



ELECTRIC CONDUCTIVITY OF CURED ARYLHYDRAZINO BISMALIMIDE-EPOXY RESINS

S. V. PATEL

Department of Chemistry, Sir P. T. Science College, MODASA - 383 315 (Guj.) INDIA

ABSTRACT

Arylhydrazino-bismaleimides (AHBM) has been prepared by the Michael addition reaction of various phenyl hydrazine derivatives with N, N' -(4, 4' -biphenyl) bismaleimide (BBM). These arylhydrazino bismaleimides (AHBM) were employed for curing commercial epoxy resins. The curing behavior of commercial epoxy resin with these AHBM compounds using 2- methyl imidazole as a catalyst has been monitored using differential scanning calorimetry. Glass fiber composites of the epoxy AHBM system have also been prepared and characterized mechanically and chemically. The electrical conductivity of all unreinforced epoxy-AHBM cured products were measured at a room temperature and it was found that the produced cured materials were having good chemical resistance, good mechanical strength and low conductivity.

Key word: Electrical conductivity, Epoxy resin, Cured

INTRODUCTION

Epoxy resins are extensively used in number of applications like molding, adhesive, paints, powder coating etc¹. Epoxy resin in their precured state is colorless to yellowish brown viscous liquids. The viscous state of epoxy resins are quite stable and are not affected by weather at room temperature. Cured epoxy resins are produced by the addition of curing agents (hardeners), such as diamines, anhydrides, thiols, etc.¹. Epoxy hardeners containing hydrazine groups have been reported² including hydrazide derivatives of carboxylic acid³⁻⁶. The objective of this study was to use an aryl hydrazine derivative of bismaleimide as the hardener, with an epoxy resin to form a cured network.

EXPERIMENTAL

Material and synthesis

Commercial epoxy resin, i.e., Novolac epoxy (NE) was obtained from Sympol Product Pvt. Ltd. Ahmedabad, India. The specifications of this epoxy resin are: epoxy

equivalent: 180-190; Viscosity: 5-15; Density: 1.22-1.24 g / cm³.

Aryl hydrazine derivatives, viz; phenyl hydrazine, 4-chlorophenyl hydrazine, 4-bromo phenyl hydrazine, 4-methyl phenyl hydrazine, 4-methoxyphenyl hydrazine, were obtained from Chiti Chem. Baroda, India, and used as received. N, N'-(4,4' - biphenyl) bismaleimide (BBM) was prepared by the method⁷. Other chemicals used were of laboratory grade.

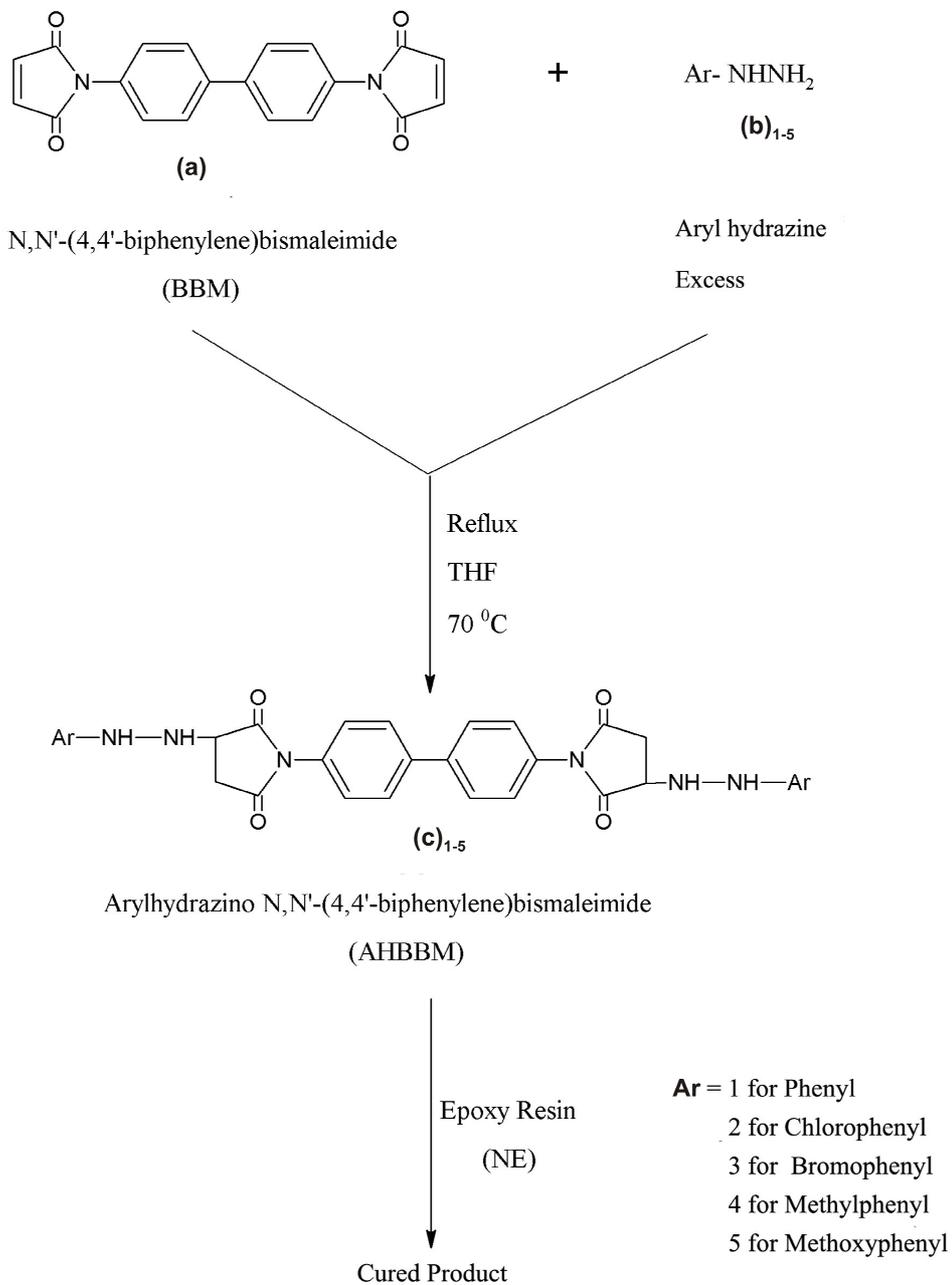
All arylhydrazino N, N'-(4,4' - biphenyl) bismaleimide (AHBBM) derivatives (**Scheme 1**) were prepared according to our earlier communication⁹⁻¹³. The unreinforced epoxy resin-AHBBM products were prepared by mixing epoxy resin (1 mol) and AHBBM derivatives (0.25 mol)⁹⁻¹³ (used for DSC study) and heated for 2 hour at curing temperature (i.e., T_p obtained from DSC experiment). The products were crushed, washed with hot water and then air-dried.

Composite fabrication

The glass-fiber reinforced composites (GRC), based on epoxy-AHBBM system were prepared by mixing a stoichiometric ratio of the epoxy resin and AHBBM (40 % wt. of total glass-fiber cloth) in THF⁹. The resulting mixture was mixed well for 10 minutes. The suspensions were then applied with a brush onto a 150 mm x 150 mm epoxy-compatible fiberglass cloth, and the solvent was allowed to evaporate. Once dried, the ten prepregs were stacked one on top of another, pressed steel plates coated with a teflon film release and compressed in a flat platen under about 0.5 MPa. The prepregs were cured by heating the press at 170°- 180° C for 12 h in an air circulating oven. The laminate so obtained was cooled at room temperature before the pressure was released. The test specimens were made by cutting the laminates and machining them to their final dimension.

FTIR and DSC

FTIR analysis was done on a Perkin Elmer-983 spectrophotometer. Curing of the epoxy resin with AHBBM compounds were monitored by DSC using a DuPont 900 DSC. The instrument was calibrated using standard material of known heat of fusion. Curing was carried out using a single heating rate of 10 K/min. The sample for this investigation was in the range of 4 to 5 mg. and an empty cell was used as a reference. Thermogravimetric analysis (TGA) of all AHBBM epoxy cured and their uncured products was carried out on a DuPont thermobalance in air at a heating rate of 10 K/min. All the mechanical and chemical properties were determined according to ASTM or ISO methods, as listed.



Scheme 1

Mechanical and chemical properties

All the mechanical and chemical properties were measured on three individual specimens and average results have been documented.

Flexural strength test

The measurement of flexural strength of the composites was carried out on a Universal Instron testing machine, Model number A-74.37, at room temperature according to the method of ASTM D-770. The crosshead was 100 mm / min.

Compressive strength test

The compressive strength was measured according to an ISO method. The sample size was 12.5 x 12.5 mm.

Impact strength test

The measurements were made with an Izod type impact tester at room temperature according to the testing methods of ASTM-256.

Hardness test

The Rockwell hardness was measured according to ASTM D-785. The sample size was 25 mm x 25 mm.

Chemical resistance test

The chemical resistance test was measured according to the ASTM D-543 method. the sample size was 20 mm x 20 mm.

Electric conductivity

For the electrical conductivity measurement, a pellet of the polymer sample was prepared by pressing a finely powdered and dried sample under hydrostatic pressure at 20,000 psi for 2 minute⁸.

A uniform thin layer of silver paste was applied to both sides of the pellet to provide electrical contacts. Average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal disks functioning as electrodes. The other ends of the electrodes were passed through the pellet holder for connections. The resistance of the pellet was measured by a million-mega ohm meter (RM 160 MK III A

BPL, India). The specific conductivity (σ) of the pellet was estimated by the usual relations from the resistance of the pellet and its diameter. The electrical conductivity (σ) of the polymer sample was measured at room temperature. The test conditions are: diameter of the pellet (d): 1.015 cm.; surface area of the pellet (A): 0.808 cm²; thickness of pellet (I): 0.19 cm.; source voltage (Vs): 8.5 V; input resistance (R): 109 ohm.

RESULTS AND DISCUSSION

The DSC study of the unreinforced epoxy-AHBBM was adopted to establish the curing temperature for bulk curing. Examination of all the DSC scans of the epoxy-AHBBM system shows a broad curing exotherm in the temperature range of 120^o- 250^oC. The exotherm was characterized by noting T_p obtained by drawing a tangent at the start of the exotherm, and at the final exotherm temperature T_f . The heat of curing (ΔH) was obtained from the area under the exotherm. The result of DSC scans for the curing of all the AHBBM resins in the presence of a catalyst are summarized in Table 1. All the samples have T_p values in the range of 100^o- 170^oC depending upon the nature of the system. The heat of curing, indicating complete reaction in the presence of catalyst.

Table 1: DSC Curing study of AHBBM-epoxy resins

| Sample* | Cure onset temperature T_i (°C) | Peak temperature T_p (°C) | Final temperature T_f (°C) | Activation energy (E_a) Kcal/mol |
|---------|--------------------------------------|--------------------------------|---------------------------------|---|
| 1 | 121 | 155 | 166 | 34.40 |
| 2 | 108 | 142 | 158 | 30.80 |
| 3 | 97 | 126 | 160 | 32.20 |
| 4 | 80 | 115 | 155 | 34.30 |
| 5 | 115 | 156 | 181 | 35.50 |

* Stoichiometric proportion of AHBBM-Novoloc epoxy resin used

IR spectra (not shown here) of all the AHBBM-epoxy unreinforced systems reveals that the discernible difference observed between cured product and parent compounds, was a band due to the epoxy ring at 910 cm⁻¹ in resin, which is almost vanished in the spectra

of all the epoxy-AHBBM cured products, indicating that curing was through the epoxy group and –NHNH- group of AHBBM, as expected.

The TGA data of all cured products are given in Table 2. Cured products start to decompose at around 250 °C, and the rate of decomposition increased between 300 °C and 500 °C. The results of TGA show that the cured products lose almost 90 % of their mass at 600 °C, which indicates that the cured products have good thermal stability.

Table 2: DSC TGA of AHBBM-epoxy resins

| Sample* | % Weight loss | | | | |
|---------|---------------|-------|-------|-------|-------|
| | 250 ° | 300 ° | 400 ° | 500 ° | 600 ° |
| 1 | 2 | 12 | 36 | 67 | 95 |
| 2 | 3 | 13 | 35 | 66 | 93 |
| 3 | 3 | 11 | 37 | 70 | 94 |
| 4 | 4 | 14 | 33 | 64 | 92 |
| 5 | 2 | 12 | 34 | 66 | 96 |

* Stoichiometric proportion of AHBBM-Novoloc epoxy resin used

The glass-reinforced composites of epoxy-AHBBM resins have a density in the range of 1.8 to 2.0 gm/cm³. The chemical resistance test reveals that all the composites have remarkable resistance towards organic solvent and concentrated HCl. However treatment with concentrated NaOH change thickness to a small amount and weight by amount 1.3 %. Mechanical properties of all composites reveals that all the composites have good mechanical strength and chemical resistance. The data are furnished in Table 3.

Examination of data reveals that electrical conductivity of each of AHBBM-epoxy resin cured materials at room temperature is found to be in the range of 2.3 to 4.2 x 10⁻¹¹ ohm⁻¹ cm⁻¹, which indicates low conductivity.

Comparison of the properties of produced cured products with those of other cured products by using same epoxy resins reveals that the produced cured products have slightly higher mechanical strength but the end cured products are dark colored. So the pigmentation could not be achieved. This would be the disadvantage otherwise the produced system could not be applicable commercially.

Table 3. Mechanical and chemical properties of glass-reinforced composites based on AHBBM-epoxy (equivalent ratio) systems

| Sample* | % Change on exposure to 25 % (w/v) NaOH | | Density (g/cm ³) | Flexural strength (MPa) (ASTM D-770) | Compressive strength (MPa) (ISO Method) | Impact strength (MPa) (ASTM D-256) | Hardness (R) (ASTM D-785) |
|---------|---|--------|------------------------------|--------------------------------------|---|------------------------------------|---------------------------|
| | Thickness | Weight | | | | | |
| 1 | 0.8 | 1.0 | 1.86 | 195 | 180 | 200 | 136 |
| 2 | 0.9 | 1.1 | 1.96 | 190 | 200 | 205 | 134 |
| 3 | 1.1 | 1.0 | 1.92 | 195 | 205 | 225 | 137 |
| 4 | 0.9 | 1.1 | 1.96 | 205 | 195 | 235 | 138 |
| 5 | 0.9 | 0.9 | 1.98 | 200 | 190 | 245 | 135 |

*Stoichiometric proportion of AHBBM-Novoloc epoxy resin used

ACKNOWLEDGEMENTS

The author is highly thankful to Masani Polymer Pvt. Ltd. Vapi (Gujarat) for providing research facilities. The author is also thankful to the Principal, Sir P. T. Science College, Modasa, for his constant encouragement and providing duty leaves.

REFERENCES

1. H. Lee and K. Naville, Hand Book of Epoxy Resin, McGraw Hill, New York (1978).
2. C. Glenda Young, US Patent, **4**, 816, 531; Chem. Abstr., **111**, 196058c (1989).
3. O. P. Baraban, A. E. Ryskina and L. V. Efimenco, Sintezi, Svoistav Zhidk, Unglevodorod Kauehakov Naikh Osnove M., 121 (1979) Zh. Khim. Abstr. No. 24T600 (1979).
4. D. P. Kochetov, F. R. Gritsenko, V. K. Grishchenko and Yu. L. Spirin, Vyskomol Soedin [A], **21**, 2171, (1979).
5. D. Aelony, J. Appl. Polym. Sci., 13227, (1969).
6. H. H. Levine, US Patent, **3**, 014, 009 (1959).
7. J. V. Crivello, J. Polym. Sci. Polym. Chem. Ed., **14**, 159, (1976).

8. M. S. Patel, J. Macromol. Phys., **325**, 57-64 (1986).
9. S. V. Patel, and J. M. Daraji, Oriental J. Org. Chem. (India), **17**, 299-302 (2001).
10. S. V. Patel and J. M. Daraji, Ultra Scientist of Physi. Sci. (India), **14**, 97-102, (2002).
11. S. V. Patel and J. M. Daraji, Anarta, J. Hem. N. G. Uni. Patan (India), **9**, 59-64 (2002).
12. S. V. Patel and J. M. Daraji, Asian J. Chem. (India), **16**, No. 2, 1143-1148 (2004).
13. S. V. Patel and J. M. Daraji, Bull. Chem. Sci. (India), **1**, 11-15 (2004).

Accepted : 06.10.2008