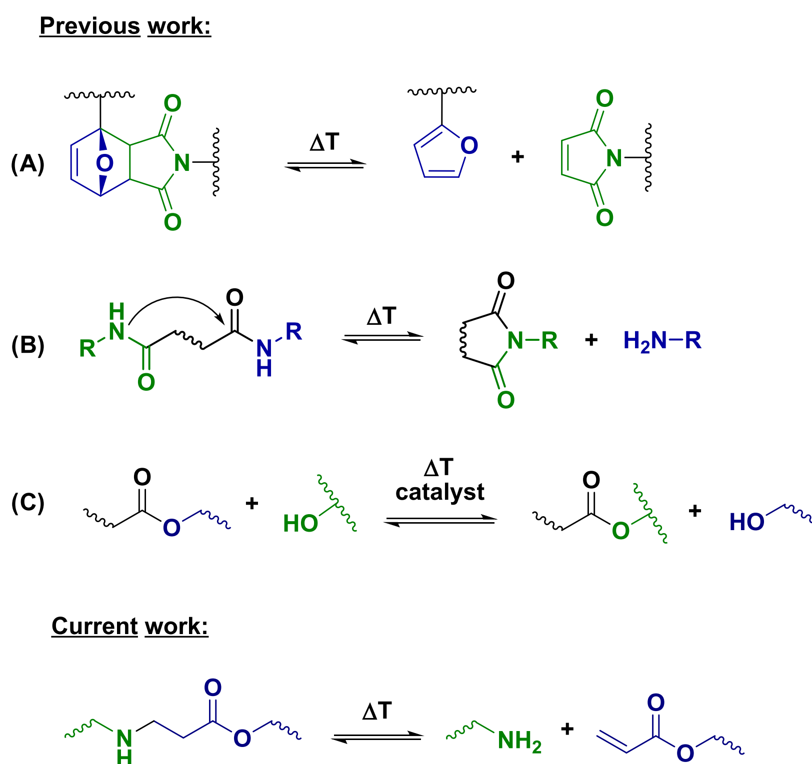

Figure 1. (Top) Overview of dynamic chemistries that have been explored for the development of on-demand debondable adhesives, and (bottom) depiction of the BAE-chemistry presented in the current study. (A) Furan-maleimide reversible adhesives described by Gandini.[22] (B) Debondable adhesives using amide-imide chemistry proposed earlier by our research group.[10] (C) Reversible adhesion via transesterification demonstrated by Roig et al.[21]

thermal debonding into cyclic imides and amines without the need for additional catalysts or other additives.[10] In two parallel studies, our research group and the one of Sijbesma and Heuts demonstrated that debonding occurs at much higher temperatures than for the furan-maleimide chemistry (i.e., above 180 °C).[25,26] As for transesterification, it has been used recently by Roig et al. to make epoxy adhesives with curing agents containing thiol and ester functionalities capable of undergoing the dynamic exchange at high temperatures (>180 °C) and only in the presence of external catalysts (Figure 1C).[21]

Recently, our research group showed that the catalyst-free Aza-Michael reaction between acrylates and amines, also known as β-amino ester (BAE) chemistry, can be of great interest for developing catalyst-free CANs.[27−29] Moreover, these studies showed that the presence of additional hydroxyl groups in the matrix enables transesterification at elevated temperature (>80 °C) in addition to the retro Aza-Michael reaction.[27,30,31] Furthermore, in bulk materials, it has been demonstrated that a dissociative pathway is prevalent with this dynamic chemistry platform, which is desired to reach a rapid decrease in adhesive strength that is needed for debondable adhesives.[32]

We herein report a one-pot, three-component reaction based on epoxides, acrylates and amines for the development of debondable adhesives inspired by this BAE chemistry (Figure S1). In this study, we envisioned that the incorporation of epoxides would be very useful to maintain a high thermal stability while at the same time enabling the debonding. The approach is fully performed with bulk chemicals, which renders the overall concept attractive for industrial uptake.[33]

EXPERIMENTAL SECTION

Materials. Pentaerythritol triacrylate (<80%, contains 100 ppm 4-methoxyphenol as stabilizer, Sigma-Aldrich), 1,6-hexanediol diacrylate (99%, contains 100 ppm 4-methoxyphenol as stabilizer, Sigma-Aldrich), 4-methoxyphenol (>98%, Sigma-Aldrich), bisphenol A diglycidylether (98%, TCI Chemicals Europe), Epikote resin 238 (DER332, epoxy equivalent weight 176 g/mol, Westlake epoxy), 1,3-bis(aminomethyl)cyclohexane (BAC), isophorone diamine (>98%, Sigma-Aldrich), Priamine 1074-LQ (Cargill), and Jeffamine T403 (Huntsman) were used without further purification unless otherwise stated.

Instrumentation. *Thermogravimetric Analysis.* The thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA 851. The dynamic thermogravimetric measurements were recorded in a nitrogen atmosphere from +25 to 800 °C, with a heating rate of 10 °C/min. The isothermal thermogravimetric measurements were recorded in a nitrogen atmosphere at 200 °C for 120 min.

Differential Scanning Calorimetry. DSC analyses were measured on a Mettler Toledo 1/700 instrument. The measurements were performed under a nitrogen atmosphere with a heating rate and cooling rate of 10 °C/min from −150 to 150 °C.

Fourier Transform Infrared Spectroscopy. IR spectra were recorded on a PerkinElmer SPECTRUM 1000 FTIR spectrometer equipped with a diamond ATR probe and the possibility to measure at high temperature.

Rheological Experiments. Amplitude Sweeps, stress-relaxation and creep measurements were performed on an Anton-Paar Physica MCR 302 rheometer and an Anton-Paar Physica MCR 302e rheometer using a plate−plate geometry. The material samples have a diameter of 8 mm and thickness of 2 mm. Amplitude sweep experiments were performed using a frequency of 10 Hz, a constant force of 1 N, and a variable shear strain that was ramped up logarithmically from 0.01 to 100%. Stress-relaxation measurements were performed with 1% strain, a constant force of 1N and a temperature range from 200 to 130 °C.

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Table 1. Screening of Different Formulations Based on Epoxy Source (BAE-1 to BAE-3), Acrylate Source (BAE-3 to BAE-4), and Amine Curing Agent (BAE-4 to BAE-7)[a]

sample	amine	acrylate	epoxy	T_g[b] (°C)	$T_{d5\%}$[c] (°C)	$T_{iso\ 200\ °C}$[d] (%)	lap shear strength[e] (MPa)
BAE-1	1,3-BAC	PETA	BADGE	94	281	−2.0	1.5 ± 0.6
BAE-2	1,3-BAC	PETA	PEO	19	263	−7.6	
BAE-3	1,3-BAC	PETA	Epikote 238	103	296	−1.8	3.3 ± 0.5
BAE-4	1,3-BAC	HDODA	Epikote 238	52	240	−11	6.0 ± 0.4
BAE-5	IPDA	HDODA	Epikote 238	39	231	−18	
BAE-6	Priamine	HDODA	Epikote 238	6	263	−9.7	
BAE-7	Jeffamine T403	HDODA	Epikote 238	15	221	−19	7.1 ± 0.2

[a]In all formulations a 1:1:1 equiv ratio of functional groups was used. [b]Determined from the second heating in DSC analysis (10 °C/min). [c]TGA onset temperatures after 5% weight loss ($T_{d5\%}$). [d]Weight loss after isothermal TGA measurement at 200 °C. [e]Lap shear strengths were obtained from a five-sample measurement at rt according to ASTM D1002.

Creep measurements were performed with between 25 and 200 °C with a 2000 Pa shear stress applied for 6000 s.

Elcometer 4340 Automatic Film applicator was used to prepare the adhesive films.

MITUTOYO IP65 μm was used to determine the thickness of the applied adhesive layer.

Tinius-Olsen H10KT tensile tester, equipped with a 5000 N load cell and environmental chamber (operating temperatures from −70 to 300 °C) was used. Lap shear tests were performed according to the ASTM 1002D standard. Additionally, an INSTRON alignment kit was used to align the grips. The tensile data were registered by using a National Instruments C-series data acquisition card. The load, displacement, and strain recorded by the FastTrack controller were measured on the same time basis. To obtain reproducible results, each experiment was repeated at least five times. For the lap shear tests performed at higher temperatures, the individual specimen were heated in the environmental chamber at specific temperatures for 10 min prior to starting the test.

General Network Synthesis. The epoxy materials were synthesized using the following procedure. At first, the acrylate and epoxy were put in a speedmixer cup and mixed for 2 min at 3500 rpm. Second, the amine was added to the cup and mixed for 5 min at 3500 rpm. The cup was transferred to a conventional oven and the material was cured at 80 °C for approximately 16 h. A transparent disk on the bottom of the cup was obtained. Removal of the disk was done by cutting the speedmixer cup.

Reprocessability. To reprocess the network, the polymer was broken into pieces and placed into a rectangular mold (A, 70 mm × 40 mm × 2 mm. B, 30 mm × 15 mm × 2 mm) for compression molding. This assembly was placed in a 180 °C preheated compression press for 1 min under 0.5 t of pressure. Then the pressure was increased to 5 tons and kept constant for 30 min. Afterward, the sample was carefully removed from the mold while still heated.

Lap Shear Specimen Preparation. Lap shear specimen preparation was adapted from the ASTM D1002 test method and includes a sequence of steps. For the tests, aluminum samples with a thickness of 1.6 mm and total length of 100 mm were used. First the specimens are sand blasted. Second, they are cleaned with two different solvents namely ethyl acetate and 2-butanone. The plates are dried overnight after which they are plasma treated with a Reylon piezo brush PZ3. Following this, the adhesive formulation is applied on one of the plate surfaces using the Elcometer 4340 Automatic Film applicator. Wet films with a thickness of 200 μm are applied to the surface on an overlap length of 15.8 mm and width of 25.4 mm. After the polymer has reached a higher viscosity (30 min after application), two plates are clamped together to avoid pushing out the adhesive. Using the Mitutoyo IP65 μm a dry bondline thickness of 100 μm was measured.

■ RESULTS AND DISCUSSION

Network Synthesis and Characterization. First, a formulation screening with different epoxy, acrylate and amine compounds was performed starting from commonly used chemicals (Table 1). For this, the typical characteristics of commercially available epoxy-based structural adhesives are targeted, including a glass transition temperature (T_g) between 40 and 100 °C, a thermal stability of the bulk materials up to 200 °C (depending on the application), and an adhesive strength of at least 7 MPa.[34−38]

For the epoxy compound, a comparison of the commonly used bisphenol A diglycidylether (BADGE), poly(ethylene glycol) diglycidyl ether (diepoxy PEG) and Epikote 238 (low-medium viscosity bifunctional epoxy resin) was performed. The three epoxy materials (BAE-1, BAE-2 and BAE-3 in Table 1) were synthesized by mixing the commonly used rigid Bisamine 1,3-bis(aminomethyl)cyclohexane (1,3-BAC), the trifunctional pentaerythritol triacrylate (PETA) and the epoxy source (1:1:1 equiv), after which the curing step occurred at 80 °C for 16 h. PETA was chosen as acrylate source because of the presence of hydroxyl groups that were expected to enhance the material properties and allow for the earlier mentioned additional transesterification pathway.[27]

The obtained networks showed a large T_g-range (19 to 103 °C) and thermal stability above 260 °C (Table 1). The diepoxy PEG-based material (BAE-2) was excluded from further investigations since its T_g (19 °C) was below the previously mentioned target. The adhesive properties of the BADGE- and Epikote 238-derived materials were tested according to ASTM D1002. BAE-3 performed better in the lap shear tests compared to the others (3.3 vs 1.5 MPa), which is assigned to the lower viscosity of the Epikote 238 compared to BADGE (5025 mPa s and 8980 mPa s at room temperature, respectively), thus ensuring better wetting of the surface, and a more effective adhesion to the substrate upon application. Therefore, Epikote 238 was selected as the epoxy compound for further formulations.[39]

Subsequently, a material (BAE-4) based on hexane-1,6-diol diacrylate (HDODA) as acrylate source was prepared with 1,3-BAC and Epikote 238 (1:1:1 equiv), to explore if a more flexible moiety compared to PETA could improve the adhesive properties. Typically, a higher chain mobility results in a more effective energy absorption and dissipation, leading to stress distribution and impact resistance improvement.[40] The T_g of BAE-4 (52 °C) was still in the targeted range and, as desired, the lap shear strength further increased to 6.0 MPa, hence approaching the targeted value (>7 MPa). In a subsequent step, a set of amines was investigated maintaining the Epikote 238 as epoxy source and the HDODA as acrylate source. Alongside 1,3-BAC (BAE-4), isophorone diamine (IPDA) (BAE-5), Priamine (BAE-6), and Jeffamine T403 (BAE-7)

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Table 2. Optimization of the Ratio between the Three Components Used in the Adhesive Formulation

sample	1,3-BAC (equiv)	HDODA (equiv)	Epikote 238 (equiv)	T_g[a] (°C)	$T_{d5\%}$[b] (°C)	$T_{iso\ 200\ °C}$[c] (%)	lap shear strength[d] (MPa)
BAE-4	1	1	1	52	240	−11	6.0 ± 0.4
BAE-8	1.5	1	1	46	266	−9	7.0 ± 0.2
BAE-9	2	1	1	41	238	−14	6.7 ± 0.6
BAE-10	1.5	1.5	0.5	12	250	−12	3.4 ± 0.5
BAE-11	1.5	0.5	1.5	75	284	−5	6.0 ± 0.5
BAE-12	1.5	0.25	1.75	64	267	−5	5.4 ± 0.4

[a]Determined from the second heating in DSC analysis (10 °C/min). [b]TGA onset temperatures after 5% weight loss ($T_{d5\%}$). [c]Weight loss after isothermal TGA measurement at 200 °C. [d]Lap shear strengths were obtained from a five-sample measurement at rt according to ASTM D1002.

Table 3. Thermal Characterization, Network Swelling Behavior and Stress Relaxation Values Obtained for the Dynamic and Nondynamic Materials

sample	T_g[a] (°C)	$T_{d5\%}$[b] (°C)	$T_{iso\ 200\ °C}$[c] (%)	swelling ratio[d] (%)	gel fraction[e] (%)	$\tau^*_{200\ °C}$[f] (s)
nondynamic reference	47	370	−0.4	259 ± 20	97 ± 2	
BAE-8 Dynamic (MEHQ)	40	260	−10	313 ± 40	94 ± 4	102
BAE-8 Dynamic (no MEHQ)	46	266	−8.7	213 ± 10	92 ± 1	296

[a]Determined from the second heating in DSC analysis (10 °C/min). [b]TGA onset temperatures after 5% weight loss ($T_{d5\%}$). [c]Weight loss after isothermal TGA measurement at 200 °C. [d]Swelling ratio obtained from a five-sample measurement in DCM at rt for 24 h. [e]Gel fraction was obtained from a five-sample measurement in DCM at rt for 24 h. [f]Calculated relaxation time ($\tau^*_{200\ °C}$) obtained by fitting to a stretched Maxwell model.

were used to synthesize adhesives applying the same ratio as previously mentioned (i.e., 1:1:1 between the epoxy, the acrylate and the amine). The two more flexible amines (Priamine and Jeffamine T403) lowered T_g to respectively 6 and 15 °C, thus below the targeted value of at least 30 °C. On the other hand, the use of IPDA resulted in a material with lower thermal stability ($T_{d5\%}$ = 231 °C, 18% weight loss at 200 °C). Therefore, after conducting this screening, it became clear that the formulation offering the best thermal properties and adhesive strength is the one based on 1,3-BAC as amine curing agent, HDODA as acrylate and Epikote 238 as epoxy source, i.e., BAE-4 (Table 1). With regard to the absolute value of lap shear strength, it should be noted that a commercial structural adhesive contains fillers and other components to further increase it (*vide infra*).Other surface preparation techniques may also be used depending on the application.

Based on these results, further optimization of the material properties was targeted by changing the ratio between the three selected adhesive components (Table 2). First, the amount of amine was increased from 1 (BAE-4) to 1.5 (BAE-8) and finally 2 equiv (BAE-9) to target a network containing not only tertiary, but also secondary amines. The latter amines were expected to promote extra intermolecular interactions that could enhance the thermal and adhesive properties.[41] However, the three materials showed relatively similar T_g-values (i.e., 52 °C, 46 and 41 °C for 1, 1.5 and 2 equiv of amines, respectively), and adhesive strength (i.e., 6, 7, and 6.7 MPa, respectively).

As sample BAE-8 showed the highest thermal stability, the amount of amine was kept constant at 1.5 equiv. and the ratio between acrylate and epoxy was varied to further optimize the formulation (BAE-10 to BAE-12). While an increase in the acrylate content compared to the epoxide resulted in an expected decrease for both T_g and lap shear strength (see BAE-10 in Table 2), the increase in the epoxy over the acrylate content (BAE-11 and BAE-12) was found to enhance T_g (>60 °C) and the thermal resistance. On the other hand, this also showed a minor negative impact on the adhesive strength (<7 MPa) and a major negative effect on the reprocessability (Figure S2) because of the lack of dynamic bonds, resulting from a reduction in the reaction of the amine with acrylate groups, in the network. Overall, the results of this extensive screening showed that the mixture 1,3-BAC: Epikote 238: HDODA (1.5:1:1), leading to adhesive BAE-8, resulted in the best performance in terms of thermal and adhesives properties. In the following sections, BAE-8 will be further referred to as the dynamic material.

In order to prevent the known acrylic homopolymerization at elevated temperatures,[27,42] 1000 ppm of the radical inhibitor 4-methoxyphenol (MEHQ) was added to the mixture and this sample was compared with a reference mixture without MEHQ as a proof of the effectiveness of the inhibitor. Both materials were tested through loop rheology whereby the stress relaxation at 180 °C was tested 5 times during 10.000s (Figures S3 and S4). While for the material in the absence of an inhibitor, the relaxation modulus increased 7×10^5 Pa after the first loop, the relaxation modulus of the sample containing MEHQ did not vary significantly, confirming the need for such inhibitor if higher temperatures are targeted. As a reference material for the lap shear tests, also a nondynamic epoxy material with similar thermal properties (T_g of 47 °C, a $T_{d5\%}$ of 370 °C), starting from 1,3-BAC and neopentyl diglycidylether (thus leaving out the acrylate compound), was synthesized in a 1:1.5 amine to epoxy ratio (Table 3).

Prior to analyzing the dynamic behavior and the debonding potential of the optimized adhesives, a better understanding of the reactivity between amine, acrylate and epoxy in this one-pot reaction is required. For this purpose, the evolution of attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum of the reaction mixture was followed over time at the curing temperature of 80 °C (Figures 2 and S5). The monitored peaks were the acrylic double bond signal at 1636 cm^{-1} and the stretching of the epoxy group at 912 cm^{-1} (Table S1). The conversion rate of acrylic and epoxy groups was calculated through the integration of their respective peaks (peak deconvolution was performed to obtain a more accurate area estimation, Figure S6). Those FTIR results indicated a rapid consumption (89%) of acrylate in the initial 10 min,

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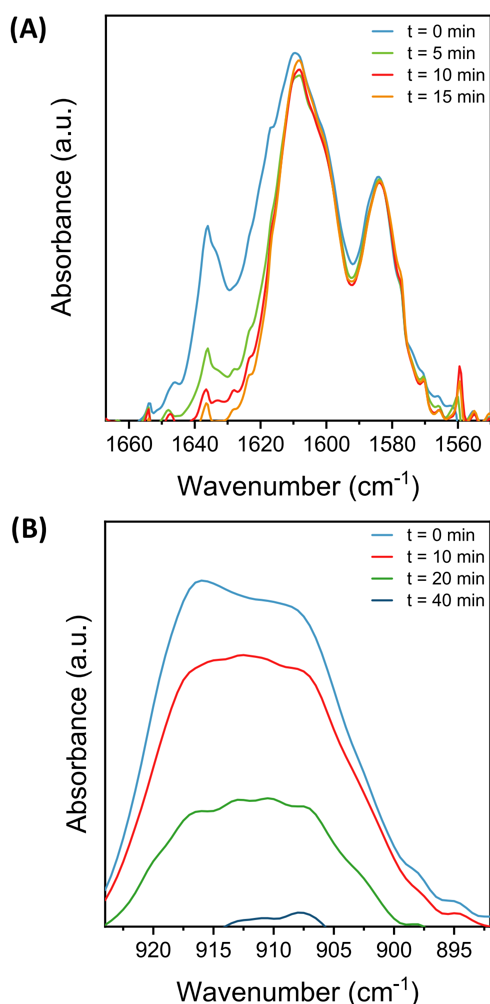

Figure 2. Zoom of the individual ATR-FTIR spectra measured at different times for (A) the acrylate signal and (B) the epoxy signal.

while the ring-opening reaction of the epoxide occurred significantly more slowly, with only 15% consumption within the same period of time (Table S2). However, conversion increased to 60% after 20 min, and the epoxy groups were completely consumed after 40 min. This indicates that most of the dynamic β-amino ester moieties are formed prior to epoxy curing.

Viscoelastic Behavior. The synthesized material was reprocessed in a preheated press at 180 °C for 30 min under 5 t of pressure to prepare disks. The presence of dynamic β-amino ester bonds allowed successful reprocessing (Figure S7) up to 5 times. The reprocessed materials were thermally characterized after every cycle as well as their network swelling and stress-relaxation behavior were analyzed (Table S3 and Figures S8–S10). Stress-relaxation experiments were then performed from 200 to 150 °C on the first reprocessed sample (Figure 3A). The initial relaxation modulus (G_0) exhibited a decrease from 3.4×10^6 to 7.3×10^5 Pa with temperature increase (150 to 200 °C), which is attributed to de-cross-linking through a dissociative mechanism (Figures 3A and S11). Concurrently, the relaxation time (τ) showed a decrease from 1.21×10^7 to 10^2 s. The stretched Maxwell model (eq 1) was preferred to fit relaxation curves over the canonical single Maxwell model due to its consideration of varying relaxation times across distinct segments of the network.

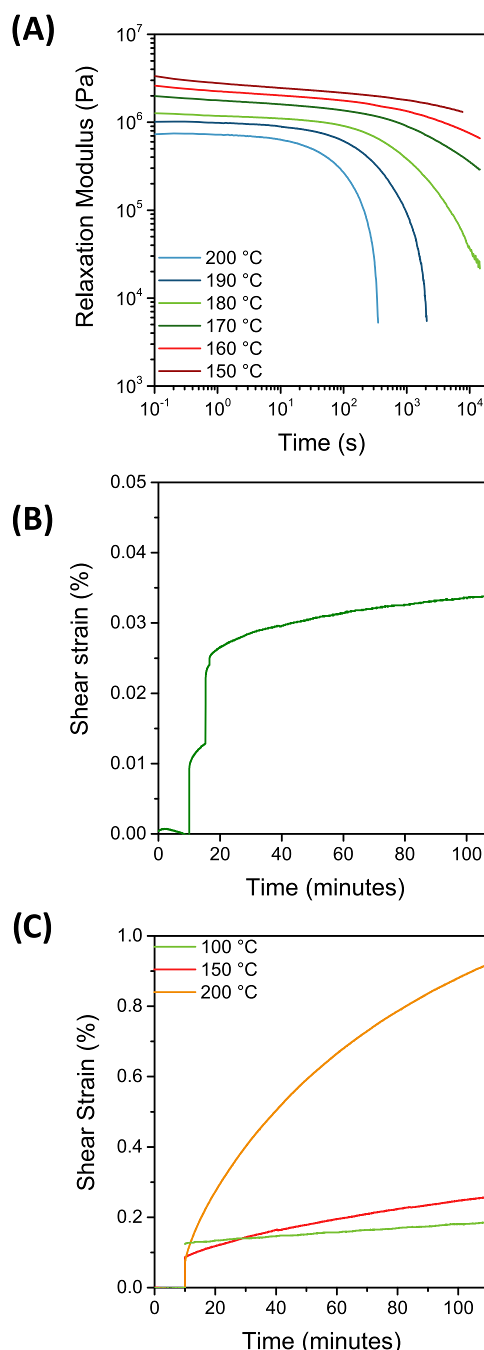

Figure 3. Stress relaxation of the BAE-8 resin with the MEHQ inhibitor from 200 to 150 °C (A) and creep experiments performed on the BAE-8 resin with the MEHQ inhibitor at different temperatures ranging from 25 °C (B) to 100–200 °C (C).

$$G(t) = G_0 e^{(-t/\tau)^\beta} \quad (1)$$

The average stretching factors (β) are in line with the ones reported in literature for the relaxation of segmental dynamics, having values between 0.8 and 0.1.[43]

CANs usually display creep resistance at room temperature because of their cross-linked structure. However, with the activation of the dynamic exchange, the material can be sensitive to creep with increasing temperature.[44] Therefore, a comparison between the reference nondynamic material and the dynamic adhesive has been performed at 150 °C. As anticipated from the heat triggered dynamic bonds, the

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permanently cross-linked specimen showed creep resistance, while the dynamic counterpart did not at such elevated temperatures (Figure S12). Further creep experiments were conducted on the dynamic adhesive at 25, 100, 150, and 200 °C, with a constant shear stress (σ) of 2 kPa for 6000 s (Figure 3B,3C). The σ value was selected to remain within the LVER (linear viscoelastic region) limits. In the creep compliance test at 25 °C, 2 kPa shear stress corresponded to 1% of shear strain (γ), this being the threshold value for the storage modulus (G') stability in the amplitude sweep experiment (Figures S13–S15).

The shear strain increases with temperature as expected from the heat triggered dynamicity. At temperatures higher than 40 °C, the material enters the rubbery regime, leading to an increased shear strain, while maintaining a good creep resistance. The latter is a necessity for the intended application as structural adhesive. At 100 °C or higher, the material deforms, as also expected from the creep and stress relaxation behavior. The resulting strain (ε) was monitored through time. From the steady-state time regime, an apparent creep rate ($\dot{\varepsilon}$) was calculated (going from 3.8×10^6 to 6.6×10^5 s^{-1}). From the Kelvin–Voigt equation ($\eta_0 = \sigma/\dot{\varepsilon}$, where is the η_0 zero shear viscosity, σ the constant shear stress and $\dot{\varepsilon}$ the apparent creep rate), the zero shear viscosity was evaluated. The lowering of η_0 (from 5.6 Pa·s to 3.0 Pa·s) value with increasing temperature was expected due to the network dissociation.[45]

Adhesive Properties. As shown above for the formulation optimization, the potential use of this dynamic material as structural adhesive was assessed using lap shear experiments (Table S4, Figures S16–S20), one of the most widely used methods to determine adhesive strength.[46] However, it is important to highlight here that a direct comparison between commercial structural adhesives and the material presented in this work is not possible due to the presence of numerous additives in the industrial formulations and specific surface treatment techniques. For this reason, the dynamic adhesive material is mainly compared to the reference nondynamic reference material (Figure 4). Even in the absence of any fillers or other additives, the epoxy material showed a good adhesive strength of 8.0 ± 1.8 MPa, comparable to the lap shear strength of the nondynamic resin (8.6 ± 2.4 MPa) and the values for other newly reported debondable epoxy adhesives.[10,21,22]

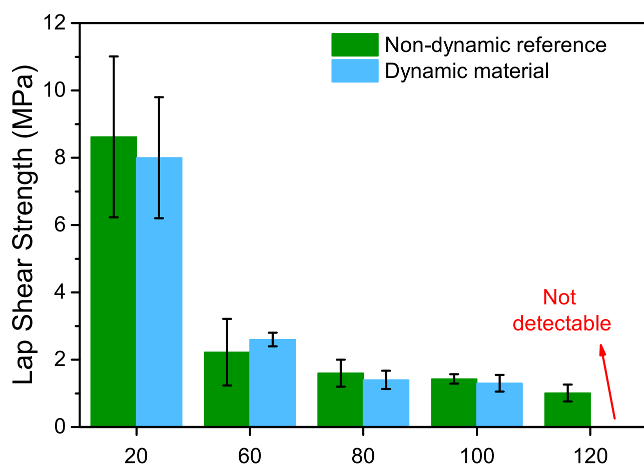

Figure 4. Comparison of lap shear strength at different temperatures (from 20 to 120 °C) between the dynamic epoxy resin (green) and the nondynamic reference epoxy material (blue).

The main target of this research was to develop an epoxy-based adhesive that allows easy debonding, thus facilitating the separation of two substrates for efficient and independent recycling. To test this ability on a proof-of-concept level, the adhesives properties of the dynamic BAE-8 were investigated at room temperature, in proximity to T_g, and at temperatures above T_g. The bond strength was determined after exposing the bonded specimen to the different temperatures for about 10 min. This was done to guarantee that the adhesive layer reached the preset temperatures. As expected, the adhesive strength exhibited a temperature-dependent decline (from 8.3 ± 1.8 MPa at RT to 1.3 ± 0.3 MPa at 100 °C). Beyond T_g, the higher chain mobility negatively impacts the adhesive strength as expected. Furthermore, at elevated temperatures, the dynamic mechanism is activated, leading to de-cross-linking. This resulted in debonding of the samples with little to no required applied force at 120 °C. When performing similar tests for the nondynamic resin, a decrease in lap shear strength can also be observed but, in contrast to the dynamic material, the lap shear tests show that the strength reaches an asymptotic value around 0.5 MPa, at which the bonded substrates do not detach manually. When visually analyzing the fracture surfaces, it can be seen that for all specimens, adhesive failure is the main type of failure (Figure S21).

CONCLUSIONS

In this paper, we demonstrated that on-demand debondable epoxy adhesives can be prepared via a one-pot approach using epoxides, acrylates and amines. ATR-FTIR spectroscopy shows that the Aza-Michael addition reaction between the amine and the acrylate is significantly faster than the ring opening reaction of the epoxide. This enables the dynamic β-amino ester linkages to be established, prior to fully curing the network. After optimization of the formulation in terms of chemicals used and ratios, a formulation of 1,3-BAC, 1,6-hexanediol diacrylate and Epikote 238 was found to perform best when aiming for a material with a T_g above 40 °C and a lap shear strength at room temperature above 7 MPa. Stress relaxation and creep experiments confirmed the dynamic nature of the epoxy resins for temperatures as low as 120 °C. The adhesive properties were tested via lap shear tests, showing a lap shear strength of around 8 MPa at room temperature, while the sample debonded completely at 120 °C in contrast to a reference nondynamic epoxy material.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c15346.

Characterization of the networks; additional IR spectra, DSC, and TGA thermograms; rheological data including amplitude sweeps, stress relaxation data and creep measurements; adhesive analysis including lap shear data and pictures of the debonded surfaces (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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