

CONFERENCE ON ADVANCES IN MECHANICAL ENGINEERING ISTANBUL 2016 – ICAME2016
11-13 May 2016, Yildiz Technical University, Istanbul, Turkey

**VISCOELASTIC AND MECHANICAL PROPERTIES OF MULTI-LAYERED-
GRAPHENE POLYESTER COMPOSITES**

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Keywords: Viscoelastic properties, mechanical properties, multi-layered graphene, polyester.

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ABSTRACT

In this study, multi-layered-graphene (MLG) reinforced unsaturated polyester (UP) were prepared by adding different weight percentage of graphene in polyester resin and subsequently cross linked using mixture of methyl ethyl ketone peroxide. The mechanical properties of polyester-graphene were also studied. The maximum increase T_g was obtained from 80.85°C to 87.59°C in case of 0.7 wt%. The Vickers microhardness (HV) was increased up to 116% compared to monolithic polyester. Flexural modulus of 0.7 wt% reinforcement recorded the highest modulus with 1.19 GPa. It was found that the addition of multi-layered graphene significantly improved the dynamic and mechanical properties of the composites.

INTRODUCTION

The field of nanoscience has become a very interesting topic in the last two decades, and the importance for nanotechnology has increased as miniaturization becomes more essential in areas which include computing, sensors, biomedical and many other applications [1]. Developments in these disciplines depend mainly on the ability to synthesize nanoparticles of various materials, sizes and shapes, as well as to assemble them efficiently into complex architectures. Currently, nanomaterials

have an enormous range of applications owing to their structural features. However, material scientists are examining materials with improved physicochemical properties that are dimensionally more suitable in the field of nanoscience and technology. In this regard, the discovery of graphene and graphene-based polymer nanocomposites is an important addition in the area of nanoscience, playing a key role in modern science and technology.

Graphene is one of the most interesting materials being investigated today. Graphene, as a nanofiller, may be preferred over other conventional nanofillers due to their high surface area, aspect ratio, tensile strength, thermal conductivity, electrical conductivity and transparency [2]. The superior properties of graphene compared to polymers are also reflected in polymer-graphene nano composites. Polymer-graphene nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared to the neat polymer [3], [4]. It was also reported that the improvement in mechanical and electrical properties of graphene based polymer nanocomposites are much better in comparison to that of clay or other carbon filler-based polymer nanocomposites [5], [6]. In recent study by Bora et al. reported that polyester resin-graphene oxide nanocomposite tensile strength was increased up to 76% and achieved 41% increase in Young's modulus [7].

Polyester resins are one of the most commonly used thermosetting polymers because of their low cost and

versatility[8]–[11]. These properties make them a potential candidate as polymer matrix to produce composites for various applications. Most of the dinghies, yachts and workboats[12] are built using composites based on various polyester resins. Polyesters are also used in coatings, construction, transportation, storage tanks, and piping [7].

When used as polymer matrix, the degree of crosslinking of polyester resins is a crucial factor to achieve desired mechanical properties, especially in the presence of nano-fillers as they can significantly influence the degree of crosslinking. In recent years, there has been an increasing interest for the incorporation of nano-fillers in polyester resins. Nano-fillers exhibit and impart a suit of remarkable properties[13] to polyester resins, as compared to other conventional micro or macro-sized fillers[14].

This research is aimed to study the dynamic and mechanical properties of multi-layered graphene (MLG) reinforced polyester composites using dynamic mechanical analyzer (DMA), Buehler Micromet II and Instron Universal testing machine.

Materials

MLG of 12 nm average thickness and 4.5 μm average lateral size with surface area of 80 m^2g^{-1} was purchased from Graphene Supermarket. The polyester resin (Norsodyne O 12335 Al) with density of 1.12 g cm^{-3} was supplied by East Coast Fibreglass UK. Butanox M-50 catalyst with -1.18 g cm^{-3} was used to cure the polyester and acquired from East Coast Fibreglass UK. The gelation time of the resin was 30 min at room temperature.

Samples production

Unsaturated polyester (UP) resin was mixed together with catalyst (methyl ethyl ketone peroxide). Using a bath sonicator, the mixture of unsaturated polyester resin, catalyst and multi-layered graphene (MLG) were stirred up for 5 minutes to achieve uniform dispersion and also to evade agglomeration. Samples of MLG-Polyester were produced at different weight fractions (0 wt%, 0.1 wt%, 0.5 wt%, 0.7 wt% and 1 wt%). The mixture then was poured into silicone mould to cure at room temperature and demould after 24 hours. The composites then were post cured at 80°C for 24 hours. The composites were prepared according to ISO 178.

Characterisation

DMA (Model 8000, Perkin-Elmer) was used to determine dynamic storage modulus (E'), and loss modulus (E'') of the samples. The loss factor $\tan\delta$ was calculated as the ratio (E''/E'). Rectangular test specimens of dimensions 20 x 10 x 3 mm were used with a single cantilever clamp. All tests were carried out by temperature sweep method

(temperature ramp from 60 °C to 130 °C at 5 °C min^{-1}) at a constant frequency of 1 Hz. The maximum force of DMA was 10 N and applied during all DMA test. The glass transition temperature (T_g) was taken as the temperature value at the peak of $\tan \delta$ curves.

Vickers microhardness test was performed using the Buehler Micromet II for the monolithic polyester and its nanocomposites. The samples were clamped and subjected to penetration of indenter. The load applied was 200 g for 10 seconds. Three-point bending test was performed using Instron Universal Testing Machine (Model 3382) according to ISO 178 with dimensions 80 x 10 x 4 mm. Five specimens were tested for each composition. The displacement rate was kept 1mm/min and the distance between span was 46mm.

RESULTS AND DISCUSSION

Dynamic mechanical analysis (DMA) is a powerful technique for studying the viscoelastic behavior of polymer-based materials [15]. The glass transition temperature of MLG-Polyester is shown in Figure 1. As expected from the single cantilever bending mode results, MLG increased the T_g as evidenced from Figure 1 and Figure 2.

The T_g increased from 80.85 °C to 82.68 °C in case of 0.1 wt% reinforcement. The maximum increase in T_g was observed in case of 0.7 wt% with 87.59 °C (6.74 °C increase). The lowest T_g was found in case of 1 wt% with 71.38°C (9.47 °C decrease). It can be seen that the incorporation of MLG significantly increased the glass transition temperature of the unsaturated polyester resin. The variation of $\tan \delta$ is shown in Figure 2. The incorporation of MLG shifted the $\tan \delta$ curve to the right for 0.1 wt%, 0.5 wt% and 0.7 wt%. In case of monolithic polyester, the mean value of $\tan \delta$ was 1.215. The $\tan \delta$ decreased with the addition of MLG especially in case of 0.1 wt%, 0.5 wt% and 0.7 wt%. At 0.1 wt% The $\tan \delta$ was 1.13, in case of 0.5 wt% the $\tan \delta$ was 1.125 in case of 0.7 wt% reinforcement. At 1 wt% of reinforcement, the $\tan \delta$ increased to 1.27. However in case of 1 wt% the $\tan \delta$ curve was shifted slightly to the left.

Figure 3 shows the storage modulus of the polyester and its composites. The highest storage modulus was obtained in case of 0.7 wt% (2.76 GPa) and the lowest value was observed in case of 1 wt% (0.57 GPa) reinforcement. The inferior storage modulus at 1 wt% of reinforcement as compared to other compositions indicates that the agglomeration may act as flaws, thus lowering the storage modulus. There was no significant effect of MLG on storage modulus after glass transition temperature. From the $\tan \delta$ and storage modulus, it can be concluded that at 0.1 wt%, 0.5 wt% and 0.7 wt% the MLG was uniformly dispersed as also reported by Rasheed et al. in their epoxy-MLG composites [16].

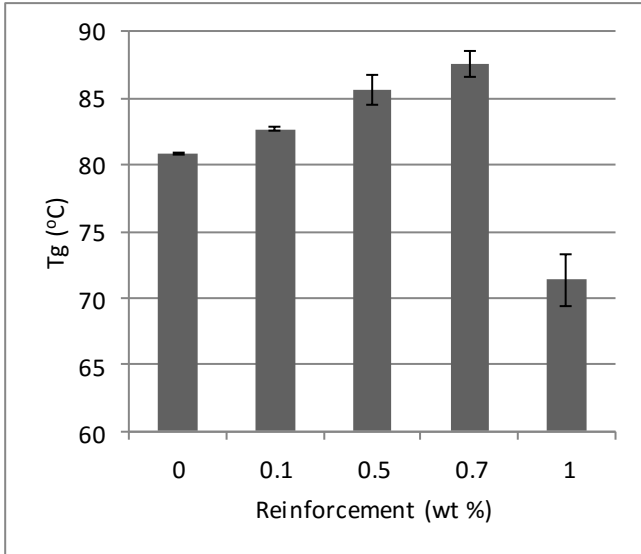


Figure 1. The variation of glass transition temperature

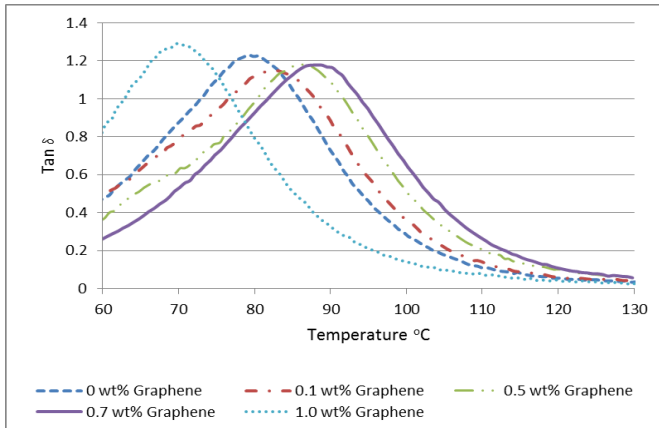


Figure 2. Tan δ curve for MLG-polyester composites

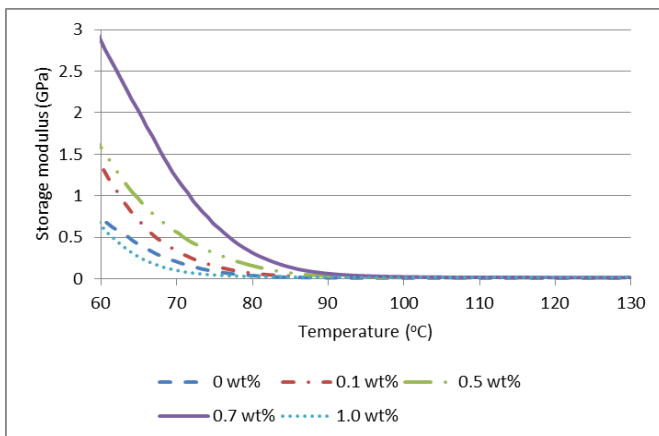


Figure 3. Storage modulus of MLG-polyester

When the MLG is homogeneously dispersed, the wrinkled texture of reinforcement along with high surface area influence the maximum exothermic heat flow temperature by restricting polymer chain mobility, as a result the T_g increase [17]. Figure 4 shows the variation of loss modulus of the monolithic polyester and its composites. The loss modulus decreased with the reinforcement of MLG in case of 0.1 wt%, 0.5 wt% and 0.7 wt%. The maximum loss modulus recorded in case of 1 wt% reinforcement with 0.1 GPa and for monolithic polyester, the loss modulus was 0.08 GPa.

The variation of Vickers microhardness for monolithic polyester and its composites is shown in Figure 5. Monolithic polyester obtained 34.86 HV. At 0.7 wt% reinforcement, the microhardness improved up to 75.28 HV (116% increase). In general the MLG incorporation improved the microhardness but in case of 1 wt% the microhardness observed was 34.82 HV (decrease 0.1%). Agglomeration of MLG caused the reduction in Vickers microhardness. The other reason of lower microhardness and other mechanical properties could be due to the bridging of reinforcement particles [18].

The flexural modulus of monolithic polyester and its composites is shown in Figure 6. In case of monolithic polyester, the flexural modulus obtained was 0.23 GPa. In case of 0.1 wt% the flexural modulus increased to 0.53 GPa which is about 130% increase. The flexural modulus steadily improved in case of 0.5 wt% (200% increase) and 0.7 wt% (417% increase). In case of 1 wt% about 156% increase in flexural modulus was observed. Figure 7 shows the maximum flexural strength of the monolithic polyester and its composites. The lowest flexural strength was observed in case of monolithic polyester with 21.15 MPa. The maximum increase of flexural strength was observed in case of 0.7 wt% with 86% increase. As for 0.1 wt% and 0.5 wt% reinforcement, the flexural strength recorded was 26.25 MPa and 38.82 MPa respectively.

The variation in flexural strain (%) is presented in Figure 8. The flexural strain was taken as the % value of strain corresponding to flexural strength. The flexural strain decreased with increasing weight fraction of 0.1 wt%, 0.5 wt% and 0.7 wt%. The lowest value of flexural strain was observed in case of 0.7 wt% where only 3% strain recorded. The highest flexural strain was observed in case of monolithic polyester, where 7.8% strain was obtained before samples fracture. The incorporation of MLG improved the stiffness of the polyester, increasing the flexural modulus and flexural strength. On the other hand, the strain values were decreased with the addition of MLG. The post curing temperature at 80°C for 24 hour significantly influenced the dynamic and mechanical properties of the nano-composites. We confirmed that the unsaturated polyester and every composite had been completely cured from the glass transition temperature. In comparison to our previous research work, for monolithic polyester in particular. The flexural modulus was significantly improved however the flexural strength of the composites slightly lower due to high crosslinking level as a result of higher post curing temperature [11].

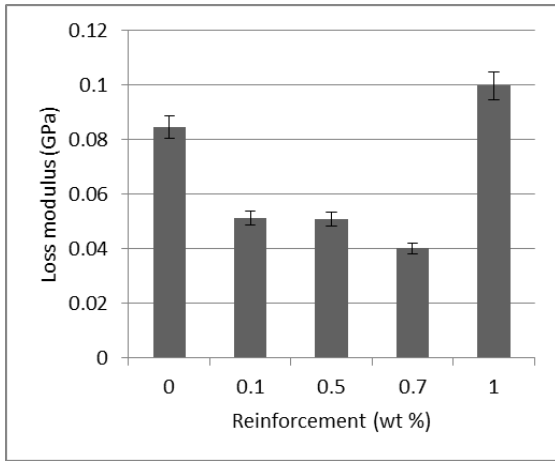


Figure 4. Loss modulus of monolithic polyester and its composites

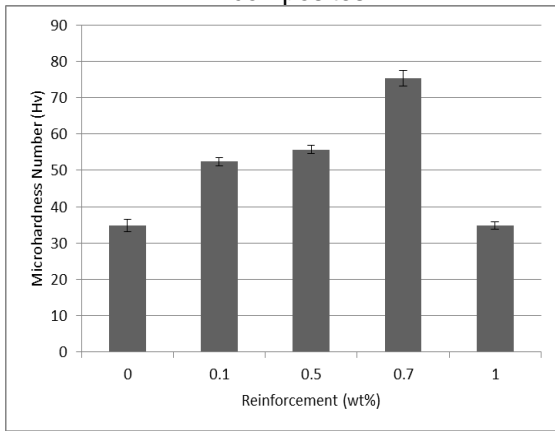


Figure 5. Variation of Vickers microhardness number (HV)

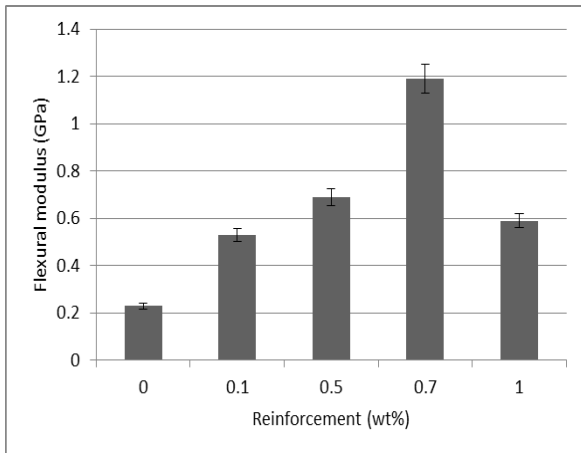


Figure 6. Flexural modulus of monolithic polyester and its composites

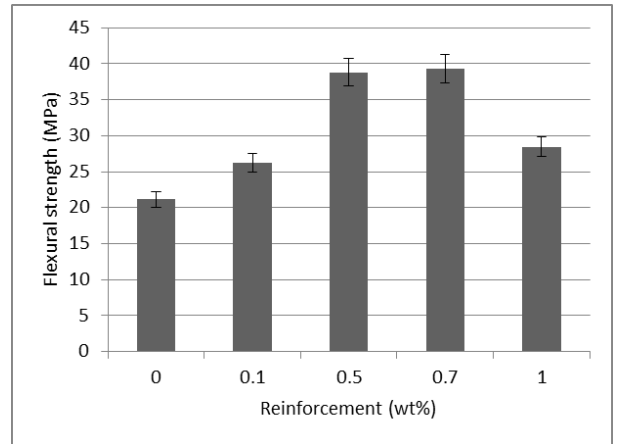


Figure 7. Flexural strength of monolithic polyester and its composites

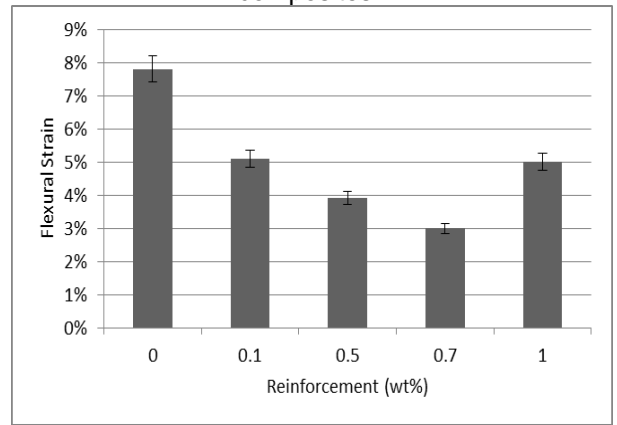


Figure 8. Flexural strain (%) versus reinforcement (wt%)

CONCLUSION

In this study, multi-layered graphene (MLG) reinforced polyester were prepared by adding different weight percentage of graphene in polyester resin and subsequently cross linked using mixture of methyl ethyl ketone peroxide. The addition of multi-layered graphene (MLG) in polyester resin significantly improved the thermal and mechanical properties of the nanocomposites. The glass transition temperature T_g increased from 80.85°C to 87.59°C in case of 0.7 wt%. The Vickers microhardness was increased up to 116% compared to monolithic polyester. Flexural modulus of 0.7 wt% reinforcement recorded the highest modulus with 1.19 GPa.

ACKNOWLEDGMENTS

The authors would like to thank Faculty of Engineering and Environment, Northumbria University and Majlis Amanah Rakyat (MARA) for the technical supports and funding provided in this research.

NOMENCLATURE

UP	Unsaturated polyester
MLG	Multi-layered-graphene
HV	Vickers microhardness
T_g	Glass transition temperature
Tan δ	Loss factor
E'	Dynamic storage modulus
E''	Loss modulus

REFERENCES

- [1] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, and J. H. Lee, "Recent advances in graphene based polymer composites," *Prog. Polym. Sci.*, vol. 35, no. 11, pp. 1350–1375, 2010.
- [2] H. Kim, A. a. Abdala, and C. W. MacOsco, "Graphene/polymer nanocomposites," *Macromolecules*, vol. 43, no. 16, pp. 6515–6530, 2010.
- [3] R. Verdejo, M. M. Bernal, L. J. Romasanta, and M. a. Lopez-Manchado, "Graphene filled polymer nanocomposites," *J. Mater. Chem.*, vol. 21, no. 10, pp. 3301–3310, 2011.
- [4] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Mater.*, vol. 6, no. 3, pp. 183–191, 2007.
- [5] T. K. Das and S. Prusty, "Graphene-Based Polymer Composites and Their Applications," *Polym. Plast. Technol. Eng.*, vol. 52, no. April 2015, p. 130227104444003, 2013.
- [6] M. S. Saharudin, R. Atif, I. Shyha, and F. Inam, "The degradation of mechanical properties in polymer nanocomposites exposed to liquid media – a review," *RSC Adv.*, vol. 6, no. 2, pp. 1076–1089, 2016.
- [7] C. Bora, P. Gogoi, S. Baglari, and S. K. Dolui, "Preparation of polyester resin/graphene oxide nanocomposite with improved mechanical strength," *J. Appl. Polym. Sci.*, vol. 129, no. 6, pp. 3432–3438, 2013.
- [8] J. K. Fink, "Unsaturated Polyester Resins," *React. Polym. Fundam. Appl.*, pp. 1–67, 2008.
- [9] M. Rahman, *Degradation of Polyesters in Medical Applications*. Manitoba, Canada.: INTECH, 2012.
- [10] S. H. Aziz and M. P. Ansell, "The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites: Part 1 – polyester resin matrix," *Compos. Sci. Technol.*, vol. 64, no. 9, pp. 1219–1230, Jul. 2004.
- [11] M. S. Saharudin, I. Shyha, and F. Inam, "The effect of methanol exposure on the flexural and tensile properties of halloysite nanoclay polyester," in *The IRES 17th International Conference, United Kingdom*, 2015, no. November, pp. 40–44.
- [12] T. Munikenche Gowda, a. C. B. Naidu, and R. Chhaya, "Some mechanical properties of untreated jute fabric-reinforced polyester composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 30, no. 3, pp. 277–284, 1999.
- [13] M. S. Saharudin, A. Jumahat, A. Z. a. Kahar, and S. Ahmad, "The Influence of Alumina Filler on Impact Properties of Short Glass Fiber Reinforced Epoxy," *Appl. Mech. Mater.*, vol. 393, pp. 88–93, 2013.
- [14] N. N. Bonnia, S. H. Ahmad, S. N. Surip, S. S. Nurul, H. N. Azlina, and H. Anuar, "Mechanical Properties and Environmental Stress Cracking Resistance of Rubber Toughened Polyester/Clay Composite," in *Advanced Materials Research*, 2012, vol. 576, pp. 318–321.
- [15] F. Inam, D. W. Y. Wong, M. Kuwata, and T. Peijs, "Multiscale Hybrid Micro-Nanocomposites Based on Carbon Nanotubes and Carbon Fibers," *J. Nanomater.*, vol. 2010, pp. 1–12, 2010.
- [16] R. Atif, J. Wei, I. Shyha, and F. Inam, "Use of morphological features of carbonaceous materials for improved mechanical properties of epoxy nanocomposites," *RSC Adv.*, vol. 6, no. 2, pp. 1351–1359, 2016.
- [17] L.-C. Tang, Y.-J. Wan, D. Yan, Y.-B. Pei, L. Zhao, Y.-B. Li, L.-B. Wu, J.-X. Jiang, and G.-Q. Lai, "The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites," *Carbon N. Y.*, vol. 60, pp. 16–27, 2013.
- [18] D. A. C. Brownson, D. K. Kampouris, and C. E. Banks, "Graphene electrochemistry: fundamental concepts through to prominent applications," *Chem. Soc. Rev.*, vol. 41, no. 21, pp. 6944–6976, 2012.

