ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 4, Issue, 06, pp.067-071, June, 2012

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

EFFECT OF UP AND DOWN-THERMAL SHOCKS ON HYGROTHERMALLY CONDITIONED E-GLASS FIBER/EPOXY COMPOSITE

Ananta Prasad Chakraverty[1*], Upendra Kumar Mohanty[1] and Bibhuti Bhusan Biswal[2]

[1]Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, Odisha, India - 769008

[2]Department of Mechanical Engineering, National Institute of Technology, Rourkela, Odisha, India - 769008

ARTICLE INFO

Article History:
Received 24th March, 2012
Received in revised form
11th April, 2012
Accepted 17th May, 2012
Published online 30th June, 2012

Key words:
Glass fiber/epoxy composite, Inter laminar shear strength, Thermal shock, Glass transition temperature, fiber pull-out.

ABSTRACT

E-Glass reinforced epoxy composites are first exposed to an environment laden with moisture (hygrothermal; 60^0C, 95% humidity) and then to up and down-thermal shocks for different lengths of time. A 3-point bend test using INSTRON-1195 is carried out to estimate inter laminar shear strength (ILSS) values of the shock treated and untreated samples (after hygrothermal exposure) separately. Low temperature DSC is carried out to record the deviation in T_g, the glass transition temperature. Hygrothermal conditioning without thermal shock reveals a general trend of lowering of ILSS values with varied exposure times. Up and down-thermal shocks are seen to affect the ILSS values differently, the lowest T_g being recorded for samples exposed to up-thermal shock after hygrothermal conditioning. Scanning electron micrographs reveal the mode of failure which includes fiber fragmentation, fiber pull-out and fiber matrix debonding.

INTRODUCTION

Structural components made of glass fiber reinforced polymer (GFRP) composites exhibit low density, higher specific strength and stiffness, superior corrosion resistance, improved fatigue properties and design flexibility (Berketis *et al.,* 2008). Added to the above epoxy resin is the material of choice in advanced fiber reinforced composites as it delivers benefits like ease of processing, excellent adhesion to various types of reinforcements, low shrinkage during curing, good thermal and chemical resistance (Kelly and Zweben, 2000). It is on this count that these materials (GFRP composites) find excessive specific utility as aerospace materials, ship building materials, automotive materials and materials of choice in civil infrastructures.

An ambience laden with moisture is most degrading for the GFRP (Chakraverty, 2010) as unlike the hydrothermal exposure where the sample is actually immersed in water, here the interface between the composite and the ambience continuously changes giving a scope for higher rates of interactions causing greater uptake of moisture and accelerating the associated damage-intending processes. The effect becomes more severe with rise in temperature as well as humidity. The combined effect of moisture laden atmosphere and temperature is called hygrothermal effect (Ray *et al.,* 1991). The chief causes of degradation under hygrothermal exposure are plasticization, hydrolysis, saponification of the resin, fiber-matrix debonding as well as matrix microcracking. Also the glass fiber may show excessive pitting, etching and cracking (Karbhari *et al.,* 2000). The hygroscopic forces may enhance the annihilation of mechanical strength and thus are a matter of concern in modern design and life time estimation of composite components (Ray, 2006 a). The epoxy networks undergo a thermally assisted oxidative degradation promoted by thermo-hygrometric ageing (Ray, 2007 a). Also the combined effect of moisture and temperature significantly weakens the fiber and the matrix as well as the concerned interface. The moisture makes the matrix pliable which results in plasticization as a consequence of lowering of the glass transition temperature, thereby lowering the modulus of the composite material (Ray, 2004 a).

Moisture diffusion in GFRP composites is a thermally activated process. An increase in time of exposure and temperature accelerates the rate of absorption of moisture leading to a non-Fickian nature of diffusion process enhancing the process of deformation and loss of adhesion across the fiber-matrix interface (Assbee, 1993). Absorbed moisture in polymeric composites under humid atmospheric condition causes its dilatational expansion. The stresses associated with moisture induced expansion lower the structural durability and damage tolerance ability of the composite material (Ray, 2006 a). This may even cause breaking of the polymeric chain by swelling in addition to plasticization by lowering of glass transition temperature as pointed out earlier (Ray, 2004 b; Ray *et al.,* 2003). The differential thermal expansion coefficient is the prime cause of thermal shock in composite material (Ray,

Corresponding author: anantac8@gmail.com

2006 b). The variation of thermal expansion between fiber and polymer matrix is responsible for the creation of stresses at the interface. Composites may not allow the stresses to be relaxed in an environment where sudden fluctuation of temperature exists. The real time application of the composite thus involves considerations related to the response of composite materials to a combined effect of moisture and temperature namely the hygrothermal effect. In particular the hygrothermal ageing of the composites followed by up-thermal and down-thermal shocks which are expected to bring in thermo-mechanical degradation due to subsequent expansion and contraction of the matrix, demands greater concern. It is in this context that the present work is an attempt at evaluating the GFRP composite exposed to the excessive degrading effect of hygrothermal ageing coupled with up and down-thermal shocks.

METHODOLOGY

Hand laying method is adopted to fabricate the eighteen layered composite specimen using liquid epoxy resin (Araldite LY556) and woven E-glass fiber with a curing agent/hardener (diamine HY951). The cut samples are put in the hygrothermal chamber, in groups, for 2, 4, 6 and 8 days at a relative humidity of 95% and 60^0C temperature. The moisture gain is estimated through weighing, as a difference between the fix weights of the unexposed composite and exposed composite for the respective periods of exposure. The up-thermal shock consisted of exposure to -40^0C in a cryogenic chamber for 5, 10, 15 and 20 minutes followed by sudden exposure to $+50^0$C in an electric oven for 30 minutes. Similarly the down-thermal shock consists of $+50^0$C exposure for 5, 10, 15 and 20 minutes followed by sudden exposure to -40^0C for 30 minutes. ILSS of differently treated specimens are determined by a 3-point bend test using INSTRON-1195. The crosshead velocity of the machine is maintained at 1 mm/min. ILSS was calculated by the formula given in equation (1) (Bond *et al.,* 2002)

$$ILSS = 0.75 \times 1000 \times (p_b / b.t)\, N/mm^2 \text{ or (MPa)} \quad (1)$$

Where p_b = breaking load (load at rapture) in KN, b = width of the specimen in mm and t = thickness of the specimen in mm. The T_g is estimated using the alternating differential scanning calorimetry (ADSC module) on Mettler-Toledo 821 with intra cooler using STAR software in the temperature range of 30^0-150^0C. The fractured surface of the specimens is examined using SEM (JEOL, JSM-6480LV).

RESULTS AND DISCUSSION

Moisture gain

As shown in Fig 1 moisture gain increases with time of exposure. The initial absorption of moisture is a direct function of time of exposure, concentration dependent and obeys Fick's 2nd law (Springer *et al.,* 1976). With the lapse of time the rate of moisture peak up is enhanced, anomalous, can't be explained by Fick's law and non-Fickian. This is in the line with the findings of Kumar et al. (Assbee, 1993). The plot also shows a continuing uptake trend even after a continued hygrothermal exposure. This trend is indicative of supplementary mechanism of moisture intake with increased time of exposure. This is because longer exposures would cause greater degradation assisting moisture uptake, delaying the saturation level of moisture in the composite body.

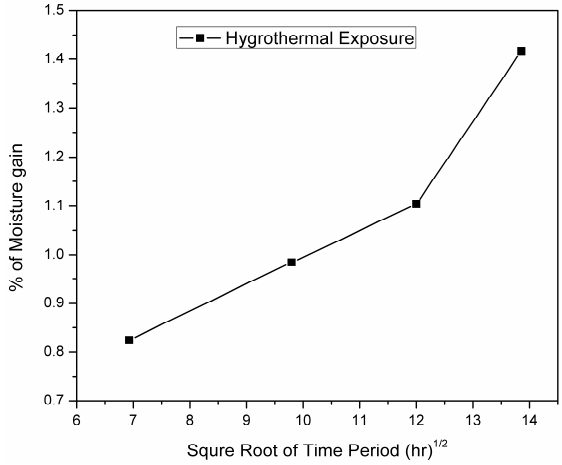

Fig. 1. Percentage of moisture gain for hygrothermally treated sample

ILSS with Hygrothermal exposure without thermal shock

As presented in Fig 2, ILSS of the treated samples show a general decreasing trend with increased exposure time.

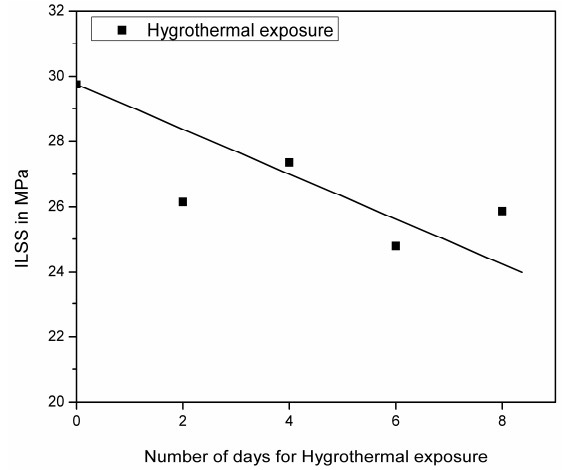

Fig. 2. Variation of ILSS of hygrothermally treated sample with time without thermal shock

This trend is attributed to the generation of double hydrogen bond in the epoxy chain. The covalent bonds between the siloxane back bone of the sizing material and the glass surface is replaced with hydrogen bonds between the oxygen atoms on the fiber glass surface, water molecules at the interphase and the hydroxyl groups on the sizing material; the replacement being caused by the ingression of moisture at the interphase (Abdel-Magid *et al.,* 2005). The loss of the covalent bonds at the interphase brings about a process of debonding of fibers from the matrix. In addition to fiber/matrix debonding microcracking in the matrix, fiber fragmentation, crack propagation etc. are caused and finally the ILSS value is lowered (Ray *et al.,* 2003). The presence of hydroxyl groups at the fiber/matrix interface helps form hydrogen bonds resulting in the weakening of the cross linking in the epoxy chain. The cross linking density decreases leading to generation of swelling stresses. Free volume inside the epoxy network increases, glass transition temperature is reduced and the

internal stresses built up during the processing of the composite are relieved. These effects make the matrix pliable causing plasticization (Ray *et al.,* 2006a; d'Almeida *et al.,* 2008). In addition to the above residual stresses are developed at the interface owing to the mismatching of the coefficient of expansion of the fiber and the polymeric-matrix. These mismatch stresses along with the internal stress relieved by plasticization weaken the thermoset resin and/or the interfacial region of laminates bringing about a general lowering of the ILSS of the composite.

ILSS with hygrothermal exposure and up-thermal shock

The experimental dada pertaining to the above is presented in Fig 3. The following are evident.

(i) The ILSS value exhibits a general increasing trend when the hygrothermally aged samples are subjected to the up-thermal shock for short durations.

(ii) A longer exposure to the up-thermal shock after hygrothermal treatment causes a decrease in the ILSS value in general.

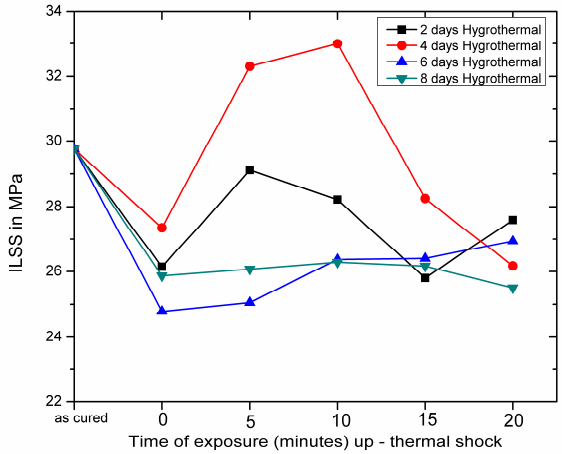

Fig. 3: Variation of ILSS of hygrothermally treated sample with the time of exposure of up-thermal shock

The increased trend of ILSS values on shorter duration of thermal shock may be attributed to the mitigation of the thermal stresses generated due to misfit of strains. On the other hand a prolonged exposure causes the deterioration of the mechanical properties as reflected by the decrease in the ILSS value. This is due to development of microcracks and crazing. More misfit stresses are generated due to differential coefficient of thermal expansion of the fiber and the matrix (Mishra *et al.,* 2010).

ILSS with hygrothermal exposure and down-thermal shock

The effect of down-thermal shock after hygrothermal exposure is illustrated in Fig 4. One has to take resort to many opposing processes responsible for the consequent increase/decrease of the ILSS when a down-thermal shock is considered. Here, after hygrothermal ageing for different lengths of time, the specimens are exposed to $+50^0$C for different lengths of time then suddenly put at -40^0C for 30 minutes. The opposing processes include enhancing of interfacial adhesion by mechanical locking due to frozen moisture; left-out porosity as a consequence of desorption of moisture during the heating cycle of the thermal shock; differential contraction during cryogenic conditioning resisting the debonding due to better adhesion at the interface (Kumar *et al.,* 2007; Ray, 2007 b); loosening of fiber-matrix contact due to relatively longer time of exposure resulting in higher moisture absorption that solidifies during cooling period; post curing shrinkage stresses caused due to hygroscopic swelling stress developed during hygrothermal exposure (Sharma *et al.,* 2008) and increase in cross linking density due to furthering of polymerization resulting in interfacial adhesion (Ray, 2004 a).

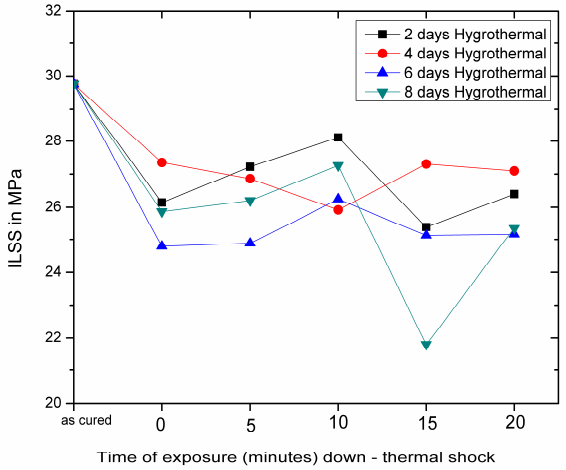

Fig. 4: Variation of ILSS of hygrothermally treated sample with the time of exposure of down-thermal shock

Glass Transition Temperature (T_g) and Up-thermal shock

Fig. 5 and Fig. 6 exhibit the variation of T_g with no-thermal shock and up-thermal shock after hygrothermal exposure, respectively.

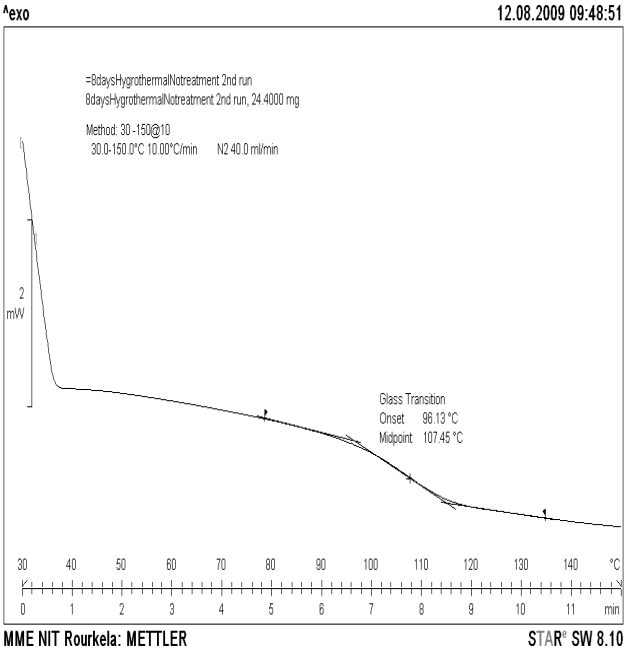

Fig 5: Glass transition temperature for 8 days hygrothermally treated sample for no-shock condition

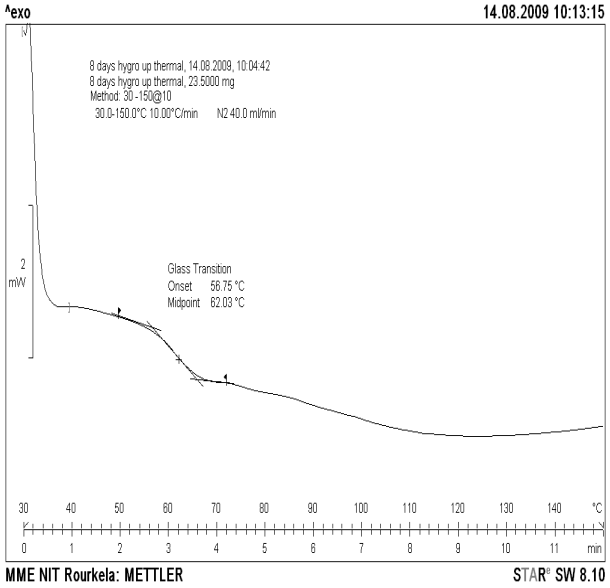

Fig 6: Glass transition temperature for 8 days hygrothermally treated sample for up–thermal shock (-40^{0}C for 20 minutes to +50^{0}C for 30 minutes)

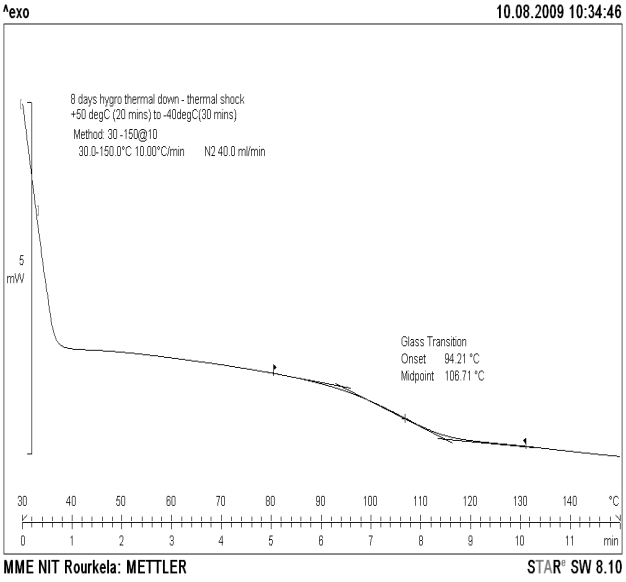

Fig 7: Glass transition temperature for 8 days hygrothermally treated sample for down–thermal shock +50^{0}C for 20 minutes to -40^{0}C for 30 minutes

The T_g value shows the greatest depression for the specimens with longest hygrothermal exposure on being subjected to up-thermal shock when compared to the same with no-thermal shock. The longest exposure to hygrothermal conditioning results in considerable moisture peak up, a large fraction of which is desorbed during the last phase (+50^{0}C) of the up-thermal shock, leaving behind some porosity in the composite body. The result is the generation of a swelling stress which is responsible for the rapid fall of the T_g. it may be appreciated that at and below the T_g 1/40th of the total volume of the material is free volume (Ray *et al.,* 2003). The generations of pores give rise to increase in the free volume in the composite body. Since the longest exposure to hygrothermal treatment results in higher quantities of moisture intake, it gives rise to higher extents of pores generated when the absorbed moisture is desorbed and the depression in T_g is noticeable, bringing in plasticization showing an early glass transition (Tsenoglou *et al.,* 2004).

Glass Transition Temperature (T_g) and down-thermal shock

Variation of T_g for specimens with longest duration of hygrothermal exposure with down-thermal shock for highest length of time (+50^{0}C 20 minutes followed by -40^{0}C 30 minutes) are presented in Fig. 7. The variation of T_g between the no-shock (Fig. 5) and down-thermal shock specimens is minimal. This may be due to the reason that lower proportions of internal voids entangling the polymer chains are created in down-thermal shock. This is due to the fact that last phase of cryogenic cycle (-40^{0}C) involved with down-thermal shock generates cryogenic compressive stresses which imparts rigidity to the polymer. The rigid polymer matrix becomes brittle and does not allow relaxation of residual stresses causing restriction in chain movements. This is the cause of less depression of the T_g from no-shock to down-thermal shock for hygrothermally exposed samples under down-thermal shock (Ray, 2006 b).

Failure Modes

The scanning electron micrographs presented in Fig 8(a), Fig 8(b) and Fig 8(c) pertain to the fracture surfaces of the specimens which are subjected to hygrothermal exposure followed by no-shock and hygrothermal exposure followed by up-thermal and down-thermal shock respectively.

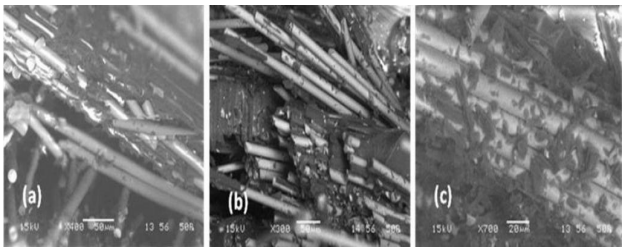

Fig 8: SEM Microstructure of 8-days hygrothermally treated sample (a) without thermal shock, (b) after up-thermal shock for maximum duration and (c) after down-thermal shock for maximum duration.

The micrographs clearly show fiber breakage, fiber/matrix debonding, loosening of contact between the fiber and the matrix as the chief modes of failure. Plasticizing effect due to the typical extreme degrading condition encountered during hygrothermal treatment and the thermal shocks are the reasons of the extreme failure modes encountered.

Conclusions

(i) Longer exposure to hygrothermal ageing assists moisture pick up.

(ii) Under the experimental conditions and the exposure time there is a continuing trend of moisture uptake revealing the delaying of saturation level of moisture in the specimens as the degrading processes get enhanced with increase of exposure time.

(iii) There is a general trend of decrease in the ILSS value with increased time of hygrothermal ageing.

(iv) Shorter durations of up-thermal shock result in an increase in ILSS value while under longer exposures the samples show a decreasing trend in the ILSS value.

(v) The ILSS initially decreases for down thermal shock while the trend is of a fluctuating nature for longer exposures.

(vi) Lowest T_g is recorded under up thermal shock for the specimens with longest hygrothermal exposure.

(vii) Under down-thermal shock the T_g variation for hygrothermally exposed samples is minimal.

REFERENCES

Abdel-Magid, B. Ziaee, S. Gass, K. and Schneider, M. 2005. The combined effects of Load, Moisture and Temperature on the properties of E-Glass/epoxy composites. Compos Struct., 71(3-4): 320-326.

Assbee, K. 1993. Fundamental Principle of Fiber reinforced Composites, Technomic Publishing Co. Lancaster, 323.

Berketis, K.S., Tzetzis, D and Hogg, P.J. 2008. The influence of long term water immersion ageing on impact damage behavior and residual compression strength of glass fiber reinforced polymer (GFRP). Materials & Design, 29(7): 1300-1310.

Bond, I. Hucker, M. Weaver, P. Bley, S. and Haq, S. 2002. Mechanical behavior of circular and triangular glass fibers and their composites. Compos Sci & Tech., 62(7-8): 1051-1061.

Chakraverty, A.P. 2010. Response of E-Glass/Epoxy Composite to Up and Down-Thermal Shocks under the Influence of Varying Environmental Condition, M.Tech(Res.)Thesis, NIT Rourkela: http://ethesis.nitrkl.ac.in/2476/

d'Almeida, JRM, de Almeida R.C. and de Lima, W.R. 2008. Effect of water absorption of the mechanical behavior of fiber glass pipes used for off shore service waters, Compos Struct., 83(2): 221-225.

Karbhari, V.M., Rivera, J. and Dutta, P.K. 2000. Effect of short-term freeze-thaw cycling on composite confined concrete. ASCE journal of Composites for Construction, 4(4): 191-197.

Kelly, A. and Zweben, C. 2000. Comprehensive Composite Materials; Vol-2: Polymer Matrix Composite, Ch-2.01: Epoxy Resins, Elsevier.

Kumar, M.S. and Ray, B.C. 2007. Mechanical Behaviour of FRP Composites at Low Temperature. Proceedings of 2nd International Conference on ICRACM, New Delhi, India.

Mishra, G. Mohapatra, S.R. Behera, P.R. Dash, B. Mohanty, U.K. , Ray, B.C. 2010. Environmental Stability of GFRP Laminated Composites: An Emphasis on Mechanical Behaviour. Aircraft Engineering and Aerospace Technology: An International Journal, 82(4): 258-266.

Ray, B.C. 2004 a. Thermal Shock on interfacial adhesion of thermally conditioned glass-fiber/epoxy composites. Materials Lett., 58(16):2175-2177.

Ray, B.C. 2004 b. Effects of crosshead velocity and sub-zero temperature on mechanical behaviour of hygrothermally conditioned glass fibre reinforced epoxy composites. Material Sci & Engg A, 379(1-2): 39-44.

Ray, B.C. 2006 a. Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites. J Colloid & Interface Sci., 298(1): 111-117.

Ray, B.C. 2006 b. Adhesion of Glass/Epoxy composites influenced by Thermal and Cryogenic Environments. J Appl Polym Sci, 102(2): 1943-1949.

Ray, B.C. 2007 a. Effect of changing Sea water Temperature on Mechanical properties of GRP Composites. Polym & Polym Compos., 15(1): 1-6.

Ray, B.C. 2007 b. Effects of Thermal and Cryogenic conditioning on Mechanical behavior of Thermally shocked Glass Fiber/Epoxy composites. J Reinforced Plastics & Composites, 24(7):713-717.

Ray, B.C. Biswas, A. and Sinha, P.K. 1991. Hygrothermal effects on the mechanical behavior of fiber reinforced polymeric composites. Metals Materials & Process, 3(2): 99-108.

Ray, P.K. Bhusan, A. Bera, T. Mohanty, U. Vadhera, S. and Ray, B.C. 2003. Mechanical behavior of Hygrothermally conditioned FRP composites after Thermal spikes. Proceedings of ETSMC, 322-332.

Sharma, N. Kumar, M.S. and Ray, B.C. 2008. Study the Effect of Hygrothermal Ageing on Glass/Epoxy Micro-composites by FTIR Imaging and Alternating DSC Techniques. J Reinforced Plastics and Composites, 27 (15): 1625-1634.

Springer, G.S. 1976. Environmental effects on epoxy matrix composites. Composite Materials: Testing and Design (5th Conference) ASTM STP: 291-312.

Tsenoglou, C.J. and Burchill, P.J. 2004. The effect of degree of cure on the corrosion resistance on vinyl-ester glass fiber composites. Composites; Part A 35 (4): 501-508.

****