

Polymer composites based on unsaturated polyester and glass nano-fibers: mechanical properties and fracture toughness

Nguyen Thanh Liem^{1*}, Hoang Dinh Kien¹, Pham Thi Lanh^{2*}

¹(Polymer Center, Hanoi University of Science and Technology, Hanoi, Vietnam)

²(Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam)

Abstract: In this study, the influence of glass nano-fibers (GNF) on toughness and other mechanical properties of unsaturated polyester resin (UPR) curing with dicumyl peroxit was investigated. Glass nano-fibers were dispersed in the matrix using high speed stirring for 15 hours along with the addition of styrene in the stirring process. The mechanical properties of GNF/UPR composites such as flexural strength, IZOD impact strength were improved slightly by the adding of glass nano-fibers. The toughness (K_{IC}) increased significantly by adding 0.2 wt% GNF, K_{IC} value, flexural strength and IZOD impact strength of 0.2 wt % GNF/UPR composites were 1.5806 MPa.m^{1/2}; 95.2 MPa and 2.25 KJ/m². These values represent improvements of 98.0%, 13.5% and 9.2% respectively, compared to the neat UPR. Scanning electron microscopy-analysis revealed the different deformation of the matrix due to the GNF.

Keywords: Unsaturated polyester, Mechanical properties

I. INTRODUCTION

Using micro/nano-fibers as additive to modify the mechanical properties of composite materials has extended the application range of this kind of materials. The glass fibers began to be used in the 1935s when Owens Corning introduced the first glass fibers. In the 1970s, synthetic-fibers industries began to develop, was the premise for the fibers reinforced materials industry [1].

Due to their remarkable properties, especially hardness and durability, GNF is suitable for combination with low density resin to create high strength composite materials. Since the early 1960s, the demand for durable and lightweight materials became urgent in the aerospace, energy, civil engineering and structural applications [1,5]. There are many different technologies to produce glass micro/nano-fibers. The electrospinning technology for producing micro/nano-fibers with specific properties has opened a new advanced composite materials that can meet the demand of many high-tech industries. When electrospun nanoparticles with large surface area, high aspect ratio and mechanical properties are better than conventional fibers, they may represent a new generation of reinforcing materials in the composite materials industries [2-4].

The mechanical properties of the fibers reinforced composite materials are primarily affected by the fibers in the matrix. The four main factors controlling the role of fibers are: (1) the mechanical properties of fibers; (2) surface interaction between fibers and polymer matrix, (3) the dispersion of fibers in resin; and (4) the orientation of fibers in composite materials [6]. Micro/nano-fibers can satisfy all of the above factors for the following reasons: micro/nano-fibers have high geometric ratio (L/d), high elongation (up to 104) due to molecular chain polymer for orientation along the chain. In addition, because of their nanoscale diameter (<500 nm), they have very high surface area, which is about 100 times higher than normal fibers. Thus, there is significant improvement in bonding at the phase separation surface and leads to better micro/nano-fibers reinforcement, which is much higher than traditional reinforcement [7-10].

II. EXPERIMENT

2.1 Materials

- Glass nano-fibers (GNF) was supplied by Nipon Inorganic Color & Chemical (Japan) with a diameter of 300 - 800 nm and a length of 500 - 1500 μ m.
- Polyester resin (polyester resin content: 62 wt%, density: 1.11 – 1.23 g/cm³ at 25°C) was supplied by Shell Chemical.
- Styrene (molecular weight of 104.15 g/mol) was purchased from Sigma-Aldrich.
- Dicumyl peroxide 98% (molecular weight: 270.37 g/mol) was purchased from Sigma-Aldrich.
- NaOH, acetone, ethanol (China)

2.2 Preparation of composites

Dispersion of GNF in unsaturated polyester resin

In this study, the dispersion of glass nano-fibers in unsaturated polyester resin was mixed using a Glass - Col high speed mechanical stirrer (about 11.000 rpm). Initially, the glass nano-fibers/unsaturated polyester system was cooled with ice and maintained at about 15 - 20°C. After stirring, the entire system consisted of glass beakers, UPR and glass nano-fibers was quantified by analytical balance, the results were recorded for comparison. During stirring, the system was sealed to prevent the styrene evaporated out of the samples. Styrene may be added to the UPR systems to avoid the lack of solvent content.

Preparation of composites materials

The UPR was well mixed with a curing agent of DCP (1.5 wt% with respect to the total mass of the GNF/UPR mixture), at 15 - 20°C for 20 minutes using a magnetic stirrer. After that, the mixture was poured into a mold coated with a release agent and cured in a vacuum oven at 140°C for 30 min.

2.3 Characterization

Both the tensile and flexural properties were measured using a mechanical tester (INSTRON 5582-100KN, USA) at $25 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ RH at a crosshead speed of $5 \text{ mm}\cdot\text{min}^{-1}$ according to the ISO 527 and ISO 178 standards, respectively. Five specimens for each type of composite materials were measured.

IZOD notched impact strength tests were also carried out on a Tinius Olsen Model 92T Plastic Impact (USA) impact tester in accordance with ISO 180. The measurements were taken at $25 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ RH. The data correspond to the average value of at least five specimens.

The fracture toughness of all cured samples was evaluated using the critical stress intensity factor (K_{IC}) according to the ASTM D5045-99 standard by single-edgenotched (SEN) tests in a flexural three-point bending setup. Testing analysis was performed using a Lloyd 500N machine. The dimensions of the single-edge notch specimen (SEN) were approximately $30 \times 6 \times 3 \text{ mm}$ with an initial notch length of approximately 2.54 mm. The specimen was then slid with a fresh razor blade to generate cracks. The span length was set to 24 mm, which is approximately four times the width of the specimen, and the load was applied with a crosshead speed of $10 \text{ mm}\cdot\text{min}^{-1}$.

The fractured surfaces of the test specimens were observed by scanning electron microscopy (SEM) using a Jeol JSM-6360LV, Japan. Prior to the SEM observations, all the samples were coated with a thin layer of platinum to avoid the build-up of an electrical charge.

III. RESULTS AND DISCUSSION

3.1. Effect of stirring time on the dispersion of glass nano-fibers in the resin

SEM images of glass nano-fibers in the resin at 1,000 and 10,000 times magnifications have been shown that the GNF exist in single state or aggregation at the micrometer size (figure 1).

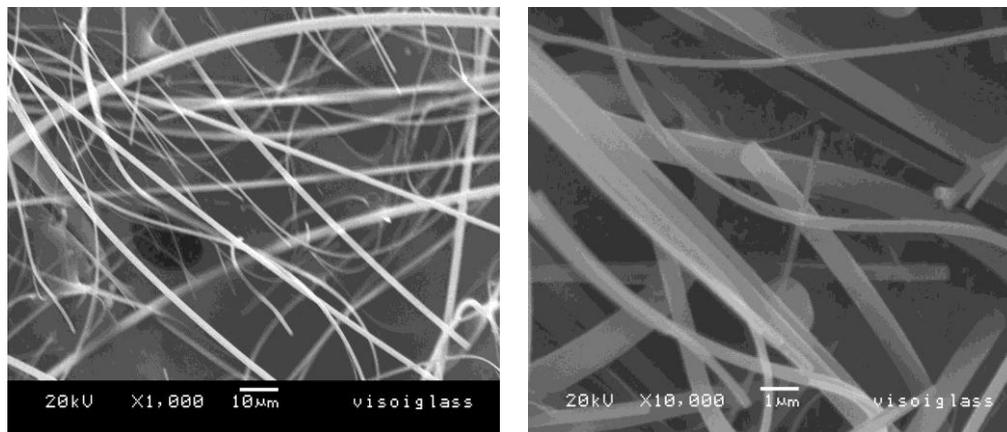


Figure 1. SEM images of glass nano-fibers at diferent magnifications

The effect of stirring time on the dispersy of GNF into the UPR was evaluated by SEM images as shown in Fig. 2.

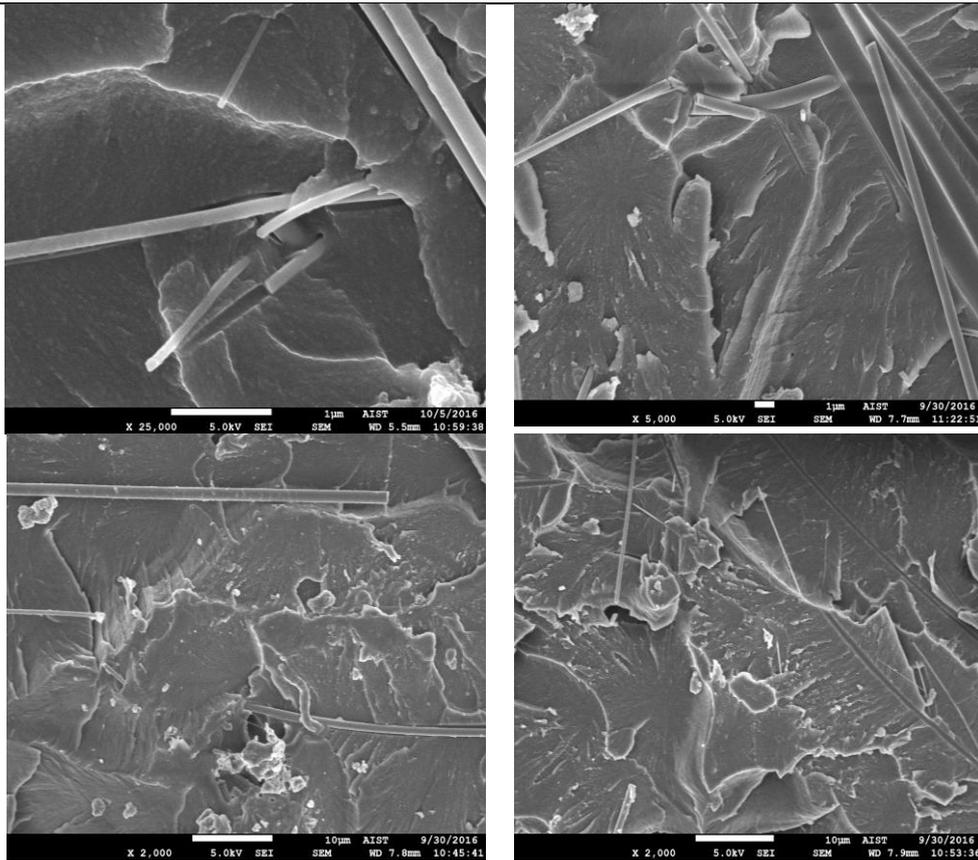


Figure 2. SEM images of fracture surface of 0.2 wt% GNF/UPR composites:
 (a): 6 hours of stirring; (b): 9 hours of stirring; (c): 12 hours of stirring; (d): 15 hours of stirring

Fig. 2 revealed that: after 9 hours and less of mechanical stirring, the bundles of fibers still be observed. For the stirring time of 15 hours, the GNF was dispersed in UPR matrix as single fibers. However, for the samples subjected to 18 hours stirring (Fig. 2(d)), there is no further improvement could be seen. Therefore, the optimum stirring time to obtain good dispersion of GNF in UPR matrix was about 15 hours.

The mechanical properties of UPR/GNF 0.2 wt% samples at different stirring time are shown in the following graphs:

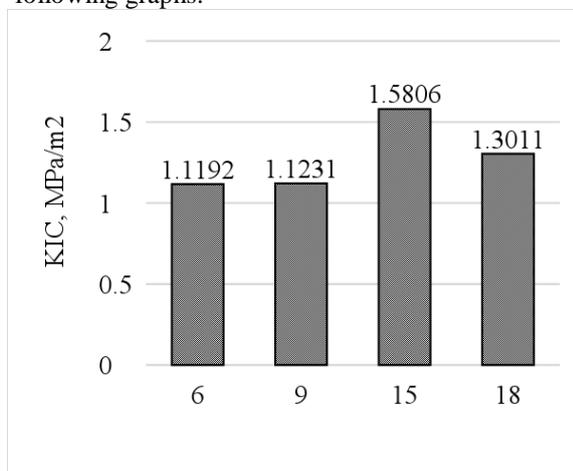


Figure 3. Effect of stirring time on K_{IC} value of UPR

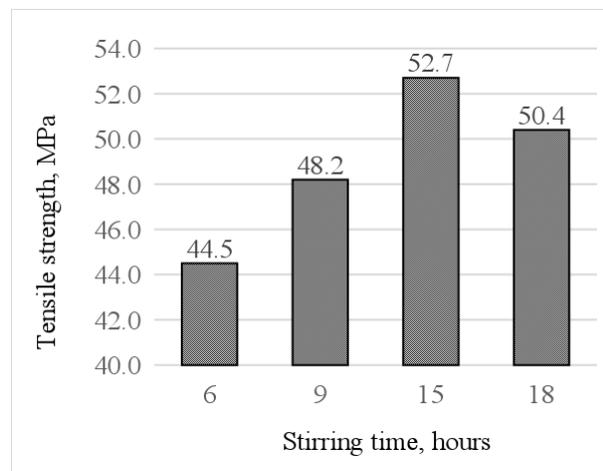


Figure 4. Effect of stirring time on tensile strength of UPR

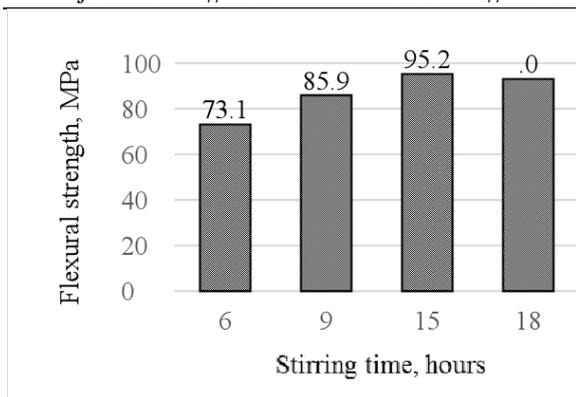


Figure 5. Effect of stirring time on flexural strength of UPR

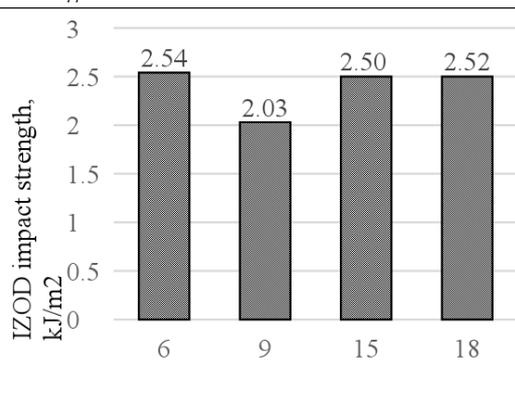


Figure 6. Effect of stirring time on IZOD impact strength of UPR

From Fig. 3, it can be seen that the K_{IC} coefficient is the maximum when the sample was stirred for 15 hours. On the other hand, at a higher stirring time (18 hours), the K_{IC} value decreased.

Figures 3, 4 and 5 also show that the samples stirred for 15 hours was the highest mechanical strength. The mechanical strengths of 9-hour and 18-hour stirring samples tended to decrease in comparison with the one of 15-hour stirring. Specifically, the highest K_{IC} value ($1.58 \text{ MPa}\cdot\text{m}^{1/2}$), tensile strength (52.7MPa), flexural strength (95.2MPa), IZOD impact strength (2.50 KJ/m^2) were recorded at 15-hour stirring samples. In this case, at 6-hour and 9-hour stirring, GNF was not evenly dispersed in UPR matrix so created the heterogeneity in the sample.

After 18-hour stirring the K_{IC} value was lower than that of the 15-hour sample but was still higher than the 6-hour and 9-hour stirring samples. However, due to excessive stirring the air bubbles and styrene losses are much higher, resulted in the reduction of mechanical properties, compared to the 15 hours stirring sample.

3.2. Effect of styrene addition

As mentioned above, the addition of styrene is required to help stabilize and enhance the properties of UPR, while also reducing the viscosity of PEKN resin during stirring.

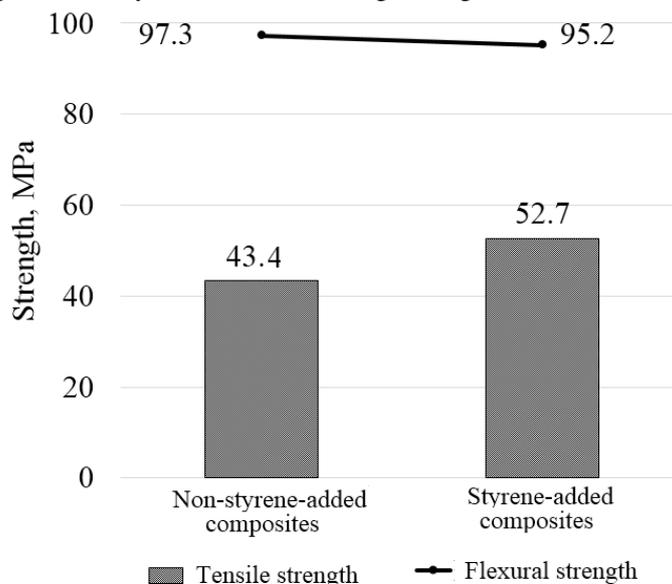


Figure 7. Effect of the styrene addition in UPR on the tensile strength and flexural strength of UPR

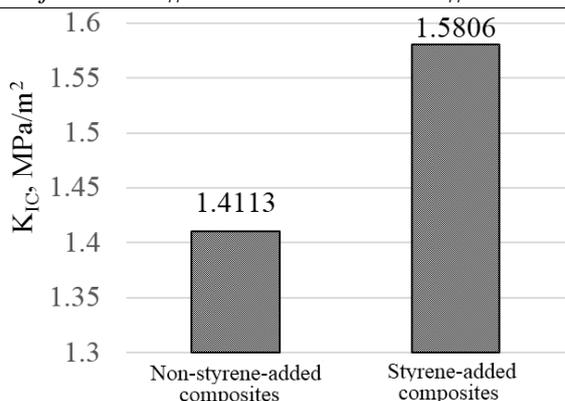


Figure 8. Effect of the styrene addition in UPR on K_{IC} value of UPR

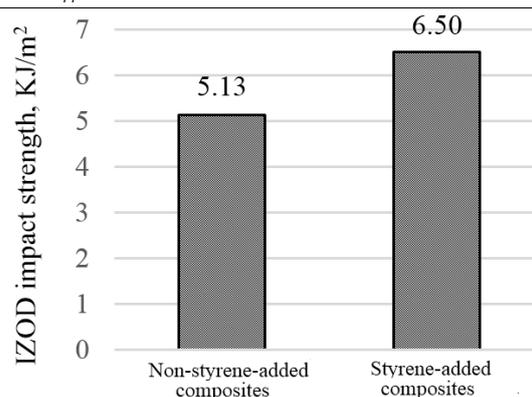


Figure 9. Effect of the styrene addition in UPR on IZOD impact strength of UPR

Figures 7, 8, 9 show that the mechanical properties of styrene added composites was higher than that of non-styrene added samples, mechanical strengths as tensile, impact strength and K_{IC} value increased by 16.0%, 26.7% and 12.1% respectively, but the flexural strength decreased about 2%.

This can be explained that a small amount of styrene was evaporated during stirring process, especially in high speed stirring the temperature of the resin increased and lead to the lack of styrene content in UPR compound. And because of styrene is not only the diluent for UPR resin but also a suture to create the tructure of composites so the mechanical properties tend to decrease.

The lack of styrene due to evaporation during stirring causes the number of cross-linkages between polymer chains of UPR to be inadequate, the viscosity of the resin increases, resulting in difficulties in processing and deterioration of the mechanical properties.

It is possible to limit the evaporation of styrene by sealing the mechanical stirrer system, controlling the system temperature by cooling the mixture container during mechanical stirring. Reducing the temperature will reduces the evaporation of styrene during stirring. However, it is not possible to completely prevent the evaporation of styrene.

Therefore, after high-speed mechanical stirring, an amount of styrene should be added to maintain the styrene content in the resin at about 40%. Experimentally, after the mechanical stirring for 15 hours, the amount of styrene needed was 12.5% of the original resin. After the addition of styrene, the mechanical properties of the resin increased considerably.

3.3. Effect of GNF on the mechanical properties of UPR

The effect of GNF on the mechanical properties of UPR was investigated. The results are shown in Fig. 10, 11 and 12.

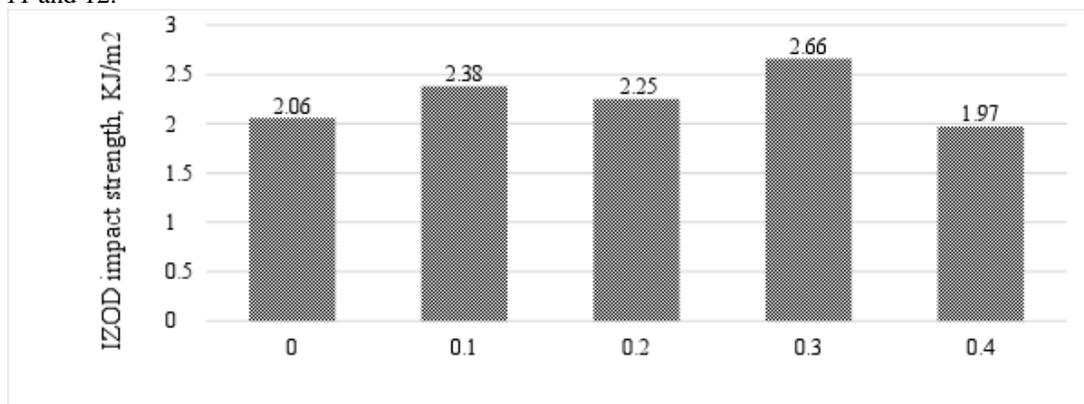


Figure 10. Effect of the GNF loading on IZOD impact strength of UPR

From Fig. 10, it can be seen that 0.3 wt% GNF/UPR sample have the highest impact strength, reached 2.66 KJ/m² compared to non-GNF or 0.4 wt% GNF/UPR composites (2.06 and 1.97 KJ/m²).

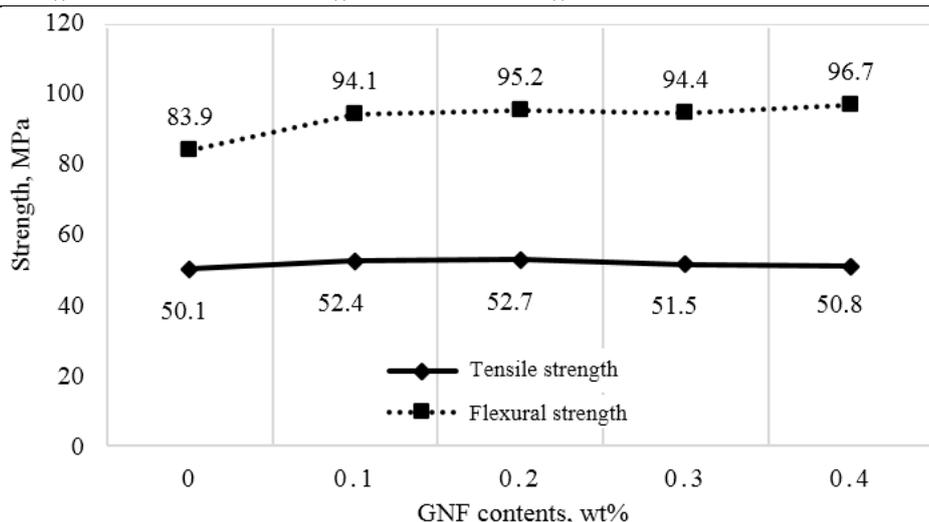


Figure 11. Effect of the GNF loading on the tensile strength and flexural strength of UPR

As shown in Fig. 11, tensile strength and flexural strength are not significantly different between GNF/UPR samples and non-GNF samples. Thus, the glass nano-fiber content seems not to affect the tensile strength and flexural strength of UPR.

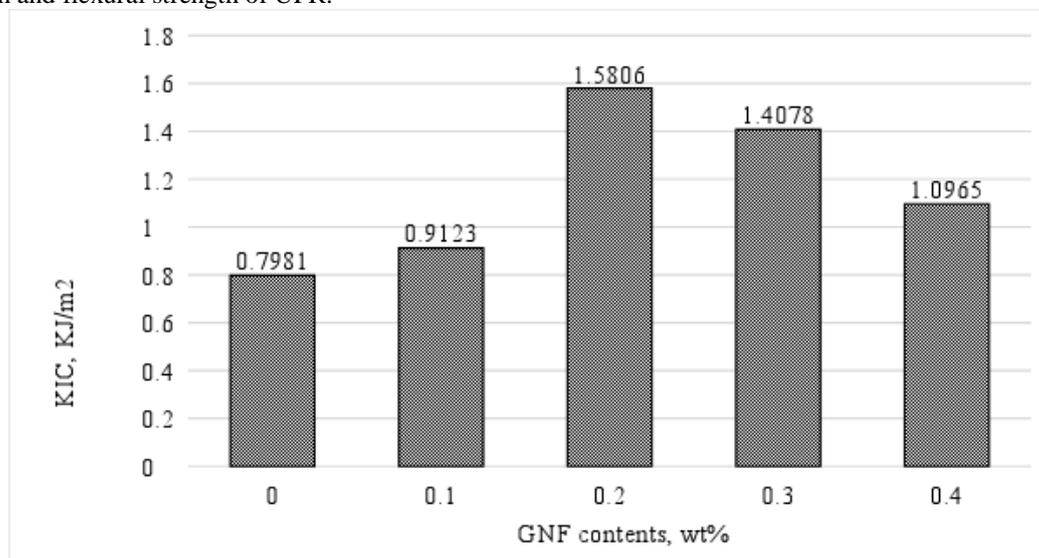


Figure 12. Effect of the GNF loading on K_{IC} value of UPR

Unlike the other mechanical strengths, the K_{IC} value of 0.2 wt% GNF/UPR is as much as two times greater than that of non-GNF composites (increased by 98.0%).

IV. CONCLUSION

In this study, GNF was used to enhance the mechanical properties of unsaturated polyester resin. The GNF was dispersed into the UPR using high speed mechanical stirring for 15 hours. The mechanical properties of GNF/UPR composites such as: tensile strength, flexural strength, IZOD impact strength and fracture toughness (K_{IC} value) were determined. The results show that, at the GNF content of 0.2 wt% and after 15 hours stirring, the tensile strength, flexural strength, IZOD impact of 0.2 wt% GNF/UPR with styrene-added did not change much compared to the neat UPR. For instance, tensile strength, flexural strength, IZOD impact strength of 0.2 wt% GNF/UPR composites were: 52.7 MPa·m^{-1/2}; 95.2 MPa, 2.25 KJ/m², increasing by 5.2%, 13.5% and 9.2%, respectively, compared to the neat UPR. However, the K_{IC} coefficient increased significantly to 98.0% in comparison with neat UPR.

V. Acknowledgements

The authors are thankful to Polymer Center and National Key Laboratory of Polymer and Composite Materials (HUST), B2017-BKA-03-PTNTĐ project and Prof. Toru Fujii (Department of Mechanical Engineering and Systems, Doshisha University, Kyoto, Japan) for financial, materials and equipment support of this research.

REFERENCES

- [1]. James A. Fadell. Method of preparing glass microfibers for use in composites and flowable microfiber products (Patent US 5585180A), 1996.
- [2]. AsokanPappu, Vijay KumarThakur. Towards sustainable micro and nano composites from fly ash and natural fibers for multifunctional applications, *Vacuum*, Vol. 146, 2017, 375-385.
- [3]. K. Song. Micro- and nano-fillers used in the rubber industry, *Progress in Rubber Nanocomposites*, A volume in Woodhead Publishing Series in Composites Science and Engineering, 2017, 41–80.
- [4]. Soraia Pimenta, Silvestre T. Pinho. Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook, *Waste Management*, Vol. 31 (2), 2011, 378-392.
- [5]. K. H. Wong, S. J. Pickering, T. A. Turner, N. A. Warrior. Compression moulding of a recycled carbon fibre reinforced epoxy composite. In: SAMPE'09 Conference, Baltimore, MD, USA, 2009.
- [6]. C.A. May. *Epoxy Resins, Chemistry and Technology*. 2nd Edition, Dekker, New York, 1998.
- [7]. M. Praeger, E. Saleh, A. Vaughan, W. J. Stewart, W. H. Loh. Fabrication of nanoscale glass fibers by electrospinning. *Applied Physics Letters*, Vol. 100 (6), id. 063114 (3 pages), 2012.
- [8]. J. Christopher Ellison, Alhad Phatak, W. David Giles, W. Christopher Macosko, S. Frank Bates. Melt blown nanofibers: Fiber diameter distributions and onset of fiber breakup, *Polymer*, Vol. 48 (11), 2007, 3306-3316
- [9]. Nguyen Tien Phong, H. Mohamed Gabr, Le Hoai Anh, Vu Minh Duc, Andrea Betti, Kazuya Okubo, Bui Chuong & Toru Fujii. Improved fracture toughness and fatigue life of carbon fiber reinforced epoxy composite due to incorporation of rubber nanoparticles, *Journal of Materials Science*, Vol. 48 (17), 2013, 6039–6047.
- [10]. Hong-Yuan Liu, Gong-Tao Wang, Yiu-Wing Mai, Ying Zeng. On fracture toughness of nano-particle modified epoxy, *Composites Part B: Engineering*, Vol. 42 (8), 2011, 2170-2175.
- [11]. Ying Zeng, Hong-Yuan Liu, Yiu-Wing Mai, Xu-Sheng Du. Improving interlaminar fracture toughness of carbon fibre/epoxy laminates by incorporation of nano-particles, *Composites Part B: Engineering*, Vol. 43 (1), 2012, 90-94.

Corresponding authors:

Nguyen Thanh Liem

Polymer Center, Hanoi University of Science and Technology, Hanoi, Vietnam

Pham Thi Lanh

Institute of Materials Science, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam