Experimental Analysis on the Effect of Surface Treatment of Glass Fibers & Nanoclay on Mechanical Properties of Glass Fiber Reinforced Polymer Nanocomposites

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***Abstract*—**The objective of this study is to analyze the effect of surface treatment on mechanical properties of Glass Fiber reinforced epoxy nanoclay nanocomposites which was manufactured using nanoclay, Nanomer 1.28E content with a fixed percentage of 3 wt. % by compression molding. Nine different samples were made with different possible combinations to compare the effect of surface treatment of glass fibers (Untreated/Silane and Acid Treated) and nanoclay (Untreated and trimethyl stearyl ammonium modified). Tensile, Impact, Flexural and Hardness tests had been done to evaluate the mechanical performance of the composites. The fine morphological modifications made on the surface of the glass fiber and nanoclay enhanced the interfacial bonding between the epoxy resin and reinforcement which in turn improved the tensile, flexural and impact properties by improvement in hardness too. The mechanical properties such as flexural strength and impact strength has slightly decreased in the composite made of Epoxy, Silane treated Glass fiber and surface modified nanoclay but instead there is an increase in tensile strength and hardness which in turn will improve the wear properties when compared to neat composite.

Keywords- *Glass Fiber Reinforced Polymer (GFRP), Montmorillonite (MMT), Glass Fiber (GF), Untretaed Glass Fiber (UGF), Modified Nanoclay (MNC), Untreated Nanoclay (UNC), Scanned Electron Microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR).*

1.Introduction

Polymer nanocomposite materials are increasingly preferred in recent years because of their low friction coefficient and the ability to sustain loads. The mechanical and tribological aspects of these materials are of great interest in automotive, aerospace, shipbuilding and other related industrial applications. Generally, the effect of fiber/filler reinforcement on the tribological behaviour of polymer nano-composites is not substantial due to lack of proper interfacial bonding. The aspect ratio of the filler material is very crucial for improvements in properties such as mechanical, electrical and thermal properties which is possible through the inclusion of nanofillers. Addition of nano-particles as a filler material between fiber and polymer composites would be one of the solution to enhance the bonding i.e. provide improvement in mechanical and tribological properties of the composite. However, diffusion of nanoparticle in the matrix hamper the formation of the well performed composite mainly due to agglomeration of nanoparticles and interfacial bonding between epoxy system and glass fibers.

Therefore, a comprehensive study of the mechanical and tribological performance with the reinforcement of nano-particles in the polymer matrix is required. In this research work, the polymer nano-composite materials will be fabricated using epoxy resin and glass fibers. Nanoclay particles will be incorporated in the composite as an interfacial bonding enhancer. The bonding characteristics between the composite matrix and nano particle will be analysed through various surface treatments. Subsequently, the mechanical and morphological properties of that polymer nanocomposite will be analyzed for enhanced performance. This research work is expected to contribute towards improved performance of Glass fiber reinforced polymer nanocomposite for high wear resistant applications such as piping and automotive industries.

Hyeong Min Yoo et al. [1] studied the mechanical behaviour of Glass fiber reinforced polymer composite where the glass fibers were surface treated with norbornene bases silane. The glass fibers were first dried at 200^{o}C for 4 hours to remove the impurities and moisture present in the fibers. The surface treatment solution was prepared with a mixture of silane, ethanol and acetic acid mixed in an appropriate mass ratio of 5:4:1. The solution was added to glass fibers in a mass ratio of 100:1. Finally the treated glass fibers were further dried at 140^{o}C for 4 hours before being reinforced with Epoxy matrix system. The mechanical testing such as shear strength, tensile strength and impact strength was carried out and shear strength was evaluated using the microdroplet pull-out test. It was observed that the shear strength increased by 40% when compared to neat specimen which replicates the improvement in interfacial bonding strength between glass fibers and resin. FTIR spectroscopy was done to analyse the quality of surface treatment and it was observed for sufficient surface functionalization using surface treatment of Glass fibers.

Ferreira et al. [2] studied the effect of surface treatment on the mechanical properties such as toughness, stiffness, static and fatigue strength of nanoclay filled polypropylene polymer matrix. Injection moulding process was used to prepare composites with fixed percentage of 3 wt.% of nanoclay. The comparison was made between organomodified nanoclay and further modified nanoclays using water mixed with acetic acid. The test results revealed that specimens with nanoclays enhanced by surface treatment had shown that the mechanical properties increased by 6% and 3% on tensile strength and modulus of elasticity. The fatigue performance of surface treated nanoclay shown results as close as neat composite but better than untreated nanoclay composite. The observation of fractured specimens through scanning electron microscopy revealed that surface treated specimens showed better clay dispersion, adhesion and no significant agglomeration.

Mengyuan Liao et al. [3] analysed the enhancement of mechanical performance for glass fiber reinforced polymer composite where the glass fibers were surface treated with polyurethane dispersion (PUD), silane treatment system and hybrid combination of silane treatment followed by PU treatment process. The composites were made using hand lay-up method and the test results revealed that PUD treated glass fiber composite had shown a better mechanical property improvement than the silane coupling treated and hybrid composites. On the other hand, the thermal properties of treated composites decreased for both silane and PUD treated glass fiber composites due to large molecular cooperative motion. Kutlay Sever et al. [4] studied the effects of mechanical performance such as tensile strength, flexural strength, interlaminar shear strength and fracture toughness for silane surface treatment of glass fibers reinforced polymer composite which was initially modified by heat cleaning and HCL acid activated. The test results revealed that the silane coating on heat cleaned glass fibers had shown beneficial effect on the interfacial adhesion between the fibers and the matrix whereby increasing the Interlaminar shear strength. On the other hand, silane coating on the acid activated glass fibers did not improve the Interlaminar shear strength of the composite because of the fiber damage caused by HCL acid solution. Somayeh Safi et al. [5] analysed the interfacial adhesion characteristics of the glass fiber reinforcement with Epoxy resin matrix whereby the glass fibers were surface silane treated. The Glass fibers were heat-cleaned to 450^{o}C for 1.5 hours for sizing and removal of impurities followed silane treatment by different combinations of GPS and TEOS (inorganic-organic silane blends). The adhesion properties were studied through the single fiber microdroplet pull-out test and the load displacement curves from the pull-out test were observed. The test results revealed that specimens containing 75:25

and 50:50 of GPS: TEOS had shown the better interfacial adhesion properties between the glass fiber and the matrix which was also analysed through SEM images. This experimentation also demonstrated that improving the mechanical interlocking between glass fiber and matrix will tailor the mechanical properties of the composite material.

Withers et al. [6] studied the mechanical properties in GFRP reinforced with organomodified nanoclay Cloisite 30B (1nm thickness and 200-300nm in length) with varying percentages of 0,2 and 4 wt.%. Cloisite 30B can create non-covalent through hydrogen bonds or covalent bond with chemical reaction with epoxy resin when moderate heat is applied. E-Glass Fiber in bi-directional [0^o/90^o] with weave yarns 1mm wide was used. The test results revealed that mechanical properties such as tensile strength, stiffness and ductility increased with nanoclay inclusion by strengthening the fiber-matrix interphase with the best results attained at 2 wt.% inclusion of nanoclay. The study also revealed that this nanoclay reinforced composite can be used for repair work for localised damages in the external surface wall of pipes and vessels installed in process and marine pipelines. Guojun Luo et al. [7] studied the enhancement of mechanical properties such as tensile and impact strength of surface treated glass fibers composites. The glass fibers were treated with film former (GFf) with certain ratio of Maleic Anhydride grafted polypropylene (MPP) and a kind of β-nucleating agent (TMB-5) through impregnation method with different ratios of 2,3 and 10 wt.%. It was observed that the mechanical properties such as mechanical and tensile properties dramatically improved with small amount of 2 wt.% of MPP to glass fibers in the matrix system. Further increase of MPP has resulted in increase of tensile strength but decrease in tensile strength. The interfacial adhesion between the glass fibers and the matrix system is analysed through the SEM images which represents that the interfacial adhesion is improved with the addition up to 2 wt.% MPP and further addition seems no improvement as there is a saturation in the addition of MPP.

Dinesh et al. [8] analysed the mechanical properties of Glass fiber reinforced polymer composite where the matrix system was reinforced with amino silane treated Glass fiber 600gsm and Iron (III) oxide particles(200nm). The addition of UP into epoxy resin has shown increased flexural and impact properties but tensile and thermal properties reduced dramatically. With the addition of reinforcement, the tensile and thermal stability had shown improvement for UP blended epoxy composites. The morphological characterization had shown that the dispersion of reinforcement is uniform which had led to improvement in mechanical and thermal properties. Gorbatkina et al. [9] studied the effect of interfacial adhesion strength of three different modifiers such as active diluents, thermostable rigid chain thermoplasts and dispersed fillers to glass fibers and epoxy resin. The different mechanism to evaluate the interfacial strength between the epoxy resin and glass fibers are analysed and it was observed that the addition of thermostable thermoplasts are more effective by providing high interfacial strength at certain concentration level than the other two fillers modification.

Moutushi Dey et al. [10] studied the effect on the interfacial bonding strength of Glass fiber and Epoxy matrix interphase through the surface modification of silane coupling agent and film former. Single fiber microdroplet test was used to determine the interfacial bonding strength between glass fiber and epoxy matrix. The test results revealed that amino silane sizing with azamide based film former had shown 47% increase in interfacial shear strength when compared to other composites which was achieved through chemical bond formation and by improving the surface roughness of glass fibers. Atomic force microscopy was used to analyse the surface morphology and found that both silane and film former components affects the failure mode at the interface of glass fibers and the epoxy system.

2.Experimental Details

2.1 Material System:

In this research work Epoxy Resin, Araldite LY 556 with a density of 1.15-1.20 and a viscosity of 10,000-12,000 MPa @ 25^{o}C with Hardener, Aradur HY 951 of density 0.97-0.99 and viscosity 10-20 MPa @ 25^{o}C were used as the matrix system both supplied by Huntsman Advanced Materials, India. Woven bidirectional E-Glass Fibers with a density of 360 gsm purchased from Javanthee Enterprises

was used as Glass Fiber Reinforcement. Nanoclay, Montmorillonite Clay(MMT) with a trade name of Nanomer Clay and Nanoclay, Montmorillonite Clay (MMT) with a trade name of Nanomer 1.28 Clay which has been surface modified with 25-30 wt. % trimethyl stearyl ammonium both purchased from Sigma Aldrich was used as Nanofiller.

2.2 Surface treatment of Glass Fibers:

The E-Glass bidirectional fibers were sized into 270x270 mm and two different surface treatments Silane treatment and Acid treatment were done. For Silane treatment, the Glass fibers were dried at 200^{o}C for 24 hours to remove moisture and impurities from the surface of the fibers. The surface treatment solution was prepared using a mixture of silane, ethanol and acetic acid mixed in a mass ratio of 5:4:1. The treatment solution was added to the glass fibers in a 100:1 mass ratio. Finally, the treated glass fibers were used after further drying at 140^{o}C for 4 hours.

For Acid treatment, the Glass Fibers are treated by soaking in two solutions 1N Sodium hydroxide and 1N Sulfuric acid separately for 24 hours at room temperature. After the fibers were thoroughly washed with distilled water to remove any sodium hydroxide and sulphuric acid and then dried in room temperature. Finally, the treated glass fibers were used after further drying at 140^{o}C for 4 hours.

2.3 Preparation of the Composites:

Glass Fibers were cut to size of 270x270mm to fit the size of the mold. The laminates are prepared using compression molding machine. At first the mold was cleaned, and wax was applied as the mold releasing agent. The Epoxy resin was mixed with hardener in the ratio of 100:10 by weight which was stirred thoroughly to attain homogenous mixing. A thin layer of epoxy is applied on the lower mold. Then the glass fibers are stacked layer by layer and the resin is applied in between each layer till final layer is placed in the mold for a 40 wt.% weight of Epoxy System. Then the upper mold half is closed and the excess resin if any will be squeezed out from the mold. Both the upper and lower mold halves have been maintained at a temperature of 100^{o}C which has been verified through the thermocouple connected and maintained at pressure of 1500psi for a duration of 30 minutes. Finally, de-molding has been done using an ejector pin to remove the composite prepared. The composites are allowed to cool down at room temperature for 24 hours.

For composites with nanoparticles inclusion the first step is to heat up the epoxy to 70^{o}C to scale back the viscosity. The next step is to disperse the nanoparticles (Natural or Surface modified) in solvent acetone. Epoxy Resin is added to the acetone/nanoclay mixture which is then mixed uniformly using ultrasonication process with a frequency of 20,000 hertz for a period of 30 minutes to eliminate the agglomeration. Then it is placed in a heated mandrel at 80^{o}C for 5 minutes to evaporate the acetone. Once acetone has been completely evaporated then it is cooled down to room temperature. Then the above process of adding hardener and preparation of composite is continued as explained in the above paragraph.

Nine different samples were prepared as per the description given in Table 1. For the samples (S1-S6) with nanoclay inclusion the weight of nanoclay inclusion is fixed as 3 wt.% of the matrix system.

2.4 Experimental Methodology:

Fig. 1 represents the samples prepared for each mechanical testing as per the ASTM Standards. The Reference Standards used for testing are ASTM D638 for tensile testing, ASTM D790 for Flexural testing and ASTM D256 for Impact testing. As mentioned in the ASTM Standards, five samples each were prepared for tensile, flexural and impact test and one 10mmx 10mm sample for micro hardness testing and the test specimens of required sizes were cut from the composite samples using water jet machining.

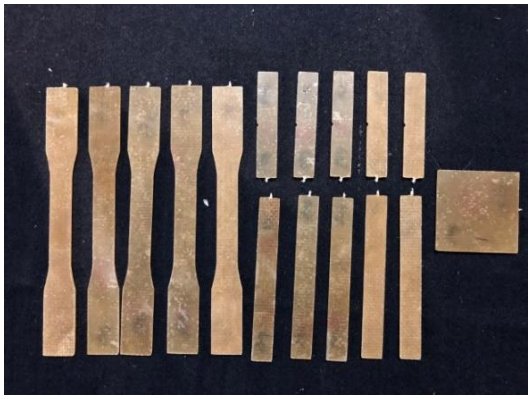

Figure 1 Mechanical Testing Samples

3 **Results and Discussion**

3.1 Tensile Testing:

Tensile testing was carried out as per the ASTM Standard D638 using the Universal Testing Machine Model F100 with cross head speed of 10 mm/min. The specimens were cut into strips of 165 mm length, 19 mm width and 3.2 mm thickness. Five identical test samples were prepared for each composite and the testing was carried out at room temperature. Average of the five specimen readings have been taken for comparison of test results. The test results as per the graph in Figure 2 have shown that the Specimen S4 with Epoxy, Silane treated Glass fiber and modified nanoclay has recorded the highest tensile strength of 315.99 MPa. The next recorded value of 300.81 MPa has been achieved for Specimen S4 which is the neat composite of Epoxy with Glass Fibers. The increase in tensile strength is due to the increase in the interfacial bonding created by the inclusion of organomodified nanoclay which in turn has shown increase in the hardness of the specimen. The lowest result was recorded with specimen with untreated glass fiber and untreated nanoclay, specimen S1 of 137 MPa which clearly indicates that surface treatment of glass fibers and nanoclay have impact on the tensile strength as well as hardness of the composite material. The test results of Specimen S4 clearly indicates that surface treatment of glass fibers and nanoclay has intercalated structure which in turn has increased the interfacial bonding between epoxy system, glass fiber and nanoclay. However, in this research work the effect of nanoclay on the mechanical properties has been done based on the literature survey that 3 wt.% inclusion has shown the optimal properties which need to be further evaluated by varying percentages of nanoclay for further research work.

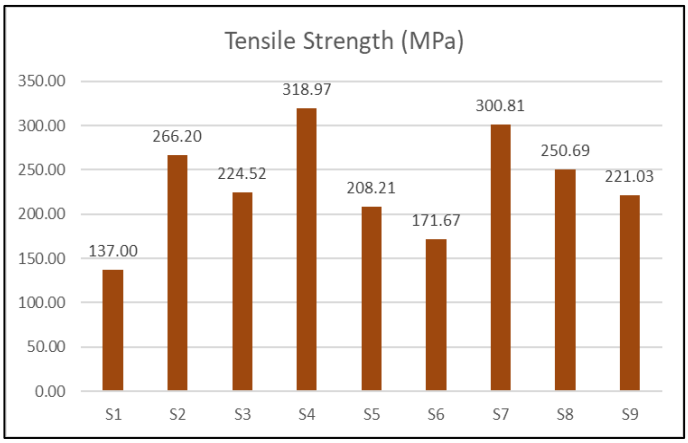

Figure 2: Graph for Tensile Test Results

3.2 Impact Testing:

Impact testing was carried out as per the ASTM Standard D790 using the Krystal Equipment Impact tester. The specimens were cut into strips of 65.5 mm length, 12.7 mm width and 3.2 mm thickness. Five Samples were prepared for each composite and the test was carried out at room temperature. Average of the five readings have been taken for comparison of test results. The test results represented in Figure 3 have shown that the neat composite i.e. Specimen 7 has the highest impact strength of 239.21 KJ/m^2. The specimen S5 with Epoxy, Acid treated Glass fiber and Untreated Nanoclay has the next highest value of 234.89 KJ/m^2. The reduction in Impact results does not show any relation with respect to hardness. So, the next value of Specimen S4 with Epoxy, Silane treated Glass fiber and Surface treated nanoclay is taken for consideration. There is a reduction of 1.8% in impact strength which is compensated by increase in hardness value of 24% when compared to neat composite where the overall mechanical properties of the composite are taken into consideration.

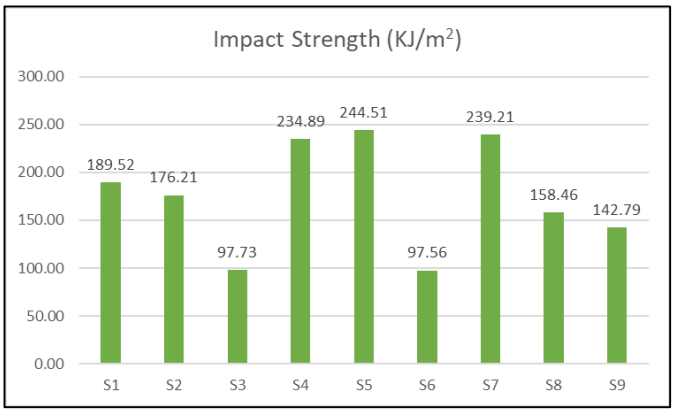

Figure 3: Graph for Impact Test Results

3.3 Flexural Testing:

Flexural testing was carried out as per the ASTM Standard D790 using the Auto Instruments GT 500, Universal Testing Machine with a fixture for conducting the three-point flex test. The specimens were cut into strips of 100 mm length, 12.7 mm width and 3.2 mm thickness with a notch of 45^o and 2.5mm depth in the center. Five identical samples were prepared for each composite and the testing was carried out at room temperature. The test results as shown in Figure 4 indicate that the sample S8 with Epoxy and Silane treated Glass fiber has the highest value of 176.58 MPa whereas the sample S4 when added with surface modified nanoclay has a value of 140.98 MPa which is 20.1% lesser than S8 which clearly indicates that silane treatment increases the flexural strength. But the reduction in flexural properties has been compensated by increase in hardness of 5.6% which is caused by the addition of surface modified nanoclay and which is the required property of the final composite. The flexural Strength (σ_{bh}), which is the maximum stress at break is calculated by using the formula:

$$\sigma_{bh} = 3FL/2bh^2$$

Where F is the breaking force in Newtons(N), L is the span between the load bearing supports in mm, b is the thickness of the specimen in mm and h is the thickness of the specimen in mm.

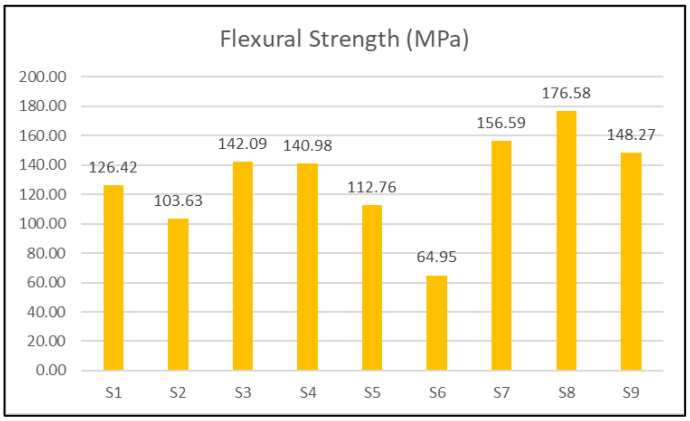

Figure 4: Graph for Flexural Test Results

3.4 Hardness:

Hardness is measure of the resistance of the material to deformation against a mechanical indentation or abrasion. The micro hardness samples are cut to size of 10mm x 10mm. All tests were carried out at room temperature and five indentations were made at different points of each sample using Micro Vickers Hardness Tester, Model 402MVD. The average of the five readings were taken as a representative sample for the hardness. The micro hardness values for different samples are plotted in the Figure 5 below based on the values mentioned in Table 1. In general, the samples with the addition of nanoclay exhibits high hardness when compared with samples made of epoxy and glass fibers. In specific, specimens with silane treated glass fibers incorporated with nanoclay exhibit high hardness than the other samples. It is observed that samples with untreated nanoclay addition has slightly higher hardness value than the surface modified nanoclay, but other mechanical properties such as tensile strength, impact strength and flexural strength need to be considered before selection of the composite for further research purpose.

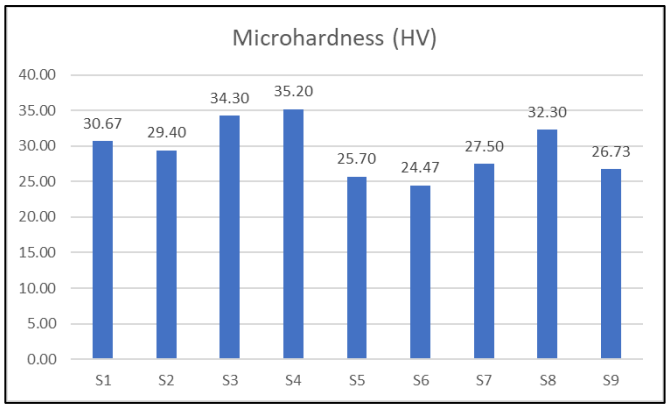

Figure 5: Graph for Microhardness Test Results

Table 1: Mechanical Test Results for Specimens

Specimen	**Description**	**Tensile Strength (MPa)**	**Flexural Strength (MPa)**	**Impact Strength (KJ/m^2)**	**Micro hardness (HV)**
S1	Epoxy + UGF + UNC	137.00	126.42	189.52	30.67
S2	Epoxy + UGF + MNC	266.20	103.63	176.21	29.40
S3	Epoxy + Silane GF + UNC	224.52	142.09	97.73	34.30
S4	Epoxy + Silane GF + MNC	318.97	140.98	234.89	35.20
S5	Epoxy + Acid GF + UNC	208.21	112.76	244.51	25.70
S6	Epoxy + Acid GF + MNC	171.67	64.95	97.56	24.47

S7	Epoxy + UGF	300.81	156.59	239.21	27.50
S8	Epoxy + Silane GF	250.69	176.58	158.46	32.30
S9	Epoxy + Acid GF	221.03	148.27	142.79	26.73

4 Conclusion

The epoxy/glass fiber/nanoclay hybrid nanocomposites were fabricated using compression molding and mechanical properties such as tensile strength, flexural strength, impact strength and micro hardness has been evaluated.The following conclusions has been made based on the experimental results:

- Flexural Strength is highest for Specimen S8 which indicates that the surface treatment of Glass fibers increases the Flexural properties. The Impact Strength has been recorded as highest value for the neat composite which is for the specimen S7.
- The hardness value has been highest for the Specimen S3 but the other properties such as tensile, flexural and impact strength has reduced drastically by 26%, 58% and 2% respectively.
- On the other hand, for the specimen S4 the tensile strength and hardness has been increased dramatically by 5% and 24% at the same time the other properties such as impact and flexural strength has been slightly reduced by 6% and 1% respectively when compared to specimen S7.
- In overall, the specimen S4 has attained the necessary matrix reinforcement with silane treated glass fibers and surface modified nanoclay which in turn has enhanced the interfacial bonding between epoxy matrix and glass fiber through the enhancement of mechanical properties. Based on the test results attained and discussion, parameters in specimen S4 will be used for further research work.

References

[1] Hyeong Min Yoo, Dong-Jun Kwon, Joung-Man Park, Sang Hyuk Yum and Woo Il Lee. (2017). Mechanical properties of norbornene-based silane treated glass fiber reinforced polydicyclopentadiene composites manufactured by the S-RIM process. *E-Polymers,17(2): 159–166.*

[2] Ferreira.J.A.M, P.N.B. Reis, J.D.M. Costa, Richardson B.C.H, Richardson.M.O.W.(2011). A Study of the mechanical properties on polypropylene enhanced by surface treated nanoclays. *Composites: Part B-42:1366–1372.*

[3] Mengyuan Liao, Yuqiu Yang, Hiroyuki Hamada. (2016). Mechanical performance of glass woven fabric composite. Effect of different surface treatment agents. *Composites Part B 86: 17-26.*

[4] Kutlay Sever, Mehmet Sarikanat, Yoldas Seki, Volkan Cecen, Ismail H. Tavman. (2008). Effects of fiber surface treatments on mechanical properties of epoxy composites reinforced with glass fabric. *J Mater Sci 43:4666–4672.*

[5] Somayeh Safi1, Ali Zadhoush1 and Mahmood Masoomi. (2017). Evaluation of interfacial properties of the silane blend sized glass fiber–epoxy composite by the microdroplet test. *Journal of Composite Materials, Vol. 51(11) 1573–158.*

[6] Withers.G. J, Yua.Y, Khabashesku.V. N, Cercone.L, Hadjiev.V. G, Souza.J.M, Davis.D.C. (2015). Improved mechanical properties of an epoxy glass–fiber composite reinforced with surface organomodified nanoclays. *Composites Part B 72, 175-182*.

[7] Guojun Luo, Wenze Li, Wenbin Liang, Guogang Liu, Yi Ma, Yanhua Niu. (2017). Coupling effects of glass fiber treatment and matrix modification on the interfacial microstructures and the enhanced mechanical properties of glass fiber/polypropylene composites. *Composites Part B III,* 190-199.

[8] Dinesh.T, Kadirvel.A, Arunprakash Vincent. (2018). Effect of Silane Modified E-glass Fibre/Iron(III)Oxide Reinforcements on UP Blended Epoxy Resin Hybrid Composite. *Springer Science + Business Media B.V., part of Springer Nature.*

[9] Gorbatkina.Yu. A, Ivanova-Mumzhieva.V. G, Kuperman. A.M. (2016). Adhesion of Modified Epoxy Matrices to Reinforcing Fibers. *Polymer Science, Series A, Vol. 58, No. 5, pp. 659–666.*

[10] Moutushi Dey, Deitzel.J.M, Gillespie Jr.J. W, Scott Schweiger. (2014). Influence of sizing formulations on glass/epoxy interphase properties. *Composites: Part A 63, 59–67.*