Reinforced polymer composite having improved fire retardant properties

SANTOSH C. BHUVA¹, KANUPRASAD D. PATEL¹*, BHARATKUMAR Z. DHOLAKIYA² and TRUPTI K. DARJI¹

¹Chemistry Department, V. P. & R. P. T. P. Science College, Vallabh Vidyanagar - 388 120 (India).
²Sardar Vallabhbhai National Institute of Technology, SVNIT, Ichhanath, Surat (India).

(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

Unsaturated polyester resin has been synthesized using phthalic anhydride, maleic anhydride and propylene glycol. Epoxy resin was synthesized using tetramobromobisphenol-A and epichlorohydrine. The synthesized halogenated epoxy resin was added to unsaturated polyester resin in different weight proportions, ranging from 0 to 20%. Composites were prepared using the prepared resin and glass fibre with benzoyl peroxide as initiator. The composites were tested for flexural strength, impact strength and rockwell hardness. The fire retardant property of the unsaturated polyester resin was also determined by Limiting Oxygen Index (LOI) test. The unsaturated polyester resin has shown good fire retardant property.

Key words: polyester resin, halogenated epoxy resin, IR spectra, Limiting Oxygen Index (LOI), mechanical properties.

INTRODUCTION

Unsaturated polyester resin (UPR) is one of the important thermosetting materials used for the fabrication of glass-reinforced plastics and polymeric composites. The widespread use of these resins is due to their relatively low cost, easy processing, excellent wetting properties with reinforcements, good balance of properties and the wide variety of grades available. UPR are the blends of unsaturated polyester with an unsaturated coreactant diluent like styrene.¹³ Natural fibre reinforced polymers are particularly used in the automotive and construction industry, ⁴⁻⁷ since natural fibres exhibit many advantageous properties such as low weight, low cost, low density, high specific properties and availability from renewable resources.

The mechanical properties of unsaturated polyester composites, reinforced with different natural fibres (sisal, jute and flax) and glass fibre were evaluated. It was found that jute composite had the best flexural and tensile strength, but the lowest impact results as a consequence of the higher interface adhesion. On the other hand, sisal fibre composites showed the lowest mechanical and water resistance properties. Woven jute and non-woven flax composites showed similar tensile properties, flexural properties and water absorption rate. Besides the good mechanical properties and low cost, it is important to evaluate the fire retardant behaviour of a material for structural applications⁸⁻⁹.

This article deals with the composites of unsaturated polyester resin, glass fibre and synthesized fire retardant additives (epoxy resin of
tetramobisphenol-A and epichlorohydrine), which gives good mechanical and electrical properties with fire retardancy. This kind of material can be used for automotive purpose, industrial use and in aerospace industries.

**EXPERIMENTAL**

**Material and Methods**

This research work deals with the preparation of unsaturated polyester resin by melt polycondensation process and preparation of halogenated epoxy resin.

**Materials used in preparation of polyester and halogenated epoxy resin**

The chemicals used in the present study were; phthalic anhydride, maleic anhydride, propylene glycol, epichlorohydrine and Tetrabromobisphenol-A. All the chemicals were obtained from Chiti-Chem. Corp. Ltd. and are of LR grade.

**EXPERIMENTAL**

Unsaturated polyester resin (UPR) was prepared by using reported method [10] by using propylene glycol, phthalic anhydride and maleic anhydride (Scheme I). This resin has been characterized by functional group analysis\(^ {10}\) (Acid value) and was below 25mg KOH/100 gms of resin. Halogenated epoxy resin was prepared by using reported method,\(^ {11-12}\) using epichlorohydrine and tetrabromobisphenol-A (Scheme II). This resin was characterized by determining Epoxide Equivalent Weight.\(^ {13}\)

Formulation of fire retardant UPR

Fire retardant unsaturated polyester resin was prepared by blending UPR with halogenated epoxy resin in different weight proportions (0%, 5%, 10%, 15% and 20%). The formulated resin was then used for the preparation of composite glass fibre as shows in Table 1.

Calculated amount of the resin and additives were mixed and homogeneous paste like mixture was made. Benzoyl peroxide was used as initiator for UPS resin system. This mixture was first layered on a glass fibre ply (6 in × 6 in). The uniform layer was made with the help of another glass fiber ply which was placed on it. The sandwich structure of resin and 10 plies of the glass fiber was carefully kneaded by a roller to impregnate the fibers completely wet into the resin, this sandwich structure was placed at the centre of pressing plate. The plate was placed in oven at 120 °C for 1 hr. After bringing it to room temperature, impact strength, flexural strength, rookwell hardness and fire resistant test were carried out.

**Characterization of resins**

Reaction was monitored by continuous determination of acid value of the reaction mass. Completion of reaction was observed with FTIR (Fig 1) and was compared data with a standard (Table 2).

During reaction, epoxide equivalent weight of epoxy resin was continuously determined and was found to be below 350 gm for liquid epoxy resin. Formation of epoxy resin was confirmed by FTIR (Fig 2) the observed data were compared with the standard ones (Table 3).

**Properties**

**Impact strength**

Izod impact strength was carried out according to ASTM D-256 (1976) standard. A zwick model No. 7900 universal testing machine was used in present work with the purpose of determining the various impact strength of thermoplastic, thermoset and composite polymer materials. For the test, specimen was cut in 1.50cm x 10cm pieces from the composite sheet. The results reported here is the average of five specimens.

**Flexural strength**

It is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses are induced due to flexural load and combination of compressive and tensile stress. Flexural properties are reported and calculated in terms of maximum stress and strain that occur at the outside surface of the test specimen. This test is carried out according to ASTM-D790 (1971). The test specimen was cut in 1.50cm x 10cm pieces from the composite sheet. The results reported here is the average of five specimens.
Rockwell hardness

The Rockwell hardness study was carried out at room temperature, according to ASTM D-785. In the present study, Rockwell hardness tester TSEW testing machine was used. A major load of 100 kef was applied for each measurement. The specimen was cut in 1.50cm x 10cm pieces from the composite sheet. The results reported here is the average of five specimens.

Fire resistant test method

An important and well established test method for evaluating flammability is Limiting Oxygen Index (LOI) test. LOI is the minimum concentration of oxygen determined in a flowing mixture of oxygen and nitrogen that will just support flaming combustion of the material. This test is carried out according to the British Standard Method (BS 2782) which describes the procedure for testing plastics samples cut from rigid sheet. The specimen was cut in 1.50cm x 10cm pieces from the composite sheet. Stanton red croft provided with an oxygen analyzer was used for the purpose.

RESULTS AND DISCUSSION

The results of flexural strength (Kg/cm²), impact strength (J/m) and Rockwell hardness (R scale) are shown in Table 4.

As seen in the Table 4, the flexural strength of composite increases with increasing percentage of halogenated epoxy resin in unsaturated polyester resin. Hardness of composite material decreases with increasing percentage of halogenated epoxy resin in unsaturated polyester resin whereas impact strength of the composite material increases with increasing percentage of epoxy resin in unsaturated polyester resin. This is due to the addition of low molecular weight epoxy resin, which is a straight

| Material                        | Wt. % of Fire retardant additive |
|---------------------------------|----------------------------------|
| UPR(gm)                         | 0% 5% 10% 15% 20%                |
| Glass fibre (gm)                | 50 51 50 55 54                   |
| Fire retardant additive (gm)    | 48 49 55 53 50                   |
| Benzoyl peroxide (2%) (gm)      | 0 2.5 4.9 7.60 10                |

Table 1: Formulation of the UPR- Glass fibre composite

| Functional group | Observed value (cm⁻¹) | Standard value (cm⁻¹) |
|------------------|-----------------------|-----------------------|
| Ar - C - Hstr    | 3079.28               | 3010-3090             |
|                  | 3442.64               | 3300-3600             |
|                  | 2878.22               | 2800-2950             |
|                  | 1724.18               | 1700-1725             |
|                  | 1041.81               | 1020-1080             |
|                  | 1071.97               |                       |
|                  | 744.1                 | 700-800               |
|                  | 780.09                |                       |
|                  | 704.04                |                       |
Table 3: IR Spectra of Epoxy resin

| Functional group | Observed value (cm\(^{-1}\)) | Standard value (cm\(^{-1}\)) |
|------------------|-------------------------------|-------------------------------|
| strAr-C-H        | 3079.28                       | 3010-3090                    |
| str-OH           | 3391                          | 3300-3600                    |
| str-CH           | 2934                          | 2800-2950                    |
| strC=H           | 1720.41                       | 1700-1725                    |
| Asym stre        | 1270                          |                               |
| Sym stre         | 1252                          | 1200-1280                    |
| Asym stre        | 1065                          | 1020-1080                    |
| Ar-CH            | 738                           | 700-800                      |
| C-Br             | 643                           | 650                           |

Table 4: Mechanical Properties UPR- Glass fibre composite

| Specimen code | Flexural strength Kg/cm\(^2\) | Izod impact strength J/M | Rockwell hardness R-scale 150 kg load |
|---------------|-------------------------------|--------------------------|--------------------------------------|
| UPS-1         | 410.41                        | 116.5                    | 160                                  |
| UPS-2         | 491.33                        | 200.0                    | 137                                  |
| UPS-3         | 578.71                        | 217.3                    | 44                                   |
| UPS-4         | 614.95                        | 254.5                    | 28                                   |
| UPS-5         | 620.56                        | 260.2                    | 20                                   |

Table 5: Fire retardant Properties

| Specimen Code | LOI value (in %) |
|---------------|------------------|
| UPS-1         | 18               |
| UPS-2         | 21               |
| UPS-3         | 23               |
| UPS-4         | 27               |
| UPS-5         | 29               |

Composites was 18-29. Material is normally considered as flame resistant if LOI is greater than 26. Thus the results of present study are in good agreement with the reported values. The result clearly indicates that the composites of the present study can be used in fire resistance application. The presence of glass fiber in the composite panel increases LOI values since the glass, at present, acts as physical barrier against the flame. The flame retarded formulation (UPR – 20% halogenated epoxy resin) shows the highest LOI value resulting from the synergistic work of additives. Composites prepared using UPR and epoxy resin gives good result. The LOI values of the composites are shown in Table 5.
Scheme 1: Preparation of Polyester Resin

Scheme 2: Preparation of Halogenated Epoxy Resin
Fig. 1: IR Spectra of Polyester resin

Fig. 2: IR Spectra of Epoxy resin
CONCLUSION

Halogenated epoxy resin and unsaturated polyester resin were synthesized as per the reported procedures\textsuperscript{12-13}. The synthesized tetrabromobisphenol-A based epoxy was added in proportions of 0, 5, 10, 15 and 20\% to the synthesized unsaturated polyester resin. The composite of these samples were prepared with glass fibre. These composites were then tested for various mechanical properties like Rockwell hardness, impact strength and flexural strength. It was observed that the addition of halogenated epoxy to unsaturated polyester resulted in the increase of flexural and impact strength (Figs. 3-4) while a decrease in Rockwell hardness was observed (Fig 5). This was due to the addition of low molecular weight epoxy resin, which is a straight chain polymer that increases flexibility, and as it is not crosslinked, it decreases the hardness. The LOI of the unsaturated polyester...
varies from 18-29. The flame retarded formulation (UP resin-15% halogenated epoxy resin) shows the highest LOI value (Fig 6) resulting from the synergistic work of additives.

ACKNOWLEDGEMENT

Authors are also very much grateful to Charutar Vidya Mandal, Vallabh Vidyanagar for providing laboratory facilities and encouragement.

REFERENCES

1. Benny Cherian A., Lity Alen Varghese and Eby Thomas Thachil, *European Polymer J.* **43**: 1460 (2007).
2. Patel K. D. and Dholakiya B. Z., *Ultra Science* **17**(2): 185 (2005).
3. Patel K. D., Dholakiya B. Z. and Patel J. V., *Chemical Engineering World* **40**: No.7, 80 (2005).
4. Li Y., Mai Y. W. and Ye L., *Compos. Sci. Technol.* **60**: 2037 (2000).
5. Dash B. N., Rana A. K., Mishra H. K., Nayak S. K., Mishra S. C. and Tripathy S. S., *J. Appl. Polym. Sci.* **78**(9): 1671 (2000).
6. Mwaikambo L. Y. and Ansell M. P., *J. Appl. Polym. Sci.* **84**(12): 2222 (2002).
7. Donnell A. O., Dweib M. A. and Wool R. P., *Compos. Sci. Technol.* **64**: 1135 (2004).
8. Liliana Manfredi B., Exequiel Rodríγuez S. and Maria, *Polymer Degradation and Stability* **91**: 255 (2006).
9. Rodríγuez E., Petrucci R., Puglia D., Kenny J. M. and Vázquez A., *J. Comp. Mater.* **39**(3): 265 (2005).
10. Hayward G., Husbands M. J. and Standen C. J. S., *A manual of resins for surface coatings*, Vol. 3: SITA Technology Ltd., London, 109 (1994).
11. Patel K. D., *Intern. J. of polymeric Mater.* **29**: 221 (1995).
12. Patel K. D., *High performance polymers*. **8**: 301 (1996).
13. Durbetaki A., *Anal. Chem.* **28**: 2000 (1956).