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Water absorption and thermal degradation behavior of graphene reinforced poly(lactic) acid nanocomposite

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Abstract

Thermal stability and high moisture absorption behaviour are major limitations of extensive application of the biodegradable poly(lactic) acid in a variety of technical application which includes the automotive sector. The use of nano fillers and appropriate processing techniques is being considered as a possible route to improve the performance of poly (lactic acid) composites. This study presents the improved performance of PLA composite via the novel processing technique of SPS. The response of the developed composite subjected to moisture absorption over a time range of 6 hrs, 12 hrs and 36 hrs indicated a negligible water uptake. Moreso, the thermogravimetric analysis (TGA) test on the composite reveals thermal stability from room temperature up until 400° C for all the samples. The thermal degradation of the composite was observed above 400°C, indicating a substantial enhancement in its thermal property.

Keywords: polylactic acid, graphene, nanocomposite, water absorption test, Thermogravimetric Analysis.

1. Introduction

Compostable and biodegradable polymers have attracted major research interest due to their potential to mitigate environmental burden. There are several ongoing attempts to replace non-degradable polymers with new sets of biodegradable ones [1,2]. Poly(lactic) acid is considered as the most promising candidate among the biodegradable polymers. Several industries such as packaging, pharmaceutical, textile, automotive, biomedical and tissue engineering are driving towards harnessing the inherent potentials of this eco-friendly polymer. It is a transparent, compostable thermoplastic made from renewable agricultural resources [3]. PLA is regarded as a green polymer because of its ability to degrade into CO_2 and H_2O [4]. It is characterized by high strength, stiffness and easy processing [5]. In spite of the numerous advantages of PLA, few of its drawback are poor water vapour/gas barrier properties and undesirable thermal stability which serve as a restriction for its extended application as bioplastics [6]. Among many approaches adopted by researchers to overcome these limitations are the development of composites, polymer bends and nanocomposites with high aspect ratio organic and inorganic fillers [7,8].

The outstanding mechanical, electrical, thermal and optical features of graphene has made it a focus for research interest in recent times [9,10]. It has shown its great potential as nano-sized fillers in polymer nanocomposite. The use of graphene in polymer material development is often geared towards the property modification of polymer nanocomposite. A significant improvement in material property can be observed even at very low concentration of graphene in a polymer matrix. This can be attributed to the inherent features in graphene. This can be observed when the property of a pristine polymer is being compared with that of a polymer nanocomposite having graphene has nano-filler. Moreso, it has also shown better mechanical and electrical properties when compared with nano clay and other carbon filler polymer nanocomposites [11,12].

The structural application of carbon-based polymer composites exposes it to a variety of environmental conditions which includes high temperature and humidity. The influence of water absorption on the physio- chemical properties of polymer composite has been examined by many researchers. Results obtained revealed that hydrothermal ageing alters the physical and mechanical properties of composite impacting on the performance of the composite in service. In addition, the absorption of water in polymer matrix composite may lead to the plasticization of the polymeric matrix with a resultant significant reduction in the glass- transition temperature and concurrent swelling [13,14]. Moreover, incorporation of fillers into polymeric matrices leads to changes in their glass transition temperature Tg, which can be attributed to the immobilisation of polymer segments close to the surface of the filler particles [15].

The factors influencing moisture absorption in composite materials are temperature, volume fraction of the filler, orientation of reinforcement, nature of filler/ reinforcement; which implies its permeability, polarity and density, area of surface exposed, diffusivity and surface protection [16]. Prolongo et al. [17], studied the water uptake of epoxy composites reinforced with carbon nanofillers. It was reported that carbon nanotubes can significantly decrease the water absorption and water diffusion coefficient by 20-30%. The maximum water content absorbed significantly decreases with the addition of nanofillers, especially in epoxy/CNT composites. The hydrophobic nature of carbon nanofillers is said to be responsible for this regardless of the hydrophilic behaviour of epoxy resin. The decrease of maximum percentage of absorbed water reaches up to 23% for epoxy composite reinforced with 0.1 wt% CNT. Chaharmahali et al. [11] worked on the effect of nano-graphene on the physico-mechanical properties of bagasse/polypropylene composites. The water absorption, thickness swelling, thermal and mechanical properties were evaluated. Results on water uptake claimed a decreased after the addition of nanographene. This was attributed to the fact that graphene layers provided a tortuous path and increased barrier property for water transport. The hydrophobic and water-repelling nature of nano graphene (NG) surface tends to immobilize some of the moisture and inhibits the water permeation in the polymer matrix. This two mechanism suggest that the water absorption has occurred on the surface layer.

This study explores the water uptake behaviour of poly(lactic) acid nanocomposite reinforced with graphene nano particle. It also considers the thermal stability property of the developed material. A very low percentage composition of graphene was added to the poly(lactic) acid matrix. A novel fabrication technique of spark plasma sintering (SPS) was employed in the developed of the nanocomposite. The samples were developed under varied process operating parameters of SPS.

2. Experimental

2.1 Materials

The PLA powder supplied by Micro Powders, Inc., NY was used for the study. According to the product description, a density of 1.23–1.25 g/cm^3 was indicated by the supplier with a maximum particle size of 180 μm and a mesh size of 80. The melting point of PLA of 150–160 ^{o}C given by the supplier. Graphene nanoplatelets (GNP) was supplied by Sigma–Aldrich. The GNP used in this experiment has an average diameter of 5μm, an average thickness of 15 nm, and a typical surface area of 50–80 m^2/g. All materials were used as received without any further purification or modification.

2.2 Fabrication of the Nanocomposite

The procedure applied in the fabrication of these nanocomposites is extensively explained in previous work on optimisation of SPS processing parameters on the density and hardness property of graphene-reinforced poly (lactic) acid nanocomposite [18]. Five percent weighted percentage of GNP was used as reinforcement in the poly(lactic) acid matrix. Design of experiment (DOE) was employed to know the numbers of feasible experimental runs. The samples were prepared through the process of spark plasma sintering at varied conditions of temperature and pressure. A specimen of 10mm thick and 30mm diameter is produced from the admixed powder at full densification by HPD 25 spark plasma sintering (SPS) machine from FCT Systeme GmbH (Raustein, Germany). The heating process ranges from room temperature to the desired temperature with a heating rate of 20 °C /min and holding time of 10 min was considered for this process. The density values were obtained from our previous study and the process parameters which produced each sample were denoted in the alphabetical code as shown in the tables.

2.3. Characterisation

2.3.1 Water Absorption.

The extent of water absorption was examined by complete immersion of the sintered samples in water at room temperature. The initial weight of the samples was recorded before immersion. The immersed composites were taken out periodically from water at a constant time interval of 6 hrs, 12 hrs, 24 hrs and 36 hrs. The water on the surface of the samples was wiped out using a tissue to know the amount of water absorbed in the composite. The amount of water absorbed in the composite was calculated by the weight difference between the samples exposed to water and the dried samples. The weight was measured using digital balance having a precision of 0.01g. The water absorption was carried out using the ASTM D 570-98 (ASTM 1998). The percentage increase in weight was calculated using

$$\textbf{Water Absorption \%} = \{(W_f - W_i) / W_i\} \times 100\ \%$$

Where W_i is the initial weight before immersion and W_f is the final weight after immersion.

2.3.2 Thermal Analysis.

The thermal stability of the nanocomposites was carried out on the GNP/PLA samples to determine the weight loss as a function of temperature. The thermal property was determined using a thermo-gravimetric analyser (TGA; TA Instrument, Model Q500, USA). A constant heating rate of 10° C/min from room temperature to 700°C was maintained under air flow.

3. Results and Discussion

3.1 Thermal stability

The TGA weight loss of the nanocomposite is shown in Figure 1. The processing technique of SPS was influential to the development of highly densified nanocomposite sample. However, there was no wide variation in the thermal stability from the room temperature to 400°C as a result of varying operating parameters (temperature and pressure) of SPS. The temperature values obtained were within close range. Although there exists a difference in the residual remaining as shown in Figure 1. A correlation was observed between the densification of the nanocomposite samples and the amount of residuals. The sample with the greatest densification has the highest residue above 400°C. The level of thermal stability witnessed could be associated with the shielding effect due to the present of flake-like nanofiller and obstructed diffusion of volatile decomposition product [19,20].

Table 1: The temperature at 5% weight loss (T5%), 50% weight loss (T50%), 75% weight loss (T75%) and the percentage of char residue at 400^{o} C.

Sample code	$T_{5\%}$ (^{o} C)	T50% (^{o} C)	T75% (^{o} C)	Residual at 400 ^{o} C	Density
A	344.93	376.13	385.31	2.261655	1.276
B	346.30	377.93	388.26	4.666572.	1.285
C	347.54	381.33	391.79	4.963210	1.288
E	349.12	379.71	390.13	4.731041	1.287
F	347.01	376.30	385.87	2.844818	1.278
G	352.15	377.92	387.26	3.34310	1.283

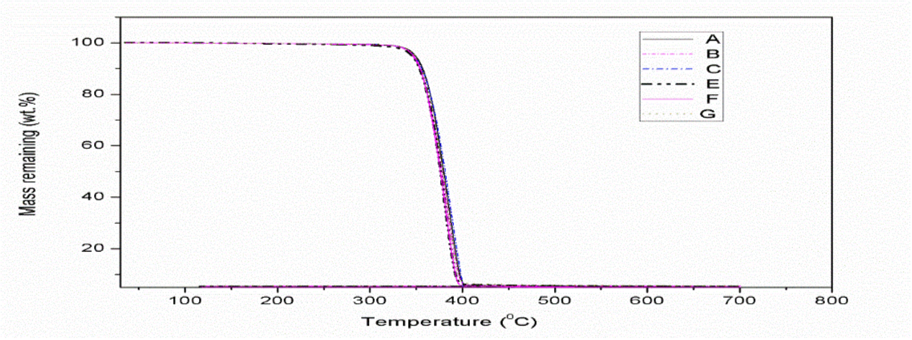

Figure 1: **TGA of Sintered GNP/PLA Nanocomposite samples under varying process conditions.**

Tables 2, 3 and 4 present the influence of graphene nanoparticle (GNP) and more importantly manufacturing process on the water absorption characteristics of GNP/PLA nanocomposite. Throughout the immersion time, a very insignificant amount of water was absorbed by the nanocomposite. This is due to the hydrophobic nature of GNP and the densification property of the sintered compact which recorded above 99% densification and minimal porosity on the developed sample. The synergetic effect brought about by the inclusion of GNP and the densified sintered compact was able to modify the hydrophilic nature of polylactic acid in the composite. A well-compacted sample of stronger adhesion between the reinforcement and the matrix was produced while the hydrophobic nature of graphene nanoplatelets surface immobilise some of the moisture, slowing down the rate of water absorption. A similar observation was found with [11] as graphene inclusion also reduced the water absorption in the developed nanocomposite immobilising some of the moisture thereby inhibiting water permeation into the polymer matrix.

Table 2: Water absorption test results for 6 hrs.

Sample code	Dry wgt. (gm)	Wgt. gained (6hrs)	Change in wgt. (gm)	% gained in wgt.	Density
A	4.31	4.32	0.010	0.2304	1.276
B	3.98	3.99	0.010	0.0025	1.285
C	4.32	4.32	0.000	0.0000	1.288
E	4.23	4.23	0.000	0.0000	1.287
F	3.71	3.81	0.100	0.0270	1.278
G	4.07	4.09	0.020	0.0049	1.283

Table 3: Water absorption test results for 12 hrs

Sample code	Dry wgt. (gm)	Wgt. gained (12hrs)	Change in wgt. (gm)	% gained in weight
A	4.31	4.33	0.02	0.00464
B	3.98	4.00	0.02	0.00503
C	4.32	4.32	0.00	0.00000
E	4.23	4.24	0.01	0.00236
F	3.71	3.81	0.01	0.02695
G	4.07	4.10	0.03	0.00700

Table 4: Water absorption test results for 24 hrs.

Sample Code	Dry wgt.(gm)	Wgt. gained (24hrs)	Change in wgt.(gm)	% gained in weight
A	4.31	4.34	0.03	0.00696
B	3.98	4.00	0.02	0.005025
C	4.32	4.33	0.01	0.002315
E	4.23	4.24	0.01	0.002364
F	3.71	3.81	0.10	0.026954
G	4.07	4.10	0.03	0.007371

4. Conclusion.

The hydrophobic nature of the nano filler, GNP in the developed PLA nanocomposite was greatly significant as it alters the hydrophilic nature/water absorbing property of polylactic (PLA) in the matrix. Thereby, resulting in an insignificant amount of water uptake in the nanocomposite. Moreso, the influence of the fabricating process in producing a highly densified nanocomposite with negligible porosity cannot be over emphasized. This also contributed to the reduction in water absorption rate of the nanocomposite. The presence of GNP as reinforcement in the nanocomposite is also responsible for the improvement in the thermal stability of the composite at a uniform steady state of around 400^o C.

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