

Filled and unfilled glass/jute-epoxy methacrylate of 1,1'-bis(4-hydroxy phenyl) cyclohexane composites: Mechanical and electrical properties

Jignesh V Patel, Jignesh P Patel, Ritesh D Bhatt & Parsotam H Parsania*

Polymer Chemistry Division, Department of Chemistry,
Saurashtra University, Rajkot 360 005, Gujarat, India
*E-mail: phparsania@aol.com, phparsania22@gmail.com

Received 12 February 2014; accepted 15 August 2015

Epoxy methacrylate of 1,1'-bis(4-hydroxyphenyl)cyclohexane has been synthesized and styrenated (EMAS) for the preparation of silica and calcium carbonate filled glass and jute composites. Both jute and glass composites displayed good tensile and flexural properties. Tensile strength is found to be improved, while flexural strength decreased due to rigid and brittle nature of the filled composites. Better improvement is observed for silica filled composites. Both tensile and flexural strengths of silica filled glass composites decreased with silica content in the composites. For calcium carbonate filled glass composites, tensile strength is found to increase with filler content up to 6% and then it is decreased with increasing filler content. For silica filled jute composites electric strength is found to increase with filler content. Calcium carbonate filled jute composites show electric strength to increase with filler content up to 6% and then it is found to decrease. For silica filled glass composites, electric strength is found to increase with filler content up to 4% and then it is decreased with filler content. For calcium carbonate filled glass composites, it is found to increase with filler content. Practically no effect of filler content is observed on volume resistivity of filled jute composites. Silica filler caused almost doubled improvement of volume resistivity. For calcium carbonate filled glass composites volume resistivity is found to increase with filler content. Comparatively calcium carbonate filled composites show better tensile and flexural properties than those of silica filled composites, while silica filled composites show somewhat better electrical properties than those of calcium carbonate filled composites. Composites may find their applications as low load bearing housing units in building and construction industries as well as in electrical and electronic industries as insulating materials.

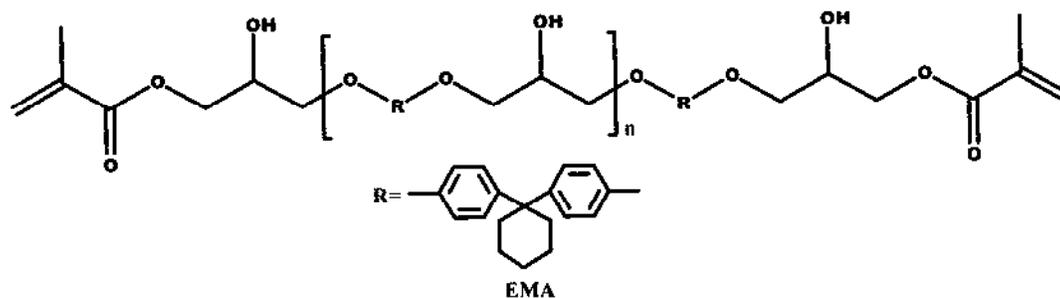
Keywords: Composites, Electrical properties, Fillers, Mechanical properties, Vinyl ester

Vinyl ester resins (VERs) can be synthesized from unsaturated polyester resins and typically consist of a bisphenol-A based dimethacrylate oligomer and styrene^{1,2}. The concentration of reactive monomer

diluent is an important consideration in the formulation of VERs for glass reinforced composites. Typical bisphenol-A based dimethacrylate oligomers are very viscous. Low concentrations of diluent hinder the wetting of the reinforcing fibers. While very high concentrations of diluent may result in inferior mechanical, thermal or chemical properties of the cured matrix. The formulation of a VER is thus a trade-off between its viscosity and the properties of the material, when cured. A third, often overlooked, consideration is the effect of diluent concentration on the kinetics of polymerization of the resin. Vinylester is a thermosetting polymer with very good chemical resistance, thermal stability, and mechanical strength³⁻⁵.

With the use of inorganic fillers, the toughening of thermo sets by means of inorganic particles has been shown to be very complicated⁶⁻⁹ and some aspects of it still appear controversial in the literature¹⁰. According to Yamamoto *et al.*¹¹ the structure and shape of silica particle have significant effect on the mechanical properties such as fatigue resistance, tensile and fracture behavior. The mechanical properties of polyester based hybrid composites are highly influenced by the type and content of the filler materials¹². Glass/vinyl ester composites with fillers are used in chemically corrosive environments such as chemical tanks and in structural laminates, where high degree of moisture resistance is desired¹³. Kumar *et al.*¹⁴ have studied the effect of various parameters on the drilling behavior of glass fiber/vinyl ester composites with and without fillers. Recently it has been reported that the characteristics of natural fiber-polymer composites containing fillers appear to be limited¹⁵⁻¹⁷.

To the best of our knowledge no work has been reported on silica and calcium carbonate filled jute and glass composites, which encouraged us to investigate present work. The main objective of the present work was to study the effect of varying proportion of silica (SiO₂) and calcium carbonate (CaCO₃) fillers on the mechanical and electrical properties of jute and glass composites of epoxymethacrylate of 1,1'-bis(4-hydroxyphenyl) cyclohexane EMA (Scheme 1).



Scheme 1

Experimental Section

Materials

Solvents and chemicals used were of laboratory grade and purified prior to their use¹⁸. Woven jute fabric (Brown jute, *Corchorus capsularis*) (Rajkot) and silane treated E-glass fabric (7 mil) (Unnati Chemicals, India) used in the present study were collected from local market. Epoxy resin of 1,1'-bis(4-hydroxyphenyl) cyclohexane (Epoxy equivalent weight²⁰ 809) was and purified according to our previous publication¹⁹. Styrene (SiscoChem, Mumbai), triethylamine (Spectrochem, Mumbai), hydroquinone (SiscoChem, Mumbai) methyl ethyl ketone peroxide (MEKP) and 6% cobalt naphthenate (free samples from EPP Composites, Rajkot) were used as received.

Synthesis of epoxy methacrylate

Into a 250 mL round-bottomed flask containing 40 g epoxy resin, 50 mL 1,4-dioxane, 16 mL methacrylic acid, 0.5 g hydroquinone and 2 mL triethylamine was placed in an oil bath. The reaction mass was refluxed for 2.5 h for desired acid value (< 2) and cooled to room temperature. Semi solid epoxymethacrylate was isolated from cold water, filtered, washed well with sodium bicarbonate solution and distilled water till unreacted acid was removed completely and dried at 50°C in an oven. The resin is soluble in chloroform, acetone, 1,4-dioxane, dimethylformamide, dimethylacetamide, etc. The resin was purified three times by dissolving in 1,4-dioxane and precipitating in large excess of water. Here after resin is designated as EMA. 250g EMA and 110 mL styrene (40%) were dissolved in chloroform. The resultant styrene solution is designated as EMAS.

Fabrication of jute and glass composites

For the fabrication of filled and unfilled Jute/Glass-EMAS composites (Table 1), required quantities of EMAS (70% of reinforcing fibers) and filler were

Table 1 — Experimental details of fabrication of filled and unfilled Jute/Glass-EMAS composites.

Composite	Fiber, g	EBCMASt, g	Filler, g
J-EMAS	120	85	0
J-EMASS-2	140	98	1.96
J-EMASS-4	142	99.5	3.98
J-EMASS-6	137	96	5.76
J-EMASS-8	158	111	8.88
J-EMASS-10	146	102	10.20
J-EMASC-2	145	102	2.04
J-EMASC-4	148	103.6	4.14
J-EMASC-6	147	103	6.18
J-EMASC-8	145	102	8.16
J-EMASC-10	147	103	10.30
G-EMAS	140	98	0
G-EMASS-2	110	77	1.54
G-EMASS-4	118	82.6	3.30
G-EMASS-6	111	77.7	4.66
G-EMASS-8	109	76.3	6.10
G-EMASS-10	110	77	7.70
G-EMASC-2	115	80.5	1.61
G-EMASC-4	114	79.8	3.19
G-EMASC-6	115	80.5	4.83
G-EMASC-8	109	76.3	6.10
G-EMASC-10	110	77	7.70

dissolved into a 500 mL beaker containing 100-130 mL chloroform at room temperature and solution was stirred mechanically for 15 min to disperse filler in the resin matrix. To this solution 1% (total mass of matrix material) each of methylethyl ketone peroxide (initiator) and cobalt naphthenate (promoter) were mixed well. The resultant solution was applied to 21cm X 21cm jute/glass fabric by a smooth brush and prepregs were allowed to dry in sunlight for about 15 min. Eight jute/Ten glass prepregs were staked one over the others and pressed between two preheated stainless steel plates under hydraulic pressure. Silicone spray was used as a mold releasing agent. The temperature was increased slowly to 110°C and

Table 2 — Mechanical and electrical properties of filled and unfilled Jute/Glass-EMAS composites.

Composite	Tensile strength, MPa	Tensile modulus, MPa	Flexural strength, MPa	Flexural modulus, MPa	Electric strength, kV/mm	Volume resistivity, Ohm cm
J-EMAS	34.5	2628.4	32.3	2105.1	1.6	5.9 X 10 ¹²
J-EMASS-2	35.2	2018.3	22.5	3268.8	1.1	1.7 x 10 ¹²
J-EMASS-4	34.1	2177.6	20.1	2944.9	1.4	1.4 x 10 ¹²
J-EMASS-6	44.7	3255.0	22.7	2995.7	2.5	1.4 x 10 ¹²
J-EMASS-8	36.6	3221.6	19.8	2024.8	3.9	1.6 x 10 ¹²
J-EMASS-10	39.7	3218.9	19.2	2228.6	4.4	1.6 x 10 ¹²
J-EMASC-2	28.7	2532.3	21.6	1482.7	3.1	1.4 x 10 ¹²
J-EMASC-4	57.1	3697.3	43.1	3161.0	2.9	1.4 x 10 ¹²
J-EMASC-6	53.3	3899.0	39.6	3363.5	3.4	1.3 x 10 ¹²
J-EMASC-8	50.8	2602.2	32.2	3169.2	1.5	1.4 x 10 ¹²
J-EMASC-10	44.6	3886.2	29.6	3604.3	2.5	1.4 x 10 ¹²
G-EMAS	220.9	8430.3	101.6	11777.6	2.1	4.5 X 10 ¹³
G-EMASS-2	212.3	8362.1	102.5	13678.3	2.8	11.7 x 10 ¹³
G-EMASS-4	221.7	8407.9	93.2	10738.2	5.9	9.6 x 10 ¹³
G-EMASS-6	216.6	8238.8	77.4	9699.4	4.8	14.4 x 10 ¹³
G-EMASS-8	177.3	4565.6	68.0	7986.2	5.3	11.1 x 10 ¹³
G-EMASS-10	162.5	3299.8	81.5	10194.4	4.6	8.7 x 10 ¹³
G-EMASC-2	227.8	7771.0	62.9	12224.1	3.2	2.9 x 10 ¹³
G-EMASC-4	240.7	8105.2	101.7	12922.0	4.1	3.2 x 10 ¹³
G-EMASC-6	242.2	8726.2	109.2	13532.2	4.5	3.3 x 10 ¹³
G-EMASC-8	232.4	9732.1	98.4	10566.2	4.8	4.1 x 10 ¹³
G-EMASC-10	226.1	10005.1	93.2	10294.8	5.6	4.8 x 10 ¹³

pressure to 2 Bar and kept for 5h, cooled to room temperature. Resultant composite sheet was peeled and edges were machined. Hereafter jute and glass composites are designated as J-EMASS-2 to J-EMASS-10 and G-EMASS-2 to G-EMASS-10 (silica filled); J-EMASC-2 J-EMASC-10 and G-EMASC-2 to G-EMASC-10 (calcium carbonate filled). Numerical figures indicate filler content in the composites.

Measurements

The tensile strength (ISO/R 527-1996 Type-I), flexural strength (ASTM-D-790-2003), electric strength (IEC-60243-Pt-1-1998) and volume resistivity (ASTM-D-257-2007) measurements were made on a Shimadzu Autograph Universal Tensile Testing Machine, Model No. AG-X Series at a speed of 10 mm/min, a high voltage tester (Automatic Electric-Mumbai) in air at 27°C by using 25/75 mm brass electrodes and a Hewlett Packard high resistance meter in air at 25°C after charging for 60 sec at 500 V DC applied voltage, respectively. Average of five measurements was considered.

Results and Discussion

Mechanical and electrical properties

Comparative mechanical and electrical properties of silica and calcium carbonate filled and unfilled

Jute/Glass-EMAS composites are presented in Table 2. Both jute and glass composites possess good tensile and flexural properties. Observed irregularity in tensile and flexural properties is probably due to visible phase separation in the composites and hence uneven distribution of filler particles resulting into variation in the properties. The maximum improvement in tensile strength of the jute composite is ~30%, when SiO₂ content in the composite was 6% and beyond that it is decreased further. Flexural strength decreased with SiO₂ content and maximum reduction of ~41% was observed for 10% SiO₂ content in the composite.

The maximum improvement in tensile and flexural strengths of the CaCO₃ filled jute composite is of ~66% and ~33%, respectively, when filler content was 4% and beyond that both decreased further.

The tensile property of SiO₂ filled glass composites practically remained constant, when SiO₂ content in the composite was 4% and then after it further decreased with SiO₂ concentration. The maximum reduction in tensile strength of ~26% is observed for 10% filler concentration. Flexural strength decreased to ~20%, when filler content in the composite was 10%. CaCO₃ filler caused overall improvement of

tensile property of the glass composite. The maximum tensile improvement in tensile strength of CaCO_3 filled glass composite was ~10%, when CaCO_3 content in the composite was 6% and beyond that it decreased further with filler concentration. Flexural property of the CaCO_3 filled composite remained practically constant upto 4%. CaCO_3 filled glass composite flexural strength is improved to ~7% and decreased to ~8% for 10% CaCO_3 filled glass composite.

In accordance to tensile strength, J-EMAS also showed maximum improvement in tensile modulus of ~23%, when SiO_2 content in the composition was 6% and beyond that it decreased and remained constant. Similarly CaCO_3 filled J-EMAS composites also showed improvement in tensile modulus. The maximum improvement of ~85% is observed when CaCO_3 content in the composite was 6%.

Practically no change in tensile modulus observed upto 4% SiO_2 content in the composite, and beyond that concentration drastic reduction in tensile modulus is observed with SiO_2 content. The maximum reduction of ~61% is observed for 10% SiO_2 filled glass composite. CaCO_3 filled glass composites showed improvement in flexural modulus upto 6% CaCO_3 and beyond that it decreased. CaCO_3 filler caused maximum improvement in flexural modulus of ~15% in flexural modulus, when CaCO_3 content was 6%. Increase of tensile strength and decrease of flexural strength is mainly due to improved interfacial adhesion (H-bonding) among filler, fiber and matrix). Due to interfacial adhesion composites lose their stiffness and as a result flexural property decreases and modulus increases. Thus, silica and calcium carbonate filled J-EMAS and G-EMAS showed good mechanical properties.

The mechanical properties of the composites depend upon type, nature of fillers, fiber and matrix, their content, degree of resin cure, arrangement of fibers within the composites, interfacial adhesion, compatibilizer, temperature, humidity, sample preparation, test method, etc.

J-EMAS showed increase in electric strength beyond 2% SiO_2 content in the composite. The maximum improvement in electric strength of ~175% is observed for 10% SiO_2 filled jute composite. CaCO_3 filled J-EMAS showed improvement in electric strength except J-EMAS-CC-8. The maximum improvement of ~113%, when CaCO_3 content was 6% and beyond that it was further decreased.

Silica and calcium carbonate fillers caused drastic improvement in electric strength of G-EMAS. The maximum improvement of 181% was observed, when SiO_2 content was 4% and beyond that it was further decreased. Similarly 6% CaCO_3 filled G-EMAS showed improvement and beyond that concentration it was remained practically constant. The maximum improvement of ~114% was observed.

Silica and calcium carbonate fillers caused drastic reduction of 71-76% in volume resistivity of J-EMAS. SiO_2 filled G-EMAS showed improvement in volume resistivity and maximum improvement of ~220% was observed, when SiO_2 content was 6% and beyond that it was found to decrease. CaCO_3 filled G-EMAS showed decrease of volume resistivity upto 8% CaCO_3 content and beyond that it was increased.

Electrical properties of the composites depend upon molecular architecture, nature of the filler, fiber, matrix, testing conditions and method, impurities, electrode geometry, etc. In present case both the fillers influenced electrical properties of the filled composites. Silica filled glass composites showed better electrical properties as compared to G-EMAS.

Filled jute and glass composites showed good electric strength as compared to unfilled composites. Silica and calcium carbonate filled J-EMAS composites showed much lower volume resistivity than that of unfilled composites probably due to more polar nature of the jute, matrix and filler. Silica filled glass composite showed much better volume resistivity than that of unfilled glass composite due to neutralization of partial charges present in the composite. In case of CaCO_3 filled glass composite volume resistivity decreased because of polar nature of glass, filler and matrix. Thus, both fillers affected electrical properties of jute and glass composites. Fairly good electric strength and volume resistivity of filled jute and glass composites signify their industrial importance as insulating materials for electrical and electronic industries.

Conclusion

Both jute and glass composites displayed good tensile and flexural properties. Tensile strength is improved, while flexural strength decreased due to rigid and brittle nature of the filled composites. Better improvement is observed for silica filled composites. Both tensile and flexural strengths of silica filled glass composites decreased with silica content in the composites.

For calcium carbonate filled glass composites, tensile strength is found to increase with filler content up to 6% and then it is decreased with increasing filler content.

For silica filled jute composites electric strength is found to increase with filler content. Calcium carbonate filled jute composites showed electric strength to increase with filler content up to 6% and then it is found to decrease. For silica filled glass composites, electric strength is found to increase with filler content up to 4% and then it is decreased with filler content. For calcium carbonate filled glass composites, it is found to increase with filler content. Practically no effect of filler content is observed on volume resistivity of filled jute composites. Both fillers influenced volume resistivity considerably. Silica filler caused almost doubled improvement of volume resistivity. For calcium carbonate filled glass composites volume resistivity is found to increase with filler content.

Comparatively calcium carbonate filled composites showed better tensile and flexural properties than those of silica filled composites, while silica filled composites showed somewhat better electrical properties than those of calcium carbonate filled composites.

Acknowledgements

Authors are thankful to director, ERDA Vadodara for electrical testing and Council of Scientific and Industrial Research for major research project funding (01(2440)/10/EMR-II, Dt. 28-12-10).

References

- 1 O'Hearn T P, *Engineering Plastics Engineered Materials Handbook*, Vol 2 (USA: ASM International), (1988) 272.
- 2 Peters S T, *Polyester and Vinyl ester Resins, Handbook of composites*, (Chapman & Hall, London) 1998.
- 3 Gryshchuk O, Karger-Kocsis J, Thomann R, Konya Z & Kiricsi I, *Compos Part A: Appl Sci Manuf*, 37 (2006) 1252.
- 4 Lee J & Yee A F, *Polymer*, 42 (2001) 577.
- 5 Fumito Y, Nozomu S, Masayoshi I & Hiroyuki K, *Polymer*, 42 (2001) 9523.
- 6 Metin S, *Compos Part-B Engg*, 59 (2014) 12.
- 7 Zhu H G, Liu M Y, Yuen R K K, Leung C K Y & Kim J K, *J Compos Mater*, (2013) DOI:10.1177/0021998312469990.
- 8 Imanika M, Takeuchi Y, Nakamura Y, Nishimura A & Lida T, *Int J Adhes*, 21 (2001) 389.
- 9 Wang H, Bai Y, Liu S, Wu J, & Wong C P, *Acta Mater*, 50 (2002) 4369.
- 10 Kawaguchi T & Pearson R A, *Polymer*, 44 (2003) 4239.
- 11 Yamamoto I, Higashihara T & Kobayashi T, *J Soc Mech Eng Int J Ser A*, 46 (2003) 145.
- 12 Patnaik A, Satapathy A, Mahapatra S S & Dash R R, *J Reinf Plast Compos*, 28 (2009) 1305.
- 13 Chauhan S, Kumar A, Patnaik A, Satapathy A & Singh I, *J Reinf Plast Compos*, 28 (2009) 2645.
- 14 Kumar S, Chauhan S R, Rakesh P K, Singh I & Davim J P, *Mater and Manuf Proces*, 27 (2012) 314.
- 15 Shao-Yun F, Xi-Qiao F, Bernd L & Yiu-Wing M, *Compo Part B: Engg*, 39 (2008) 933.
- 16 Kumar R, Yakabu M K & Anandjiwala R D, *Compos A Appl Sci Manuf*, 41 (2010) 1620.
- 17 Cho J, Joshi M S & Sun C T, *Compos Sci and Technol*, 66 (2006) 1941.
- 18 Vogel A I, Furniss B S, Hannaford A J, Smith P W G & Tatchell A R, *Vogel's Textbook of Practical Organic Chemistry*, 5th Edn, (Longman Scientific and Technical, New York, NY) 1998.
- 19 Sanariya M R, Godhani D R, Baluja S & Parsania P H, *J Polym Mater*, 15 (1998) 45.
- 20 Adroja P P, Koradiya S B, Patel J P & Parsania P H, *Polym Plast Technol Eng*, 50 (2011) 52.