Mechanisms for Initiating Thermal Degradation of Certain Anhydride-Cured Epoxides

GERALD J. FLEMING, *U.S. Naval Ordnance Laboratory,*
*Silver Spring, Maryland 20910*

Synopsis

The mechanisms initiating the unusual thermal degradation of epoxy resins cured with methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride were investigated.   Two mechanisms were elucidated, each assuming greater importance than the other depending upon the severity of the thermal environment.   One is an internal acid-initiated mechanism operating from 240 to 350°C. under slow heating rates.   The other is a reverse Diels-Alder reaction which operates above 350°C., usually under instantaneous pyrolysis conditions such as encountered in ablation.   These two mechanisms, working simultaneously, promote further crosslinking of the resin system giving rise to a greater amount of carbonaceous residue than would otherwise be expected.

INTRODUCTION

The study reported here was initiated as a result of the unusual thermograms and excellent ablative performance in hyperthermal environments of epoxy resins cured with methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (NMA).   The relatively great amount of carbonaceous char remaining after controlled pyrolysis (TGA) to 550°C. and after instantaneous pyrolysis under hyperthermal conditions was not consistent with the overall structure of an NMA-cured epoxy.   Generally, the amount of char produced in TGA and in some hyperthermal environments, is proportional to the crosslink density and the amount of aromaticity in the original structure.   However, NMA lends no aromaticity to the polymer system and seems to give a low crosslink density (Table I).   Therefore, it seems apparent that a constructive degradation mechanism is operative.   It is the purpose of this paper to put forth and substantiate the mechanism for the initiation of this degradation.

EXPERIMENTAL

An epoxy novolac, DEN 438, was the basic resin used in this study, although similar corollary work with NMA was done with a number of other epoxy resins including Epon 1031.[1,2]   The curing agents employed were designed to elucidate the mechanism of degradation.   The resins and curing agents are given in Figure 1.   In this work the structure of NMA
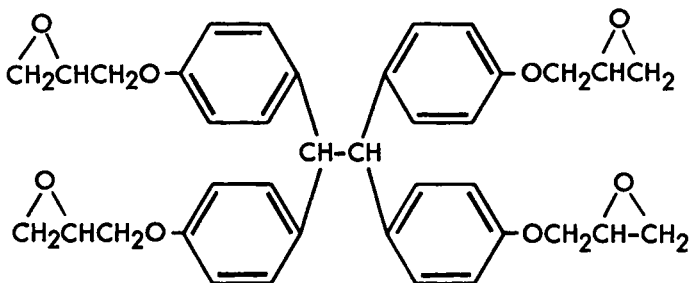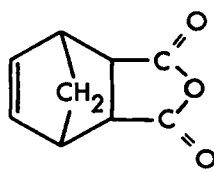
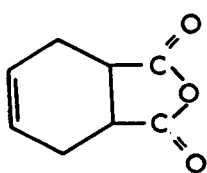Tetraglycidyl ether of tetraphenylene ethane (Epon 1031)
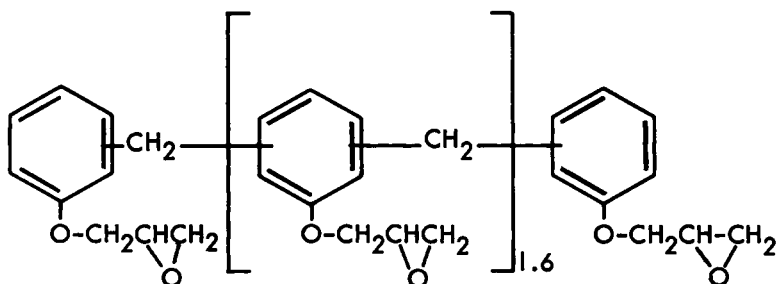
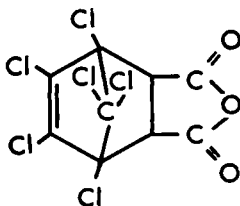Polyglycidyl ether of phenol–formaldehyde novolac (DEN 438)
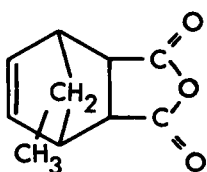
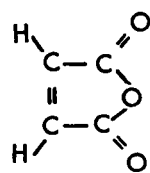Methylbicyclo[2.2.1]hept-5-ene-2,3-
dicarboxylic anhydride (NMA)

Bicyclo[2.2.1]hept-5-ene-
2,3-dicarboxylic anhydride (NA

Tetrahydrophthalic
anhydride (THPA)

1,4,5,6,7,7-Hexachloro-
bicyclo[2.2.1]hept-5-ene-
2,3-dicarboxylic anhydrine
(chlorendic anhydride)

Maleic anhydride

Fig. 1.   Epoxy resins and curing agents used in NMA mechanistic study

TABLE I
Crosslink Density and Char Formation Data

Resin system	S.A., %	Crosslink density	Highest crosslink density for resin[a]	Char at 550°C., %
DEN 438 + NMA	85	38.9	17.8	25.2
DEN 438 + NA	85	38.7	17.8	25.5
DEN 438 + THPA	85	30.9	17.8	14.5
DEN 438 + NMA	95	62.0	17.8	22.0
DEN 438 + NMA	90	38.5	17.8	22.0
DEN 438 + NMA	75	40.4	17.8	22.0
DEN 438 + NMA	65	43.0	17.8	22.0
DEN 438 + NMA	55	47.0	17.8	22.0
DEN 438 + chlorendic anhydride	85	39.5	17.8	21.5
DEN 438 + maleic anhydride	85	29.8	17.8	30.0
Epon 1031 + NMA	85	46.4	32.0[b]	22.0

[a] Obtained with $BF_3NH_2C_2H_5$.

[b] Obtained with 4,4'-diaminodiphenylsulfone.

was varied by deleting the methyl group as in nadic anhydride (NA), and then by deleting the methylene bridge and the methyl group as in tetrahydrophthalic anhydride (THPA), to determine the effect each of these has on the thermal degradation of epoxy resin systems.

Resins and Chemicals

The resins and chemicals employed in this work together with their purity and origin are given in Table II. The resin systems were cured with 85% of the stoichiometric amount of the anhydride (S.A.). Catalytic amounts (0.5% or less) of N,N-benzyldimethylamine were used when the reactivity of the resin and curing agent made it necessary to expedite the cure. Cure schedules for the systems varied somewhat depending on the system's reactivity, but in all cases, a 2-hr. postcure at 200°C. was given. After the postcure, the resins were ground into a fine powder (+60–80 mesh) for the subsequent studies.

Thermogravimetric Analysis

Thermogravimetric analysis was performed on an apparatus constructed around an Ainsworth Model RV-AU-2 semimicro vacuum recording balance and a West Model JSBG-2 temperature programmer.[3] In general, a 20-mg. sample (+60–80 mesh) was used for thermal analysis. The sample and balance were evacuated to 0.05 mm. Hg and a heating rate of 5°C./min. was used. Three variables were recorded during the analysis: time, temperature of sample, and weight loss. The last two of these are plotted as thermograms with the x and y axis for temperature and weight loss, respectively.

TABLE II

Resins and Curing Agents Used in NMA Study

Resin or chemical	Type	Purity	Manufacturer
DEN 438	Epoxy novolac	Unspecified	Dow Chemical
Epon 1031	High functionality aromatic epoxy resin	Unspecified	Shell Chemical Co.
Kopoxite 159	Resorcinol diglycidyl ether	Unspecified	Koppers Company, Inc.
Nadic methyl anhydride (NMA)	Acid anhydride	Unspecified	Miller-Stephenson Chemical Co.
Nadic anhydride (NA)	Acid anhydride	Recrystallized	Synthesized by author
Tetrahydrophthalic anhydride (THPA)	Acid anhydride	Baker Grade	J. T. Baker Chemical Co.
Maleic anhydride (MA)	Acid anhydride	Baker Grade	J. T. Baker Chemical Co.
N,N-Benzyldimethylamine	Tertiary amine	Practical	Eastman Organic Chemicals

Vapor-Phase Chromatography and Micro Pyrolysis

An F and M Scientific Corporation Model 80 pyrolysis unit was connected directly to an F and M Model 720 dual-column gas chromatograph. The sample (approximately 1.0 mg.) was placed between two platinum–rhodium foils and inserted into the injection port of the chromatograph. The sample was then pyrolyzed for 10 sec. at 1000°C. The ensuing degradation products were swept directly to the columns via the carrier gas. The columns used in this work were 6-ft. stainless steel ($1/4$ in.) with a 10% silicone gum rubber (SE-52) liquid phase on 60 to 80 mesh Diatoport W solid support. Helium carrier gas was used with a pressure of 20 psig and a flow rate of 60 ml./min. Normal injection port, detector, starting, and finishing column temperatures were 210, 350, 75, 325°C., respectively. The chromatograph was programmed at 15°C./min. temperature rise.

Semimicro Pyrolysis

A semimicro pyrolysis unit was constructed which is capable of using samples up to 300 mg. This apparatus is operated under vacuum (0.05 mm. Hg) and heat is supplied via a Marshall Furnace controlled and programmed at 5°C./min. by a West Model JSBG-2 temperature programmer. Condensable pyrolysis products are trapped in tubes cooled by Dry Ice. These trapped degradation products were then subjected to gas chromatographic and infrared spectroscopic analysis.

Crosslink Density

A relative value for the crosslink density of every system in this study was obtained by the method of Dannenberg and Harp.[4] In this method, a powdered sample of the resin system is placed in a desiccator containing solvent vapor (1,2-dichloroethane) and then evacuated and allowed to equilibrate for 24 hr. The sample is then removed from the desiccator and weighed. The greater the increase in weight, the lower is the crosslink density.

Infrared Spectroscopy

Infrared spectra of the resin systems were taken on a Perkin-Elmer 337 grating infrared spectrophotometer. These were usually taken from Nujol mulls between sodium chloride windows. Spectra of liquid compounds were taken as capillary films between salt windows.

DISCUSSION AND RESULTS

Structure and Synthesis of NMA

Methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (NMA, III) is synthesized commercially from methylcyclopentadiene and maleic anhydride via a Diels-Alder reaction as shown in eq. (1).

$$\text{I} \quad + \quad \text{II} \quad \rightleftharpoons \quad \text{III} \tag{1}$$
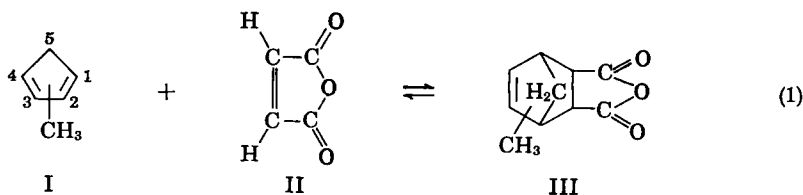
The methylcyclopentadiene which is generally used in this synthesis is a mixture of the three possible monomer and six possible dimer isomers as is shown in a chromatogram of methylcyclopentadiene (Table III). According to Csicsery,[5] on the basis of NMR studies on methylcyclopentadiene, the chief isomer is the 2-methyl (1.9-min. retention), with considerably lesser amounts of the 1- and 5-methyl in that order. Therefore, it is reasonable that the 2-methylcyclopentadiene adduct (IV) with maleic anhydride will be obtained in the greatest amount.
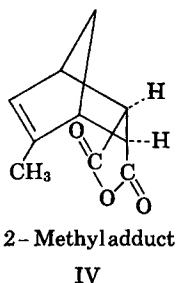
2 – Methyl adduct

IV

TABLE III

Gas Chromatographic Retention Times for Major Components of Pyrolysis

|		Retention time, min.			
Nadic methyl anhydride	Methyl-cyclopentadiene	DEN + 438 + NMA (1000°C.)	Epon 1031 + NMA (1000°C.)	DEN 438 + MA (1000°C.)	Epon 1031 + NMA (350°C.)
2.5	1.2	0.5a	0.6a	0.5a	0.6
5.7	1.9a	0.8	1.1	0.8	2.8
11.0	2.3	1.2	1.3	1.2	3.1
11.8a	7.7	1.4	1.4	4.3	5.1
12.6a	8.0	1.6	2.1a	4.8a	6.0
	8.5	2.3a	2.5	5.6a	7.4
	8.8a	2.7	7.3	7.1a	11.8
	9.2a	4.2	8.3	8.1	12.6a
	9.5a	5.6	8.6	8.3	
		7.3	11.8		
		8.2	12.6		
		11.8			
		12.6			

a Denotes major constituents.

Diels-Alder adducts have traditionally been reported to be endo adducts and indeed the reaction of a cyclic diene (cyclopentadiene), with maleic anhydride was reported by Alder to be strictly endo.[6] However, he did mention that under favorable driving conditions, the endo product would be converted to the more thermodynamically stable exo form.[7] Also, it has recently been recognized by many that there is an equilibrium of exo and endo products, albeit initially the endo product may be formed. NA has been shown to exist in this equilibrium mixture, although there is some disagreement as to how this equilibrium is established.[8,9] Also, it has been pointed out that the Diels-Alder adduct of furan and maleic anhydride goes completely exo in an ethereal solution.[10] All of this suggests that NMA may be an equilibrium mixture of the endo and exo forms which will be of some importance in discussing the degradation mechanisms.
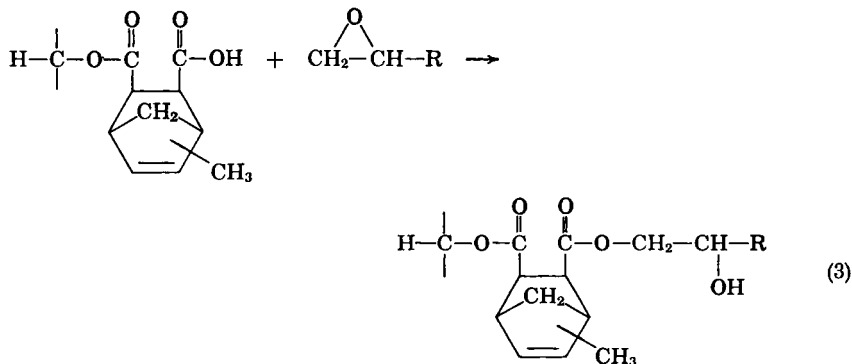

endo   exo
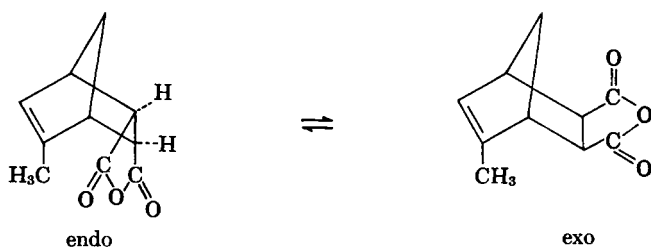
Cure Mechanism of Epoxy Resins with NMA

The cure mechanism of epoxy resins with NMA is fairly straightforward and conventional and is given in eqs. (2)–(4).
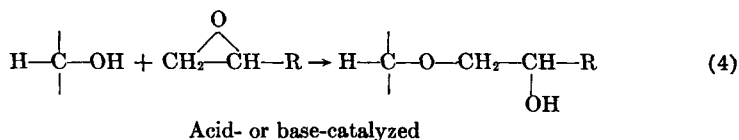
Formation of monoester:

(2)
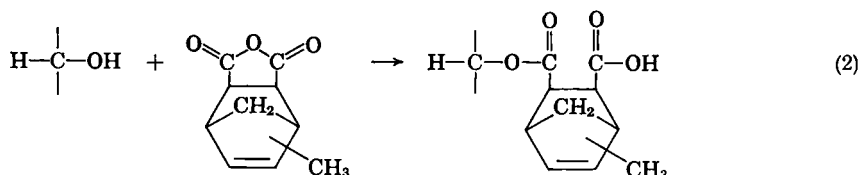
Formation of diester:

(3)

Etherification reaction:

$$H-\overset{|}{\underset{|}{C}}-OH + CH_2-\overset{O}{\overset{\triangle}{CH}}-R \rightarrow H-\overset{|}{\underset{|}{C}}-O-CH_2-\underset{\underset{OH}{|}}{CH}-R \qquad (4)$$

Acid- or base-catalyzed

In the first step, eq. (2), the anhydride reacts with an hydroxyl group of the resin, thus opening the anhydride ring to give a monoester-monoacid. The hydroxyl group on the resin is present due to: (a) a residual amount of unreacted hydroxyl after the epoxidation of the monomeric phenolic compound or (b) base-catalyzed polymerization of the epoxy resin during expoxidation. Reaction of a tertiary amine catalyst with the anhydride which in turn can react with an epoxide group will also give the monoester-monoacid specie. The mechanism for this catalyst initiation is well covered in the literature.[11-14]

In the second step, eq. (3) the monoester-monoacid reacts with an epoxide group to give the diester and another hydroxyl which can react as in eq. (2). A third reaction which is possible is the reaction of an epoxy with an hydroxyl group under acid or base catalysis to given an ether. Initially, as noted by Dearborn and Fuoss,[15] the kinetics favor the monoester and diester formation. However as the polymerization proceeds, reaction (4)
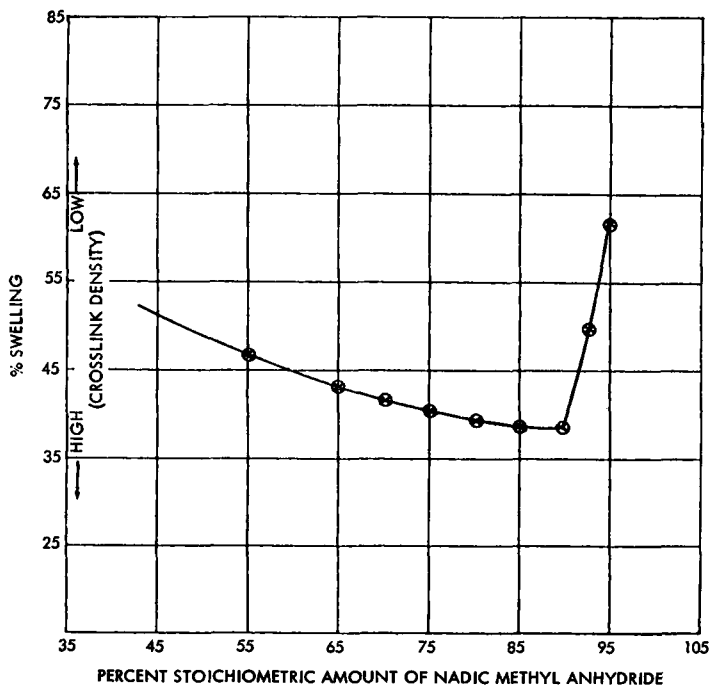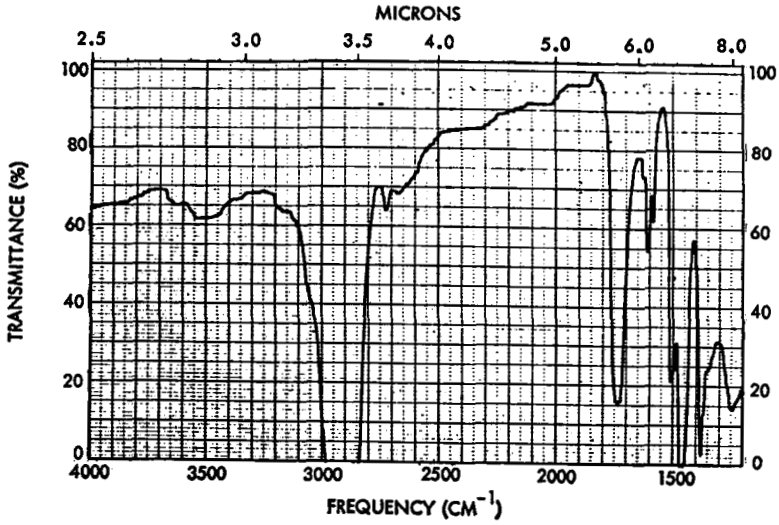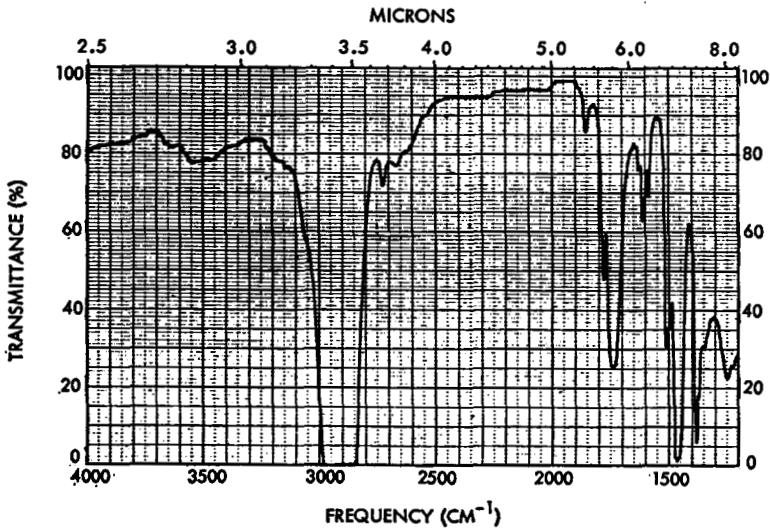

Fig. 2.   Crosslink density vs. per cent stoichiometric amount of NMA for the Resin System DEN 438 + NMA.

MICRONS

(a)

MICRONS

(b)

Fig. 3. Infrared spectra of DEN 438 + NMA: (a) 85% S.A.; (b) 95% S.A.

assumes importance and competes with reactions (2) and (3). Also, depending on the final properties desired, the polyester–polyether ratio in the polymerized resin can be altered by varying the stoichiometric amount (S.A.) of anhydride. This is shown for one property, crosslink density, which is plotted against the per cent stoichiometric amount of NMA (Fig. 2). Usually 85% S.A. is employed for maximum consumption of anhydride, allowing for 15% etherification. A portion of the infrared

spectrum for DEN 438 cured with 85% and with 95% S.A. of NMA is given in Figure 3. Note in the spectrum of the 85% S.A. of NMA (Fig. 3a) that there is no absorption at 1775 and 1850 cm.$^{-1}$, which indicates the absence of anhydride carbonyl. However, at 1740 cm.$^{-1}$, there is a large absorption indicating ester carbonyl. In the case of the resin cured with 95% S.A. of NMA (Fig. 3b) all three carbonyl bands are present, indicating incomplete consumption of anhydride. Both systems were subjected to the same cure and catalyst conditions. Epoxide consumption was nearly complete in each system as was evidenced by the absence of the epoxide group absorption at 910 cm.$^{-1}$ (not shown).

Mechanisms for Initiating Degradation

Two mechanisms for initiating thermal degradation of NMA-cured epoxy resins are proposed. Both are simultaneously operative under certain temperature conditions, but one is usually quite dominant depending on the degree of thermal activation that the system experiences. They are as given in eqs. (5) and (6).

Acid-initiated mechanism:
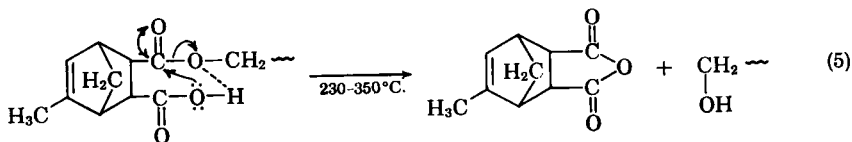
Reverse Diels-Alder mechanism:
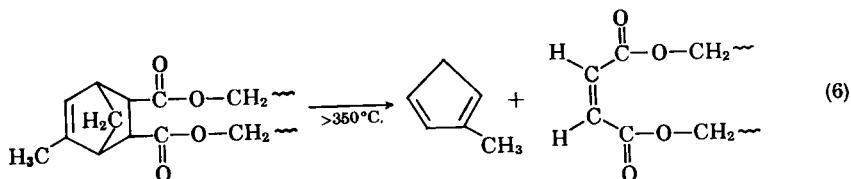
The first mechanism, the acid-initiated one, is operative in the temperature range of 230–350°C. It is postulated that there is an incomplete conversion of monoester-monoacid to diester in the epoxy system which would also explain the low crosslink density. This may be due to partial steric hindrance of the completion of the reaction by the methylene bridge so that a fairly large amount of the NMA molecules do not convert to the diester but stay in the monoester-monoacid form. Also, the stereochemical structure of NMA seems to be such that there is a good possibility of hydrogen bonding between the acid hydrogen and the ester oxygen, which would hinder the diesterification. However, when thermally activated, a nucleophilic attack on the ester carbonyl coupled with a proton transfer would give the initial anhydride and a hydroxyl (on the resin). The initial rupture of the anhydride ring to form monoester-monoacid is not greatly hindered, as is evidenced by the infrared spectra of epoxy resins cured

with 85% S.A. of NMA which show virtually no anhydride carbonyls.[2] However, gel times for NMA-cured systems compared to similar tetra-hydrophthalic anhydride-cured systems (similar except for the absence of the bridge methylene and pendant methyl group) are usually about three times longer and often require catalysts for reasonable cure times. This would seem to indicate steric inhibition since the electronic factors for the two systems do not differ greatly. Depending upon the stereochemical structure of NMA (i.e., endo, exo, or a mixture of both), the kinetics of the monoester and hence diester formation would be altered, and thus the final ratio of polyester to polyether mentioned before, could be substantially altered, and thereby affect the thermal properties. A typical weight loss in the region of 230–350°C. resulting from the acid-initiated degradation is shown (Fig. 4).

The second mechanism for initiating thermal degradation is a reverse Diels-Alder reaction. This mechanism functions mainly above 350°C., although not to the complete exclusion of the acid-initiated mechanism. It is usually operative under conditions of instantaneous pyrolysis such as often encountered in ablative environments. When this reaction occurs, the backbone of the polymer is left virtually intact with a double bond at every prior NMA site. Further crosslinking and possible ring formation could occur (constructive degradation) via free radicals formed in this pyrolysis through the olefinic linkages. This would explain why greater quantities of char are formed with NMA-cured systems than with similar systems such as tetrahydrophthalic anhydride-cured epoxides.

Thermogravimetric Results

The plateau effect (230–350°C.) exhibited in the thermograms (Figs. 4–7) is typical of all NMA- and NA-cured epoxides.[2] No exceptions have been found to this by the author.

The structure of NMA was varied to determine if the pendant methyl was affecting the behavior of NMA (this was done with NA) or if the methylene bridge was the dominating factor in its behavior (this was done with THPA which has no methylene bridge or pendant methyl group). The results of this part of the study with 85% S.A. of each curing agent are given in tabular and thermogravimetric form (Fig. 5 and Table I). The physical properties and thermal performance of DEN 438 cured with NMA and NA are almost identical for each system: the initiation of degradation (~250°C. for both), crosslink density (38.9 and 38.7, respectively), and the amount of char at 550°C. (25.2% and 25.5%, respectively). However, the properties of the DEN 438 sample cured with THPA are quite different with degradation initiating at a lower temperature, a different thermogravimetric curve, a higher crosslink density value (30.9), and only 14.5% char at 550°C. (approximately $^1/_2$ of that of the other systems). Therefore, it seems that the pendant methyl group has little effect, while the methylene bridge is all important in the cure and thermal properties of epoxy resins.
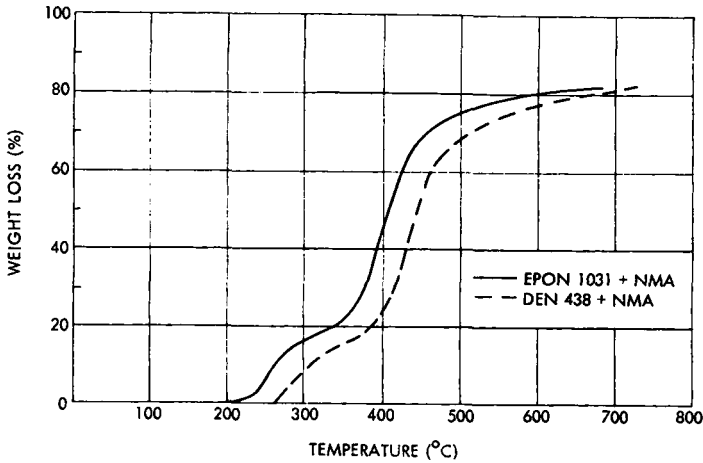
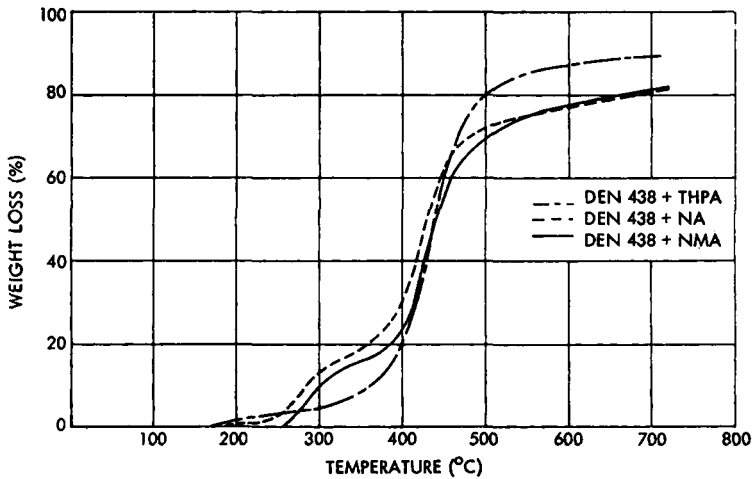Fig. 4. Thermograms of DEN 438 + NMA and Epon 1031 + NMA.

Fig. 5. Thermograms of DEN 438 + THPA, DEN 438 + NMA, DEN 438 + NA.

Based on the crosslink density measurements for these three systems, the hypothesis stated earlier in this paper that there is a considerable amount of monoester-monoacid in NMA cured epoxides seems to be substantiated, since THPA has a similar structure in bulk and character yet gives almost a 25% increase in crosslink density. Therefore we can conclude that NMA-cured epoxides have considerable monoester-monoacid formation which apparently is sterically hindered from completion to diester by the methylene bridge and by possible hydrogen bonding.

Chlorendic anhydride was also used to cure DEN 438 to determine if the electron-withdrawing and bulky chlorine groups would affect the cure and thermal properties of the system. Again we can see from the thermo-
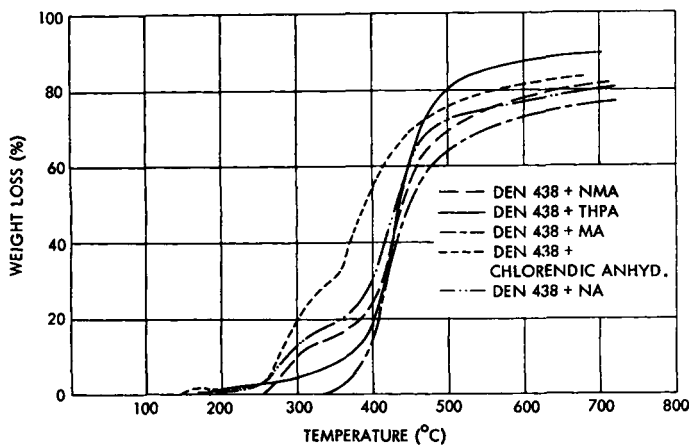
Fig. 6. Thermograms of DEN 438 and various anhydride curing agents of the Diels-Alder type.
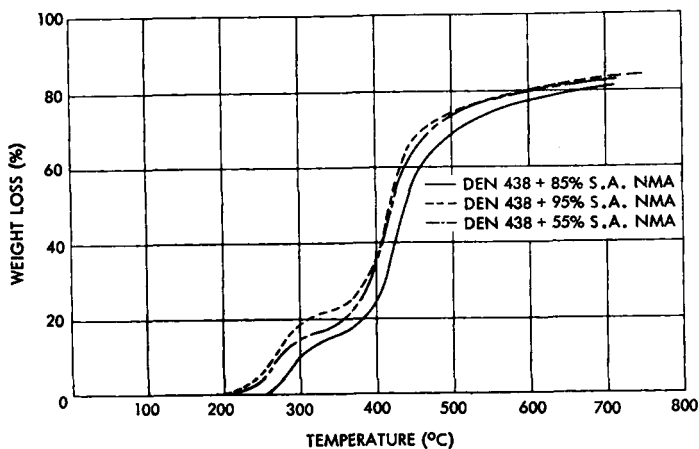

Fig. 7. Thermograms of DEN 438 + NMA at various stoichiometric amounts of NMA.

grams (Fig. 6) that the initial degradation is in the 250–350°C. range. This is much higher (~30% initial decomposition) than that of NMA-cured systems (~20% initial decomposition). This is probably due to the additional steric hindrance by the bulky chlorine groups resulting in a greater amount of monoester-monoacid which would in turn result in a greater initial weight loss. Further evidence that a reverse Diels-Alder reaction does not occur here but that the acid-initiated mechanism does, is given by the fact that all the bridged compounds in this study (NMA, NA, chlorendic anhydride) initiate degradation at 230–350°C. Reverse Diels-Alder reactions for these three materials would be expected to occur at different temperatures.

Semimicro Pyrolysis

The pyrolysis of several epoxy resin systems, typified by Epon 1031 + NMA and DEN 438 + NMA, was performed. The degradation products up to 350°C. were collected and examined by infrared spectroscopy and gas chromatography. Chromatographic data are given in tabular form (Table III).

If the mechanism giving rise to the plateau effect in the thermograms is due to a reverse Diels-Alder, one would expect to find evidence of methyl-cyclopentadiene. However, for the pyrolysis products for Epon 1031 + NMA (350°C.) there are no peaks between 0.6 and 2.8 min. retention time as there are for methylcyclopentadiene; yet at 11.8 and 12.6 min., large peaks occur which are identical to those for NMA. This would indicate an acid-initiated mechanism. Further evidence of this mechanism is given in the infrared spectrum of these same degradation products (Fig. 8). This spectrum is identical to that of pure NMA (Fig. 9). The predominant
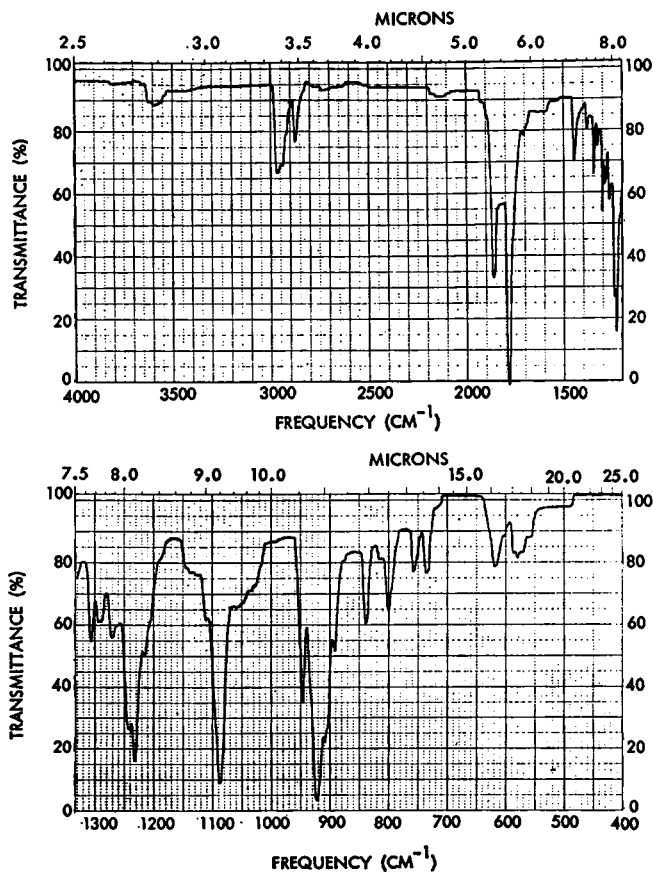

Fig. 8. Infrared spectrum of pyrolysis products to 350°C. of the system Epon 1031 + NMA (85% S.A.)
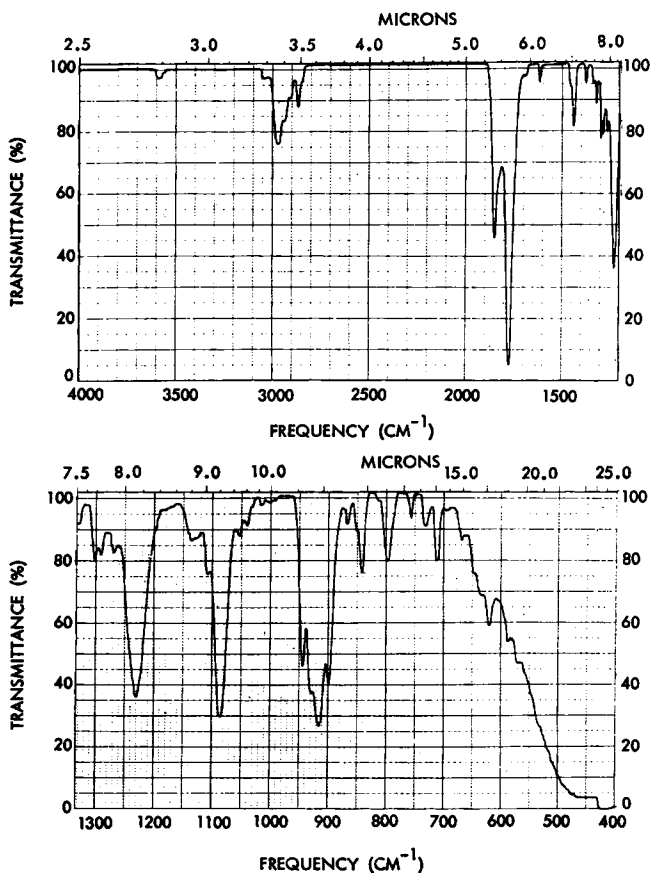
Fig. 9. Infrared spectrum of nadic methyl anhydride.

absorptions are the anhydride carbonyls at 1780 and 1855 cm.$^{-1}$ and the >C—O—C< bond at 1230 cm.$^{-1}$. An infrared spectrum of pure methyl-cyclopentadiene is also given and is obviously quite different from that of NMA (Fig. 10). The broader absorption at 3500–3600 cm.$^{-1}$ of Figure 8 compared to Figure 9 is due to slight hydrolysis of the anhydride.

A similar pyrolysis as described above was performed on the system DEN 438 + NMA. An infrared spectrum of the degradation products up to 350°C. was taken, and again the degradation product seems to be almost pure NMA (Fig. 11). Therefore, we may conclude on the basis of this evidence, that the acid-initiated degradation is mainly operative in the range of 230–350°C. for NMA-cured epoxides.

Micro Pyrolysis

Several NMA-cured epoxy resins were instantaneously pyrolyzed at 1000°C. and their degradation products were swept directly into a gas chromatograph (see Experimental). Similar chromatographic conditions
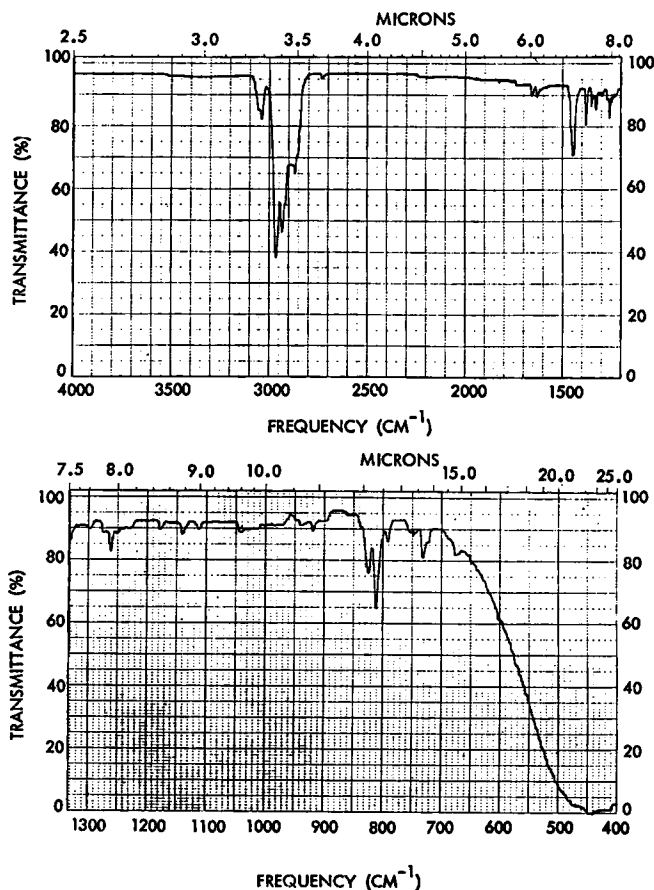
Fig. 10. Infrared spectrum of methylcyclopentadiene.

were imposed on these products as were imposed on pure NMA and methyl-cyclopentadiene. The results of the pyrolysis of Epon 1031 + NMA and DEN 438 + NMA are given in Table III. If the acid-initiated mechanism were the main one operating at this temperature, one would expect to find the major NMA isomers at 11.8 and 12.6 min. retention. However, if a reverse Diels-Alder were operative here, one would expect to find evidence of the three methylcyclopentadiene isomers at approximately 1.2, 1.9, and 2.3 min. retention, with separations of 0.7 and 0.4 min., respectively, between the isomers. For the system Epon 1031 + NMA retention times of 1.4, 2.1, and 2.5 min. were obtained, with separations of 0.7, and 0.4 min. For the system DEN 438 + NMA retention times of 1.6, 2.3, and 2.7 min. were obtained, with separations of 0.7 and 0.4 min. In both cases, as for methylcyclopentadiene, the main isomer was the second isomer with the third in trace amount. Also, in both cases, small amounts of NMA were found at 11.8 and 12.6 min.
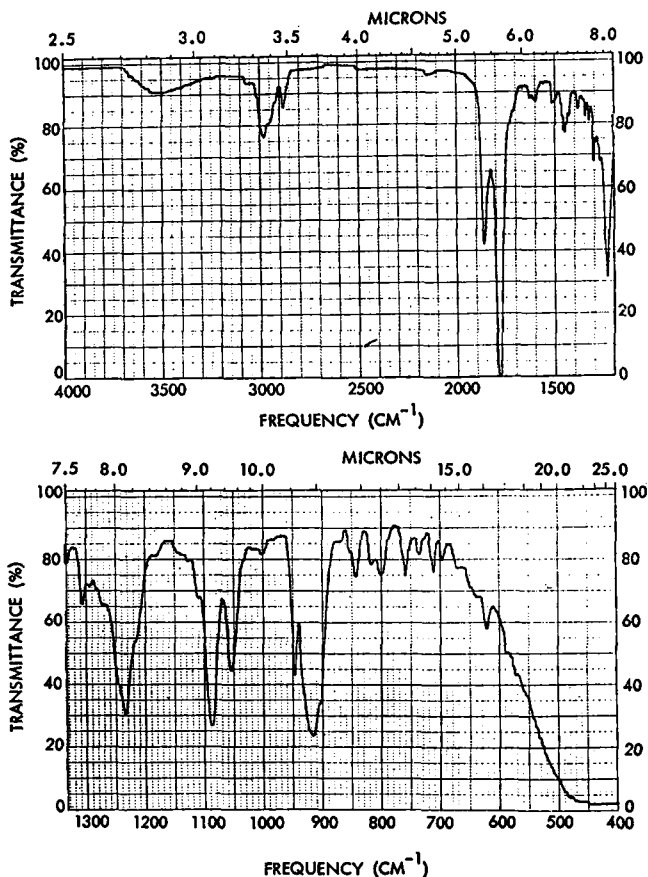
Fig. 11. Infrared spectrum of pyrolysis products to 350°C. of the System DEN 438 + NMA (85% S.A.)–benzene solution–benzene reference.

retention times. Data on a similar pyrolysis of DEN 438 + maleic anhydride were included to show that retention times for methylcyclopentadiene and for NMA were not generated by the resin.

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Résumé

On a étudié les mécanismes qui initient la dégradation thermique inhabituelle des résines époxy traitées à l'anhydride méthyl-bicyclo[2.2.1]hept-5-ène-2,3-dicarboxylique. Deux mécanismes ont été interprêtés, chacun supposant une prédominance de l'un par rapport à l'autre suivant la sévérité des conditions thermiques. L'un consiste en un mécanisme initié par l'acide interne, et agit de 240°C à 350°C à faibles vitesses de chauffage. L'autre consiste en une réaction de Diels-Alder inverse, et agit au-dessus de 350°C habituellement dans les conditions de pyrolyse instantanée, comme on en rencontre dans les cassures. Ces deux mécanismes, agissant simultanément, favorisent le pontage ultérieur de la résine, et donnent naissance à une quantité plus élevée de résidu charbonneux que l'on n'aurait sinon attendue.

Zusammenfassung

Die Startmechanismen für den ungewöhnlichen thermischen Abbau von mit Methyl-bicyclo-[2.2.1]-hept-5-en-2,3-dicarbonsäureanhydrid gehärteten Epoxyharzen werden untersucht. Zwei Mechanismen wurden gefunden, von den der eine oder der andere je nach der Stärke der Wärmeeinwirkung grössere Bedeutung annimmt. Der eine ist ein innerer, säure-gestarteter Mechanismus, der zwischen 240 und 350°C bei niedriger Erhitzungsgeschwindigkeit wirksam ist. Der andere besteht in einer umgekehrten Diels-Alderreaktion, welche oberhalb 350°C unter den Bedingungen einer plötzlichen Pyrolyse, wie sie bei Ablationsprozessen auftreten, wirksam wird. Diese beiden, gleichzeitig auftretenden Mechanismen, fördern die weitere Vernetzung des Harzsystems und liefern so eine grössere Menge von Verkohlungsrückständen, als zu erwarten wäre.