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Syntheses of hexafunctional epoxy resin of bisphenol-C-formaldehyde and unsaturated polyester resin for the fabrication of jute and glass hybrid composites and evaluation of mechanical, electrical and water absorption characteristic properties

Jignesh P. Patel and **Parsotam H. Parsania***

Polymer Chemistry Division, Department of Chemistry, Saurashtra University, Rajkot - 360005, Gujarat, India

*E-mail: phparsania@aol.com, phparsania22@gmail.com
*Tel. and fax: +91-281-2577633

ABSTRACT

Hexafunctional epoxy resin of bisphenol-C-formaldehyde (HEBCF) and unsaturated polyester resin of maleic anhydride and propylene glycol (PER) were synthesized and used for the preparation of jute and glass hybrid composites. The composites were prepared by hand layup followed by compression molding technique. Both types of the hybrid composites possess good mechanical properties. G-HEBCF-PER possesses almost doubled mechanical properties than J-HEBCF-PER except Barcol harness, which is comparable. G-HEBCF-PER and J-HEBCF-PER possess moderate electrical properties due to their polar nature. G-HEBCF-PER and J-HEBCF-PER possess excellent hydrolytic stability, high water absorption tendency (~ 18%) and long equilibrium time (456h) due to presence of hydrophilic hydroxyl and other polar groups in the hybrid composites. The hybrid composites may be useful for low load bearing and marine applications.

***Keywords*:** multifunctional epoxy resin; unsaturated polyester resin; hybrid composite; mechanical and electrical properties; hydrolytic stability

1. INTRODUCTION

Epoxy resins have been widely applied in many areas such as aerospace and electronics industries in the form of surface coatings, structural adhesives, advanced composites and packaging materials due to their well-balanced properties. For example, epoxy resins possess excellent thermal stability, moisture resistance, chemical stability, superior electrical and mechanical properties and good adhesion to many substrates [1–4]. Multifunctional epoxy resins are well known for their improved mechanical, chemical, thermodynamic and electrical properties [5-8]. Other advantages of multifunctional epoxy resins are their high glass transition temperatures, high decomposition temperatures, long term high temperature performance and good wet strength performance. Multifunctional epoxy resins have two important limitations because of their intrinsic brittle nature and considerable moisture absorption tendency from environment, which adversely affect most physico-mechanical properties of the fabricated articles. Both these drawbacks increase by enhancing the crosslink density of the network.

Epoxy based fibre composites have become more commonly used in automobile, electronic devices, construction and aerospace industries. This is attributed to the attractive mechanical properties, dimensional stability and corrosion resistance of the composites [9-12]. Recently epoxy based hybrid composites have been extensively used in many engineering and industrial applications. For the best choice of load bearing complex engineering applications superior adhesive properties and better mechanical strength are the key factors for the composite materials.

In comparison with the synthetic fibre composites; natural fibres are characterized by their attractive price, low density and lower abrasion. The energy consumption needed for production of synthetic fibres is much more than that needed for a similar quantity of natural fibres [13]. Unlike the synthetic fibres, natural fibres have a wide variation in diameter and length, which in turn affects the composite expected mechanical behaviour. The variation in dimensions is contributed to fibre type, fibre maturity, harvesting time as well as processing methods adopted for the extraction of fibres, which all affect the diameter, stability of the fibre. Source, age, separating techniques, moisture content and the history of fibre also play an important role in the filament and individual fibre properties [14,15]. The implementation of natural fibres in thermoplastic composites is attractive for different industrial sectors like automobiles and construction [15].

Although the tensile strength and Young's modulus of jute are lower than those of glass fibres. The specific modulus of jute fibre is superior to that of glass when compared on modulus per cost basis, jute is far superior. The specific strength per unit cost of jute too approaches that of glass. Where high strength is not a priority, jute may be used fully or partially to replace glass fibre. The need for using jute fibres in place of the traditional glass fibre partly or fully as reinforcing agent in composites stems from its lower specific gravity (1.29 gcm^{-3}) and higher specific modulus (40 GPa) of jute compared with those of glass (2.5 $gcm^{-3}$and 30 GPa, respectively).

Apart from much lower cost and renewable nature of jute, much lower energy requirement for the production of jute (only 2% of that for glass) makes it attractive as a reinforcing fibre in composites. High moisture uptake (approx. 12.5% at 65% relative humidity and at 20 °C) is a major drawback of natural fibres as reinforcement due to presence of hydrophilic hydroxyl and other polar groups present in natural fibres. This leads to poor

wettability with resin and poor interfacial adhesion bond between fibre and hydrophobic matrices. Environmental performance of such composites is generally poor due to delamination under humid conditions. Thus, it is essential to pre-treat the fibre to reduce its moisture absorption and to improve its wettability with the resin.

To the best of our knowledge no work has been reported on jute and glass fibre reinforced hybrid composites of hexafunctional epoxy resin of bisphenol-C-formaldehyde in combination with unsaturated polyester resin. However few reports on other multifunctional epoxy resins found in the literature [5-8]. In present investigation it was thought to be of interesting to use hexafunctional epoxy resin of bisphenol-C-formaldehyde (Scheme-I) and unsaturated polyester resin (Scheme-II). Jute and glass hybrid composites were fabricated by hand layup followed by compression molding technique. The jute and glass composites are characterized for their mechanical, electrical and water absorption properties.

2. EXPERIMENTAL

2. 1. Materials

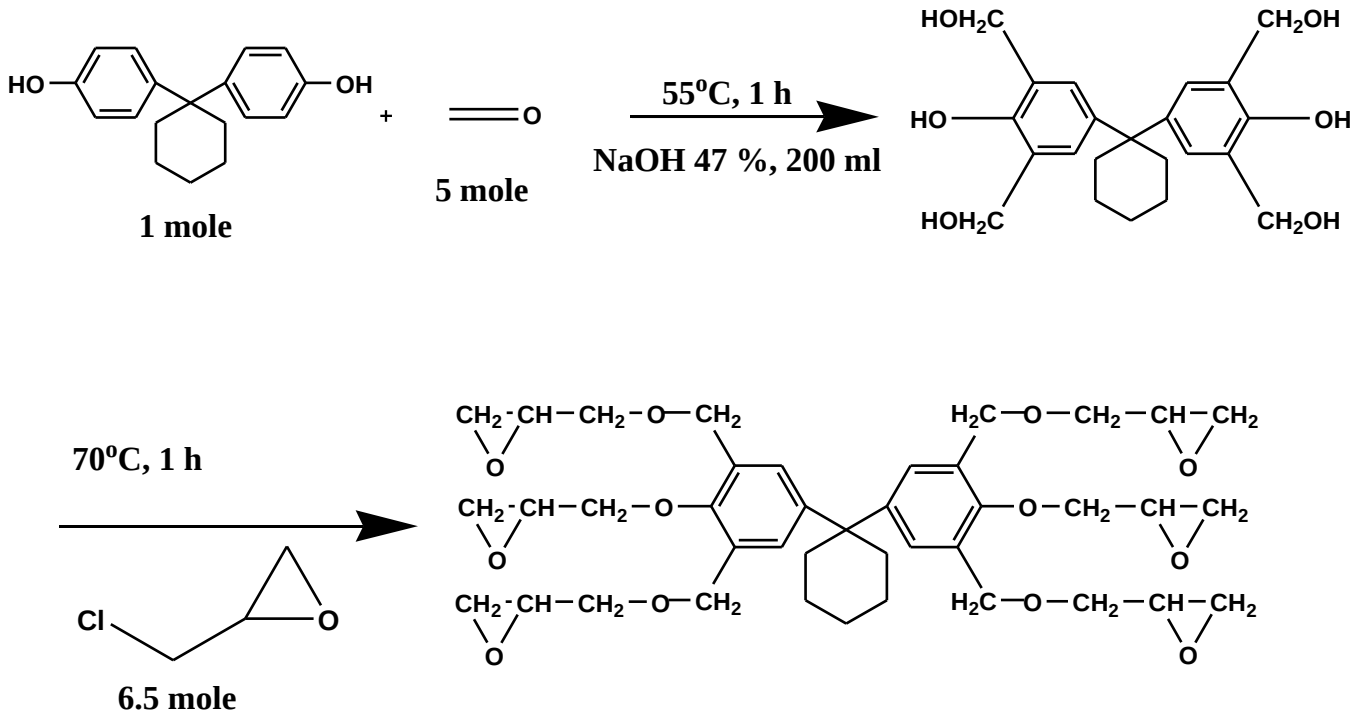
Solvents and chemicals used were of laboratory grade and purified prior to their use [16]. Bisphenol-C was synthesized and crystallized according to our previous publication [17]. Maleic anhydride, propylene glycol and toluene were supplied by Loba Chemie, Mubai. Formaldehyde, sodium hydroxide, methanol and 1,4-dioxane were supplied by was supplied Allied Chemicals Vadodara, Epichlrohydrin was supplied by Spectrochem, Mumbai. Woven silane treated E-glass fabric (7mil) was supplied by (Unnati Chemicals, India Ahmedabad) and jute fabric was purchased from local market, Rajkot.

2. 2. Synthesis of hexafunctional epoxy resin of bisphenol-C (Scheme I)

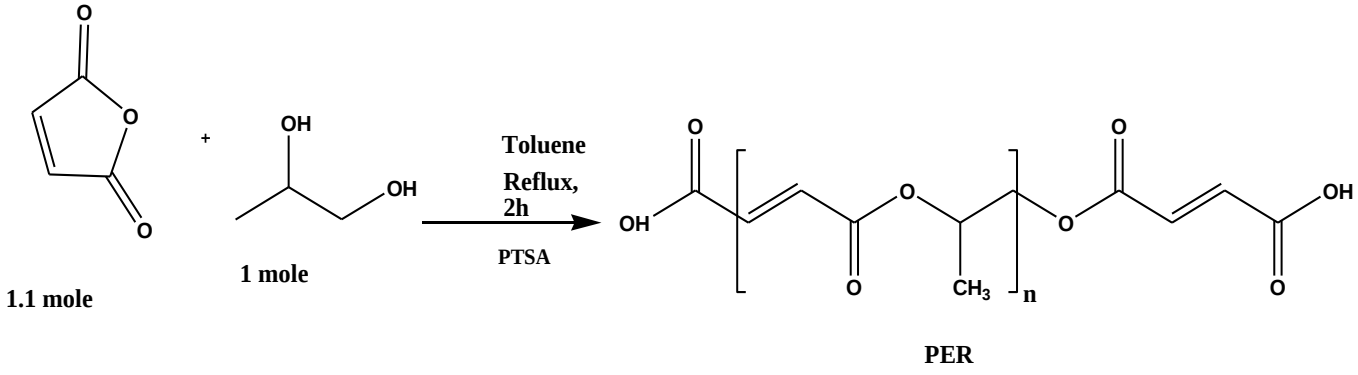
A 2 lit three neck flask equipped with a mechanical stirrer and condenser was placed into a thermostat bath. To this flask 1.0 mol (268 g) bisphenol-C, 5.0 mol (405.5 ml of 37-41 % fomaldehyde and 200 ml of 47% NaOH were placed and stirred at 55 °C for 1h. Then, 6.5 mol (510 ml) epichlorohydrin was added slowly with stirring and stirred the reaction mass at 70 °C for 1h, cooled to room temperature and neutralized using dilute hydrochloric acid solution. Separated brownish viscous resin was collected into a 2 lit plastic beaker and washed well with hot distilled water several times and dried at 70 °C. The resin is soluble in 1,4-dioxane, N,N-dimethylformamide and dimethylsulfoxide. Hereafter resin is designated as HEBCF. Epoxy equivalent of HEBCF was determined according to pyridine-pyridinium chloride method. Average epoxy equivalent weight of three measurements was 2128.

2. 3. Synthesis of unsaturated polyester resin (Scheme II)

A 2 lit three neck round bottomed flask equipped with a Dean and Stark apparatus, mechanical stirrer and thermometer was placed in an oil bath. To this flask 2.2 mol (205.6 g) maleicanhydride, 1.0 mol (76 ml) propyleneglycol and 0.5% (1.74 g) p-toluenesulphonic acid catalyst were charged and temperature was raised to reflux with stirring for 2h with continuous removal of released water. The yield was 365 g. The acid value was determined titrimetrically by using 0.1 M methanolic potassium hydroxide and phenolphthalein as an indicator. The average acid value of three measurements was 29.6 and carboxyl equivalent was 12.6 g/100 g resin.



Scheme – I. Synthesis of hexafunctional epoxy resin of bisphenol-C (HEBCF).



Scheme II. Synthesis of unsaturated polyester resin (PER).

2. 4. Fabrication of jute and glass hybrid composites

A 2lit beaker containing 425.6 g HEBCF was dissolved in 425.6 ml 1,4-dioxane. Into another beaker 100.8 g PER was dissolved in 100.8 ml 1,4-dioxane. Two solutions were mixed together and stored in a 2.5 lit bottle. The required quantity of mixed matrix material (Table 1) was applied to 24 cm x 24 cm glass/jute fabrics with a smooth brush. The solvent was allowed to evaporate at 100 °C for 1h and ten glass / eight jute prepregs were stacked one over the other between two teflon sheets which were kept between two preheated stainless

steel plates and pressed under 2 bar pressure at 120 °C for 6 h and at 150 °C for 2h. Hereafter hybrid composites are designated as G-HEBCF-PER and J-HEBCF-PER. The samples were machined according to standard test methods.

Table 1. Experimental detail of glass and jute hybrid composites.

Composite	Glass fabric, g	Jute fabric, g	Resin solution, ml
G-HEBCF-PER	134	-	268
J-HEBCF-PER	-	217	434

3. MATERIALS CHARACTERIZATION

Fourier transform infrared (FTIR) spectra (KBr pellet) of HEBCF-PER and J-HEBCF-PER were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 400 cm^{-1}.

Tensile (ASTM-D-638-01) and flexural (ASTM-D-790-03) tests were carried out on a W & T Avery LTD Type 1010 Model No E-46234 (Birmingham, England) at a speed of 10 mm/min. Izod impact (ASTM-D-256-96) measurements were carried out on an Izod Impact Tester, Type A1300, Model E-46204 (Birmingham, England).

Barcol hardness (ASTM-D-2583-95) tests were performed on a Barcol Hardness Tester Model 934-1. Dielectric strength (IEC-60243-Pt-1-1998) measurements were carried out on a high voltage tester (Rajsan electromech Makarpura, Baroda) and volume resistivity (ASTM-D-257-2007) measurements were carried out on a Hewlett Packard high resistance meter in air at 25 °C after charging for 60 sec at 500 V DC applied voltage. Water absorption (ASTM-D-570-98) study was carried out at 30 °C by a change in mass method.

4. RESULTS AND DISCUSSION

4. 1. Mechanical and electrical properties

The mechanical performance and durability of composite materials are mainly governed by types of reinforcement, the matrix, and interfacial bond strength [18]. Strength, stiffness, and stability of fibres and matrix are very important for long term service of composites. Tensile properties of materials are most widely useful for engineering design and understanding quality characteristics of polymeric materials.

Flexural properties are useful for quality control and classification of materials with respect to bending strength and stiffness. Impact strength is the ability of a material to resist fracture under applied stress at high speed. The hardness is related to the strength and elastic characteristics of the polymers.

The tensile strength, flexural strength, flexural modulus, impact strength and Barcol hardness of the glass and jute composites are presented in Table 2. It is observed that both J-HEBCF-PER and G-HEBCF-PER showed good above mentioned mechanical properties due

to good interfacial adhesion. G-HEBCF-PER showed approximately two times mechanical properties than J-HEBCF-PER except Barcol hardness. Improved flexural property is due to flexible PER blocks in the crosslinked resin matrix and as a result observed modulus was low in both the composites. The interaction of jute with resin is also confirmed by spectra of HEBCF-PER and J-HEBCF-PER (Figure 1).

The peak shape and shifting of OH and C=O stretching frequencies of HEBCF-PER from 3555, 3271 and 1732 cm^{-1} to 3545, 3341 and 1740 cm^{-1} in J-HEBCF-PER confirmed interaction of OH groups of jute with the OH and ester groups of the resin, i.e. H-bond formation. Mechanical properties of the composites depend upon nature of matrix material and reinforcement, interfacial adhesion, degree of cure, fillers, compatibilizers, humidity, temperature, test conditions, etc.

For engineering application of the material scratch and wear resistance are very important. International Cast Polymer Alliance (ICPA) [19] has recommended Barcol hardness between 45 and 65 for scratch and wear resistant materials. A lower number indicates incomplete cured material, while higher number indicates too brittle material [19]. The surface hardness also depends on the resin, concentration of filler materials and other factors. Barcol hardness of both the composites below recommended range signified under curing of HEBCF and therefore both the hybrid composites may not be very useful as scratch and wear resistant material.

Table 2. Mechanical, electrical and water absorption data of G-HEBCF-PER and J-HEBCF-PER.

Property	G-HEBCF-PER	J-HEBCF-PER
Thickness, mm	6.34	6.87
Tensile strength, MPa	76.3 ±1.3	34 ±1.7
Flexural strength, MPa	134 ±1.2	74.3 ±0.6
Flexural modulus, MPa	4210	2574
Impact strength, kgm^{-2}	40.3 ±2.1	20.7 ±2.1
Barcol hardness	35	28
Electric strength, $kVmm^{-1}$	8.36	5.63
Volume resistivity, Ωcm	3.7×10^{9}	2.4×10^{8}
%Water absorption@ 24h	9.23	13.36
% Equilibrium water absorption	18.2	18.4
Equilibrium water absorption time, h	456	456
Diffusivity Dx, $m^2 s^{-1}$, 10^{-12}	1.98	0.48

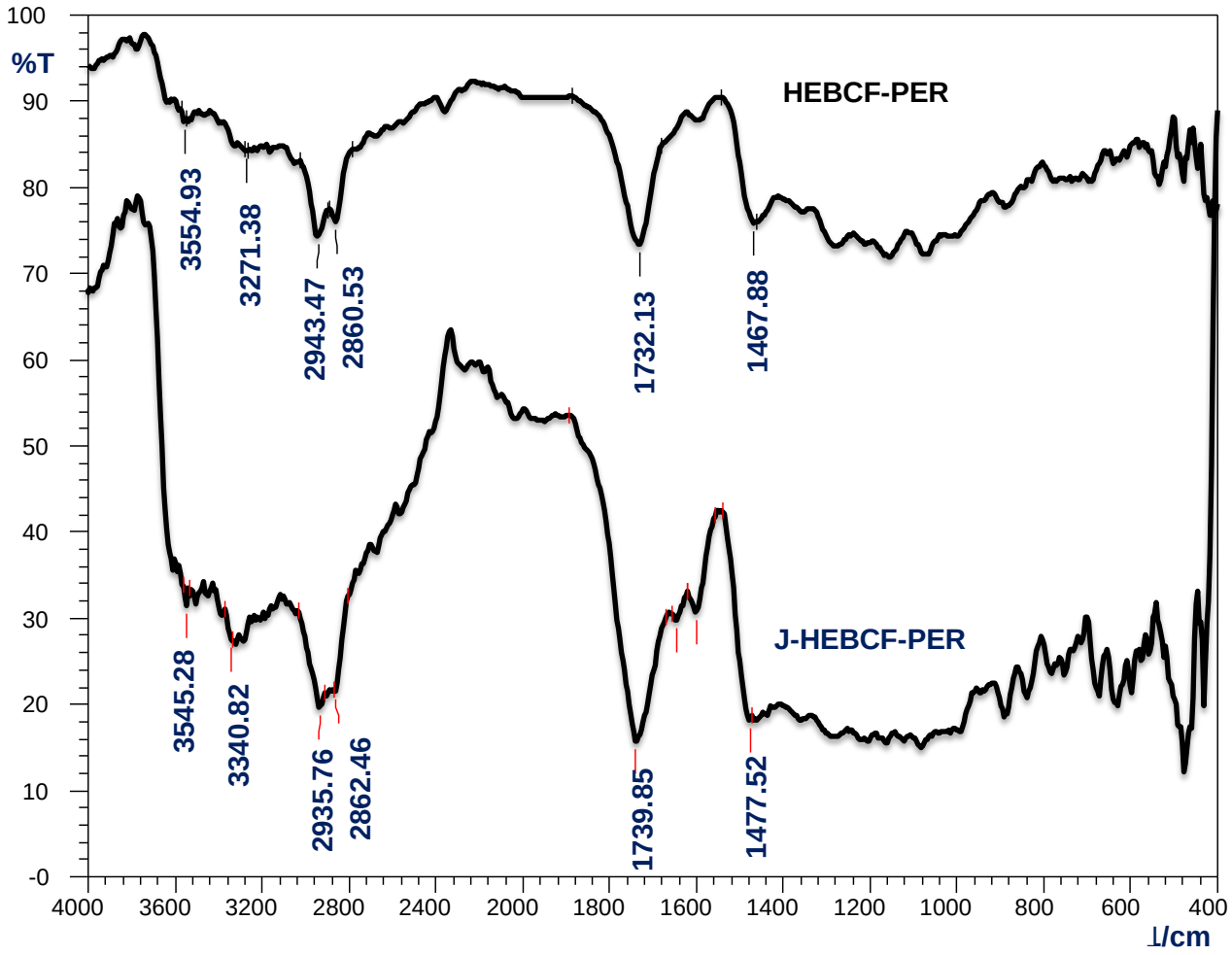


Figure 1. FTIR spectra of HEBCF-PER and J-HEBCF-PER.

Volume resistivity and electric strength data are useful for comparing relative insulation quality of material selection, to evaluate the effect of material composition and environment. Mechanical and electrical properties of the materials are useful to material scientists to design materials with specific properties.

Electric strength and volume resistivity data of G-HEBCF-PER and J-HEBCF-PER are presented in Table 2. It is observed that both the hybrid composites showed moderately good studied electrical properties due to presence of polar groups in the resins and jute fibre. G-HEBCF-PER showed 15.4 and 1.5 times volume resistivity and electric strength, respectively than that of J-HEBCF-PER.

Electrical properties of the fibre reinforced composites depend upon several factors like humidity, impurities, degree of resin cure, temperature, nature of resin, fillers and additives, geometry, electrode area and electrode material, sample thickness, time of voltage application, current frequency, and extent of ageing. Both the composites may be useful for low load bearing housing applications.

5. WATER ABSORPTION

The % water absorbed in the composites with the passage of time at 30 °C for G-HEBCF-PER and J-HEBCF-PER is presented in Figure 2 from which it is observed that the % water absorption increased with time, reached maximum and remained practically constant, when equilibrium was established. The % water absorption 24h, equilibrium water content and equilibrium time for both the composites are reported in Table 2. G-HEBC-PER (18.2%) and J-HEBCF-PER (18.4%) showed same water absorption tendency and equilibrium time (456h). Absorbed water plays a significant role in influencing mechanical behaviour and long-term durability of the polymers and polymer matrix composites. High water absorption tendency of G-HEBCF-PER and J-HEBCF-PER is mainly due to presence of polar hydrophilic hydroxyl groups present in HEBCF and jute, solvation phenomenon and probably also due to microcracks formation [20,21].

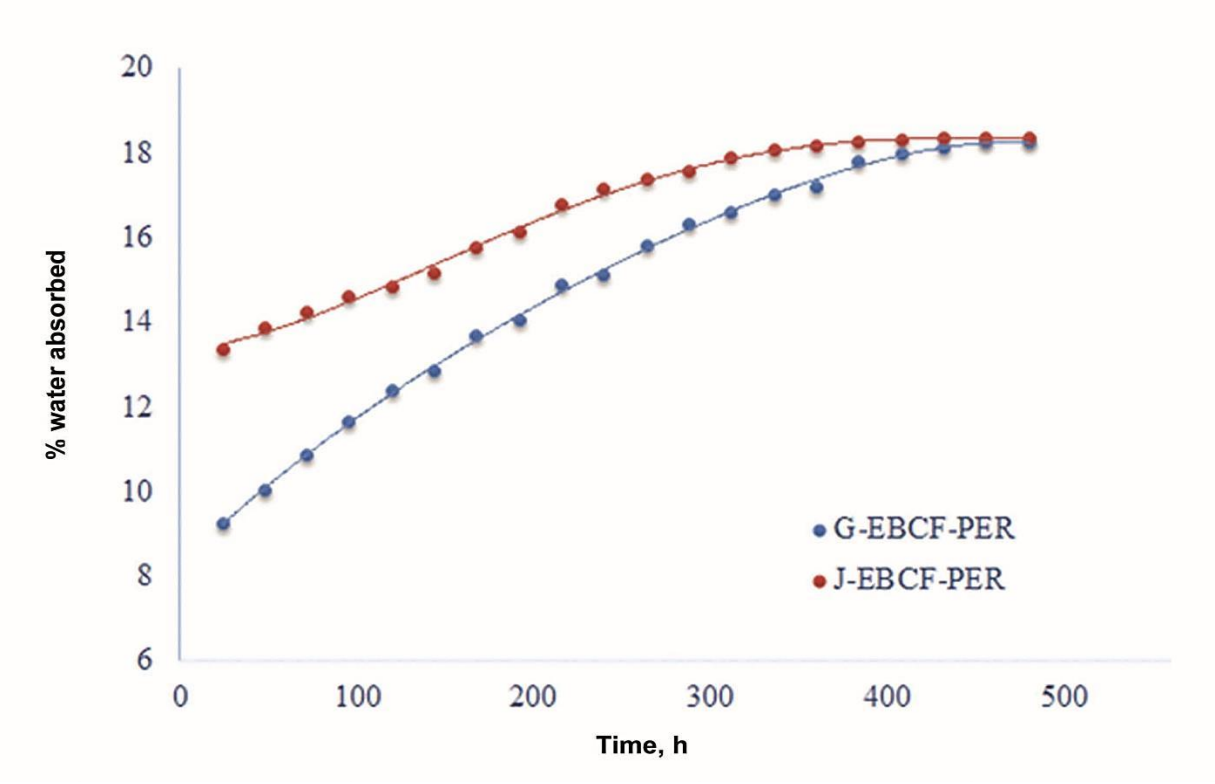


Figure 2. The plots of % water absorbed against time for G-HEBCF-PER and J-HEBCF-PER at 30 °C.

Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character. Viscoelastic nature of polymers and cracks are responsible for non-Fickian diffusion. Water absorption continues till the cell walls are saturated with water. Beyond saturation point, water exists as free water in the void structure leading to delamination or void formation [22].

Absorbed water leads to weakening of interface and accelerates delamination, which decreases the strength of the composites [23]. Absorbed water causes hydrolytic degradation of both matrix and interface during service [24].

Formation of voids and blistering result into high water absorption tendency [20,25]. Water absorption in fibrous composites depend upon temperature, fibre loading, fibre orientation, permeability of fibres, surface protection, area of the exposed surface, diffusivity, void content, hydrophilicity of the individual components, etc.

Assuming unidirectional diffusion, water absorption in semi-infinite plate exposed on both sides to the same environment was calculated according to Eq.1:

$$M = \frac{W_m - W_d}{W_d} X\ 100 \qquad \ldots 1$$

where: M = % water absorbed at time t, W_m = weight of moist sample and W_d = weight of dry sample. Diffusivity of water in the composites was determined according to Eqs. 2 and 3.

$$M = \frac{4M_m}{h}\sqrt{\frac{t}{\pi}}\sqrt{D_x} \qquad \ldots 2$$

$$D_x = \pi\left(\frac{h}{4M_m}\right)^2 (slope)^2 \qquad \ldots 3$$

where M_m = equilibrium water content, D_x = diffusivity, t = time (s) and h = sample thickness (m).

The diffusivity of water in the composites is reported in Table 2 from which it is observed that G-HEBCF-PER showed four times diffusivity as compared to J-HEBCF-PER probably due to void and microcracks formation in the glass composites. Excellent hydrolytic stability of both the composites suggested that composites may be useful for marine applications.

6. CONCLUSIONS

HEBCF showed good solubility in common solvents and high epoxy equivalent. Both the composites showed good mechanical and moderate electrical properties. Both composites showed high water absorption tendency, excellent hydrolytic stability and long equilibrium time due to presence of hydrophilic hydroxyl and other polar groups in the composites. The composites showed same water absorption behaviour and equilibrium time.

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References

[1] Lin C H, Wang Y R., Feng Y R., Wang MW., Juang TY. "An approach of modifying poly(aryl ether ketone) to phenol-containing poly(aryl ether) and its application in preparing high-performance epoxy thermosets." *Polymer* (2013) 54: 1612-1620.

[2] Li T, Qiu H J, Liu Y, Zhong X H, Yu Y F, Serra A. "Hyperbranched polyester as additives in filled and unfilled epoxy-novolac systems." *Polymer* (2013) 53: 5864-5872.

[3] Xu K., Chen M C., Zhang K, Hu J W. "Synthesis and characterization of novel epoxy resin bearing naphthyl and limonene moieties, and its cured polymer." *Polymer* (2004) 45: 1133-1140.

[4] Muthuvel M., Ranganath G, Janarthanan K, Srinivasan K. "Characterization study of glass fiber reinforced hybrid composite material". *International Journal of Engineering Research and Technololgy* (2013) 2: 335-344.

[5] Musto P. Martuscelli E. Ragosta, G. Mascia L. "Cure kinetics and ultimate properties of a tetrafunctional epoxy resin toughened by a perfluoro-ether oligomer". *Polymer* (2001) 42: 5189-5198.

[6] Xie M R, Wang Z G, Zhao Y F. "Synthesis and properties of a novel, liquid, trifunctional, cycloaliphatic epoxide." *Journal of Polymer Science Part A: Polymer Chemistry* (2001) 39: 2799-2804.

[7] Lin L L, Ho T H Wang C S. "Synthesis of novel trifunctional epoxy resins and their modification with polydimethylsiloxane for electronic application". *Polymer* (1997) 38: 1997-2003.

[8] Wang C S, Li M C. "Synthesis and modification of a naphthalene-containing trifunctional epoxy resin for electronic applications." *Journal of Applied Polymer Science* (1998) 70: 1907-1921.

[9] Srihari S, Revathi A and Rao RMVGK. "Hygrothermal effects on RT-cured glass-epoxy composites in immersion environments Part B: moisture absorption characteristics." *Journal of Reinforced Plastics and Composites* (2002) 21: 993-1001.

[10] Ellyin F and Rohrbacher C. "Effect of aqueous environment and temperature on glass-fibre epoxy resin composites." *Journal of Reinforced Plastics and Composites* (2000) 19: 1405-1427.

[11] Deng S and Ye L. "Influence of fibre-matrix adhesion on mechanical properties of graphite/epoxy composites: III. Impact on dynamic mechanical properties." *Journal of Reinforced Plastics and Composites* (2000) 19: 689-703.

[12] Patel VA, Bhuva BD and Parsania PH. "Performance evaluation of treated untreated jute carbon and glass carbon hybrid composites of bisphenol-C based mixed epoxy phenolic resins." *Journal Reinforced Plastics and Composites* (2009) 28: 2549-2556.

[13] Joshi SV, Drzal L, Mohanty A, Arora S. "Are natural fibre composites environmentally superior to glass fibre reinforced composites". *Composites Part A: Applied Science and Manufacturing.* (2004) 35(3): 371-376.

[14] Zimmermann T, Reimann P, Thommen V, Eckstein D. "Cellulose fibrils in wood cell walls and their potential for technical applications." *Empa Activities* (2006) 2007: 24.

[15] Mussig, J. "Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications; CV Stevens; Wiley: United Kingdom", (2010); Vol. 1, Chapter 2, 89-219.

[16] Vogel, AI.; Tatchell, AR.; Funis, BS.; "*Hannaford, AJ.; Smith, PW G. Vogel's Textbook of Practical Organic Chemistry, 5th Ed., Addison Wesley Longman Ltd., U. K"*. (1998), 395.

[17] Rao MV, Rojivadia AJ; Parsania PH. and Parekh HH. "A convenient method for the preparation of bisphenols". J. Indian Chem. Soc., (1987) 64: 758-59.

[18] Biro DA, McLean P, Deslandes Y. "Application of the microbond technique: Characterization of carbon fibre-epoxy interfaces." *Polymer Engineering & Science*. (1991) 31(17): 1250-1256.

[19] International Cast Polymer Alliance, *Solid Surface Properties and Applications*, ICPA, Arlington, (2003), 8 pp.

[20] Bao L-R, Yee AF. "Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fibre composites." *Polymer* (2002) 43(14): 3987-3997.

[21] Espert A, Vilaplana F, Karlsson S. "Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties." *Composites Part A: Applied Science and Manufacturing*. (2004) 35(11): 1267-1276.

[22] Gassan J, Bledzki AK. "The influence of fibre-surface treatment on the mechanical properties of jute-polypropylene composites." *Composites Part A: Applied Science and Manufacturing.* (1997); 28(12): 1001-1005.

[23] Collings T. "In Handbook of Polymer–Fibre Composites;" Jones FR, Ed. Longman Scientific and Technical: UK, (1994).

[24] Crank, J.; Park, G. S. "*Diffusion in Polymers, Academic Press: New York,"* (1968).

[25] Tyberg C, Bergeron K, Sankarapandian M, Shih P, Loos A, Dillard D, "Structure-property relationships of void-free phenolic–epoxy matrix materials." *Polymer*. (2000) 41(13): 5053-5062.

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