WOOD FIBER COMPOSITES WITH ADDED MULTI-FUNCTIONALITY

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Abstract
Graphene nanoplatelets (GNPs) are used to enhance the mechanical properties and functionality of wood plastic composite (WPC) targeting applications such as de-icing or anti-icing and fast thermal diffusivity. The GNPs are integrated into neat polymer using a masterbatch containing functionalized graphene by melt compounding through a twin-screw extruder without the use of any coupling agent or compatibilizer. The same manufacturing process (melt compounding) but with the use of compatibilizer is employed to produce WPC with nano-doped matrix. The effect of different GNP loadings (up to 15 wt.%) on morphology, crystallinity, mechanical and thermal conductivity of the nanocomposites and the WPCs was investigated. It was found that both strength and modulus of nanocomposites, in tension and bending, were increased with the addition of GNPs. With the aid of MAPE compatibilizer WPCs show higher flexural strength and modulus than neat polymer. GNP has marginal effect on the flexural stress but further increases flexural modulus of WPC. The preliminary results related to the thermal conductivity of studied materials indicate that the incorporation of GNP may be beneficial for faster and more uniform heat distribution in WPC.

1. Introduction

Growing environmental concerns and dwindling fossil resources have led to increasing need for sustainable solutions. Wood plastic composites (WPC) containing wood flour or wood fibres dispersed in a polymer matrix, mostly thermoplastic, have been largely utilised in applications where timber is usually used, e.g., decking and fencing. WPC are said to have advantages over natural untreated wood such as higher resistance to insects and rotting, lower moisture absorption and less maintenance need [1]. WPC is most commonly processed using the side-streams of wood industry and recycled plastics is quite often used as matrix, hence is beneficial for increasing the added value of forest resources and reducing plastic waste disposal in landfill. However, in places where there is abundant forest resources, such as the Nordic countries, timber is still preferred over WPCs in products such as fencing and decking boards. Therefore, it is very important to increase the functionalities of WPCs without comprising or even improving their structural properties for innovative products that can have extended use in more versatile and/or high-end applications. Integration of functional nano-particles in WPC can be a promising aproach for such purposes [2].

Different nano-particles have been used in bio-based composites, such as nano-clay [3], carbon nanotubes [4] and graphene [5], to mention only a few. Due to extremely large specific surface area and

high aspect ratio these nano-particles can provide effective reinforcement at nano-scale. Besides, they can influence other material properties such as electrical and thermal conductivity. Graphene, as an example, can have a surface area of 2600 $m^2 g^{-1}$ [6], possesses an intrinsic stiffness of 1 TPa [7], thermal conductivity of around 5000 $W \cdot K^{-1} m^{-1}$ [8] and electrical conductivity of 3000 $S \cdot m^{-1}$. If dispersion of these nano-particles can be achieved, their superior properties are expected to be transferred into the composites leading to an enormous improvement in properties. To aid their homogeneous dispersion in the polymer matrix and improve their particle-polymer adhesion, the surface of the nano-particles is often functionalized or the addition of a compatibilizer is utilized.

Nano-clay and TiO_2 nano-powder were used to increase fire retardancy and antibacterial characteristics of polystyrene [9] and polyethylene [10] based WPC. Sheshmani et al. [5] reported the improvement of mechanical, thermal and water resistance properties of wood plastic composites by the incorporation of small amount of graphene. Loading of 0.8 wt.% graphene resulted in improvement in tensile strength of about 20% and water uptake reduction of 35%. Idumah et al. [11] reported an increase of thermal conductivity by 88% by the addition of 3phr of exfoliated graphene in addition to the improvement of mechanical properties and water uptake resistance of kenaf fibres reinforced polypropylene composites. To the best knowledge of the authors, the use of graphene to enhance conductivity of WPC has seldom been reported.

The current work reports the method to process graphene modified high density polyethylene (HDPE) nanocomposites and graphene modified WPC based on the same HDPE matrix, which has high industry relevance and low environmental impact and is apt to be scaled up. Results of mechanical properties of nano-doped materials in combination with study of microstructure and morphology, as well as initial qualitative assessment of thermal conductivity are reported in this paper.

2. Experimental

2.1. Materials

HDPE (MG9647S) in the form of pellets was purchased from BOREALIS (1220 Vienna, Austria). HDPE based graphene masterbatch (heXo HDPE1-V20/35) in pellet form was purchased from NanoXPLOre (Montreal, Canada). The masterbatch contains 35 wt.% of dispersed graphene nanoplatelets (GNP) which are functionalized at the edges of nanoplatelets using a patented method leading to an oxygen content of less than 5%. According to the information provided by the supplier, the GNP has an average thickness of 20 nm and flake size of 50 μm, the number of layers in one platelet is ~40. The wood flour (WF) is sawdust of spruce and pine wood with 75% of its particles in the size range 200- 400 µm. Maleic anhydride HDPE (MAPE), E265, kindly provided by DuPont, was used as compatibilizer in WPC.

2.2. Composite processing

GNP masterbatch was mixed with HDPE according to selected ratios (2, 6 and 15 wt.% GNP) and then fed into a twin co-rotating screw extruder ZSK25 (Krupp Wener & Pfleiderer GmbH, Germany) with a temperature range of 180-200 °C and a mass flow of 8 kg/h. The rotation speed of head screw was 120 rpm. The WPC was processed in the same extruder. Wood flour was dried in the oven at 100 °C overnight before being fed into the extruder. All constituents of WPC in pellets form (HDPE, MAPE and GNP masterbatch) were mixed then fed into the extruder through the main feeder and the wood flour was fed through the side feeder. The compounds were first extruded with a rotation speed of 300 rpm and a mass flow of 10 kg/h and pelletized, then extruded again with a rotation speed of 120 rpm and a mass flow of 8 kg/h. Measured amounts of the extrudate were heated at 220 °C for 30 minutes before compression molded under a pressure of 100 bar into circular plates with a diameter of 320 mm and thickness of 4 mm using a conventional 310-ton compression molding press (Fjellman, Sweden). Table 1 lists the compositions of the manufactured materials.

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Table 1. Composition and coding of studied materials

Sample Code	HDPE (wt.%)	GP (wt.%)	MAPE (wt.%)	WF (wt.%)
HDPE0	100	0	0	0
HDPE2	98	2	0	0
HDPE6	94	6	0	0
HDPE15	85	15	0	0
WPC	58.5	0	1.5	40
WPC7.5	50.9	7.6	1.5	40
WPC15	43.5	15	1.5	40

2.3. Characterization

Tensile properties were measured using an Instron 3366 universal testing machine (Instron, UK) equipped with 10 kN load cell at a crosshead speed of 5 mm/min, following the guidelines of ASTM D638 on 15 mm wide, 200 mm long rectangular specimens. Stiffness was determined from the linear region of stress-strain curve within strain interval of 0.05%-0.25%. Strain was measured using an extensometer with gauge length 50mm mounted in the middle of the sample. Tensile yield stress was obtained as the 0.2% offset yield stress (ASTM D638). Average values of 5 specimens are reported.

Flexural properties were measured using an Instron 4411 benchtop universal machine equipped with 5 kN load cell on samples of dimensions 75 mm, 16 mm and 4 mm (length, width and thickness) with support span to thickness ratio of 16:1. Samples were strained with a speed of 10 %/min for the nanocomposites and 4.7 %/min for the wood composites, following the ASTM D790. The flexural strength was determined for the nanocomposite as the maximum stress at 5% flexural strain. However, due to the more brittle behaviour of composites with WF such strain could not be reached; thus the flexural strength presented for WPC was the ultimate flexural strength.

The Morphology of studied composites was characterized by a scanning electron microscopy (JEOL JCM-6000 Neoscope) on freeze-fractured surfaces sputter-coated with thin layer of gold (<15 μm).

The degree of crystallinity and transition temperatures of processed nanocomposites was studied using a differential scanning calorimeter (Mettler Toledo 180) in a nitrogen controlled environment. Reported values are the average of minimum of 5 specimens per sample. Each specimen was heated at a rate of 10 °C/min up to 220 °C and held at that temperature for 5 minutes to remove the thermal history then cooled down to 25 °C at a rate of 20 °C/min. Both the peak melting temperature and the onset of the endothermic event, indicated by the intersection of the tangential line with the constructed baseline, are reported. Degree of crystallinity ($\%X_c$) was calculated using Eq. 1

$$\%X_c = \frac{\Delta H_f}{\Delta H_f^0} \times \frac{1}{1 - W_{GP}} \times 100 \tag{1}$$

where ΔH_f is the measured enthalpy of fusion of the studied material, ΔH_f^0 is the enthalpy of fusion of 100% crystalline HDPE, 245 J/g from literature [12] and W_{GP} is the weight fraction of the GNP in nanocomposite.

A Testo 870 series thermal camera (Nordtec Instrument AB) was used to provide preliminary information of how heat can be transferred in the studied composites placed on an electrically heated plate connected to a thermal regulator to keep the temperature at 70 °C. The thermal camera was placed on a constant distance and angle over the specimen (Fig.1). Thermal images were processed by use of Testo IRSoft program to extract data for processing and analysis. The temperature profile is mapped

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along the line in the middle of the sample (see thick black line on the right image of Fig.1). In order to obtain single value from each specimen for comparison the average temperature over 10mm distance on the temperature profile line is calculated at different time intervals (see red circle in the right image of Fig.1). Since only relative changes in temperature is of interest, the material ability to emit heat was not elaborately studied here. It should be noted that this is just a preliminary study for qualitative comparison and more accurate and standardized method is to be used in the future for quantification and validation.
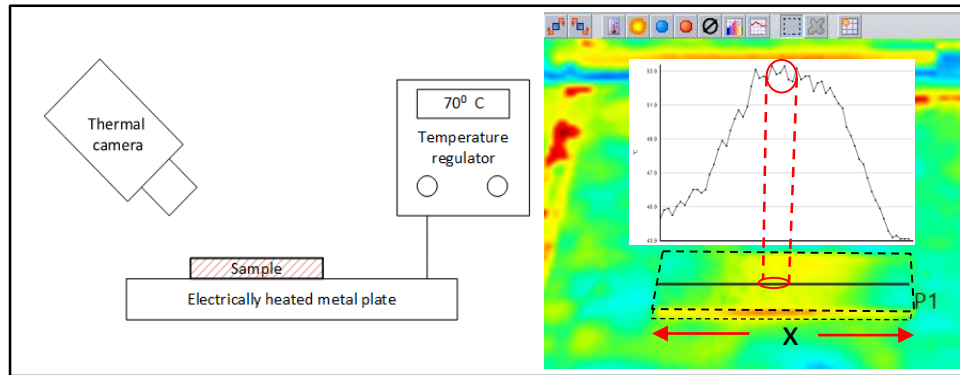

Figure 1. Thermal functionality measurement: schematic of the setup (left) and data extraction (right)

3. Results and Discussion

Fig.2 shows the tensile and flexural properties of studied composites. Tensile/flexural strength and moduli increased with the addition of nano- and/or micro- reinforcement. The stiffness and tensile strength of the nanocomposite with 15 wt.% GNP is 2 and 1.5 times as high as that of neat HDPE (for neat polymer tensile modulus is 1.9 GPa and strength 8.6 MPa), respectively. The addition of wood flour has increased the bending stiffness and strength by 2.2 and 1.8 times with respect to neat HDPE (for neat polymer flexural modulus is 1.2 GPa and strength 28 MPa), respectively. The addition of the GNPs increased flexural modulus of WPC even more while strength was almost unaffected.
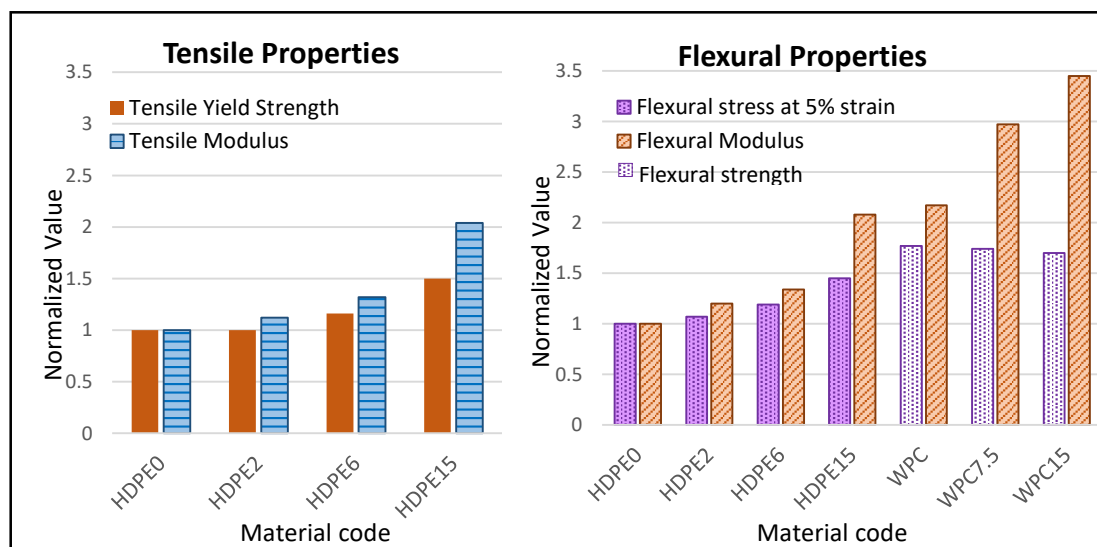

Figure 2. Mechanical properties of materials: tensile and flexural stiffness, yield stress (0.2% offset) and flexural strength (stress at 5% strain for nano-composites, stress at failure for WPC).

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Fig. 3 shows SEM images of the neat polymer, the nanocomposites and the WPC at different GNP loadings. In general, it can be stated that the distribution of the GNP is considered to be homogeneous, however, big flakes that could be aggregates of GNP were still observed in the sample (dashed arrow). The surface morphology is changing with more GNP added. HDPE shows fibril-like ductile surface and plasticized regions while the sample containing 15 wt.% GP shows a smoother surface with less topology which is characteristic for a brittle material. The fractographs of GNP modified WPCs also show a good bonding between the wood flour and the polymer matrix which can be attributed to the use of the compatibilizer. GNPs seem to be very well embedded in the matrix as they were rarely spotted individually. On the other hand, some voids could be seen within the material (enclosed in ovals) that might explain only modest increase of flexural strength.
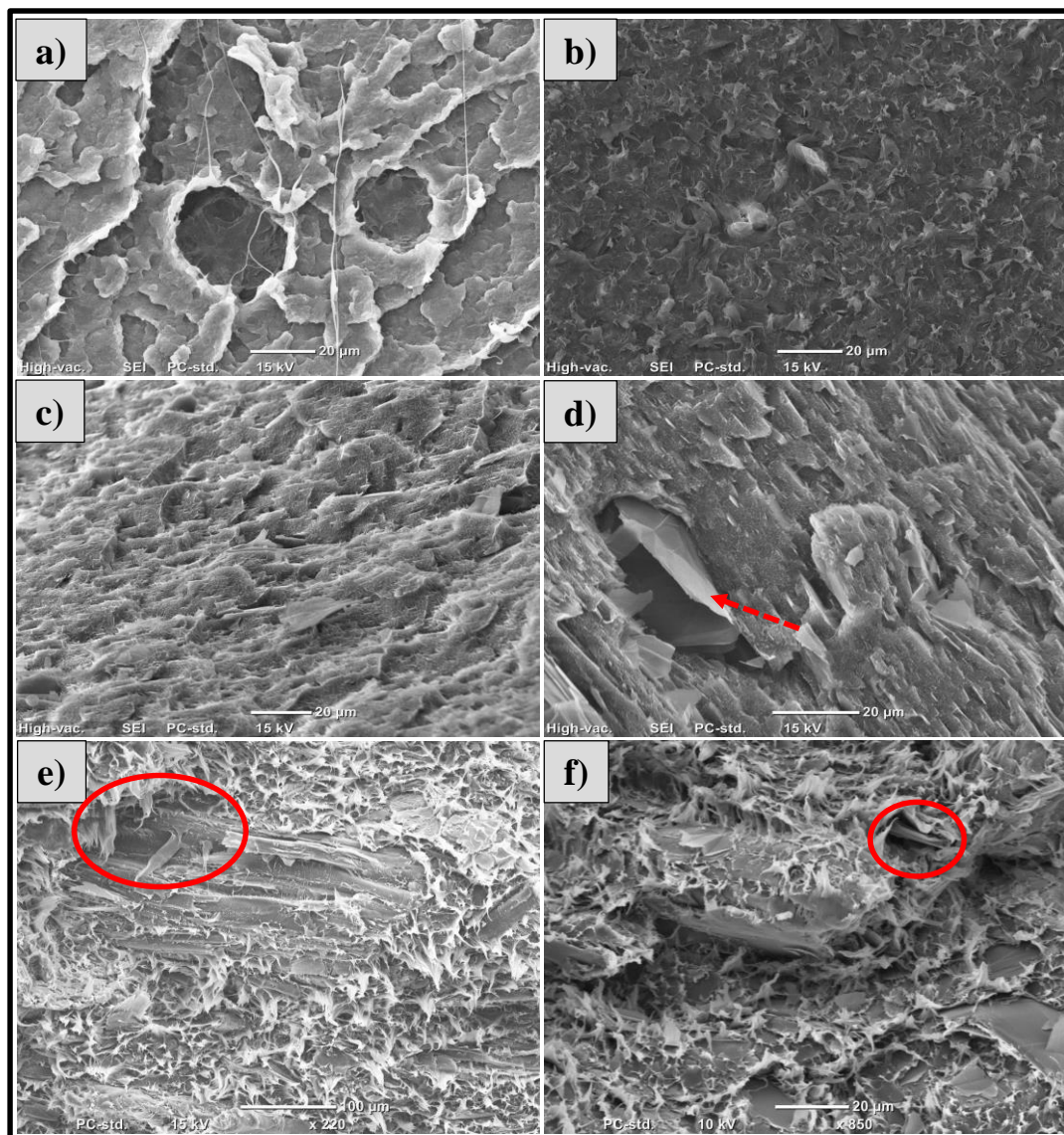

Figure 3. SEM micrographs of the fractured surfaces of a) HDPE0, b) HDPE2, c) HDPE6, d) HDPE15 e) WPC7.5 and f) WPC15. Find the significance of the markings in the text.

Table 2 shows the characteristic values measured during melting and crystallization process for the thermal properties of the tested samples. It can be observed that the addition of GNP hardly has any effect on the melting and crystallization temperatures of HDPE. On the other hand, the addition of

graphene has slightly increased the degree of crystallinity of HDPE regardless the GNP loading. This could be because GNPs act as a nucleating agent leading to more crystallites which are smaller in size.

Table 2. DSC results of the different composites.

Sample code	T_O* (°C) [std]	T_m*(°C) [std]	T_c*(°C) [std]	X_c*(%) [std]
HDPE0	125.3 [0.15]	133.1 [0.9]	116.4 [0.9]	89.3 [1.3]
HDPE2	125.0 [0.7]	133.7 [0.5]	117.1 [0.5]	91.2 [0.6]
HDPE6	125.3 [0.3]	133.4 [0.4]	117.3 [0.5]	91.1 [1.0]
HDPE15	125.1 [0.5]	133.3 [0.7]	117.7 [0.8]	91.1 [1.7]

*T_O, T_m, T_c: onset, melting and crystallization temperatures respectively. X_c: degree of crystallinity. [std]: standard deviation

The graphs in Fig. 4 (on the left) show the temperature profiles across the middle line of the sample recorded by the thermal camera at two time intervals; before and after thermal equilibrium had been reached. It should be noted that the profiles presented in the figure are experimental data fitted by a high order polynomial function. This has been done for better visualization (and easier comparison) of the data to remove and smooth out the local fluctuations. It can be seen that the temperature rise is concentrated in the central area of samples without wood flour regardless of the addition of GNPs; while WPC, with and without GNPs, show temperature rise in a wider area, indicating that wood flour is beneficial for more homogeneous temperature distribution. This is more prominent at early stages of experiment. However, without the addition of GNPs, the WPC shows stronger temperature fluctuation than the GNP modified WPC. Comparing temperatures at specific data point and certain time instances between the different samples (the right graph in Fig. 4) reveals that the addition of wood reduces the temperature rise compared to the pure polymer as wood sawdust have a reported thermal conductivity of 0.02-0.14 W·m^{-1}·K^{-1} which is less than that of HDPE (0.4 W·m^{-1}·K^{-1}). However, the addition of GNPs increases the efficiency of both the polymer and the wood composite to transfer heat as the order of temperature elevation at the same position and time is in the order WPC7.5>HDPE15>HDPE>WPC. This can be directly explained by the imparted functionality from the highly conductive carbonaceous particles.
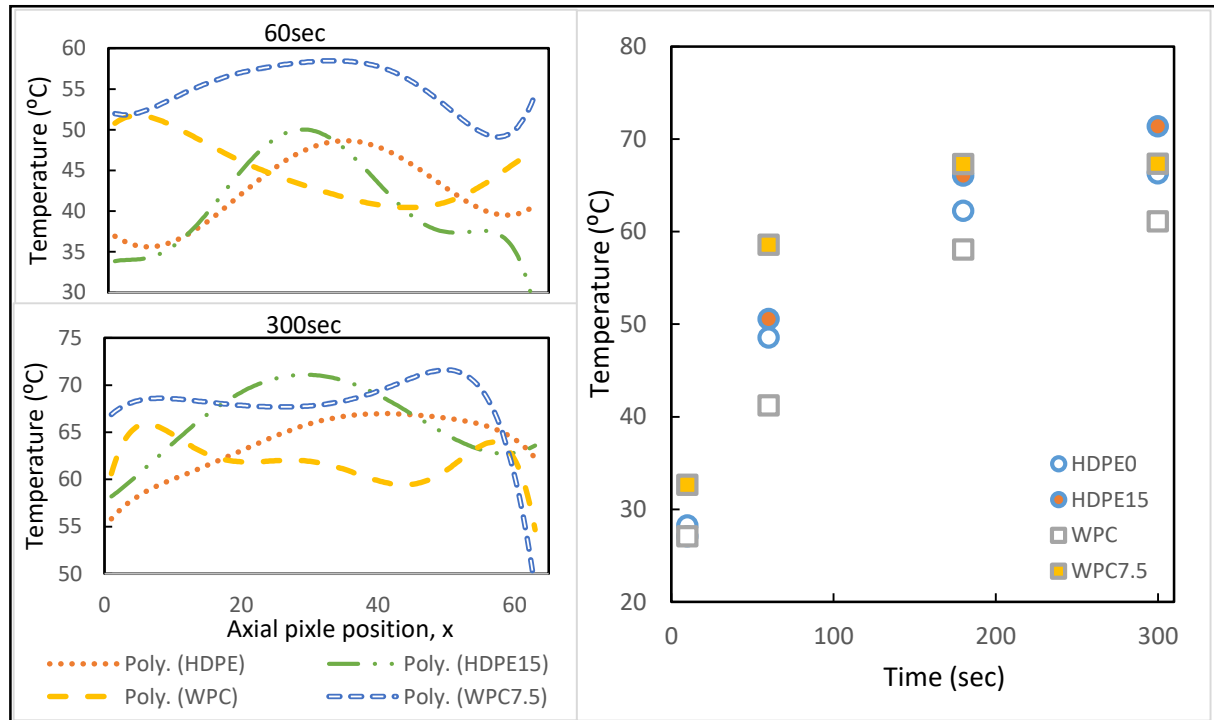
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Figure 4. Fitted temperature profiles at two time instances across the middle line of the sample (left); the average temperature at 10mm at the centre of the line at different time intervals (right).

4. Conclusions

Graphene modified nanocomposites and WPC based on an HDPE matrix were processed through melt compounding in a twin-screw extruder by using a graphene/HDPE masterbatch with 35 wt.% GNPs functionalized at the edges. In the nanocomposites processed without the addition of compatibilizer, both tensile strength and stiffness increased with addition of GNPs. This indicates a uniform dispersion of GNPs in the polymer and good adhesion between GNPs and HDPE. The flexural strength and stiffness of WPC were improved with the addition of wood flour compared to neat HDPE, which can be attributed to the positive influence of MAPE on good dispersion of wood flour and wood-polymer bonding. The addition of GNP has marginal effect on the flexural strength of WPC but further enhanced the flexural modulus. The addition of GNPs increases the efficiency of both the polymer and the wood composite to transfer heat as the order of temperature elevation at the same position and time is in the order WPC7.5>HDPE15>HDPE>WPC. Further measurements of thermal conductivity are required for quantification and verification of these preliminary results

Acknowledgments

References

1.   Agarwal S, Gupta R.K. Improving the mechanical properties of wood plastic composites. In: *Applied Rsearches in Polysaccharides*. Research Signpost, 2015.

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2. Sumithra H, Sidda Reddy B. A review on tribological behaviour of natural reinforced composites. *Journal of Reinforced Plastics and Composites, 2017*

3. Lei Y, Wu Q, Clemons CM, Yao F, Xu Y. Influence of nanoclay on properties of HDPE/wood composites. *Journal of Applied Polymer Science,* 106(6):3958–66, 2015.

4. Hapuarachchi TD, Peijs T. Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for polylactide and its natural fibre reinforced composites. *Composites Part A Applied Science and Manufacturing*,41(8):954–63, 2010.

5. Sheshmani S, Ashori A, Arab Fashapoyeh M. Wood plastic composite using graphene nanoplatelets. *International Journal of Biological Macromolecules*, 58:1–6, 2013.

6. Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A. Graphene: The new two-dimensional nanomaterial. *Angewandete Chemie - International Edition*, 48(42):7752–77, 2009.

7. Kim H, Abdala AA, MacOsko CW. Graphene/polymer nanocomposites. *Macromolecules*, 43(16):6515–30, 2010.

8. Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, et al. Superior thermal conductivity of single-layer graphene. *Nano Letters*, 8(3):902–7, 2008.

9. Devi RR, Gogoi K, Konwar BK, Maji TK. Synergistic effect of nanoTiO2 and nanoclay on mechanical, flame retardancy, UV stability, and antibacterial properties of wood polymer composites. *Polymer Bulletin*, 70(4):1397–413, 2013.

10. Gong G, Nyström B, Joffe R. Enhanced thermal stability and flame retarding properties of recycled polyethylene based wood composites via addition of polyethylene/nanoclay masterbatch. *Plastics, Rubbers and Composites*, 42(6):244–55, 2013.

11. Idumah CI, Hassan A. Characterization and preparation of conductive exfoliated graphene nanoplatelets kenaf fibre hybrid polypropylene composites. Synthetic Metals, 212:91–104, 2016.

12. INOS olefins & Polymers USA, Typical engineering properties of high density polyethylene.