



## SYNTHESIS AND CHARACTERIZATION OF PVA NANOCOMPOSITES FILMS

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### ABSTRACT

Nanocomposite films of PVA (polyvinyl alcohol) with GF(graphene flakes), GO (Graphene oxide) and graphene as nanofillers have been synthesized. Nanocomposites were prepared containing various weight amounts of nanofiller (0.3, 1, 1.5, 2 and 3%) within PVA matrix. Film is casted on clean glass plate through solution casting method and dried in oven. Here we report a simple and practical approach to synthesize graphene-reinforced poly (vinyl alcohol) (PVA) composite films by incorporating others filler into PVA aqueous solution. Futher the investigation of thermal Properties was used using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal analysis shows increment in stability with increasing nanofillers content.

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### 1. INTRODUCTION

Graphene, consisting of a single layer of carbon atoms, was firstly discovered by Professor Geim and co-workers at Manchester University in 2004 through a simple table top experiment. Due to its unique two dimensional (2D) nanostructure, graphene exhibits ultrahigh Young' modulus of 1 TPa and ultimate strength of 130 GPa,[1] high thermal conductivity of 5000 W/(m·K) [2]and the highest known electrical conductivity up to 6000 S/cm [3].All of these make graphene be the "super-star" in material science, and is considered as a promising candidate for modifying polymers [4]

Because of their unique mechanical, electrical, optical, and thermal properties, the various allotropes of carbon such as diamond, graphite, graphene, and fullerene with various geometrical shapes (spherical, ellipsoidal, layered, single sheet, tubes, and buds) have attracted enormous interest from both scientific and engineering standpoints. They have extraordinary potential applications in electronics, sensors and actuators, solar

cells and data storage, optics and photonics, medical and biological applications, tissue engineering and biomaterials, and functional nanocomposites [5].

Graphene has been experimentally studied for over 40 years, and measurements of transport properties in micromechanical exfoliated layers, of graphene grown on (SiC), large- area graphene grown on copper (Cu) substrates, as well as a variety of studies involving the use of chemically modified graphene (CMG) to make new materials, have in part led to a surge in the number of publications and in the amount of, e.g., National Science Foundation grants recently awarded in the USA [6].

Graphene oxide (GO) has been popularly used as nanofiller for fibre reinforced polymer composites. GO can be chemically coated onto the surfaces of either carbon fibre or carbon fabric to augment the interfacial bonding properties through surrounding polymer matrix of the composites. Recently, GO is also used as a dielectric material for the purpose of energy storage. A thin layer of GO film is inserted between carbon fabric layers which act an electrode to form a structural capacitor. Due to the increasing demand for unmanned air vehicles (UAVs), the energy storage capacity and weight of battery always limit their flight duration [7].

The control of graphene flake size distribution by manipulating synthesis conditions is largely ignored in the literature. Only the use of centrifugation for selectively removing small sized graphene flakes from the product suspension has been reported. To the best of our knowledge, a systematic study on the effect of synthesis variables on the graphene flake size distribution is not reported for liquid phase methods. For these methods, the matter is made complicated by a scatter in the layer numbers of the product graphene since the effect of a synthesis variable on the size of a flake depends on its layer numbers [8]

Polyvinyl alcohol, also known as PVOH, PVA, or PVAL, is a synthetic polymer that is soluble in water. It is effective in film forming, emulsifying, and has an adhesive quality. It has no odour and is not toxic, and is resistant to grease, oils, and solvents. It is ductile but strong, flexible, and functions as a high oxygen and aroma barrier. By annealing amorphous PVA films above 85°C, the glass transition temperature, semi-crystalline

films of PVA were prepared [9]. PVA is a hydroxyl rich and water-soluble polymer, which can form strong interfacial interaction with GO through the formation of hydrogen bonds with GO. The strength and modulus of PVA matrix can be enhanced greatly by adding small amount of GO [4].

PVA is widely used in the production of adhesives, fibers, paper, membranes, drug release media and pharmaceutical products. It is tasteless, odourless and possesses good mechanical properties. Unlike other polymers, which are normally produced via polymerization, PVA is produced from hydrolysis of polyvinyl acetate [10].

In this research we study and selected polyvinyl alcohol (PVA) it is hydroxyl rich and water soluble, which can form strong interfacial interaction with GO through the formation of hydrogen bond with GO and very easily forms. We also study the formation of PVA with the others carbon likes as GF and G. From that we can determine the thermal properties of PVA nanocomposites before and after hydrolysis reaction. What is more, we found that the composite films had better barrier properties for water compared with pure PVA.

## **2. MATERIAL AND METHODS**

### **2.1. Materials**

Graphene(G) was purchased from ITO graphene industry. Graphene oxide(GO), graphene flakes(GF) and polyvinyl alcohol(PVA) were purchased from ACS material, Sigma Aldrich, Aldrich respectively.. All other reagents were of analytical grade and were used without further purification.

### **2.2. Methods**

#### **Preparation of G/PVA nanocomposites**

2 g of PVA was dissolved in 30 ml DI water at 95°C under hot plate to form an aqueous solution. Subsequently, graphene powder (at 0.3 wt.% of PVA) was sonicated in 20 ml DI water to form a black colloidal solution. The as obtained solutions were mixed together under vigorous stirring for about 2 hours at 60 °C to form a colloid. Therefore, vigorous stirring of the aqueous graphene mixed PVA colloid is required to ensure complete and uniform mixing. Finally, 10 ml of this homogeneous G mixed PVA colloid was poured

onto a Teflon petri dish, and kept in a vacuum dryer at 40 °C for 48 h. The dried films (hereafter, PVA-G) was peeled off the substrate for further characterizations.

### **Preparation of GO/PVA nanocomposites**

2 g of PVA was dissolved in 30 ml DI water at 95°C under hot plate to form an aqueous solution. Subsequently, graphene oxide powder (at 0.3 wt.% of PVA) was sonicated in 20 ml DI water to form a yellowish brown colloidal solution. The as obtained solutions were mixed together under vigorous stirring for about 2 hours at 60 °C to form a colloid. Therefore, vigorous stirring of the aqueous graphene oxide mixed PVA colloid is required to ensure complete and uniform mixing. Finally, 10 ml of this homogeneous GO mixed PVA colloid was poured onto a Teflon petri dish, and kept in a vacuum dryer at 40 °C for 48 h. The dried films (hereafter, PVA-GO) was peeled off the substrate for further characterizations.

### **Preparation of GF/PVA nanocomposites**

2 g of PVA was dissolved in 30 ml DI water at 95°C under hot plate to form an aqueous solution. Subsequently, graphene flake powder (at 0.3 wt.% of PVA) was sonicated in 20 ml DI water to form a black colloidal solution. The as obtained solutions were mixed together under vigorous stirring for about 2 hours at 60 °C to form a colloid. Therefore, vigorous stirring of the aqueous graphene flake mixed PVA colloid is required to ensure complete and uniform mixing. Finally, 10 ml of this homogeneous GF mixed PVA colloid was poured onto a Teflon petri dish, and kept in a vacuum dryer at 40 °C for 48 h. The dried films (hereafter, PVA-GF) was peeled off the substrate for further characterizations.

<b>PVA(%)</b>	<b>Fillers(%)</b>
99.5	0.5
99	1.0
98.5	1.5
98	2.0
97	3.0

Table 1. The composition of the samples with different percentage of PVA and fillers

### 2.3. Characterization

TGA was carried out under a nitrogen atmosphere with a Mettler thermal analyzer at a 30-790 °C with heating rate of 10 °C min<sup>-1</sup>. The thermal behaviour was investigated via differential scanning calorimetry (DSC, Mettler-DSC822) on square shaped coupons (2-10 mg) over 30-350 °C with a heating rate of 5 °C min<sup>-1</sup>. The water absorption of the composites was determined according to ASTM D570-98.19 oven-dried graphene/PVA films (2 cm × 2 cm) were immersed in distilled water at 30 °C for 24 h. Every 12 hour the samples were weighted to calculate the ratio of adsorption.

$$\text{Adsorption ratio } WA(t) = \frac{(W_t - W_0)}{W_0} \times 100 \% \quad \text{Eq-1}$$

where  $WA(t)$  is the water absorption at time  $t$ ,  $W_0$  is the original weight and  $W_t$  is the weight of the sample at a given immersion time  $t$ .

### 3. RESULTS AND DISCUSSION

Table 2 showed that the comparison absorption for PVA pure and PVA nanocomposites at 1.5% nanofillers for 0, 4, 9 and 24 hours. At 24 hours, water absorption of pure PVA was at 28.63%. However, PVA nanocomposites using GO, GF, G the water absorption decreased at 23.7 %, 19.21 % and 16.78 % respectively. PVA absorption of the water was improved when added with the different filler. Thermal properties of PVA improve with the additional of fillers.

Figure 2 showed TGA curves of nanocomposites. TGA curves utilized to determine thermal transitions of polymer nanocomposites. Figure 2 (a) shown that  $T_g$  was happened at 150°C while for Figure 2 (b) it happen at 135°C and figure 2(c) happen at 170°C.  $T_g$  mean the glass transition temperature and this mean at this time it getting more heat flow. This mean it also got an increase in the heat capacity of our polymer. This happen because the polymers have a higher heat capacity above the glass transition temperature than they do below it. It also shown that different type of nanocomposites also effect to the  $T_g$  happened.

Figure 2(a) showed that  $T_m$  was occurred at  $250^{\circ}\text{C}$  while figure 2(b) showed that  $T_m$  was happened at  $240^{\circ}\text{C}$  and figure 2(c) showed that happened at  $245^{\circ}\text{C}$ . This is also shown that different type of nanocomposite also effected to  $T_m$  happen at the polymer.  $T_m$  is the melting temperature that mean the polymer's reach the melting temperature. Those polymer crystals begin to fall apart, that is they melt. The chains come out of their ordered arrangements and begin to move around freely. It is also show the melting endothermic of PVA crystallites. The PVA sample used in this study is essentially atactic but has a degree of crystallinity of about 40%. Furthermore, PVA is a semi crystalline polymer in which high physical interactions between polymers chains exist, due to hydrogen bonding between hydroxyl groups.

Figure 2(a) showed that  $T_c$  happened at  $300^{\circ}\text{C}$ , figure 2(b) happened at  $300^{\circ}\text{C}$  while figure 2(c) also happened at  $300^{\circ}\text{C}$ . So from that we see that  $T_c$  happened at the same temperature. We can observed that crystallization for PVA and nanocomposites was same. When polymers fall into these crystalline arrangements, they give off heat. The temperature at the lowest point of the dip is usually considered to be polymer's crystallization temperature or  $T_c$ . Because the polymer gives off heat when it crystallizes, it's an exothermic transition.

The thermal stability of the PVA and the filler materials was studied by TGA. In Figure 1, the TGA termograms of PVA and three samples G, GF and GO with compositions ranging from 0.3 to 2 wt % are compared. There was effect that can be observed: as expected, the weight loss percentage depends on the composite material composition.

The decomposition temperature of PVA increases from about 250 to  $400^{\circ}\text{C}$  with adding fillers. The reason for the increment in polymer stability is not well understood, but it may be related to the restriction in polymer chain mobility and to the reduction of diffusivity of attacking agents within the polymer matrix, both attributable to polymer-filler interactions. The pure PVA started to degrade at  $250^{\circ}\text{C}$ . Considering that the PVA decomposes completely within the composite material. To verify this point, the thermal degradation of PVA with G, GF and GO mixtures were determined. In figure 1, the results obtained show that PVA blend of 1 wt % of the different fillers have the highest

temperature to decomposed which is at 300 – 450 °C compared to 0.3, 1.5 and 2 wt % of fillers.

Time (hours)	Weight loss of Fillers %			
	PVA	PVA/GO	PVA/GF	PVA/G
0	9.97%	8.35%	6.42%	5.75%
4	30.29%	26.46%	25.88%	23.90%
9	28.67%	25.18%	22.65%	21.03%
24	28.63%	23.70%	19.21%	16.78%

Table 2. Water absorption of nanocomposites at 1.5% nanofillers

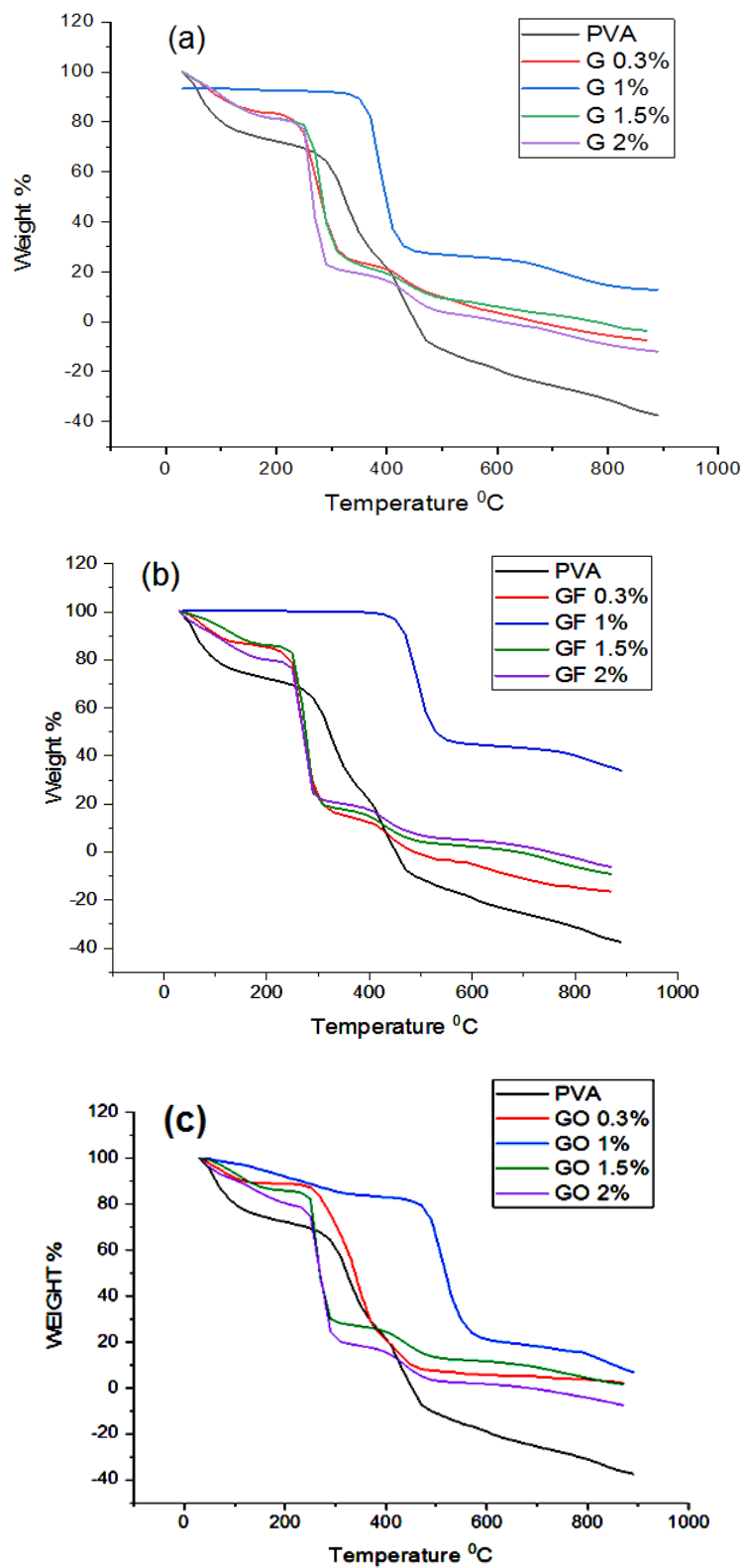


Figure 1. Thermal gravimetric analysis of (a) PVA/G, (b) PVA/GF (c) PVA/GO nanocomposites



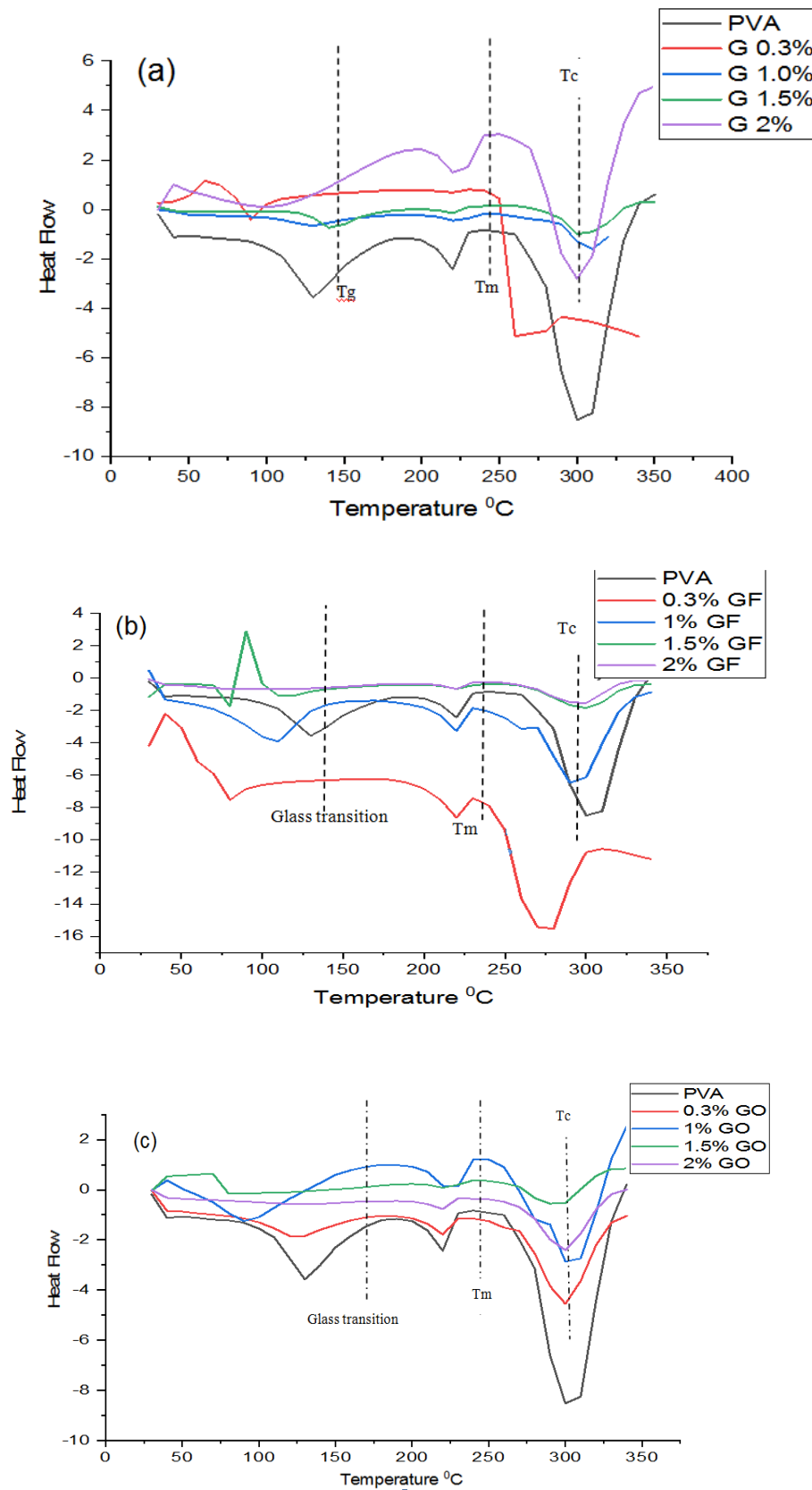


Figure 2. DSC curve of (a) PVA/G (b) PVA/GF (c) PVA/GO nanocomposites

#### 4. CONCLUSIONS

We have successfully synthesis and characterize PVA nanocomposites films by incorporating other filler such as GO,GF and G into PVA aqueous solution. The sample prepared 0.3, 1, 1.5, 2 and 3wt% of fillers. The film containing 3 wt.% shows better result in term of reducing water absorption and improving the thermal properties. The result showed that GO/PVA was the highest thermal properties compare to other filler. This study opens a new route for optimizing interface structure and improving the comprehensive performances of graphene/polymer nanocomposites. Moreover, with a small increase in the amount of fillers, the surfaces of PVA films transform from hydrophilic to hydrophobic, greatly improving the water resistance of PVA.

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