

The Processing of Epoxy/1 wt%-graphene Nanocomposites: Effects of Ethanol on Flexural Properties

Mohd Shahneel Saharudin, Syafawati Hasbi, Asmimi Zulkifli, Nurul Fatimah Zailani

Abstract: Four different types of nanocomposites were successfully produced using solution casting technique. Graphene was dispersed in four different ethanol concentrations; 0g, 1g, 2.5g, and 5g. In general, it can be observed that ethanol is an excellent agent for 1 wt% graphene dispersed in the epoxy matrix. The maximum increase in flexural properties, impact strength and microhardness were observed in 1 wt% graphene dispersed in 1g ethanol. The flexural strength and modulus increased by 62% and 61% respectively. The highest impact strength was recorded for 1 wt% graphene dispersed with 1g ethanol, where an improvement of 9.5% was observed. The maximum Vickers microhardness was recorded to improve 3% compared to monolithic epoxy. SEM images revealed that graphene can impede the advancing cracks and significantly change the fracture mode from a straight fracture path to radially emanated path. It is worth to point out that if ethanol is not completely evaporated during processing, it can cause porosity which is unfavourable to the mechanical properties of the nanocomposites.

Keywords : Nanocomposites, Epoxy, Flexural properties, graphene dispersion.

I. INTRODUCTION

Epoxy resins are typically used in aerospace, automotive, building and construction application due to their distinct mechanical properties, favourable thermal stability, ease of processing, compatibility with other fibers and excellent chemical and water resistant [1], [2].

However, this material has low toughness; hence adding nano particles can improve its properties. The inclusion of graphene into epoxy can considerably increase the physical and chemical performance of matrix at low content providing that the filler is homogeneously dispersed in the matrix [3].

In 2004, graphene was discovered by Andre Geim and Kostya Novoselov [4]. This unique material has received limelight as mother of all graphitic materials owing to its

superlative mechanical, electrical and thermal properties [5]. According to Wei et al., recently the European Commission has invested almost 1 billion in funding in research associated with graphene in academic and commercial institution [6].

Graphene is incorporate in the epoxy to improve its mechanical properties. Significant improvement could be seen when the graphene is uniformly dispersed where the dispersed graphene shared the external stress and blocks the advancing cracks. However, for practical applications, graphene is not suitable to disperse in epoxy just by simple mixing, as graphene tends to accumulate in the matrix [7]. Poorly dispersed graphene could act as a stress raiser and causes stress concentration, which decreases the mechanical properties of composites [3]. Homogenous dispersion graphene in the liquid matrix is very difficult to achieve due to its large surface area [8]. Besides that, the strong van der Waals force attracts graphene to each other which leads to reaggregation of graphene as reported in the literature [9]. Achieving a good dispersion of graphene-reinforcement is one of the difficult challenges in the processing of epoxy/graphene nanocomposites [10]. According to Zhang et al., uniform dispersion of graphene create high surface area of filler which affects the polymer chain that facilitate the improvement of the whole nanocomposite properties [11].

Mittal and Vikal stated that the easiest method for processing epoxy/graphene nanocomposites is by manipulating the surface of graphene which enable direct dispersion of organic solvents [12]. This adds to better physical or chemical interface between the functionalized graphene and polymeric matrices. Several studies describe how the surface alteration of graphene has been carried out by reinforcing surfactant such as amine, organic phosphate, silane, and plasma [13], [14].

As a commonly used surfactant, ethanol is widely known to disperse graphene, however, the dispersing efficiency of ethanol at low content (such as 1 wt%) for graphene in an epoxy matrix is still unknown. In order to evaluate its dispersing performance, epoxy/1 wt%-graphene nanocomposites were produced and their mechanical properties were studied. To date, there has been no specific research publication discussing on the effects of ethanol content on the properties of the epoxy/1wt% graphene nanocomposites [6], [15].

Therefore, this study provides a new insight for the preparation of epoxy/1

Revised Manuscript Received on July 22, 2019.

* Correspondence Author

Mohd Shahneel Saharudin, Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI), Kuala Lumpur, Malaysia. Email: mshahneel@unikl.edu.my

Syafawati Hasbi*, Faculty of Mechanical Engineering, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, Kuala Lumpur, Malaysia. Email: syafawati@upnm.edu.my

Asmimi Zulkifli, Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI), Kuala Lumpur, Malaysia. Email: asmimizulkifli@gmail.com

Nurul Fatimah Zailani, Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI), Kuala Lumpur, Malaysia. Email: nurulfatihahzailani@gmail.com

The Processing of Epoxy/1 wt%-graphene Nanocomposites: Effects of Ethanol on Flexural Properties

wt%-graphene nanocomposites at various ethanol contents and examines the usage of ethanol solvent in the processing of epoxy/graphene nanocomposites.

II. MATERIALS AND SAMPLES PREPARATION

Graphene (nanoplatelets) of 2 μm particle size and thickness in few nm with a surface area of 300 m^2/g and purity of 99.2% was purchased from Sigma Aldrich, UK. The graphene of 1 wt% was dispersed in 4 different ethanol contents of 0g, 1g, 2.5g, and 5g. The dispersion of graphene in ethanol was carried out using a bath sonicator (Fig. 1) for 5 minutes followed by mixing with epoxy resin. The temperature of the ethanol and epoxy mixture was increased to 60 $^{\circ}\text{C}$ for 10 min to remove the solvent. Then, the hardener was added in the epoxy-graphene mixture. Subsequently, the mixture was hand mixing for another 5 minutes before vacuum degassing took place for 15 minutes. The mixture was poured into silicone mould to cured for 6 hours at room temperature before post-curing took place at 150 $^{\circ}\text{C}$ for 6 h as shown in Fig. 2 [16].

The silicone rubber and curing agent used in this research were supplied by Portal Trading, Penang, Malaysia. The gelation time is 25 minutes. The mixture of silicone rubber and the curing agent were poured into an acrylic mould and cured at room temperature for 24 hours. The ratio between the silicone rubber and hardener was 98:2.

The epoxy and hardener used in this research were Miracast 1517A and Miracast 1517B supplied by Miracon Sdn. Bhd., Seri Kembangan, Malaysia. The epoxy has a density of 1.13 g/cm^3 while the hardener has 1.1 g/cm^3 density. This epoxy system is a standard resin for composite industry and has low viscosity. The low viscosity of the hardener prevent the reinforcement agglomeration by improving the dispersion state and fast curing [15]. The resin was left 40 minutes at room temperature for gelation.



Fig. 1. Sonication of 1 wt% graphene in epoxy resin using bath sonicator.



Fig. 2. Post curing of samples at 150 $^{\circ}\text{C}$ in a drying oven.

III. CHARACTERIZATION

A flexural test was performed using Victor Universal Testing Machine (Victor VE 2302). Five specimens were prepared and tested for each composition. For flexural test, the displacement rate was set to 1mm/min. The test properties were conducted based on ASTM D790 using specimen with 3 mm thickness as shown in Fig. 3. Buehler Micromet II was used for Vickers microhardness test for the monolithic polyester and its nano composites in air and after methanol exposure. 200 g of load was applied for 10 s and the readings were taken on specimens based on standard ASTM D790. Brooks Charpy Impact Tester UK was used for the impact test and was performed based on the standard ASTM A370 (Fig. 4). Mini SEM (Thermo Fisher, USA) was used for Scanning Electron Microscopy analysis. The samples were taken from broken flexural specimens.

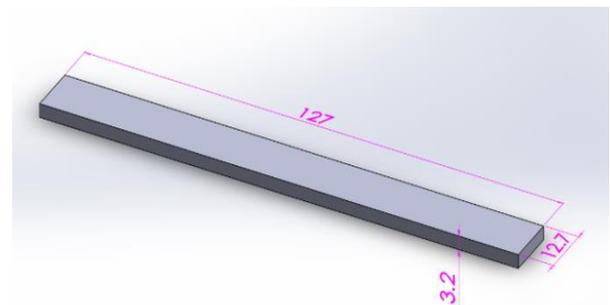


Fig. 3. Illustration of the flexural sample in mm (ASTM D790)

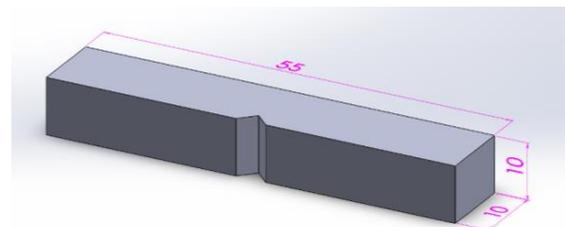


Fig. 4. Illustration of the impact test sample in mm (ASTM 370)

IV. RESULTS AND DISCUSSION

The variation of flexural strength of monolithic epoxy and epoxy/1 wt% graphene nanocomposites prepared with different ethanol dosages is shown in Fig. 5. Monolithic epoxy (ME) recorded 113 MPa of flexural strength. For 1 wt% graphene dispersed without ethanol, the flexural strength increased by 5%. Due to the strong van der Waals, it can be observed that after the sonication process in bath sonicator, graphene has a tendency to reaggregate in the matrix [17]. In the case of 1 wt% graphene dispersed in 1g ethanol, the flexural strength improved by 62%. In the case of 1 wt% graphene dispersed in 2.5g ethanol, the flexural strength increased by 24% compared with monolithic epoxy. The flexural strength recorded the lowest value for graphene dispersed in 5g ethanol.

Flexural modulus of monolithic epoxy and epoxy/1 wt% graphene nanocomposites prepared with different ethanol dosages is shown in Fig. 6. Monolithic epoxy recorded 7.6 GPa of flexural modulus. In the case of graphene dispersed without ethanol, the flexural modulus increased by 42%. The flexural modulus further increased up to 61% in the case of 1wt% Graphene dispersed in 1g ethanol. In the case of graphene dispersed in 2.5g ethanol, the flexural strength increased by about 18.7%. The flexural modulus dropped 22% compared with a flexural modulus of monolithic epoxy. This can be associated with retained ethanol which acts as a stress raiser and thus deteriorating the flexural modulus [18]. Ethanol was not completely removed during the stirring process at 60°C possibly due to insufficient time needed to evaporate.

The variation of flexural strain for monolithic epoxy and epoxy/1wt% graphene nanocomposites prepared with different ethanol dosages is shown in Fig. 7. In general, monolithic epoxy recorded the highest flexural strain compared with all samples reinforced with 1 wt% graphene. This is due to the fact that graphene has outstanding properties of carbonaceous materials, such as high strength and stiffness [19]. Besides that, graphene had decreased the length of the polymeric chain as well as of the number of rigid particles from the polymeric matrix [20].

The variation of impact strength is shown in Fig. 8. It can be seen that monolithic epoxy (ME) exhibit the lowest impact strength compared with other samples reinforced with 1 wt% graphene. The highest impact strength was recorded in the case of 1 wt% graphene dispersed with 1g ethanol, where an improvement of 9.5% was observed. The minimum improvement of impact strength was seen in the case of graphene sonicated in 5g ethanol where 6.8% improvement was observed. The reason for this impact strength improvement is that, when the fracture path becomes more tortuous as cracks deviate around the strong reinforcement, the increase in crack microlayers offers extra work to fracture [19].

The variation of microhardness for monolithic epoxy and epoxy/1 wt% graphene nanocomposites is shown in Fig. 9. The maximum Vickers microhardness was seen in the case of epoxy/1wt% graphene processed with 1g ethanol. An increase of 3% microhardness was recorded. The lowest improvement in microhardness was observed in the case of graphene dispersed in 5g ethanol where only 0.5%

improvement was recorded. The result shows some air entrapment and restriction in the movement of polymer chains due to the reinforcement of graphene. The graphene tends to fill in the porosity in the matrix and restricts the movement of polymer chains that increase the microhardness. As mentioned earlier, the porosity was visible on produced samples due to air entrapment during samples preparation where the volatiles were not able to escape in the curing process.

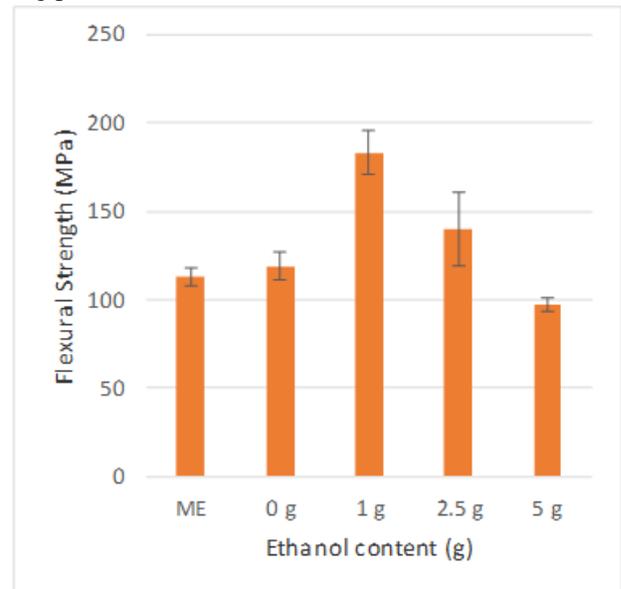


Fig. 5. Flexural strength of epoxy/graphene nanocomposites prepared with ethanol

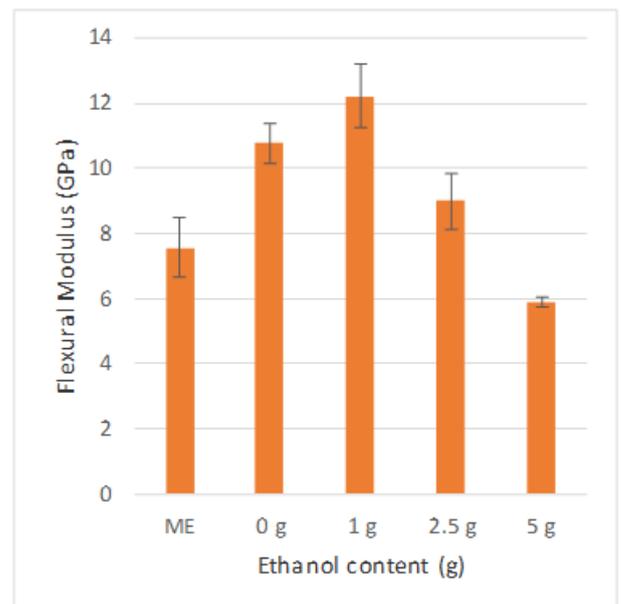


Fig. 6. Flexural modulus of epoxy/graphene nanocomposites prepared with ethanol

V. SEM ANALYSIS

Fig. 10 shows the SEM images taken from flexural samples for monolithic epoxy and epoxy-1 wt% graphene prepared with ethanol. It can be seen that for monolithic epoxy (Fig. 10 (a)), the crack propagates in straight lines when the maximum load is reached. The crack moves without diversions and this can be associated with lower resistance which is very typical for unreinforced epoxy [21]. Fig. 10 (b) shows the SEM image of epoxy-1 wt% graphene sample. The crack started from a defect point and radially emanated as shown below. Dispersion of graphene in ethanol improved the dispersion in the epoxy matrix. The homogenous dispersion and improved chemical interaction between graphene and epoxy matrix contributed to the excellent flexural properties. In contrast, poor graphene dispersion raises stress and lowering its mechanical properties due to stress concentration [18].

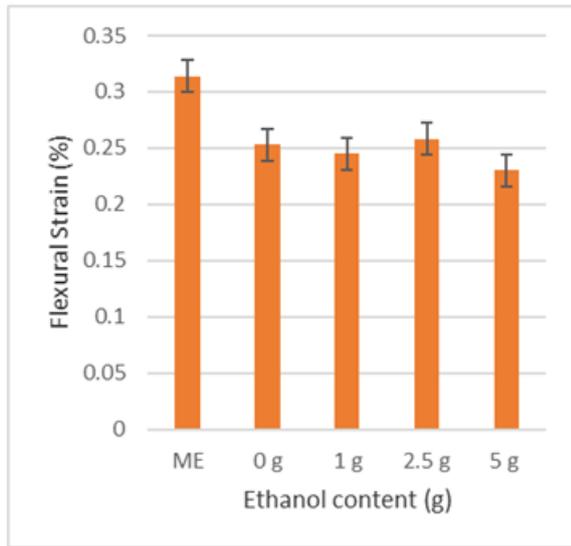


Fig. 7. Flexural strain of the nanocomposites prepared with ethanol

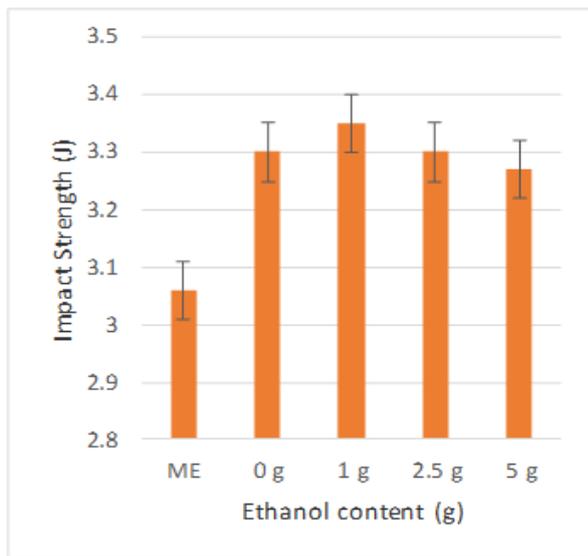


Fig. 8. Impact strength of the nanocomposites

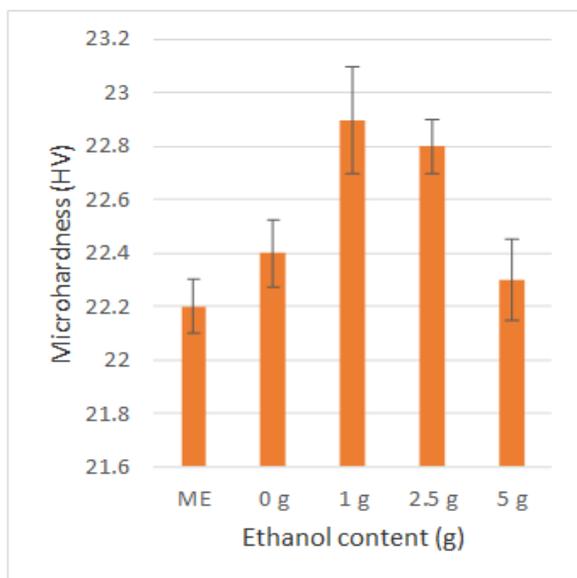


Fig. 9. Microhardness of the nanocomposites

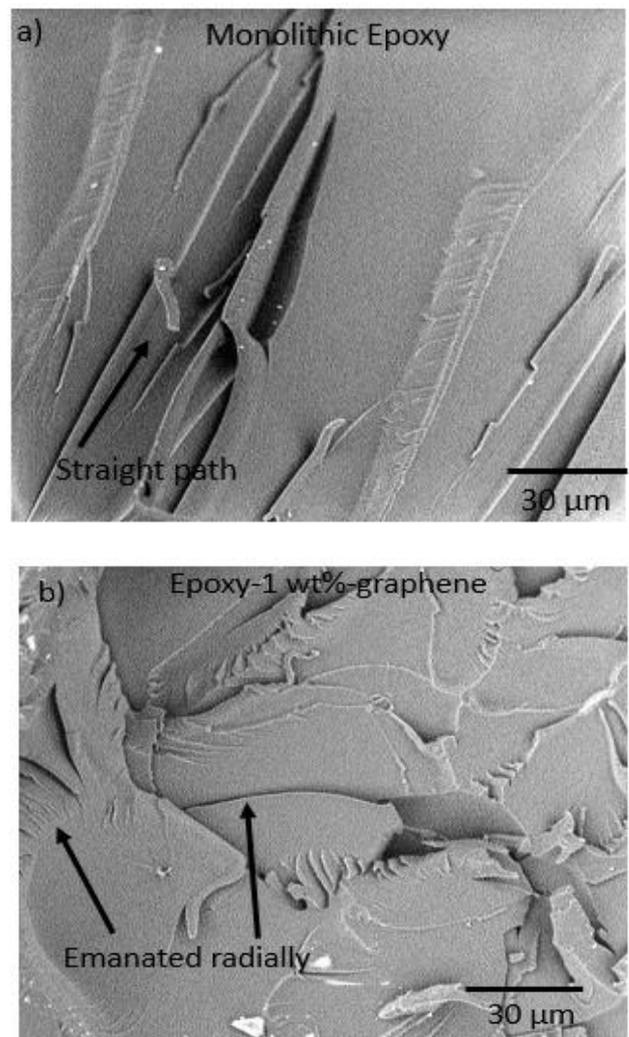


Fig. 10. SEM images of (a) monolithic epoxy and (b) epoxy-1wt% graphene prepared with 1g ethanol

VI. CONCLUSION

Four different types of nanocomposites were successfully produced. It was found that ethanol is an excellent dispersant agent for 1 wt% graphene dispersed in the epoxy matrix. The maximum increase in flexural properties, impact strength and microhardness were observed in the case of 1 wt% graphene dispersed in 1g ethanol. The flexural strength and modulus increased by 62% and 61% respectively. The highest impact strength was recorded for 1 wt% graphene dispersed with 1g ethanol, where an improvement of 9.5% was observed. The maximum Vickers microhardness was recorded to improve 3% compared with monolithic epoxy. SEM images revealed that graphene can obstruct the advancing cracks and significantly change the fracture mode from straight fracture path to radially emanated path. It is worth to point out that if ethanol is not completely evaporated during processing, it causes porosity which is unfavourable to mechanical properties. Further research need to be carried out as the results would differ if ethanol is completely removed at higher temperature during mixing process of graphene and epoxy.

REFERENCES

1. J. Wei, M. S. Saharudin, T. Vo, and F. Inam, "Dichlorobenzene: an effective solvent for epoxy/graphene nanocomposites preparation," R. Soc. Open Sci., vol. 4, no. 10, Art. no. 170778, 2017.
2. M. S. Saharudin, A. Jumahat, A. Z. Kahar, and S. Ahmad, "The Influence of Alumina Filler on Impact Properties of Short Glass Fiber Reinforced Epoxy," in Applied Mechanics and Materials, 2013, vol. 393, pp. 88–93.
3. M. S. Saharudin, I. Shyha, and F. Inam, "Viscoelastic and mechanical properties of multi-layered-graphene polyester composites," in 2nd International Conference on Advances in Mechanical Engineering, 2016, pp. 41–45.
4. A. K. Geim, "Graphene: status and prospects," Science, vol. 324, no. 5934, pp. 1530–4, 2009.
5. A. K. Geim and K. S. Novoselov, "The rise of graphene," Nat. Mater., vol. 6, no. 3, pp. 183–191, 2007.
6. J. Wei, T. Vo, and F. Inam, "Epoxy/graphene nanocomposites – processing and properties: a review," RSC Adv., vol. 5, no. 90, pp. 73510–73524, 2015.
7. V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, and S. Seal, "Graphene based materials: Past, present and future," Prog. Mater. Sci., vol. 56, no. 8, pp. 1178–1271, 2011.
8. I. Shyha et al., "Micro-Machining of Nano-Polymer Composites Reinforced with Graphene and Nano-Clay Fillers," in Key Engineering Materials, 2018, vol. 786, pp. 197–205.
9. J. Wei, M. S. Saharudin, T. Vo, and F. Inam, "Effects of surfactants on the properties of epoxy/graphene nanocomposites," J. Reinf. Plast. Compos., vol. 37, no. 14, pp. 960–967, 2018.
10. B. Tan and N. L. Thomas, "A review of the water barrier properties of polymer/clay and polymer/graphene nanocomposites," J. Memb. Sci., vol. 514, pp. 595–612, 2016.
11. Y. Zhang, Y. Wang, J. Yu, L. Chen, J. Zhu, and Z. Hu, "Tuning the interface of graphene platelets/epoxy composites by the covalent grafting of polybenzimidazole," Polymer (Guildf.), vol. 55, no. 19, pp. 4990–5000, 2014.
12. V. Mittal, "Functional polymer nanocomposites with graphene: a review," Macromol. Mater. Eng., vol. 299, no. 8, pp. 906–931, 2014.
13. S. Ganguli, A. K. Roy, and D. P. Anderson, "Improved thermal conductivity for chemically functionalized exfoliated graphite/epoxy composites," Carbon N. Y., vol. 46, no. 5, pp. 806–817, 2008.
14. A. Celzard, E. McRae, J. F. Mareche, G. Furdin, M. Dufort, and C. Deleuze, "Composites based on micron-sized exfoliated graphite particles: electrical conduction, critical exponents and anisotropy," J. Phys. Chem. Solids, vol. 57, no. 6, pp. 715–718, 1996.
15. J. Wei, R. Atif, T. Vo, and F. Inam, "Graphene Nanoplatelets in Epoxy System: Dispersion, Reaggregation, and Mechanical Properties of Nanocomposites," J. Nanomater., vol. 2015, Art. no. 561742, 2015.
16. M. S. Saharudin, S. Hasbi, N. Mohd Rashidi, and M. S. Jamal Nordin, "Effect of short-term water exposure on mechanical properties of

multi-layer graphene and multi-walled carbon nanotubes-reinforced epoxy nanocomposites," J. Eng. Sci. Technol., vol. 13, no. 12, pp. 4226–4239, 2018.

17. J. Wei, M. S. Saharudin, T. Vo, and F. Inam, "N,N-Dimethylformamide (DMF) Usage in Epoxy/Graphene Nanocomposites: Problems Associated with Reaggregation," Polymers (Basel), vol. 9, no. 6, p. 193, 2017.
18. R. Atif, I. Shyha, and F. Inam, "The degradation of mechanical properties due to stress concentration caused by retained acetone in epoxy nanocomposites," RSC Adv., vol. 6, no. 41, pp. 34188–34197, 2016.
19. R. Atif, I. Shyha, and F. Inam, "Mechanical, Thermal, and Electrical Properties of Graphene-Epoxy Nanocomposites—A Review," Polymers, vol. 8, no. 8, Art. no. 281, 2016.
20. M. Bastiurea, M. S. Rodeanu, D. Dima, M. Murarescu, and G. Andrei, "Thermal and Mechanical Properties of Polyester Composites With Graphene Oxide and Graphite," Dig. J. Nanomater. Biostructures, vol. 10, no. 2, pp. 521–533, 2015.
21. M. Saharudin, J. Wei, I. Shyha, and F. Inam, "The degradation of mechanical properties in halloysite nanoclay-polyester nanocomposites exposed in seawater environment," J. Nanomater., 2016.

AUTHORS PROFILE



Dr. Mohd Shahneel Saharudin is a senior lecturer and head of section at Universiti Kuala Lumpur, Malaysia Italy Design Institute (UniKL MIDI). His research interest is focusing on the development of nanocomposite materials for aerospace, coating and medical applications.

He is an active member of the Institute of Mechanical Engineering (IMEchE, UK) and a registered European Engineer (Eur Ing) with European Federation of National Engineering Associations (FEANI). From 2017 to 2019, he and his team developed an economical fracture toughness and tensile machine for environmental stress cracking resistance study.



Syfawati Hasbi is a lecturer at National Defence University (NDU), Kuala Lumpur, Malaysia. She obtained her MSc Mechanical Engineering from University of Malaya in 2012 and MEng Mechanical Engineering from University of Sheffield, UK in 2009. She has published several articles in peer reviewed mechanical engineering journals.



Asmimi Zulkifli is final year student in BEng Tech Product Design (Hons) at Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI). She earned her Diploma at Institut Kemahiran Tinggi Belia Negara Temerloh (IKTBN), in Automotive Engineering (major in Product Design). Her current research interest is on mechanical performance of graphene/epoxy nanocomposites



Nurul Fatimah Zailani is a final year student at Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI). She is a final year student of BEng Tech Product Design (Hons) at Universiti Kuala Lumpur Malaysia Italy Design Institute (UniKL MIDI). She obtained her Diploma of Engineering Manufacturing in Product Design from KKTMM (Kolej Kemahiran Tinggi MARA) Balik Pulau.