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Strengthening epoxy adhesives at elevated temperatures based on dynamic disulfide bonds†

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Epoxy resins incorporating aromatic disulfide bonds demonstrated improved adhesive properties with increasing temperature below their glass transition points. This behaviour was explained in terms of the relatively low topology freezing transition temperature of these materials as compared with their glass transition temperatures.

Thermosetting structural adhesives have a wide range of applications, including in the aerospace, automobile and infrastructure industries, because they tend to add less weight than conventional mechanical fastening methods. The majority of such adhesives are composed of crosslinked network polymers such as epoxy resins, and provide excellent dimensional stability, good mechanical properties and superior creep and chemical resistance.[1–6] However, although these substances are often required to be stable under harsh high temperature conditions, the adhesive strength of traditional thermosetting resins tends to be reduced with increases in temperature. The development of materials with greater adhesive strength at high temperatures would enable the reliable application of environmentally-friendly adhesive joints in lightweight automobiles or various infrastructure components.

To this end, our group has focused on the use of dynamic covalent chemistry (DCC) to develop adhesives that maintain their strength at higher temperatures. Network polymers with dynamic covalent bonds generally behave as conventional thermoset resins but can exhibit thermoplastic characteristics as a result of reversible bond exchange reactions in response to specific external stimuli, such as heating or exposure to ultraviolent (UV) radiation or ultrasound.[7–11] To date, Diels–Alder reaction,[12–14] olefin metathesis,[15] imine/amine exchange,[16] siloxane/silanol exchange,[17] disulfide metathesis,[18] transamination,[19] and transesterification[20,21] have all been utilized to devise exchangeable bond systems. The introduction of adaptable bonding into thermoset resins using these approaches provides a variety of unique properties, including self-healing and the ability to reprocess, remold and recycle these materials. However, the adhesive properties of such resins have not yet been fully exploited because these adaptable bonding systems (typically based on transesterification) require the use of insoluble catalysts that can damage metal substrates. In addition, the prolonged reaction times that are required may induce thermal degradation and poor mechanical strength, both of which can limit the applications of resins as structural adhesives.

Epoxy resins based on exchangeable aromatic disulfide exhibit exceptional thermal and mechanical stability and can be synthesized using catalyst-free reactions. These materials also provide rapid exchange rates and healing efficiency compared with other dynamic bonding systems. Even though the degradation, self-healing characteristics and electrical resistance properties of epoxy resins incorporating disulfide bonds have been examined,[22–25] the adhesive characteristics of these substances, especially the effects of temperature on adhesion, have not been fully elucidated. The present study therefore performed a detailed examination of the adhesive characteristics of epoxy resins having aromatic disulfide bonds. The results of this work demonstrate unusual thermal strengthening of adhesive joints at elevated temperatures. These results are discussed herein with regard to the thermal properties of epoxy resins with adaptable bonding systems, especially with regard to glass transition temperature (T_g) and topology freezing transition temperature (T_v).

Ester and disulfide bonds were introduced into aromatic epoxy networks to obtain model epoxy adhesives with adaptable bonding (Scheme 1). The disulfide system comprised bis(4-glycidyloxyphenyl)disulfide (BGPDS, termed the **1a** herein) and dithiodianiline (DTDA, **2a**) as the epoxy monomer and diamine hardener, respectively. The diglycidyl ether of bisphenol A

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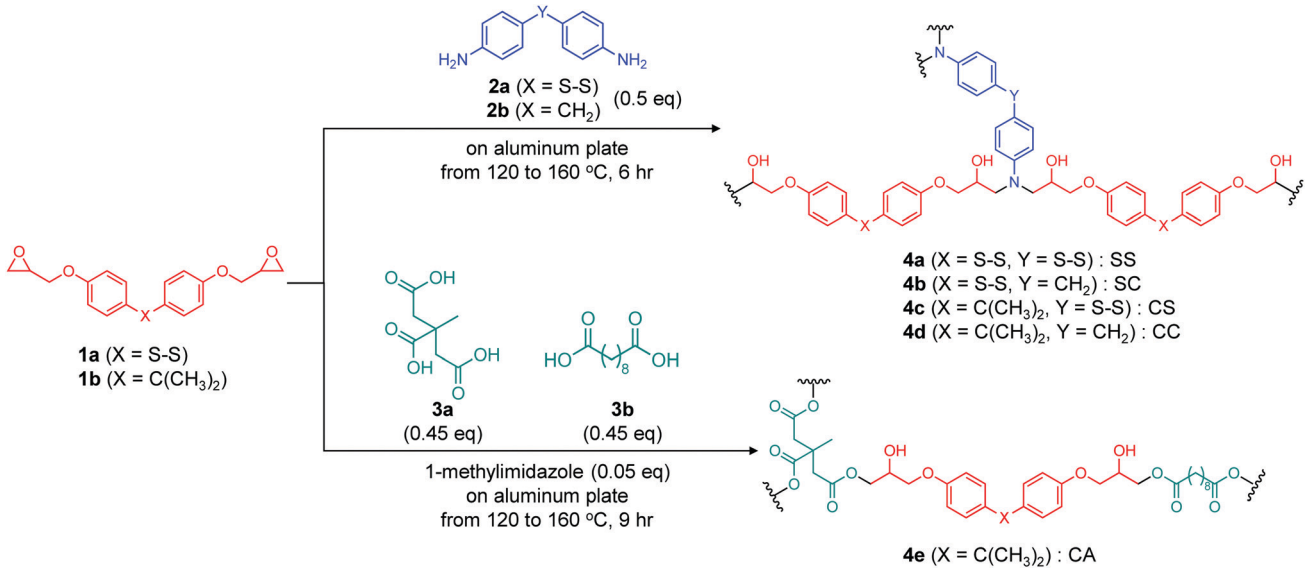

Scheme 1 Synthesis and chemical structure for all epoxy-based network in this study.

(DGEBA, **1b**) and diaminodiphenyl methane (DDM, **2b**) were employed as controls analogues of BGPDS and DTDA, respectively, without disulfide bonding. The chemical reactivities of the aromatic disulfide in the epoxy monomer and amine hardener were assumed to be almost identical. The epoxy adhesives were synthesized by combining the epoxy monomer (either **1a** or **1b**) and the diamine hardener (**2a** or **2b**) followed by mixing at 90 °C for 30 min in stoichiometric ratios (2 : 1) of the ingredients. The mixture of the epoxy monomer and hardener was transferred onto the pre-treated aluminium substrates. This was followed by curing at 120 °C for 2 h, 140 °C for 2 h and 160 °C for 2 h. Aluminium substrates were employed because these are chemically inert with regard to thiols and because aluminium is an important lightweight structural material.[26,27] To systematically elucidate the effects of adaptable bonding, the epoxy monomer and amine hardener with/without disulfide bonding were prepared in all combination, to give specimens referred to herein as SS (**4a**), SC (**4b**), CS (**4c**) and CC (**4d**) (Scheme 1). Note that the extent of disulfide bonding in the SS, SC and CS samples was in the ratio of 3 : 2 : 1, which meant the most content of disulfide bonding in the SS sample. For comparison purposes, a previously reported epoxy network with ester bonding (referred to as CA sample (**4e**) herein) was prepared by mixing citric acid and sebacic acid followed by the addition of DGEBA together with 1-methylimidazole as a catalyst. This mixture was subsequently precured at 120 °C for 3 h, followed by full curing at 160 °C for 6 h. The ratio of CA (**4e**) for DGEBA, citric acid, sebacic acid, and 1-methylimidazole was 1 : 0.45 : 0.45 : 0.05. An excess of the epoxy monomer was added to this composition so as to increase the crosslinking density.[28] Details of the sample preparation conditions are provided in Table S1 (ESI†). Prior to the adhesive tests, the thermomechanical properties of these epoxy adhesives were evaluated. Specifically, T_g, T_v, activation energy of stress relaxation (E_a) and storage modulus (E') were determined based on dynamic mechanical analysis (DMA) (Table 1).

Table 1 Thermal and mechanical properties of all epoxy networks in this work

Item	T_g (°C)	T_v (°C)	E_a (stress relaxation) (kJ mol^{-1})	Storage modulus (25 °C) (GPa)	Storage modulus (T_g + 30 °C) (MPa)
SS	133.7	−26	37.7	1.93	15
SC	144.0	67	65.5	2.22	30
CS	160.5	91	85.9	1.88	20
CC	177.9	—	—	1.88	200
CA[28]	73	105	106	1.5–1.8	4–5

It is important to note that the viscoelastic behaviour of polymer networks having adaptable bonding systems can be characterized by two transition temperatures. One is associated with the transition between glassy and rubbery states, which is related to intramolecular chain motions. Segmental chain movements will occur above T_g, resulting in dramatic decrease of mechanical strength. On the other hand, rigid structure below T_g will limit the movement, so that the mechanical strength only slightly decreases with increasing temperature within this region. The other transition mode is associated with the topology freezing transition, which occurs at the point at which the material exhibits a viscosity of 10^{12} pa s. T_v is generally considered as the critical point at which the exchange rate becomes sufficiently rapid such that bond breaking and bond rearrangement can occur dynamically. This transition temperature is calculated by varying the sample temperature during a stress relaxation test, as shown in Fig. 1. In this process, the relaxation times at different temperatures are obtained based on the Maxwell model, defined as the time required for a 63% drop in the effective modulus, after which these times are plotted as a function of temperature in the manner of an Arrhenius plot (Fig. 2). The T_v values determined for the epoxy networks having disulfide and ester bonds in the

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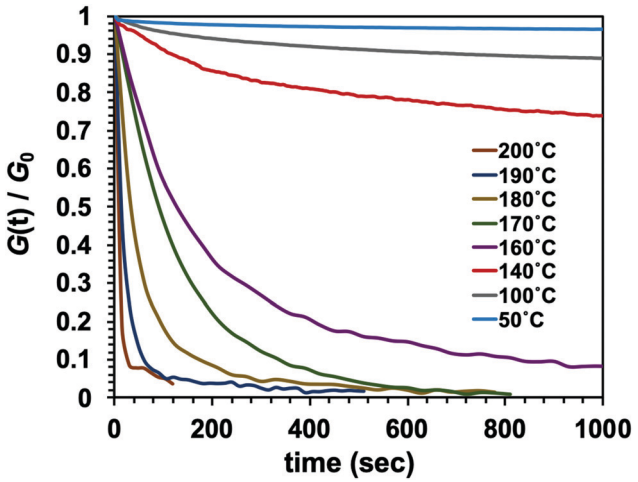

Fig. 1 Normalized stress relaxation curves of dynamic epoxy networks SS at different temperatures.

present work are summarized in Table 1,[28] while the T_v and T_g values for various adaptable bonding epoxies reported in the literature are presented in Table S2 (ESI†). It should be noted that the viscoelastic properties of the dynamic covalent systems could be classified into two categories based on the relationship between the T_v and T_g values of the materials.[8,10] In the case of the T_v value was much greater than the T_g value, (that is, the CA sample), as shown in Fig. 3(a), the heating of the thermosetting epoxy to temperatures within the intermediate region II (between T_g and T_v) was expected to induce a transition from a glassy to rubbery state and so provide increased chain mobility. As a consequence, the material would acquire the properties of an elastomer, but would not present the exchange reaction such as transesterification in this region. Upon further heating above T_v (region III), the exchange reaction started so that the polymer would change from an

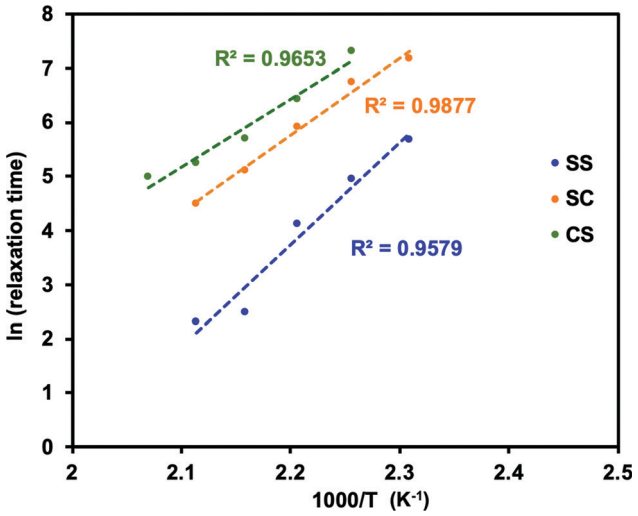

Fig. 2 Fitting line of the relaxation time to Arrhenius equation for dynamic epoxy networks SS, SC, and CS (R-square = 0.9579, 0.9877, and 0.9653, separately).

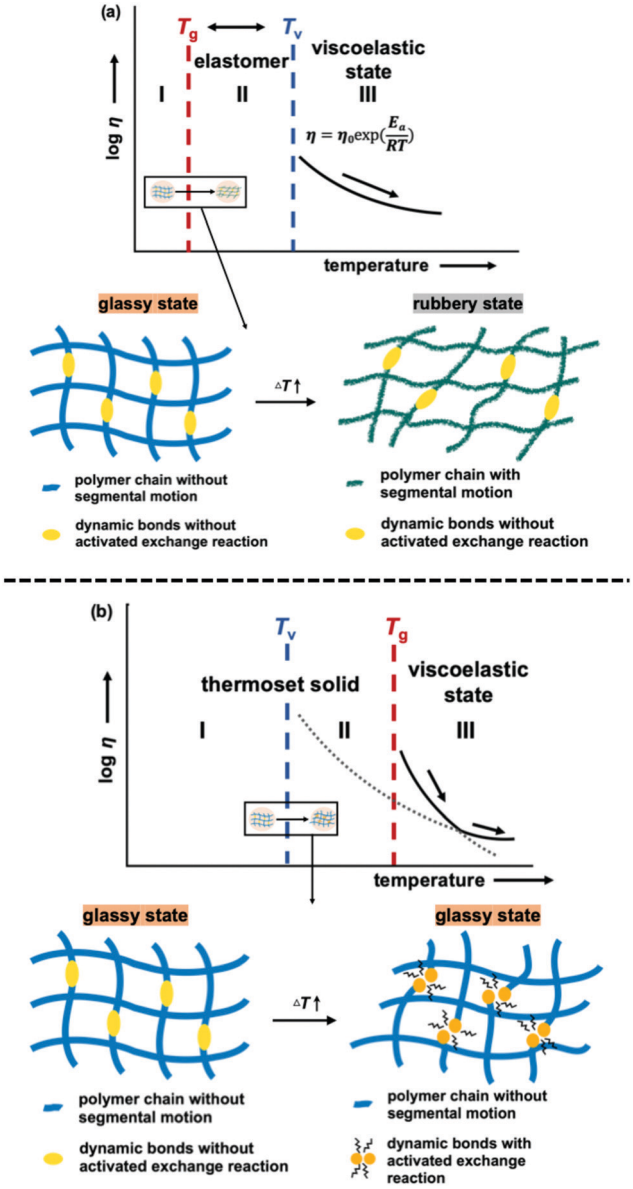

Fig. 3 Comparison for the effect of glass transition temperature (T_g) and topology freezing transition temperature (T_v) on viscosity and viscoelastic behavior of dynamic systems (a) $T_v > T_g$ (b) $T_g > T_v$.

elastomer to a viscoelastic liquid. In contrast, the epoxy samples with aromatic disulfide bonding (that is, the SS, SC and CS specimens) had T_g values higher than their T_v values, as can be seen from Fig. 3(b). Here, the intrinsically rapid exchange reaction associated with disulfide bonding was able to take place in the epoxy network even within the intermediate temperature region II (above T_v and below T_g). In this scenario, although the exchange reaction involving the disulfide bonds was able to proceed at temperatures in excess of T_v, a lack of chain motion below T_g would be expected to limit the segmental movement of the epoxy network, resulting in rigid and glassy structure. Above T_g (region III), these samples also transitioned to viscoelastic liquids because the chain motions were able to proceed along with active exchange reactions

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associated with the disulfide bonds. The data show that a higher content of aromatic disulfide bonding in the network lowered the T_v value. This effect is attributed to the increased probability of exchange reactions with higher densities of disulfide bonds, which accelerated the bond cleavage and bond reorganization. This behaviour can also be explained by considering activation energy, and the activation energy value for the stress relaxation of each composition was obtained from the data in Fig. 2 based on the Arrhenius equation. The resulting values are presented in Table 1. Although the exchange reaction of dynamic bonds would result in relaxation, significant rearrangement of whole polymer network would also be required for stress release. In the present work, the SS specimen was found to have the lowest activation energy for stress relaxation among all the compositions. Both the T_v values and activation energies demonstrate that higher concentrations of aromatic disulfide bonds promoted the stress release because of the easier reorganization of the polymer network and the increased possibility of exchange occurring.

Most importantly, the viscoelastic properties derived from the T_g and T_v of these materials had a significant effect on their performance as adhesives. The single lap shear test is a standard means of assessing adhesive strength and so the room temperature lap shear strength of each epoxy sample was ascertained. In these trials, each epoxy was applied to a pretreated aluminium substrate followed by curing at temperatures that exceeded both the T_v and T_g of the epoxies with dynamic covalent bonding (see ESI,† for details). In addition, to evaluate recycling and rebonding ability, the used aluminium specimens were rebonded to their original configurations by hot-pressing. Each epoxy showed a relatively high initial shear strength in the range of 13 to 19 MPa (Fig. 4). Thus, introducing disulfide bonds into the epoxy adhesive did not significantly affect the adhesive strength, regardless of whether such bonding resulted from the phenolic epoxy or the aromatic amine hardener. After rebonding, the shear strength of the epoxy with adaptable bonding was found to be 83 to 95% of the initial shear strength, while the sample without adaptable bonding (that is, the CC specimen) did not exhibit any adhesion when rebonding was attempted. These results can be explained in terms of both the viscoelastic nature of the epoxy network and the exchange reaction associated with the adaptable bonding system. In the case that an epoxy adhesive with adaptable bonding was heated above both its T_g and T_v, the material behaved as a viscoelastic liquid within region III (see Fig. 3). Simultaneously, the bond exchange reaction proceeded among the adaptable bonds at a rapid rate to restore the polymer network, resulting in recovery of the shear strength. Evidence for these effects is provided by the correlation between the recovery of shear strength and the amount of disulfide bonding, such that the shear strength of the SS sample was 95% of the original value. This was higher than the recovery percentages showed by the other two compositions (the SC and CS). Moreover, the CC sample (without exchangeable dynamic bonding) could not adhere again once it was cleaved. These results confirm that a high degree of adaptable bonding is required to allow the efficient recovery of the polymer network, leading to restoration of the adhesive strength. Similarly, the CA sample also showed good recovery of shear strength when heated to a viscoelastic state because of the presence of dynamic ester bonds, although a longer recovery time was needed. As a result, there were no significant differences between the rebonding strengths of the epoxies with the disulfide and ester bonds when the specimens were repaired by heating above both T_g and T_v. However, there were obvious differences in adhesive behaviour after heating to within region II, intermediate between T_v and T_g. For this reason, the adhesive properties of the epoxy specimens with adaptable bonding were evaluated in this intermediate region. Although there have been several reports concerning the adhesive characteristics of adaptable bonding systems to date, the effect of temperature on these properties has not yet been fully established, especially in the range between T_v and T_g. Even so, this temperature range is important because it may coincide with temperatures applied during industrial bonding processes. Variations in adhesive properties in this temperature range were examined by preparing two SS and CA film samples and adhering these specimens at 80 °C using a compressive force of 10 kN. Here it is important to note again that the SS sample had a T_g (134 °C) higher than its T_v (−26 °C), whereas the CA sample had a T_g (73 °C) lower than its T_v (105 °C). The pressing temperature of 80 °C was chosen so as to be intermediate between the T_v and T_g of both materials (Fig. 3). The subsequent testing of these specimens indicated that the SS showed good adhesive properties (Fig. 5a) while the CA film pieces did not adhere but simply deformed from their original shapes during testing (Fig. 5b). When the SS film was heated to 80 °C, the bond exchange reaction was initiated but chain motions of the epoxy network could not proceed efficiently because the material was below its T_g. Therefore, the film shape could be maintained such that it exhibited solely good adhesion. At the same temperature, the transesterification process in this polymer is thought to have been dormant, while chain motions would have been able to

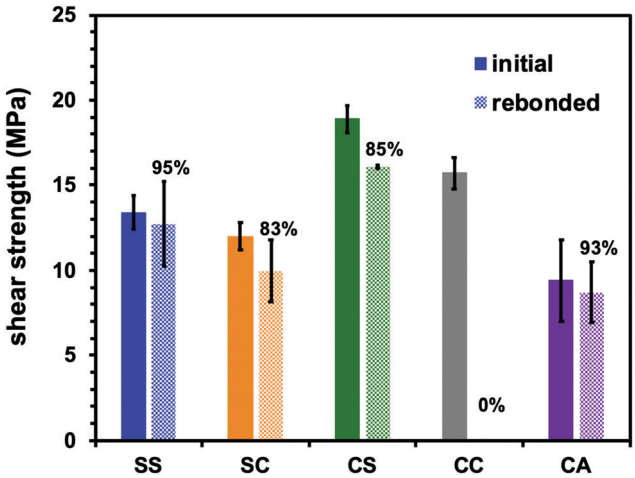

Fig. 4 Single lap shear strength for initial and rebonded dynamic epoxy adhesive networks at room temperature.

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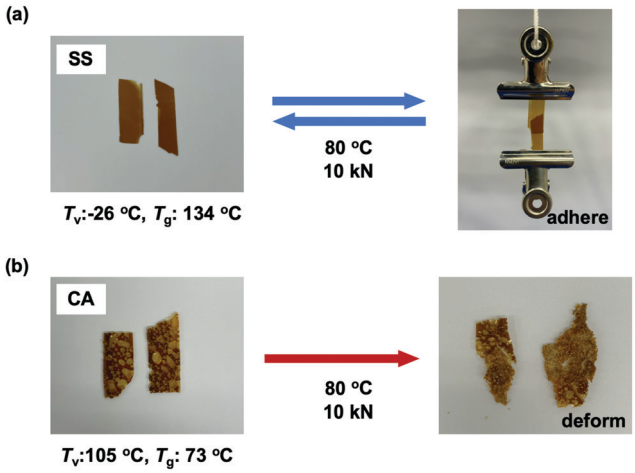

Fig. 5 Demonstration of exchange and healing behaviour at 80 °C for formula (a) SS and (b) CA.

occur. Therefore, only deformation of the film occurred without adhesion between the CA films.

The effect of temperature on the Young's modulus and adhesive strength values of the adaptable bonding specimens was further assessed by performing single lap shear strength tests at temperatures ranging from ambient to 200 °C (Fig. 6 and 7). As can be seen from Fig. 6, the Young's modulus values of all compositions were slightly decreased with increases in temperature below the glass transition point but dramatically declined upon heating above T_g. This was the case for both the dynamic systems and the conventional thermoset polymers. Consequently, the heat-induced change in the mechanical properties of the adhesive resins is primarily ascribed to the glass–rubber transition. However, when epoxy resins are applied as adhesives, their adhesive strength shows more complicated behaviour that can be placed into two categories. In the case of a standard thermosetting adhesive, the adhesive strength tends to gradually

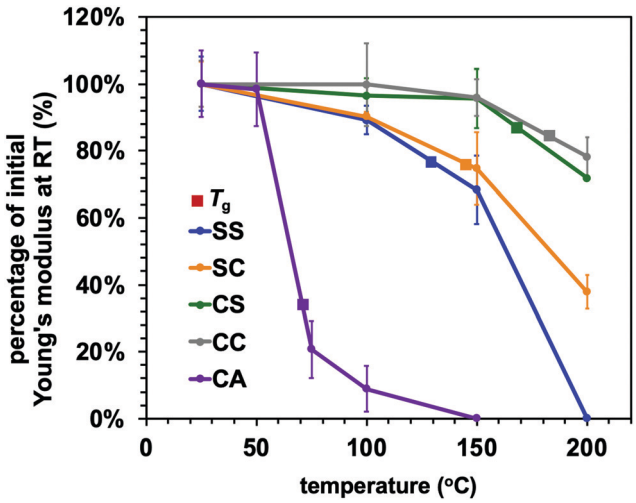

Fig. 6 Temperature-dependent Young's modulus for all adhesive epoxy networks.

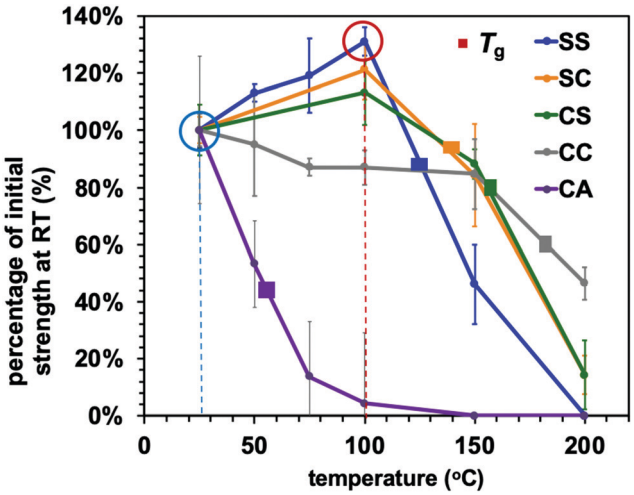

Fig. 7 Temperature-dependent single lap shear strength for all adhesive epoxy networks.

decrease with increases in temperature and then drastically drop at the T_g of the material, as is also observed for bulk resins (see Fig. 6).[29–31] This effect originates from the transition from a glassy to rubbery state. Similar to these typical thermoset adhesives, the lap shear strength of the CC sample transitioned from moderate to very poor over the temperature range of 150 to 200 °C, which contains the T_g of the sample CC (178 °C).

Conversely, the epoxy samples with disulfide bonds (the SS, SC and CS) exhibited unusual increases in lap shear strength on heating from room temperature to 100 °C. In particular, the SS specimen showed a 30% increase in lap shear strength at 100 °C as compared with room temperature (Fig. 7). In general, epoxy adhesives accumulate internal stresses in their three-dimensional network structures as a result of volume shrinkage during the curing process and the cooling process after curing. When external forces are applied to these polymer networks at room temperature, these materials therefore tend to exhibit brittle fracture because of cracks caused by internal stress and/or decreases in the elongation of the three-dimensional network structure, resulting in the cleavage of chemical bonds. In addition, considering that thiols will not readily react with aluminium/aluminium oxide surfaces, the exchange reaction of the disulfide bonds is thought to be the primary means of relieving localized internal stress *via* rearrangement of the polymer network. To confirm the occurrence of efficient exchange reactions among the aromatic disulfide bonds, diphenyl disulfide and dithiodianiline were dissolved in dimethyl sulfoxide (DMSO) as low molecular weight model compounds. The nuclear magnetic resonance (NMR) spectra of these solutions (Fig. S5, ESI†) indicate that the exchange reactions of these compounds proceeded even at room temperature.[32] Although it should be noted that the rapid exchange of disulfide bonds may be more limited in a rigid polymeric structure at room temperature, we assumed that the dissociation and association of disulfide bonds could still occur within such fixed networks. Increasing the temperature would be expected to enhance both the bond cleavage and recombination rates as

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well as the probability of exchange and rearrangement. As a result, epoxy networks containing disulfide bonds will become tougher at higher temperatures because of the rapid exchange and reorganization that occur above T_v. At the same time, if the sample is below its T_g, the mechanical strength of the adhesive resin will be maintained owing to its rigid structure. As a sample approaches its T_g, its adhesive strength will greatly decrease and adhesive joints will tend to break, as is observed with conventional polymeric materials. The present data establish that a high density of aromatic disulfide bonds strengthened the adhesive effect. However, when the CA sample was heated, the bond strength was drastically decreased. This effect can likely be attributed to the frequent chain motions in the sample (because of its relatively low T_g of 73 °C) but lack of exchange reaction, as transesterification did not occur.

The T_g of a polymer reflects its transition from a rigid brittle solid to a flexible rubbery state due to chain movement. In addition, the effect of temperature on polymers containing adaptable bonds is also often evaluated based on T_v. Both T_v and T_g are associated with changes in viscosity, but for entirely different reasons. The T_g transition originates from changes in intramolecular chain motion, while T_v is attributed to intermolecular bond exchange processes. This difference leads to dissimilar phenomena in terms of adhesive properties. Specifically, bonding strength is greatly decreased above T_g but adhesion may be strengthened while the occurrence of fractures is minimized as a result of bond exchange reactions above T_v. Compared with other dynamic covalent bonds, aromatic disulfide systems tend to have low T_v and high T_g values, which increase the rates of dissociation, diffusion and association of the disulfide bonds and widen the temperature range over which these materials can be applied as industrial adhesives. On the contrary, adhesives with transesterification bonds will show high T_v and low T_g values, and so undergo glass transition before toughening.[19,23–25,28,33,34]

In summary, this work represents the first observation of improved adhesion behaviour at elevated temperatures as a result of adaptable aromatic disulfide bonding. An improved understanding of disulfide-based networks may permit the development of new dynamic systems and broaden the potential range of material design.

Conclusions

This study demonstrated the application of epoxy polymers incorporating aromatic disulfide bonds as adhesives. The improved adhesive properties of these materials at elevated temperatures below the glass transition region (compared with other dynamic systems and traditional thermosets) is ascribed to their extremely low T_v and activation energy values. These factors resulted in tougher adhesion because the easier rearrangement of aromatic disulfide bonds allowed the release of internal stress. This study also established that a high density of disulfide bonds accelerated the exchange process by increasing the likelihood of bond cleavage and rearrangement, which in turn improved adhesion.

With regard to industrial applications, epoxy-based adhesive systems with dynamic disulfide bonding represent an environmentally-friendly and economical option. These resins not only show good adhesion properties and permit simple rebonding procedures, but also demonstrate improved high-temperature adhesive performance as a result of the incorporation of exchangeable disulfide bonds that expand their usable temperature range. These factors could permit the development of next-generation adhesives based on dynamic covalent chemistry and should be further investigated in the future. The knowledge gained from the present study should also be applicable to other epoxy adhesive systems, especially because bisphenol A is often used in epoxy adhesives.

Notes

The Maxwell relationship viscosity = $G{\cdot}t$ was used to determine the relaxation times for T_v calculations. Here, G is the shear modulus, calculated as $G = E'/2(1 + \nu)$ where ν is Poisson's ratio for a rubber (with a value of 0.5) and E' is the storage modulus for each composition in a rubbery state as determined using DMA. The E' values for the SS, SC and CS compositions in the rubbery state were 15, 30 and 20 MPa, respectively.

Conflicts of interest

There are no conflicts to declare.

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References

1 E. M. Petrie, *Handbook of Adhesives and Sealants*, McGraw-Hill Education, New York, 2nd edn, 2007.
2 S. Ebnesajjad and A. H. Landrock, in *Adhesives Technology Handbook*, ed. S. Ebnesajjad and A. H. Landrock, William Andrew Publishing, Boston, 3rd edn, 2015, pp. 1–18.
3 J. Shields, in *Adhesives Handbook*, ed. J. Shields, Butterworth-Heinemann, 3rd edn, 1984, pp. 1–6.
4 S. Pruksawan, S. Samitsu, Y. Fujii, N. Torikai and M. Naito, *ACS Appl. Polym. Mater.*, 2020, **2**, 1234–1243.
5 S. Pruksawan, G. Lambard, S. Samitsu, K. Sodeyama and M. Naito, *Sci. Technol. Adv. Mater.*, 2019, **20**, 1010–1021.
6 S. Pruksawan, S. Samitsu, H. Yokoyama and M. Naito, *Macromolecules*, 2019, **52**, 2464–2475.
7 C. J. Kloxin and C. N. Bowman, *Chem. Soc. Rev.*, 2013, **42**, 7161–7173.
8 W. Denissen, J. M. Winne and F. E. Du Prez, *Chem. Sci.*, 2016, **7**, 30–38.
9 W. Zou, J. Dong, Y. Luo, Q. Zhao and T. Xie, *Adv. Mater.*, 2017, **29**, 1606100.

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10 G. M. Scheutz, J. J. Lessard, M. B. Sims and B. S. Sumerlin, *J. Am. Chem. Soc.*, 2019, **141**, 16181–16196.
11 J. M. Winne, L. Leibler and F. E. Du Prez, *Polym. Chem.*, 2019, **10**, 6091–6108.
12 B. J. Adzima, H. A. Aguirre, C. J. Kloxin, T. F. Scott and C. N. Bowman, *Macromolecules*, 2008, **41**, 9112–9117.
13 G. Zhang, Q. Zhao, L. Yang, W. Zou, X. Xi and T. Xie, *ACS Macro Lett.*, 2016, **5**, 805–808.
14 S. Das, S. Samitsu, Y. Nakamura, Y. Yamauchi, D. Payra, K. Kato and M. Naito, *Polym. Chem.*, 2018, **9**, 5559–5565.
15 C. Liu, E. Park, Y. Jin, J. Liu, Y. Yu, W. Zhang, S. Lei and W. Hu, *Angew. Chem., Int. Ed.*, 2018, **57**, 1869–1873.
16 P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi and W. Zhang, *Adv. Mater.*, 2014, **26**, 3938–3942.
17 P. Zheng and T. J. McCarthy, *J. Am. Chem. Soc.*, 2012, **134**, 2024–2027.
18 A. Rekondo, R. Martin, A. Ruiz De Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *Mater. Horiz.*, 2014, **1**, 237–240.
19 A. Chao and D. Zhang, *Macromolecules*, 2019, **52**, 495–503.
20 D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965–968.
21 K. Yu, P. Taynton, W. Zhang, M. L. Dunn and H. J. Qi, *RSC Adv.*, 2014, **4**, 10108–10117.
22 S. P. Black, J. K. M. Sanders and A. R. Stefankiewicz, *Chem. Soc. Rev.*, 2014, **43**, 1861–1872.
23 A. Ruiz De Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez and I. Odriozola, *Mater. Horiz.*, 2016, **3**, 241–247.
24 A. Takahashi, T. Ohishi, R. Goseki and H. Otsuka, *Polymer*, 2016, **82**, 319–326.
25 F. Zhou, Z. Guo, W. Wang, X. Lei, B. Zhang, H. Zhang and Q. Zhang, *Compos. Sci. Technol.*, 2018, **167**, 79–85.
26 S. L. Nesbitt, J. A. Emerson and J. P. Bell, *Int. J. Adhes. Adhes.*, 2000, **20**, 429–436.
27 C. Vericat, M. E. Vela, G. Corthey, E. Pensa, E. Cortés, M. H. Fonticelli, F. Ibañez, G. E. Benitez, P. Carro and R. C. Salvarezza, *RSC Adv.*, 2014, **4**, 27730–27754.
28 F. I. Altuna, C. E. Hoppe and R. J. J. Williams, *RSC Adv.*, 2016, **6**, 88647–88655.
29 R. D. Adams, J. Coppendale, V. Mallick and H. Al-Hamdan, *Int. J. Adhes. Adhes.*, 1992, **12**, 185–190.
30 L. F. M. da Silva and R. D. Adams, *Int. J. Adhes. Adhes.*, 2007, **27**, 216–226.
31 L. D. R. Grant, R. D. Adams and L. F. M. da Silva, *Int. J. Adhes. Adhes.*, 2009, **29**, 535–542.
32 S. Nevejans, N. Ballard, J. I. Miranda, B. Reck and J. M. Asua, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27577–27583.
33 Z. Ding, L. Yuan, Q. Guan, A. Gu and G. Liang, *Polymer*, 2018, **147**, 170–182.
34 X. Yang, L. Guo, X. Xu, S. Shang and H. Liu, *Mater. Des.*, 2020, **186**, 108248.

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