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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

Note: Thermally removable epoxy adhesives incorporating thermally reversible diels-alder adducts

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Online publication date: 08 September 2010

To cite this Article Aubert, James H.(2010) 'Note: Thermally removable epoxy adhesives incorporating thermally reversible diels-alder adducts', *The Journal of Adhesion*, 79: 6, 609 – 616

To link to this Article: DOI: 10.1080/00218460309540

URL: <http://dx.doi.org/10.1080/00218460309540>

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NOTE

THERMALLY REMOVABLE EPOXY ADHESIVES INCORPORATING THERMALLY REVERSIBLE DIELS-ALDER ADDUCTS

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Thermally reversible adhesives are prepared through the reaction of aliphatic diamines and a diepoxy compound containing two Diels-Alder adducts. The diepoxy compound is formed via the Diels-Alder reaction between two epoxy-containing furans and a bismaleimide. The adhesive displays a T_g of -40°C and a constant shear modulus up to approximately 90°C . At temperatures exceeding 90°C the retro Diels-Alder reaction occurs, which leads to a significant loss in modulus. The loss of modulus is reversible with temperature. A thermally reversible adhesive is proposed based upon the loss of modulus at an elevated temperature, i.e., adhesives bonds are easily broken at elevated temperature where the modulus is low.

Keywords: Epoxy; Diels-Alder; Diamine; Adhesion; Thermally reversible; Thermally removable

INTRODUCTION

Adhesives are normally chosen to join materials together indefinitely without consideration to disassembly. Yet disassembly can be an important aspect of manufacturing if one considers the entire life cycle of the product. For example, recycling requires that bonded parts be

Received 15 April 2002; in final form 30 November 2002.

I would like to thank Patti Sawyer for sample preparation, Mark Stavig for the mechanical properties measurements, and Dave Tallant and Manuel Garcia for the FTIR analysis. Sandia National Laboratories is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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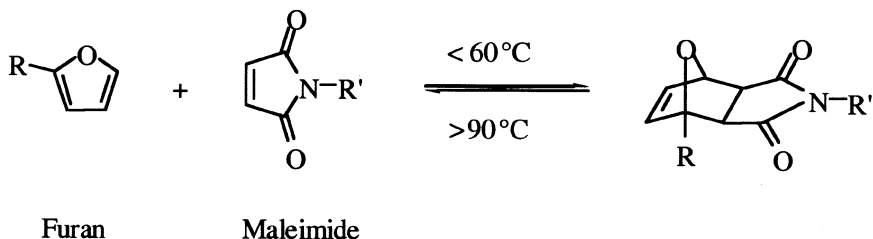


FIGURE 1 Reversible Diels-Alder reaction between furan and maleimide.

taken apart. In other instances there may be an economic incentive to repair or to upgrade an expensive component. If the components are bonded, then the bond must be easily broken to avoid collateral damage. An enabling technology for these options is a removable adhesive.

Typically, adhesive bonds are taken apart after heating to a temperature above the softening point of the adhesive (glass transition temperature) and then prying them apart. Our approach to a thermally removable adhesive takes this idea one step further. It relies upon the use of a thermally reversible chemistry that results in very low modulus at an elevated temperature. The modulus is three orders of magnitude lower than in the rubbery region. Only low force is then needed to separate the bonded components, and this decreases the chance of collateral damage.

We are developing removable adhesives based upon thermally reversible Diels-Alder chemistry [1] as shown in Figure 1. The Diels-Alder adduct is formed between a diene (the furan) and a dienophile (the maleimide) below 60°C. Above 90°C the adduct opens to form the original furan and maleimide moieties. By choosing R in the diene to contain a reactive epoxy group, we are able to formulate removable elastomeric adhesives that cure *via* conventional epoxy cure reactions. This work builds upon our recent results—Loy *et al.* [2] and McElhanon *et al.* [2–3]—which demonstrated epoxy resins containing Diels-Alder adducts that were utilized in removable epoxy foams. Previously, McElhanon *et al.* [4] demonstrated the use of Diels-Alder adducts in the preparation of thermally responsive dendrimers. Chen *et al.* [5] recently demonstrated a self-healing polymer that contains Diels-Alder adducts.

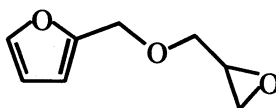
EXPERIMENTAL

1,1'-(methylenedi-4,1-phenylene)-bismaleimide (95%), furfuryl glycidyl ether (95%), and technical-grade nonylphenol are obtained from Aldrich Chemical Co., (Milwaukee, WI, USA). Diamine curatives,

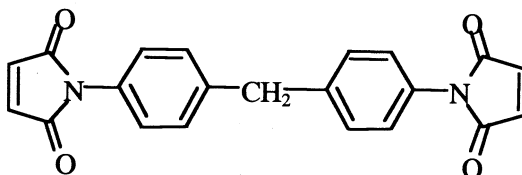
polyoxypropylenediamines (Jeffamine[®] 230 (DP ~ 2.86) and Jeffamine[®] 2000 (DP ~ 34.2)) are obtained from Huntsman Chemical Co. (Houston, TX, USA). All reagents were used as received. Some of their structures are shown in Figure 2.

An adhesive, RA100, is prepared by first dissolving the bismaleimide in furfuryl glycidyl ether at 95°C while stirring in a round-bottom flask with reflux condenser. When cooled below 60°C, the resin, RR1 (adduct of the furfuryl glycidyl ether and the bismaleimide, Figure 3), is a solid. A typical Fourier transform infrared (FTIR) absorption spectrum of this epoxy resin and the components is shown in Figure 4 and indicates that the adduct forms under these conditions. Because the resin is a solid below 60°C, it is necessary to blend in the curatives at an elevated temperature, typically 95°C, where the resin is liquified. At 95°C it is expected that the Diels-Alder adduct will open and

Furfuryl glycidyl ether



1,1'-(methylenedi-4,1-phenylene)-bismaleimide



Jeffamine[®] diamine curatives

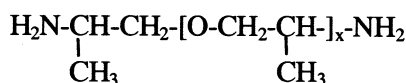


FIGURE 2 Ingredients of one thermally removable adhesive formulation, RA100.

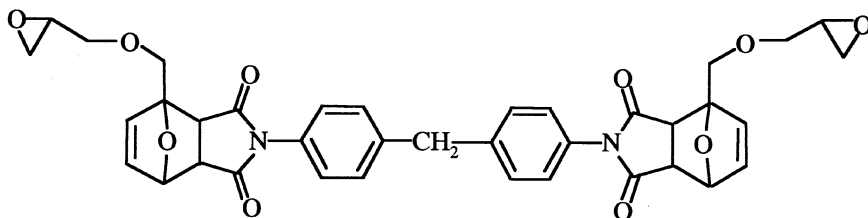


FIGURE 3 Epoxy resin, RR1, adduct of furfuryl glycidyl ether and 1,1'-(methylenedi-4,1-phenylene)-bismaleimide.

expose the maleimides to reaction with the amines (Michael addition [6]). In an attempt to substantially avoid this unwanted reaction, we minimize the time of exposure to only 15 min. This time is sufficient to melt the resin and to dissolve the curatives. The time appears to be short enough to avoid the Michael addition based upon the reversible nature of the resulting adhesive. If this dissolution time is much longer, then the resulting cured elastomer is not reversible. The clear uniform solution is then cooled to 60°C and cured for 72 h. The formulation of this adhesive is listed in Table I.

Dynamic mechanical analysis (DMA) data are collected using a Rheometrics ARES Dynamic Spectrometer (Rheometrics Corp., Piscataway, New Jersey, USA). The dynamic testing is performed on a disk of 25 mm diameter and 2 mm thickness, at a frequency of 1 Hz and with the temperature ramped at a rate of 3°C/min. Prior to the test, the sample is heated to softening and the normal force adjusted until full contact between the sample and plates is obtained. Thermal mechanical analysis (TMA) using a PerkinElmer DMA 7E (PerkinElmer Analytical Instruments, Shelton, Connecticut, USA) is used to determine the glass transition temperature at a temperature ramp rate of 3°C/min.

Lap-shear samples are prepared using 1100 aluminum and 304 stainless steel coupons (Metal Samples, Co., Munford, AL, USA). The adhesive bond thickness is 0.127 mm (0.005 inches) and the area of adhesion is 6.45 cm². Pull tests are performed using the 4505 instron load frame with the 10 kip load cell (Instron Corp., Canton, Massachusetts, USA). The grip-to-grip distance is 8.89 cm and the crosshead speed is 0.127 cm/min. Lap-shear samples are prepared after a standard surface preparation consisting of grit blasting with 50 μm aluminum oxide powder (S.S. White Technologies, Piscataway, New Jersey, USA), followed by cleaning with Brulin[®] cleaner (The Brulin Corporation, Indianapolis, Indiana, USA). No coupling agent is used.

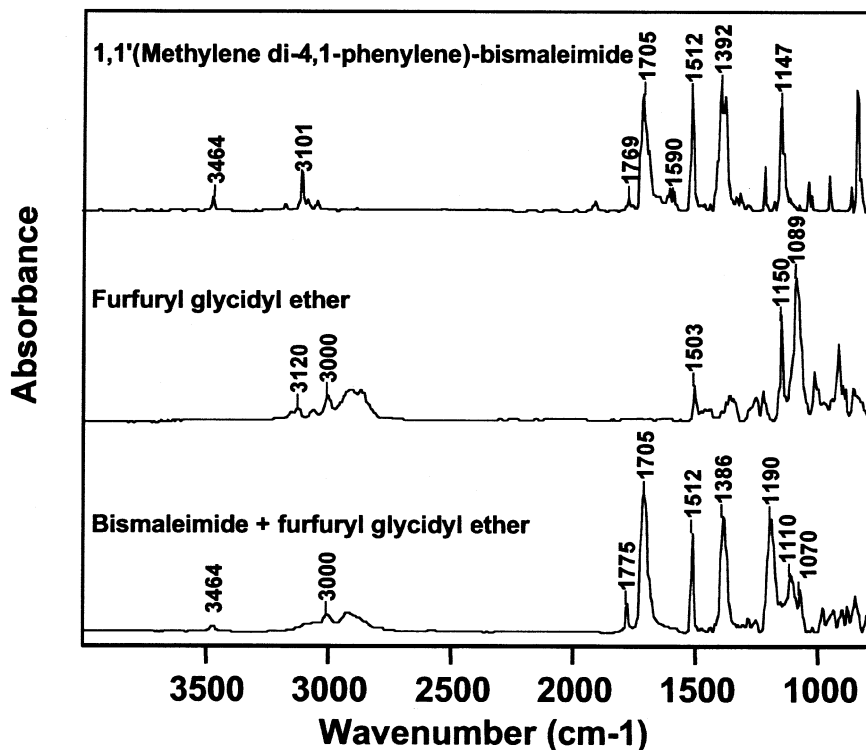


FIGURE 4 FTIR absorption spectra of furfuryl glycidyl ether (FGE), 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (MDPBM), and their Diels-Alder adduct, RR1. IR bands (3101 , 3120 , 1590 , 1392 , and 1386 cm^{-1}) related to nonaromatic alkene groups in the reactants (imide ring in MDPBM and the furfuryl group in FGE) disappear or are significantly modified in the IR spectrum of the adduct. The IR band due to the furfuryl ring (1503 cm^{-1}) of FGE is not present in the adduct. Imide carbonyl (≈ 1770 and 1705 cm^{-1}) bands of MDPBM are largely unchanged in the adduct. The C-N stretch mode increases in frequency from 1147 cm^{-1} (spectrum of MDPBM) to 1190 cm^{-1} (spectrum of adduct), indicating that the bonding of the imide ring has changed. Finally, changes in the frequencies of the ether modes (1150 and 1189 cm^{-1} in FGE; 1110 and 1070 cm^{-1} in the adduct) suggest that the environment around the C-O-C bond changes as a result of adduct formation.

RESULTS AND DISCUSSION

Our goal is to develop an elastomeric adhesive in order to bond two metals that have different coefficients of thermal expansion. The adhesive must also allow for the thermal removal of the adhesive bond

TABLE 1 RA100 Thermally Removable Epoxy Adhesive Formulation Including an Epoxy Resin, RR1, that Contains Two Diels-Alder Adducts, and Commercial Curatives

Resin	RR1	
Curing agent #1	Jeffamine [®] 230 (Huntsman)	10.8 phr*
Curing agent #2	Jeffamine [®] 2000 (Huntsman)	61.7 phr
Curing agent #3	Nonylphenol	13.4 phr

*Parts per hundred resin.

without damage to the metal pieces or other components of the assembly. The low modulus of the RA100 adhesive may possibly accommodate the differential movement of the metals under thermal stress. The RA100 formulation results in an elastomeric adhesive with a broad glass transition temperature of approximately -40°C as determined by thermal mechanical analysis. This is due to the use of long chain diamine curatives, in particular the Jeffamine[®] 2000, and the plasticizing effect of the nonylphenol.

The average lap-shear strength (5 samples) of RA100 with 1100 aluminum coupons is 4.09 MPa (standard deviation (SD) 0.39 MPa) and with 304 stainless steel coupons is 4.56 MPa (SD 1.75 MPa). The failure mode is primarily cohesive with some adhesive failure. For comparison purposes, we prepared identical coupons with a commercial elastomeric adhesive, Sylgard[®] 184 (Dow Corning, Midland, Michigan, USA). The average lap-shear strength (6 samples) is 3.36 MPa (SD 0.78 MPa) with 1100 aluminum coupons and with 304 stainless steel coupons is 4.65 MPa (SD 0.98 MPa). The failure mode is primarily adhesive. The lap-shear strength of the thermally removable epoxy adhesive is, therefore, similar to this commercial elastomeric adhesive. The lap-shear strengths could obviously be increased with the use of primers, but for our application we do not need higher strength. Lap-shear strength at high temperature ($>90^{\circ}\text{C}$) are so low that they cannot be measured with this technique (*i.e.*, the coupons essentially fall apart) due the retro Diels-Alder reaction.

The thermal removal of the adhesive is further demonstrated by DMA data. Figure 5 shows the shear modulus as a function of temperature for one representative adhesive sample as described above. At about 90°C the modulus falls by more than 10^3 as some of the Diels-Alder adducts are expected to open, *i.e.*, the retro Diels-Alder reaction. If the adhesive is cooled, the modulus recovers as the Diels-Alder adducts are expected to reform. This process is reversible for numerous cycles. The modulus at temperatures below 60°C is typical for an

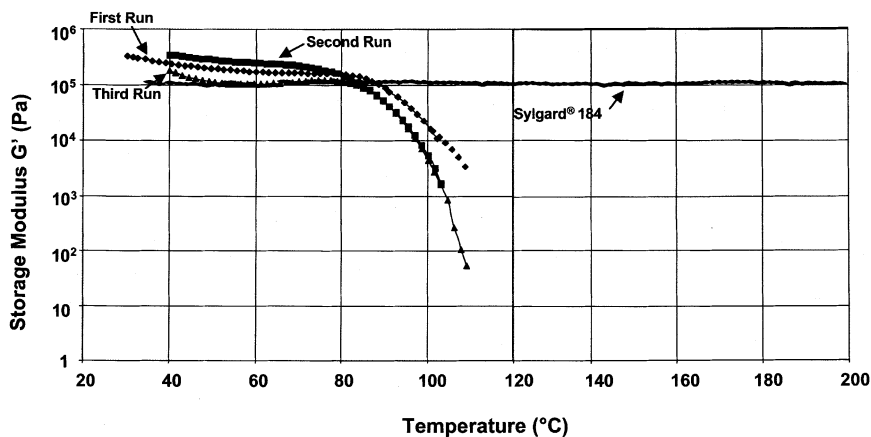


FIGURE 5 DMA of shear modulus as a function of temperature for the thermally removable epoxy adhesive heated and cooled sequentially for three temperature cycles and for a commercial elastomeric adhesive, Sylgard 184[®].

elastomeric adhesive, such as Sylgard[®] 184 (also shown in Figure 5). As expected for this cross-linked elastomer, the modulus does not vary significantly with temperature.

The reversible nature of the modulus loss, and presumably the thermally reversible chemistry, is limited by an uncharacterized side reaction that occurs when the adhesive is held above 90 $^{\circ}\text{C}$ for an extended period of time. The side reaction could involve exposed maleimides reacting with excess amine or exposed maleimides reacting together. If the adhesive is held at an elevated temperature for a long period of time (> approximately 1 h), then the modulus actually increases and the adhesive is no longer thermally reversible. The same phenomenon occurs with temperature cycling. If the cumulative time that the adhesive is at an elevated temperature (> 90 $^{\circ}\text{C}$) exceeds approximately 1 h, then the modulus increases and the adhesive is no longer thermally reversible. We hope to characterize the nature of this side reaction in our future work.

The thermally removable adhesive can be prepared as thin sheets that can later be applied as a hot melt. Films of adhesive (nominal thickness of 0.254 mm (0.010 inches)) were prepared using a Gardco[®] (Paul N. Gardner Company, Inc., Pompano Beach, Florida, USA) drawdown machine. Applying this as a hot melt requires an application temperature sufficient for the adhesive to flow and wet surfaces, approximately 110 $^{\circ}\text{C}$. For our application, we cut the adhesive sheet to the appropriate size and heated at least one of the metal surfaces to be

bonded to above 110°C. The hot surface is brought into contact with the adhesive, the adhesive softens and wets both metal surfaces, and is then cured at 60°C to form the bond.

CONCLUSION

We have prepared elastomeric epoxy adhesive with moduli and lap-shear strengths comparable with a commercial elastomeric adhesive, but which contain a high density of Diels-Alder adducts. Above approximately 90°C, the retro Diels-Alder reaction was expected to occur, which lowered the modulus of the adhesive by a factor of more than 10^3 . Lap-shear strength testing above 90°C was not possible because the modulus was so low that lap-shear samples fell apart. At sufficiently high temperatures (> approximately 110°C), the adhesive flowed, which allowed it to be applied as a hot melt.

We propose that the use of thermally reversible Diels-Alder adducts incorporated into our adhesive provides a mechanism for a thermally removable adhesive. At temperatures above approximately 90°C, adhesive bonds could be easily taken apart. The adhesive bond can be formed and liquified repeatedly for at least three cycles. Extended dwell times at elevated temperatures (> 90°C) resulted in uncharacterized side reactions that limited the reversibility.

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