

Thermal Properties of an Epoxide Resin Cured with Bicyclo Diels-Alder Anhydride Adducts

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Synopsis

The thermal properties of polymers derived from resorcinol diglycidyl ether cured with several bicyclo Diels-Alder anhydride adducts have been investigated. Increased char yields and decreased rates of weight loss were observed for these systems as compared to polymers cured by Diels-Alder adducts from acyclic dienes. This is explained on the basis of a reverse Diels-Alder reaction which these bicyclo adducts undergo at lower temperatures than do adducts from acyclic dienes.

Introduction

The Diels-Alder reaction has been successfully employed in a wide variety of organic syntheses since its inception and subsequent elucidation by O. Diels and K. Alder in 1928.¹ Recently, it has been profitably used to synthesize anhydride curing agents for epoxide resins such as methyl norbornene-2,3-dicarboxylic anhydride (NMA). Glass fiber-reinforced composites made with epoxide resins and cured with NMA exhibit excellent mechanical properties. In addition, NMA-cured epoxides have unusual thermal properties which have been noted and discussed previously.² An initial weight loss in the range of 200–300°C (as measured by thermogravimetry) was observed prior to main polymer degradation. This was attributed to a combination of two mechanisms: (1) a reverse Diels-Alder reaction, which liberates a diene, and (2) an internal ring closure mechanism which regenerates the initial anhydride from unreacted monoester-monoacid. This latter reaction was also observed by Sugita and Ito for monoanhydride-cured epoxide resins.³

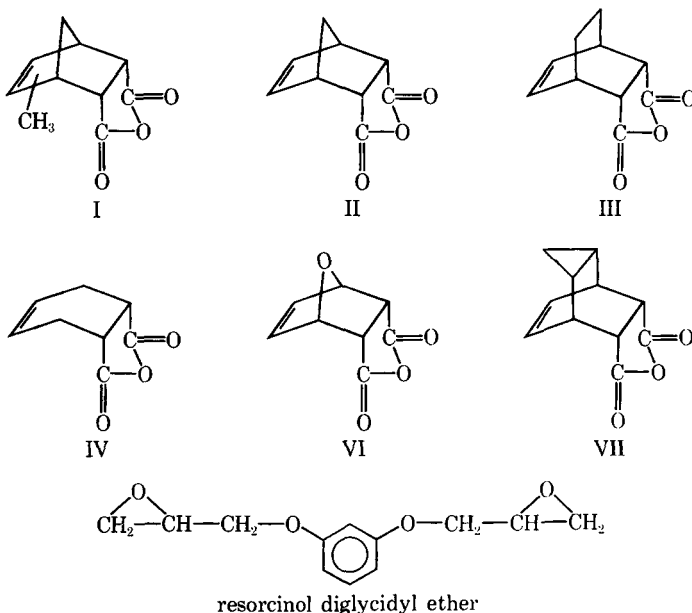
Under very high temperatures quantitative enhancement of char residues was observed for NMA-cured systems compared to nonbridged Diels-Alder anhydride adducts such as tetrahydrophthalic anhydride.⁴ This is attributed to the reverse Diels-Alder reaction of the bridged adduct which generates an activated olefinic linkage at every NMA site while leaving the polymer backbone intact. The olefinic bond is a crosslinking site (via free radicals formed during initial stages of resin degradation) which leads to increased crosslink density, and this in turn favors higher char yields.

Also, it is possible for the diene liberated in the reverse Diels-Alder reaction to undergo polymerization itself, resulting in further crosslinking and higher char yields. To investigate further the thermal properties afforded to polymer systems by these reactions, a series of bicyclo Diels-Alder anhydride curing agents were obtained or synthesized, and used to cure an epoxide resin. The thermal analysis of these materials is the subject of this report.

EXPERIMENTAL

Materials

Several Diels-Alder anhydride adducts (I-VII) were synthesized or obtained commercially for this study. The synthesis, properties, and suppliers of these adducts are given below.



Methyl-5-norbornene-2,3-dicarboxylic Anhydride (I). This Diels-Alder adduct is synthesized from methylenecyclopentadiene and maleic anhydride. It was obtained from the National Aniline Division of Allied Chemical Corporation. As received and used, it is a straw-colored, semi-viscous liquid. It is a mixture of structural and stereo isomers, the main structural isomer being the adduct from 2-methylenecyclopentadiene and maleic anhydride.⁵

5-Norbornene-2,3-dicarboxylic Anhydride (II). This adduct is synthesized from cyclopentadiene and maleic anhydride. It was obtained from the Monomer-Polymer Laboratories of the Borden Chemical Company.

It was recrystallized from benzene to give white crystals with a melting point of 163°C.

Bicyclo(2.2.2)-5-octene-2,3-dicarboxylic Anhydride (III). This adduct is synthesized from 1,3-cyclohexadiene and maleic anhydride. It was obtained from the Aldrich Chemical Company as a white, crystalline solid with a melting point of 141–142°C, and was used without further purification.

Endo-cis-1,2,5,6-Tetrahydrophthalic Anhydride (IV). This adduct is synthesized from 1,3-butadiene and maleic anhydride. It was obtained from J. T. Baker Chemical Company as a white solid with a melting point of 101–103°C. It was used without further purification.

Maleic Anhydride (V). This anhydride was obtained from the J. T. Baker Chemical Company, and was recrystallized to give white crystals with a melting point of 54°C.

Resorcinol Diglycidyl Ether. The epoxide resin used in this study, resorcinol diglycidyl ether, was obtained from CIBA, designated as ERE-1359. The as-received resin was then vacuum-distilled at 155°C at a pressure of 0.3 mm Hg. The resulting clear, colorless resin crystallizes at room temperature and has an epoxide equivalent weight of 113 (theory 111.1) and a chlorine content of <0.1%.

Diels-Alder Adducts Synthesized

7-Oxo-bicyclo(2.2.1)-5-heptene-2,3-dicarboxylic Anhydride (VI). This adduct was reported by Diels et al. previously,⁶ and was synthesized for this study as follows. To 476.6 g (7.0 mole) of furan in a round-bottomed flask, fitted with stirrer, was added 98.1 g (1.0 mole) of maleic anhydride at room temperature. Over a period of 1 hr the maleic anhydride dissolves, the flask becomes warm, and the product crystals fill the flask. The solid product is then suction-filtered to give a quantitative yield of the adduct (166.0 g) which melts with decomposition (reverse Diels-Alder) at 125°C. The infrared spectrum of the product is in agreement with the adduct structure.

3,6-Cyclopropylene- Δ 4-tetrahydrophthalic Anhydride (VII). This adduct was synthesized according to the procedure of Kohler et al.⁷ from 1,3,5-cycloheptatriene and maleic anhydride. This unusual reaction involves the conversion of 1,3,5-cycloheptatriene into its valency tautomer norcaradiene due to thermal activation or as an integral part of the Diels-Alder addition, as noted by Alder and Jacobs.⁸ Dreyden and Burgert also discussed the reaction and structure of the triene.⁹ Thus, to a three-necked flask fitted with stirrer and reflux condenser was added 19.6 g (0.2 mole) of maleic anhydride, 18.4 g (0.2 mole) of 1,3,5-cycloheptatriene, and 200 g of xylene solvent. The contents of the flask were then refluxed for 5 hr and allowed to stand overnight at room temperature; 80 ml of cyclohexane was added to the cool mixture. Suction filtration of the product gave a near-quantitative yield of product (33.1 g), which was recrystallized from isopropanol to give colorless needles with a melting point of

102.5°C. The infrared spectrum of the product is in agreement with the adduct structure.

Polymerization

Eighty-five per cent of the stoichiometric amount of the anhydride adducts was used with 0.5% *N,N*-benzylidimethylamine catalyst to cure the resorcinol diglycidyl ether. Except for the furan-maleic anhydride adduct, VI, gelation was effected at 100°C for several hours followed by a stepwise cure to 170°C over a period of 24 hr. This was followed by a 2-hr post cure at 200°C.

The system cured with VI was gelled at 80°C and then cured at 90–95°C for 24 hr. The low temperature of decomposition (125°C) for this anhydride necessitated this cure. Mixed curing agents such as the I + VI system were used in equimolar amounts of each constituent with the total quantity of the mixture yielding 85% of the stoichiometric amount required for curing the resin.

Thermogravimetry

The cured polymer samples were ground to a fine powder (+60–80 mesh) and checked for completeness of cure by infrared spectroscopy. They were then heated in *vacuo* (0.05 mm Hg) at a programmed rate of 5°C/min in a thermobalance described previously.¹⁰ Three variables—time, temperature of sample, and weight loss—were automatically recorded. The temperature and weight loss readings were then put on an *X-Y* plot along with the derivative (dC/dT) to give the rates of weight loss.

RESULTS AND DISCUSSION

It should be remembered in the ensuing discussion that the thermal properties of interest in this work were the char yield on degradation, the rates of weight loss, and explanation of these in relation to the structure of the Diels-Alder adduct. In general, it was found that bicyclo Diels-Alder adducts undergo a reverse reaction liberating the diene prior to main resin degradation. This reaction does not rupture the main backbone of the resin system. It does leave an activated olefinic bond which is capable of undergoing crosslinking reactions during degradation via free radicals produced therein. This increased crosslinking results in lower rates of weight loss and higher char yields than in systems where reverse Diels-Alder reactions do not occur before main resin degradation. The maximum rates of weight loss for the bridged Diels-Alder adducts (Fig. 1), which undergo the reverse before the main resin degradation, are identical to that for the maleic anhydride-cured system (4%/min). This is reasonable and to be expected, because after the reverse reaction, the same polymer system should be present (B), as shown in eqs. (1)–(5).

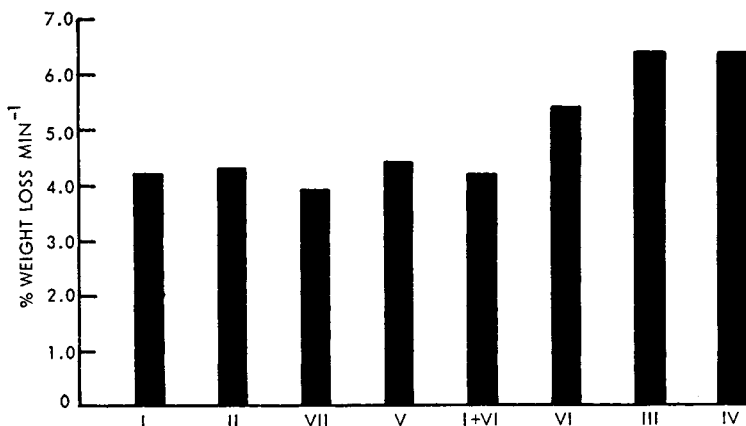
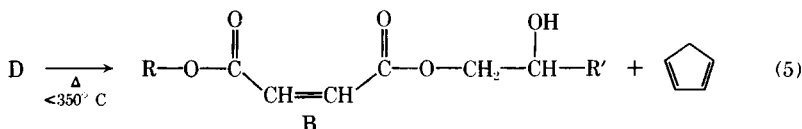
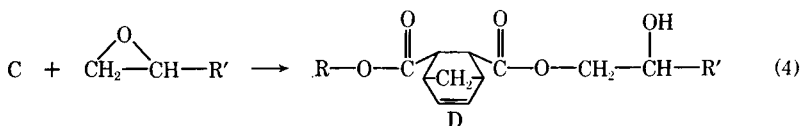
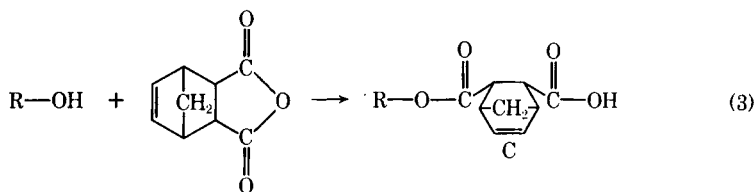
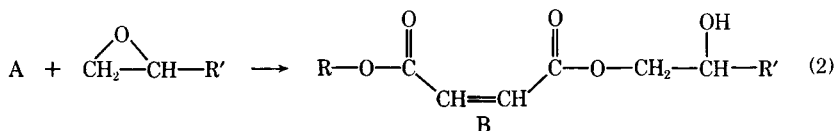
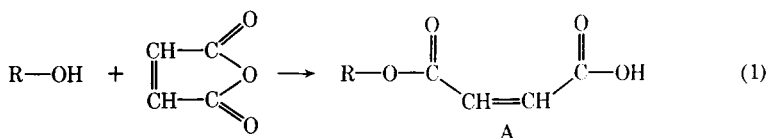


Fig. 1. Maximum rates of weight loss for resorcinol diglycidyl ether cured with Diels-Alder anhydride adducts. $dT/dt = 5^\circ\text{C}/\text{min}$ *in vacuo*.



The cure mechanism of epoxide resins by the bicyclo Diels-Alder adducts is identical to that for other anhydrides. The initial step involves the opening of the anhydride ring to give monoester-monoacid with subsequent reaction of this moiety with an epoxide group to give the diester. Also, a

third and competing reaction at elevated temperatures is that between epoxide and hydroxyl resulting in etherification.

Under vacuum, the diene liberated in the reverse Diels-Alder reaction is usually removed before it can react in any manner. Under atmospheric or positive pressure inert environments it may, depending on the diene, polymerize, add to the reactive olefin bond in the polymer backbone, and further increase crosslink density prior to main resin degradation.

The difference in thermal properties between epoxide resins cured with Diels-Alder adducts from cyclic and acyclic dienes is shown in Figure 2. The polymer system cured with II exhibits the usual performance of bicyclo Diels-Alder adducts with a reverse Diels-Alder reaction occurring first with a loss of the diene and followed by a plateau in thermal stability prior to the initiation of main resin degradation at 325–350°C. The initial weight loss to 350°C for the systems cured with IV and V is accounted for by the regeneration and subsequent loss of original anhydride from incompletely cured monoester-monoacid.² Undoubtedly, this occurs in the case of II, as in all monoanhydride-cured systems, but is masked by the reverse Diels-Alder reaction. The system cured with IV (an adduct from an acyclic

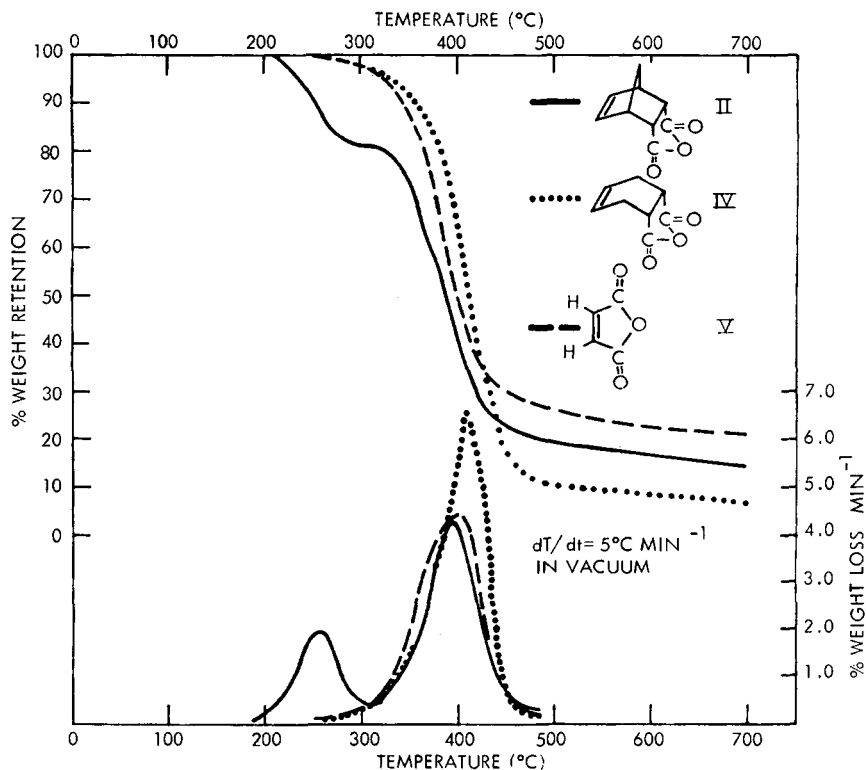


Fig. 2. Thermograms and rate-of-weight loss plots for resorcinol diglycidyl ether cured with several anhydrides.

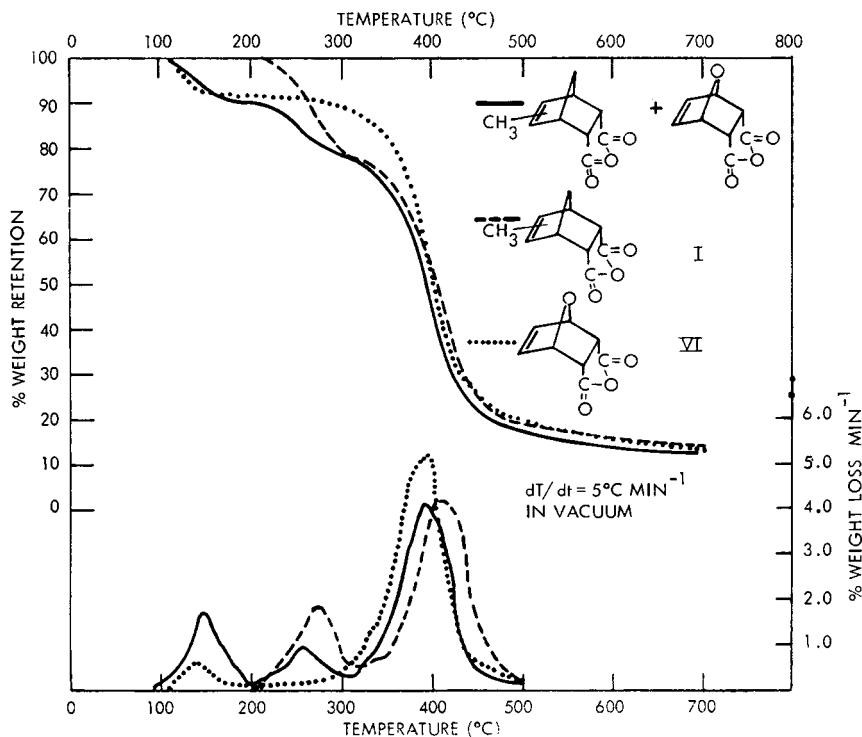


Fig. 3. Thermograms and rate-of-weight loss plots for resorcinol diglycidyl ether cured with several anhydrides.

diene) exhibits no reverse Diels-Alder reaction prior to main resin degradation, and thus its thermal performance is characterized by a higher rate of weight loss and a lower char yield. The system cured with maleic anhydride (V) gives the same maximum rate of weight loss as II (as it should according to previous discussion), but it has a higher char yield since it is not an adduct and therefore does not lose the weight of diene that II does.

The thermograms and rate plots for two more adducts (I and VI) are shown in Figure 3. The furan-maleic adduct (VI) undergoes the reverse at 125°C. Thermal stability is then retained until main resin decomposition. The yield of furan at 110–150°C. is not quantitative. This is believed to be due to some dissociation of the adduct during cure. The thermogram of the resin cured with I exhibits the reverse prior to 300°C, with subsequent stabilization and then main resin degradation. The system cured with a 50–50 mixture of I and VI exhibits the expected composite thermogram with breaks in the curve occurring in the regions of the respective reverse Diels-Alder reactions.

In Figure 4, the thermogram of the Diels-Alder adduct of cycloheptatriene and maleic anhydride (VII) is in agreement with our discussion above, and the reported temperature of the reverse Diels-Alder adduct of 250–

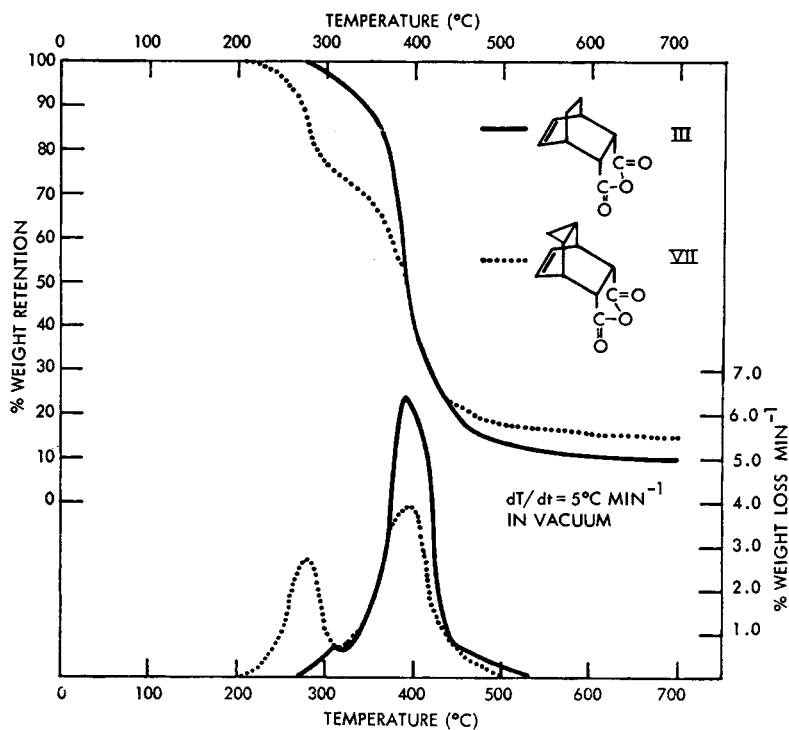


Fig. 4. Thermograms and rate-of-weight loss plots for resorcinol diglycidyl ether cured with several anhydrides.

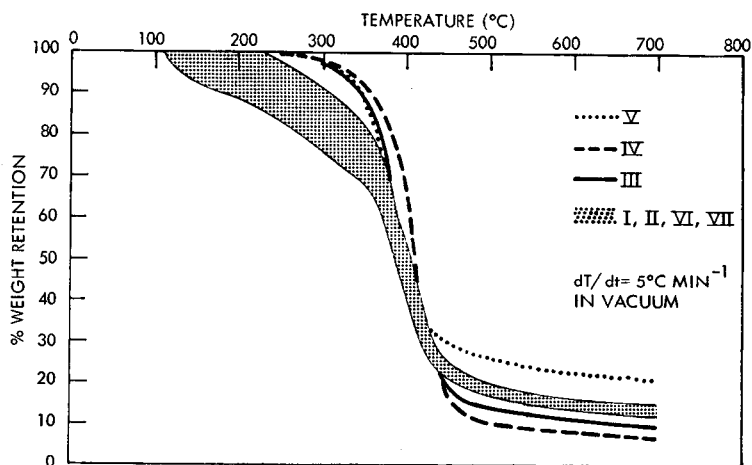


Fig. 5. Summary of thermograms of resorcinol diglycidyl ether cured with several anhydrides.

260°C.⁹ The adduct from 1,3-cyclohexadiene and maleic anhydride (III) is reported to undergo a reverse at 310–325°C.¹¹ This is evidently too high a temperature and too close to the temperature of main resin degradation for enhanced crosslinking to occur; thus, performance of this system is similar to that of IV with a higher rate of weight loss and a lower char yield.

A summary of the thermograms of the above systems is shown in Figure 5. Noteworthy are the differences in char yield of the Diels-Alder adduct from the acyclic diene, IV, and the grouping of higher char yields of those systems from cyclic dienes that undergo a reverse Diels-Alder reaction prior to main resin degradation.

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