The Mechanism of the Thermal Degradation of Aromatic Amine-Cured Glycidyl Ether-Type Epoxide Resins

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Synopsis

A mechanism is proposed for the thermal degradation of aromatic amine-cured glycidyl ether-type epoxide resins which is based on the results of previous work in this field. The significance of the degradation mechanism to the thermal stability of aliphatic amine-cured epoxides and aromatic amine-cured cycloaliphatic epoxides is discussed.

INTRODUCTION

The literature in the field of the thermal degradation of epoxide resins up to July 1966 was reviewed by Bishop and Smith.[1] At this time, no clear picture of the mechanism of degradation on a molecular level had emerged.[1] Since then, a considerable amount of work[2-8] has been done on the thermal degradation of one particular resin/hardener system, viz., the diglycidyl ether of bisphenol A (DGEBPA), either pure or a commercial product containing small quantities of higher molecular weight homologues:
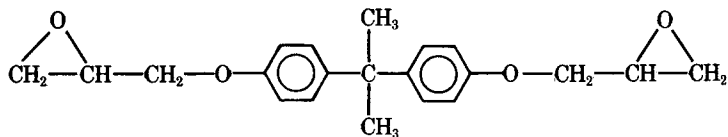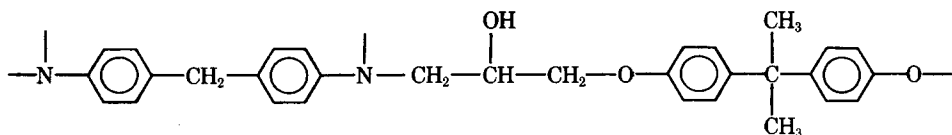

DGEBPA

cured with p,p'-diaminodiphenylmethane (or methylenedianiline, DDM):
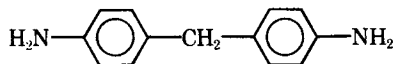
DDM

This resin–hardener combination is a typical representative of the class of cured resin with which this paper is concerned. The cured resin's structure may be represented by the part formula

1539

The thermal degradation of DGEBPA cured with DDM has the following characteristics:

1. Water is a major product,[7,8,9] in fact, the major product at lower degradation temperatures (300–350°C).[7]

2. Phenolic compounds are major products. These include phenol, p-isopropylphenol, p-isopropenylphenol, bisphenol A, 2-benzofur-5-yl-2-(p-hydroxyphenyl)propane, and, at higher temperatures, ethyl-substituted phenols and cresols.[2,4,5,7,8,9] There is evidence that phenolic products with the bisphenol A nucleus intact predominate at lower degradation temperatures but not at high temperatures.[4,7]

3. Compounds containing the benzofuran structure such as 2-benzofur-5-yl-2-(p-hydroxyphenyl)propane, 2,2-bis(benzofur-5-yl)propane, and benzofuran are produced at low temperatures (304°C).[4,7]

4. Products containing the aniline structure are formed; N,N,N′,N′-tetramethyl-p,p′-diaminodiphenylmethane, N,N-dimethylaniline, N-methylaniline, N,N-dimethyl-p-toluidine, N-methyl-p-toluidine,[7] aniline, and p-toluidine[5] have been isolated and identified. There is some evidence that the N-methylaniline structure predominates at lower degradation temperatures (304°C),[7] whereas N-unsubstituted anilines are formed at higher temperatures (500°C).[5]

5. In addition to the above compounds which are formed in appreciable quantities together with a large number of minor compounds not yet identified,[7] traces of aliphatic compounds volatile at room temperature and permanent gases have been identified,[7,9] e.g., acetaldehyde, chloromethane, carbon dioxide, ethene, carbon monoxide, ethane, methane, and nitrogen. Methylcyclopentadiene has been identified by Lee[9] as a product of degradation at 450°C. Hydrogen has also been found[8] as a product of hot wire pyrolysis.

6. Degradation leads to an involatile residue[2,6,7] whose structure is complicated but shows evidence of dehydration and unsaturation and which has been shown to contain long-lived free radicals.[6]

7. A reduction in crosslink density due to degradation can be detected at temperatures as low as 240°C.[2] At 290°C, considerable chain breaking occurs fairly rapidly and is accompanied by only small weight loss.[2]

8. Degradation by the hot wire pyrolysis method has been shown to give products which differ somewhat from those formed during degradation by other techniques such as vacuum pyrolysis.[8] Large amounts of acetone, acetaldehyde, and hydrogen are formed by hot wire pyrolysis.[8] This is probably an indication of some catalytic activity of the metal filament and the very high temperatures (up to 700°C) used in this method. Results of such studies must be used with caution in interpreting uncatalyzed degradation of bulk resin at lower temperatures.

9. Degradation of labeled resin has indicated that products containing carbon atoms from the 1 or 3 position of the glyceryl group are formed at lower temperatures than those containing the 2 carbon atom of the isopropylidene group.[3] In addition, methane has been shown to arise from both the glyceryl and isopropylidene groups whereas ethylene, acetaldehyde, and acetone are formed only from the glyceryl group.[8] Phenolic products are formed from the bisphenol A group as expected.[8]

On the basis of these results, mechanisms have been proposed for the degradation. A dehydration reaction has been repeatedly postulated[2,4,6,7,8,9] together

with homolytic scission of aliphatic carbon-to-carbon, carbon-to-oxygen, and carbon-to-nitrogen bonds.[2,4,6,7,9] Recent work[10,11,12] on model compounds for this resin–hardener system has elucidated the nature of the dehydration reaction and has identified the reaction responsible at low degradation temperatures for products containing the benzofuran and N-methylaniline groupings.

Sufficient data are now available that a mechanism for the degradation of the DGEBPA system can be proposed. In service, this material is unlikely to encounter temperatures above 350°C. The set of reactions which follow are intended to apply to uncatalyzed degradation under nonoxidizing conditions and, in addition, at temperatures to which this material may occasionally be subjected under harsh service conditions.
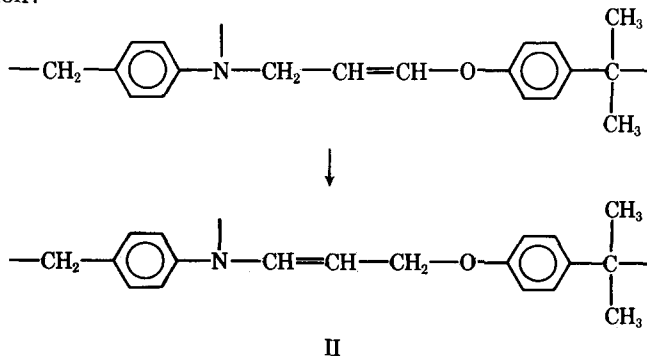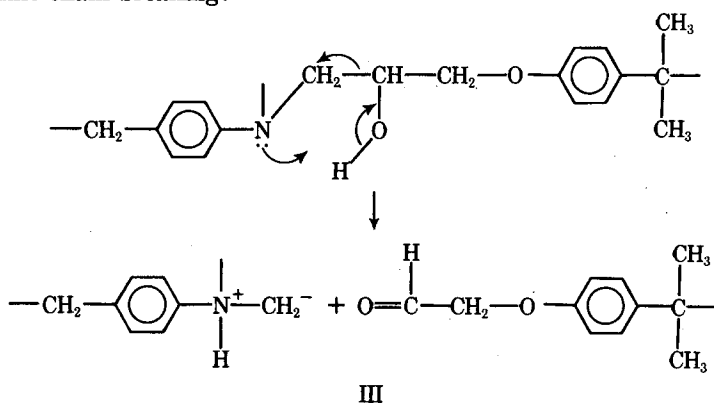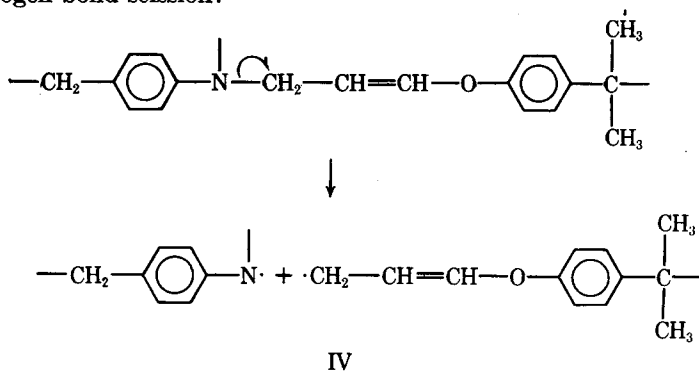
MECHANISM

Major Reactions

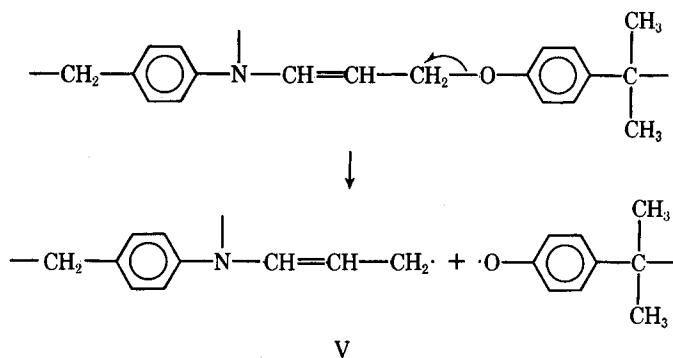Dehydration:

I

Isomerization:
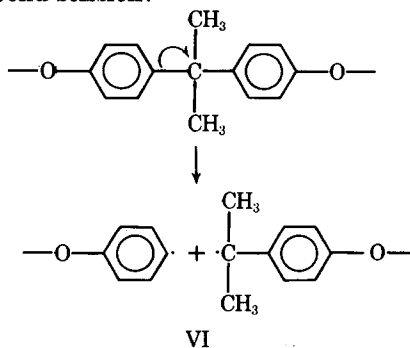

II
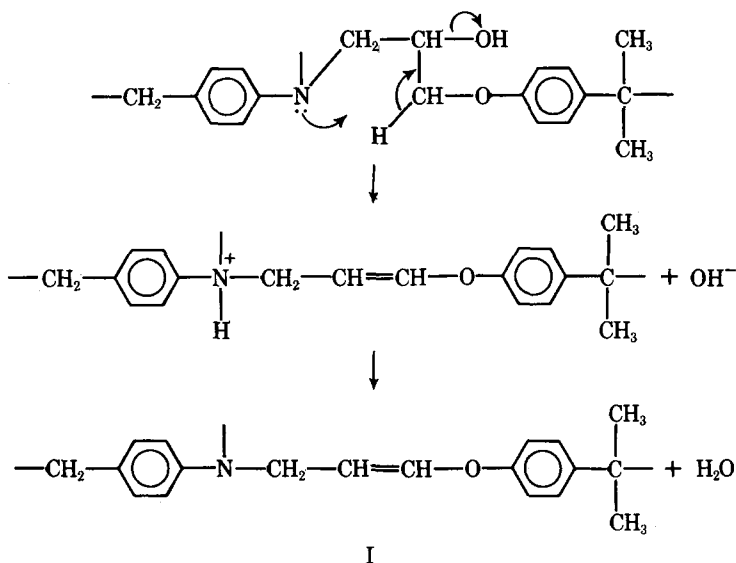
Nucleophilic chain breaking:

III

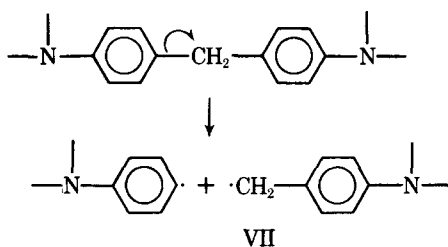Allyl-nitrogen bond scission:

IV

Allyl-oxygen bond scission:

V

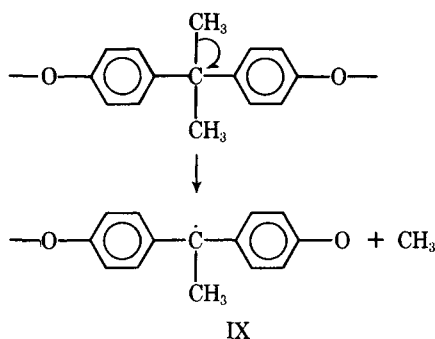Aryl-isopropylidene bond scission:
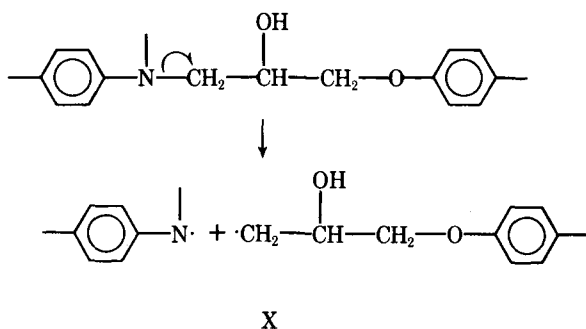

VI

Aryl-methylene bond scission:

VII

Crosslinking reaction VIII: The nature of this reaction is discussed further below.

Minor Reactions

Loss of methyl:

IX

Chain breaking before dehydration:

X

DISCUSSION

The nucleophilic character of the nitrogen present, which is responsible for the epoxide ring opening reaction during cure, is also responsible at higher temperatures for the breakdown of the resin's structure.   The available evidence indicates that reactions I and III predominate at low degradation temperatures and, at higher temperatures, are accompanied increasingly by reactions VI and VII. Thus, products in which the bisphenol A and diaminodiphenylmethane nuclei are retained predominate at lower degradation temperatures,[4,7] whereas lower molecular weight products predominate at higher temperatures.[2,5,8,9]   Bowen[3] showed that the cure linkage is degraded at lower temperatures than the isopropylidene group.

Water is produced in major quantities during degradation.[7,8,9] A specific de-hydration reaction rather than formation of water by secondary processes has been postulated repeatedly.[2,4,6,7,8,9] Both reactions I and III are responsible for water production. The phenoxyacetaldehyde structure formed in III is a direct precursor for the benzofuran structure via a cyclization-dehydration re-action. The formation of benzofuryl structures as major products[4,7] indicates that this is an efficient secondary process under degradation conditions. Re-action III is also responsible for the major quantities of products with the N-methylanilino structure formed at lower temperatures by rearrangement of the nitrogen ylide structure.[10]

Reaction I is formulated as an intramolecular rather than an intermolecular reaction. Steric factors, including the lack of mobility of any particular portion of the network relative to another because of its tightly crosslinked structure, make an intermolecular attack extremely improbable. Work with atomic models shows[12] that in reaction I the nitrogen can approach the γ-hydrogen in a strain free conformation. Similarly, in reaction III, the nitrogen can approach the hydroxyl hydrogen closely without strain. In fact, infrared spectra indicate the presence of hydrogen bonding between the nitrogen and oxygen in the cured resin.[13]

In contrast with reaction III, reaction I is not a direct chain-breaking reaction but leads to unsaturated structures, directly and via reaction II. These struc-tures contain weak allyl-nitrogen and allyl-oxygen bonds, respectively, which may scission homolytically (reactions IV and V) to give anilino and phenoxy radicals which form anilino and phenolic products by hydrogen abstraction. These products are formed in major quantities during degradation.[2,4,5,7,8,9]

An alternative reaction to V is a Claisen rearrangement:
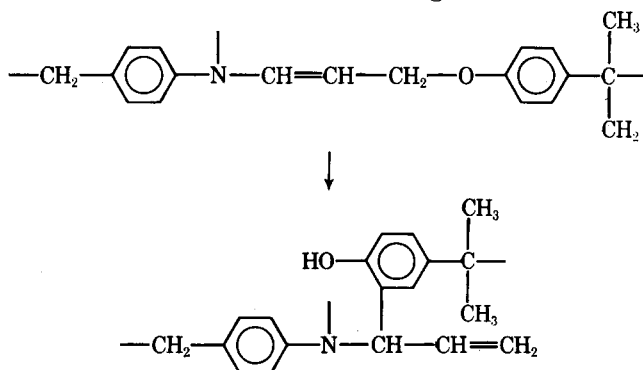
Steric factors, such as the tightly crosslinked structure of the resin and the bulky nature of the groups involved, make this reaction improbable, at least in the early stages of degradation. It is significant that no evidence of a Claisen rearrange-ment was found in the degradation of diphenoxypropene.[11]

Electronic rearrangement and hydrogen abstraction by the propenyl radical formed in reaction IV will lead to allyl phenyl ether structures which probably rearrange to o-allylphenols via a Claisen rearrangement which is not, in this case, sterically hindered. o-Allylphenol was a product of the degradation of the model compound 1-(N-ethylanilino)-3-phenoxypropan-2-ol.[10] Electronic rearrange-ment and hydrogen abstraction by the radical formed from reaction V may lead to allylanilino structures which were also found as a product of the degradation

of the same model compound.[10]   Degradation of the model compound also led to N-substituted skatole and tetrahydroquinoline, 2- and 3-chromenes, and 2- and 3-methyl benzofurans.[10]   Analogous products are probably formed by degradation of the resin.   Lee[9] attributed peaks in the mass spectrum of the degradation products of DGEBPA/DDM to 2-chromenyl structures; but, in fact, the relevant peaks are more likely due to the presence of o-allylphenolic or 2- and 3-methylbenzofuryl structures, since the molecular ion in the 70-eV mass spectrum of 2- and 3-chromenes is very small.   Lee[9] found significant quantities of methyl-cyclopentadiene among the degradation products.   It is likely that this is formed by a reaction of propenyl radicals produced by reactions IV and V with allyl groups from the same source.[7]

Reactions I and III are competing reactions.   The evidence available indicates that, whereas III predominates at lower temperatures (N-methylanilino products are formed in larger quantities at 304°C than anilino products[7]), at higher temperatures, III becomes less important (Sugita[5] found only aniline and toluidine, not methyl substituted, at 500°C).   This implies that compounds with the benzofuran structure are major products only at lower temperatures, as is the case.[7]

It has been pointed out[7] that considerable crosslinking must accompany chain breaking during degradation.   Crosslinking is most likely the result of radical recombination.   The production during degradation of most of the products requires homolytic bond breaking.   The formation of a stable product requires, in most cases, abstraction by a radical of a hydrogen atom from a suitable site so that radical sites remain in the resin which may recombine.   This is a random process dependent only on the near approach of two radical sites.   During degradation, therefore, the resin structure remains crosslinked but is being progressively randomized.   There is evidence for free-radical formation during degradation.[6]

Reactions IX and X can give rise to the small amounts of methane, ethane, acetaldehyde, and carbon monoxide formed.   Acetaldehyde which may be formed by
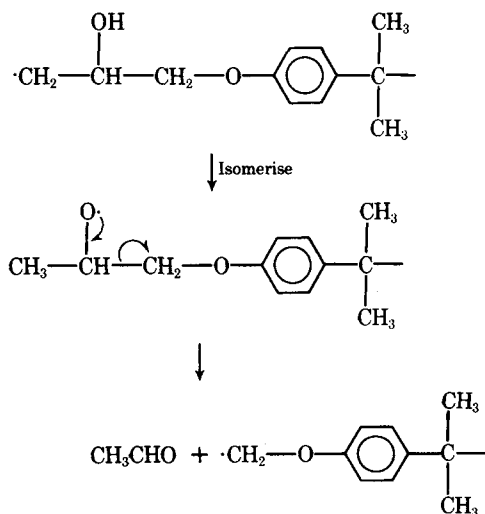

pyrolyzes to form methane, carbon monoxide, and ethane.[14]

CONCLUSIONS

The mediocre heat stability of aromatic amine-cured epoxide resins is a direct result of the incorporation in these structures of nucleophilic centers in the form of the hardeners' nitrogen atoms. It is, therefore, an intrinsic defect of this resin–hardener system. This paper has been concerned solely with the inherent stability of this material; under normal service conditions, oxidation and the possible presence of fillers will profoundly modify its performance.[11]

Aliphatic amines are much stronger bases than aromatic amines.[15] Epoxide resins cured with aliphatic amine hardeners contain in their structure strong nucleophiles. The poor heat resistance of these materials is a direct result.

Cycloaliphatic epoxide resins containing cyclohexene epoxide rings are not as susceptible to nucleophilic degradation as glycidyl ether types. In the structure of the cured resins, the nitrogen atom cannot approach the γ-hydrogen atoms to initiate a nucleophilic dehydration such as reaction I:
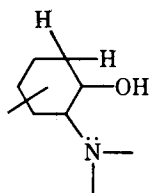
The analogy of reaction III involving nucleophilic abstraction of the hydroxylic proton can occur:
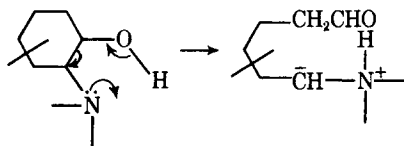
but in this case, the reaction is not a chain-breaking reaction. Cycloaliphatic epoxides cured with aromatic amines should, therefore, be more thermally stable than glycidyl ether types; this is borne out in practice.[16]

It is clear that a reduction in the basicity of aromatic amine hardeners (by, for example, suitably substituting the phenyl ring adjacent to the nitrogen) would affect an increase in the thermal stability of resins cured with them. Unfortunately, such a modification will also result in a decrease in reactivity and hence necessitate unacceptably high cure temperatures.

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