

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Biaspartimide-diamines as Curing Agents for Epoxy Resins

Devendra Kumar^a; Alka D. Gupta^b

^a Defence Materials and Stores, Research and Development Establishment, Kanpur, India ^b Department of Chemical Engineering, Indian Institute of Technology, New Delhi, India

To cite this Article Kumar, Devendra and Gupta, Alka D.(1985) 'Biaspartimide-diamines as Curing Agents for Epoxy Resins', Journal of Macromolecular Science, Part A, 22: 8, 1101 – 1107

To link to this Article: DOI: 10.1080/00222338508063317

URL: <http://dx.doi.org/10.1080/00222338508063317>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Biaspartimide-diamines as Curing Agents for Epoxy Resins

DEVENDRA KUMAR

Defence Materials and Stores
Research and Development Establishment
Kanpur 208013, India

ALKA D. GUPTA

Department of Chemical Engineering
Indian Institute of Technology
New Delhi 110016, India

ABSTRACT

Various 4,4'-bis{N²-[4-(4-aminophenoxy)phenyl]aspartimido}diphenylmethane-type bisaspartimide-diamines have been used as solventless curing agents for epoxy resins. The thermal curing was performed at 170, 190, and 230°C to give a tough brown polymer. Thermogravimetric analysis of the polymer obtained showed thermal stability up to 330°C and char yields of 45% in N₂ at 800°C and 12% in air at 700°C. The thermal curing reaction was monitored using FT-IR. The synthesized polymers are useful for making composites, laminates, and adhesives.

INTRODUCTION

Epoxy resins cured with amines have been most commonly utilized as matrix resins for making high strength composites, laminates, and adhesives. In an attempt to develop thermally stable matrix resins,

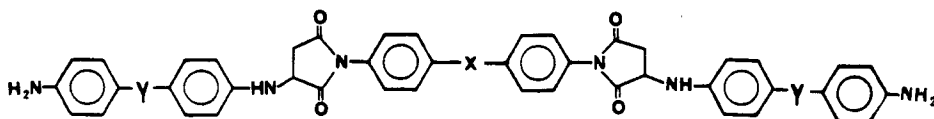
curing of epoxy resins, without use of a solvent, utilizing various recently synthesized [1] bisaspartimide-diamine has been examined. The use of bisaspartimide-diamine is expected to serve the dual purpose of providing flexibility and heat stability because in these linear bisaspartimides the functional primary aromatic amino groups are separated through preimidized segments. The incorporation of longer chain segments into the polymer matrix is known to provide flexibility to the tridimensional polymeric network by changing the effective length between the crosslinking points, enabling the system to absorb energy without catastrophic failure. Solventless curing is preferred by industry to avoid void formation in the cured matrix.

In this paper we report the results of thermal curing of epoxy resins with bisaspartimide-diamines and the thermal stability of the resulting polymers.

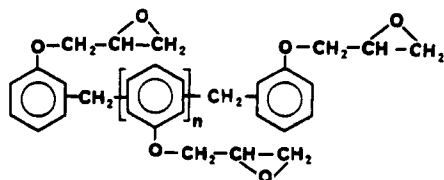
EXPERIMENTAL

Materials and Reagents

Various 4,4'-bis{N²-[4-(4-aminophenoxy)phenyl]aspartimido}diphenylmethane-type bisaspartimide-diamines were synthesized [1] by involving a Michael-type reaction of an aromatic bismaleimide (1 mol) with an aromatic diamine (2 mol) and characterized as reported by us [1]. The bisaspartimide-diamines used in this study are 4,4'-bis{N²-[4(4-aminophenoxy)phenyl]aspartimido}diphenylmethane (I) and 4,4'-bis{N²-[4-(4-aminobenzyl)phenyl]aspartimido}diphenylmethane (II).



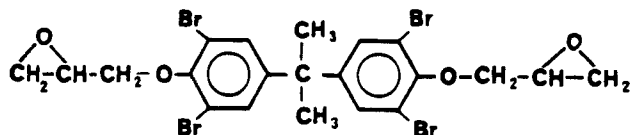
- I $X = CH_2, Y = O$
 II $X = Y = CH_2$



$$n = 1.6$$

III

Epoxy resins used in this work were commercially obtained. Among those studied were DEN 438 (III), the polyglycidylether of phenol-formaldehyde novolac from Dow Chemical U.S.A., and DER 542 (IV), the diglycidylether of tetrabromo bisphenol-A, also from Dow Chemical U.S.A.



IV

Curing of DEN 438 with Bisaspartimide-diamine

The yellow powder of bisaspartimide-diamine (1.29 g) (I) was added to DEN 438 epoxy resin (1.72 g) (III) heated to 120°C. This was cured by heating in an aluminum cup placed in a hot air circulation oven previously maintained at 170°C for 2 h and 190°C for 1 h. It was further heated at 230°C for 30 min. A tough brown polymer was obtained.

In a slightly changed procedure, a solution of the diamine and epoxy resin was obtained by adding a few drops of dioxane or N,N'-dimethylacetamide and then curing was performed under similar conditions.

Epoxy resin DER 542 was similarly cured with bisaspartimide-diamines.

Characterization of the Polymers

IR Spectroscopy. The spectra of the polymers were recorded on a NaCl disk with a Nicolet FT-IR Spectrophotometer.

DSC Analysis. Differential scanning calorimetry was performed on a DuPont 1090 Thermal Analyzer System. Measurements were made at a heating rate of 10°C/min.

TG Analysis. Thermogravimetric analysis were performed on a Stanton Redcroft Model 750/770. Measurements were made at a heating rate of 10°C/min in nitrogen and air atmospheres.

RESULTS AND DISCUSSION

Bisaspartimide-diamine (I) and (II) were synthesized and characterized using FT-IR, ¹H-NMR, and ¹³C-NMR as reported by us [1]. These were crystallized with acetone to fine yellow powders. Epoxy

resins DEN 438 (III) and DER 542 (IV) have epoxy equivalents of 176-181 and 330-380, respectively.

Preliminary investigations showed that both the epoxy resins noted can be cured with bisaspartimide-diamine to thermally stable, tough, polymeric materials. The results presented here are based on the curing reaction of DEN 438 and bisaspartimide diamine (I) without use of any solvent.

The IR spectrum of DEN 438 neat film formed on a NaCl disk showed absorption bands at 915 and 862 cm^{-1} due to the presence of epoxy groups [2] and bands at 1113-1040 cm^{-1} due to ether bonds.

The curing reaction of epoxy resin DEN 438 with bisaspartimide-diamine (I) was monitored using FT-IR. A film of uncured resin was made on a NaCl disk. This NaCl disk was heated under identical con-

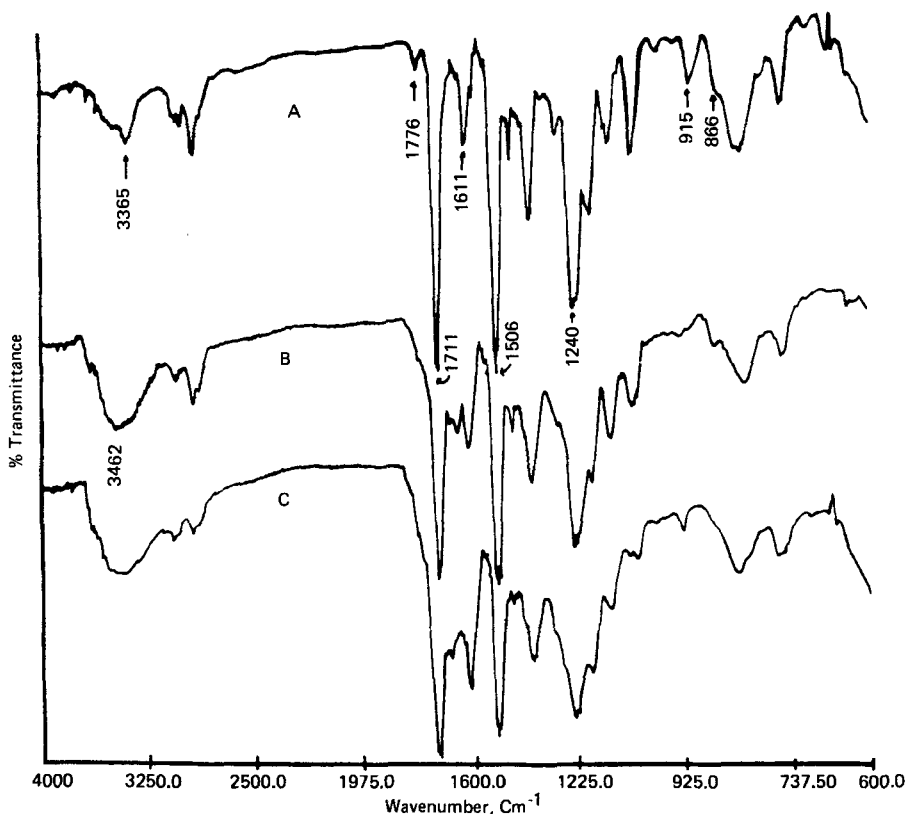


FIG. 1. (A) Infrared spectrum of uncured resin (bisaspartimide-diamine I + DEN 438 III). (B) Infrared spectrum obtained after heating at 170°C for 2 h and 190°C for 1 h. (C) Infrared spectrum of the cured resin.

ditions along with the sample under curing. Figure 1(A) showed the IR spectrum of the uncured sample. In this spectrum the presence of epoxy (915 and 866 cm^{-1}) and imide (1776 and 1711 cm^{-1}) is clearly indicated along with the presence of aromatic (1506 cm^{-1}), phenoxy (1240 cm^{-1}), aliphatic ether (1135 - 1034 cm^{-1}), and amino (3470 , 3365 , and 1611 cm^{-1}) groups. Figure 1(B) shows the IR spectrum obtained after curing at 170°C for 2 h and 190°C for 1 h. At this stage the epoxy groups are seen as absent because the original bands at 915 and 866 cm^{-1} have disappeared along with the broad band at 3462 cm^{-1} . The latter may be due to the formation of hydroxyls. This indicates opening of the epoxide ring and most likely involves addition of amino groups. On further curing of this sample at 230°C for 30 min, the IR spectrum (Fig. 1C) follows the same pattern with broadening of the entire spectrum. This type of broadening is usually observed in the IR spectra of polymers.

The DSC analytical curve for the reaction mixture bisaspartimide-diamine I + DEN 438 in air before curing is given in Fig. 2. Three exothermic peak temperatures (Texo) were observed at 190 , 260 , and 363°C . Beyond 420°C the large exotherm indicated mainly decomposition. The peak with Texo at 363°C may be due to the polymerization, isomerization, and partial decomposition of the epoxy part [3, 4]. The first two peaks with Texo at 190 and 260°C represent polymerization.

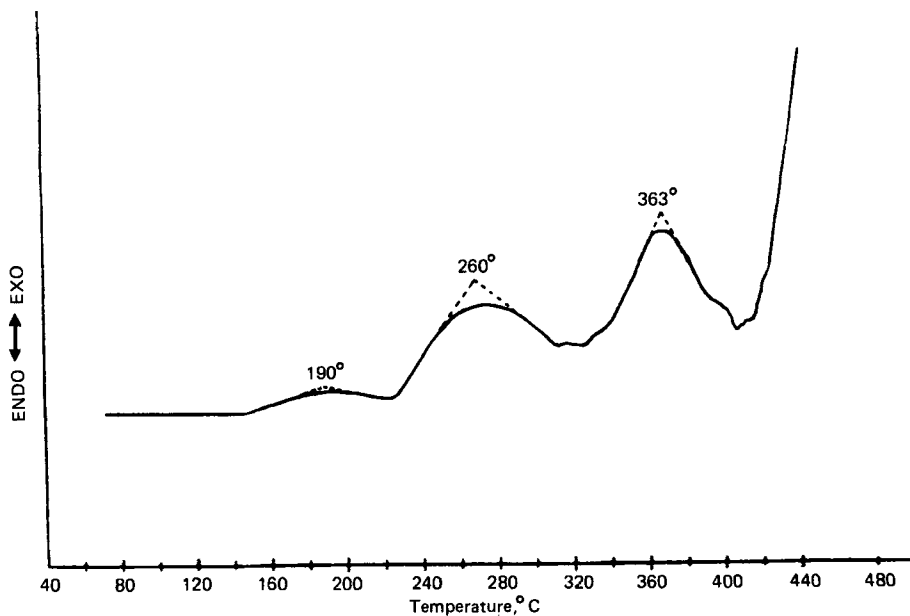


FIG. 2. Differential scanning calorimetry of uncured resin in air at heating rate of $10^\circ\text{C}/\text{min}$.

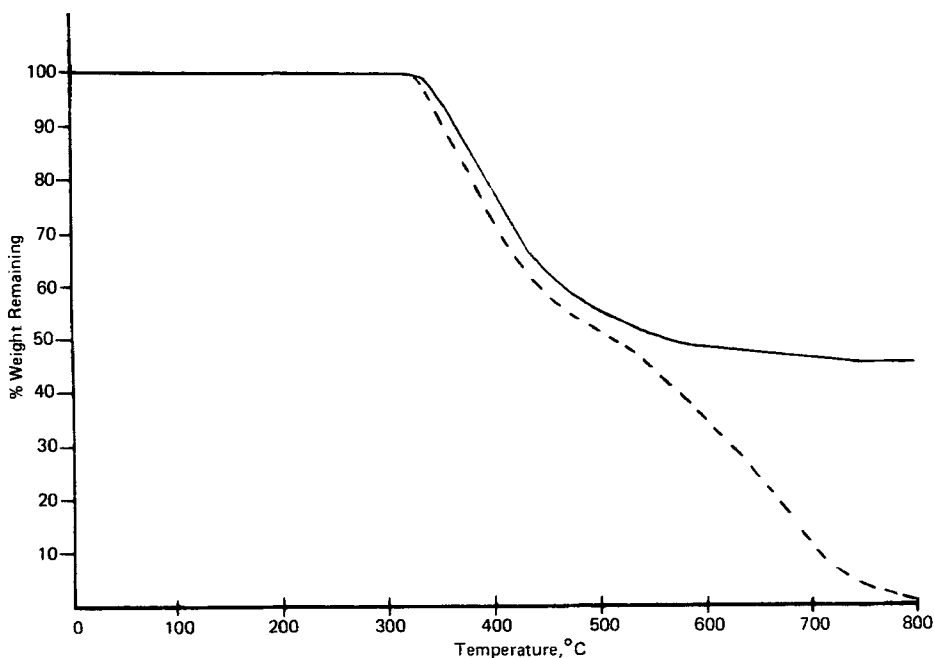


FIG. 3. Thermogravimetric analysis of cured resin (—) in N₂ and (---) in air. Heating rate, 10°C/min; flow rate, 20 mL/min.

The relative thermal stability of the polymer obtained was investigated by dynamic thermogravimetry in air and nitrogen atmospheres (Fig. 3). The polymer was stable up to 330°C and started losing weight above that temperature. Anaerobic char yield was found to be 45% at 800°C. Two-step decomposition was observed in air for this polymer in the 330-470 and 470-740°C temperature ranges, with a char yield of 12% at 700°C.

Similar polymerization studies were carried out using DER 542 epoxy resin, but the resulting cured polymers were found to be comparatively less thermooxidatively stable.

CONCLUSION

Thermally stable polymer has been obtained by a solventless curing of DEN 438 epoxy resin with bisaspartimide-diamine. It has an anaerobic char yield of 45%. This type of polymer is expected to be useful for the preparation of laminates, composites, and adhesives.

ACKNOWLEDGMENT

The authors wish to thank Dr J. K. Nigam, Director, Shriram Institute for Industrial Research, New Delhi, for FT-IR measurements.

REFERENCES

- [1] D. Kumar, G. M. Fohlen, and J. A. Parker, J. Polym. Sci., Polym. Chem. Ed., **21**, 245-267 (1983).
- [2] H. Lee and K. Nivelles, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967.
- [3] L. H. Lee, J. Polym. Sci., **A3**, 859 (1965).
- [4] H. C. Anderson, Anal. Chem., **32**(12), 1592 (1962).

Accepted by editor April 4, 1984

Received for publication April 20, 1984