

## Poly(vinyl alcohol)/GO-MMT Nanocomposites: Preparation, Structure and Properties<sup>\*</sup>

Muhammad Raheel<sup>a,b</sup>, Kun Yao<sup>a</sup>, Jiang Gong<sup>a</sup>, Xue-cheng Chen<sup>a\*\*</sup>, Dong-tao Liu<sup>a</sup>, Yi-chao Lin<sup>a</sup>, Dong-mei Cui<sup>a</sup>, Muhammad Siddiq<sup>b\*\*</sup> and Tao Tang<sup>a\*\*</sup>

<sup>a</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

<sup>b</sup> Department of Chemistry, Quaid-i-Azam University, Islamabad 045320, Pakistan

**Abstract** A facile, efficient and environment friendly method is established to prepare poly(vinyl alcohol) (PVA) based graphene oxide-montmorillonite (GO-MMT) nanocomposites in aqueous media. GO-MMT nanohybrid is obtained by the combination of GO and MMT in water without any reducing or stabilizing agents. The formation of GO-MMT nanohybrid is due to the hydrogen bonding and crosslinking effects. The sodium ions within MMT sheets act as crosslinkers between GO sheets and MMT platelets. The resultant nanocomposites are characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and mechanical testing. Compared to that of pure PVA, PVA nanocomposites show enhanced thermal stabilities and mechanical properties, which results from strong interfacial adhesion of the nanoadditives in PVA matrix. The further increase in the tensile strength and modulus results from strong interaction between PVA chains and layered GO-MMT as well as good mechanical properties of GO-MMT hybrid, compared to PVA/GO and PVA/MMT nanocomposites.

**Keywords:** Clay; Graphene oxide; Nanocomposites; Poly(vinyl alcohol).

### INTRODUCTION

So far various types of inorganic nanofillers have been extensively studied for polymer reinforcements. The most widely used nanofillers are one-dimensional (nanotubes, nanorods, nanofibers), two-dimensional (layered silicates, clays) and three dimensional (silica, diamond)<sup>[1–3]</sup>. Over the past decade, graphene oxide (GO) as a layered carbon material has attracted great interest due to its superior mechanical, thermal and permeability properties. GO is readily soluble in polar solvents like water due to the presence of oxygen atom on the surface, as a result, GO can be uniformly dispersed in some polar mediums under sonication<sup>[4]</sup>. There have been reports about GO incorporating into a variety of polymer matrices as a filler to significantly improve mechanical and other properties<sup>[5–11]</sup>. Sodium montmorillonite (MMT) is made up of two silicate sheets mounted over an aluminate sheet combined as a unit by van der Waals and weak ionic forces<sup>[12]</sup>. MMT shows hydrophilic character and can form stable suspensions in water, which provides the compatibility of MMT with water soluble polymers<sup>[13]</sup>. Based upon the dispersion state of clay sheets in a polymer matrix, three different kinds of

<sup>\*</sup> This work was financially supported by the National Natural Science Foundation of China (No. 51233005), CAS-TWAS 2012 Fellowship Award and Higher Education Commission (HEC) of Pakistan.

<sup>\*\*</sup> Corresponding authors: Xue-cheng Chen (陈学成), E-mail: xchen@ciac.ac.cn

Muhammad Raheel, E-mail: m\_sidiq12@yahoo.com

Tao Tang (唐涛), E-mail: ttang@ciac.ac.cn

Received May 4, 2014; Revised September 2, 2014; Accepted September 28, 2014

doi: 10.1007/s10118-015-1586-2

polymer/clay composites can be prepared, including conventional composites, intercalated nanocomposites and exfoliated nanocomposites<sup>[1]</sup>. Polymer/MMT composites with well-dispersed states of MMT show considerable improvements in thermal, barrier, mechanical and flame retardant properties<sup>[14, 15]</sup>. Poly(vinyl alcohol) (PVA) is a typical hydrophilic water soluble polymer, which has been most extensively used in flexible water soluble packaging films, textile sizing and in paper coating<sup>[16]</sup>. These applications arouse the attention in improving thermal, mechanical and other properties of PVA. Environment friendly processing and biodegradability of PVA make it fit for many fields of applications<sup>[17, 18]</sup>.

Hybrid nanomaterials, such as carbon nanotube (CNT)-GO and CNT-MMT, are very attractive for polymer reinforcement applications. This is because of the combined benefits from 2-D GO (or MMT) and 1-D CNTs making 3-D architecture which in turn is capable for providing excellent functionalities and properties in the final composite materials. Zhang *et al.*<sup>[19]</sup> incorporated CNT-MMT hybrid into nylon-6 and found the impressive mechanical properties compared to the corresponding neat polymer. Also CNT-MMT hybrid was used to modify PVA and epoxy resins for improving thermal and dynamic mechanical properties<sup>[20]</sup>. Cai *et al.*<sup>[21]</sup> prepared CNT-GO thin films by casting the solutions on glass cover-slips and found that electrical conductivity of the films was increased with increasing the content of CNTs. Jehng *et al.*<sup>[22]</sup> demonstrated the construction of high-sensitivity H<sub>2</sub>O<sub>2</sub> sensors by incorporating a three-dimensional CNT-MMT network in Nafion polymer membranes. Wang *et al.*<sup>[23]</sup> dispersed single wall carbon nanotubes (SWCNT) and GO by RNA and then subsequently reduced GO and removed the RNA by post-treatment with NaBH<sub>4</sub> and NaOH/HNO<sub>3</sub> consequently. Kim *et al.*<sup>[24]</sup> developed a CNT-GO double layer as a laser desorption/ionization platform. The films exhibited durability against mechanical stress. Zhang *et al.*<sup>[25]</sup> explored an electrochemical platform based on the self-assembly of CNT-GO hybrid, combined with horseradish peroxidase (HRP) and found excellent electrocatalytic behavior of the resultant composite. Han *et al.*<sup>[26]</sup> prepared CNT-GO by electrostatic spray technique combined with an efficient ultrasonic treatment and discovered excellent redox reversibility towards VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> redox couples for vanadium redox flow batteries. Dong *et al.*<sup>[27]</sup> produced stable aqueous dispersion of hydrophobic SWCNTs and GO nanosheets without using any surfactant. Wang *et al.*<sup>[28]</sup> prepared CNT-GO fibers by using a coagulation spinning technique. The hybrid fiber displayed a synergetic enhancement of mechanical strength, electronic conductivity and electrical actuation performance. In a word, hybrid nanomaterials from the combination of different nanomaterials are very charming in the modification of polymers and other applications, compared to single nanomaterial.

Inspiring by the studies from CNT-GO and CNT-MMT, in this work, we synthesized GO-MMT nanohybrid with the expectation of extraordinary reinforcement properties. The formation of GO-MMT nanohybrid is a result of two contributing factors, *i.e.* the hydrogen bonding interaction and the crosslinking effects originated from sodium ions (Na<sup>+</sup>) acting as “crosslinkers” between GO sheets and MMT nanoplatelets. These two types of physical interactions between GO sheets and MMT nanoplatelets lead to the formation of GO-MMT hybrids in water<sup>[29]</sup>. The resultant GO-MMT hybrid was introduced into PVA matrix to improve thermal and mechanical properties. Structural and morphological characterizations are carried out by XRD, SEM and TEM. DSC measurements are used to characterize the crystalline properties of the nanocomposites. Thermal and mechanical properties are evaluated by TGA and tensile testing experiments, respectively. A synergistic effect between GO and MMT in PVA/GO-MMT nanocomposites on improving thermal and mechanical properties of PVA is observed.

## EXPERIMENTAL

### Materials

MMT used in this work was purchased from Kunimine Industries Co., Ltd., Japan. PVA was provided by Beijing Yili Fine Chemicals Co., Ltd., China. The average polymerization degree of PVA was (1750 ± 50) (molecular weight: 77000 g/mol). Deionized water was used throughout the experiments. H<sub>2</sub>SO<sub>4</sub> (purity 95.0%–98.0%) and graphite flakes (purity ≥ 99.85%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. H<sub>3</sub>PO<sub>4</sub> (purity ≥ 85.0%), H<sub>2</sub>O<sub>2</sub> (purity ≥ 30%), KMnO<sub>4</sub> (purity ≥ 99.5%), and HCl (purity 36.0%)

–38.0%) were obtained from Beijing Chemical Works, China. Ethanol (purity  $\geq 99.7\%$ ) was purchased from Tianjin Fu Yu Fine Chemical Co., Ltd., China. All the reagents were used as received.

#### ***Preparation of Graphene Oxide***

The modified Hummers method was utilized for the preparation of GO. A mixture of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  in 9:1 (360:40 mL) was prepared and mixed to graphite flakes (3.0 g, 1 wt. equiv.) and  $\text{KMnO}_4$  (18.0 g, 6 wt. equiv.) at 40 °C. The mixture was heated to 50 °C and stirred for 12 h, cooled to room temperature and poured onto ice (400 mL) with 30%  $\text{H}_2\text{O}_2$  (3 mL). Then, the mixture was sifted through a metal U.S. Standard testing sieve (W.S. Tyler, 300  $\mu\text{m}$ ) and then filtered through polyester fiber. The filtrate was centrifuged (4000 r/min for 4 h), and the supernatant was decanted away. The remaining solid material was then washed with 200 mL of water, 200 mL of 30%  $\text{HCl}$ , and 200 mL of ethanol; for each wash, the mixture was sifted through the U.S. Standard testing sieve and then filtered through polyester fiber with the filtrate being centrifuged (4000 r/min for 4 h) and the supernatant was decanted away. The material remaining after this extended, multiple-wash process was coagulated with 200 mL of ether and the resulting suspension was filtered over a PTFE membrane (pore size 0.45  $\mu\text{m}$ ). The solid obtained on the filter was vacuum-dried overnight at room temperature, obtaining the final product<sup>[30–33]</sup>.

#### ***Preparation of GO-MMT Hybrid***

For the preparation of GO-MMT (1:3 by weight) hybrid, GO (0.03 g) was dispersed in distilled water by sonication (0.5 h) and mixed with a dispersion of MMT (0.1 g) in distilled water (100 mL) at room temperature. Then the mixture was continuously stirred at room temperature for 96 h. Solid GO-MMT hybrid was separated from liquid by centrifugation (10000 r/min, 20 min). The obtained solid was dried under vacuum at 60 °C for 24 h to remove the solvent.

#### ***Preparation of Nanocomposites***

1 g of PVA was dissolved in distilled water (10 mL) at 90 °C. 0.01 g (1 wt%) or 0.05 g (5 wt%) of GO-MMT nanofiller was dispersed in distilled water by sonication separately at room temperature. The nanofiller dispersion was added to PVA solution, and the resulting mixture was refluxed at 100 °C for 6 h. Then the mixture was cooled to room temperature, air dried by being spread on a polystyrene petri dish and kept under vacuum at 60 °C for 24 h. For reference purposes PVA nanocomposites with 1 wt% and 5 wt% loading levels of GO and MMT were also prepared under the similar conditions. The resultant samples were designated as PVA/GO1, PVA/GO5, PVA/MMT1, PVA/MMT5, PVA/GO-MMT1, and PVA/GO-MMT5. The number “1” and “5” represented the weight percentage of the fillers in the nanocomposites.

#### ***Characterization***

The interlayer spacing of GO, MMT, GO-MMT and their respective nanocomposites were examined by X-ray diffraction (XRD) analysis with a D8 advance X-ray diffractometer operating at 40 kV voltage and 200 mA current using monochromatic  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) source. The morphology of the nanofillers was observed by means of a transmission electron microscope (TEM, JEM-1011) with an accelerating voltage of 100 kV. TEM samples were prepared by placing several drops of GO, MMT or GO-MMT water dispersions on carbon-coated copper grid and subsequently dried in an oven. The dispersion state of fillers in PVA matrix is investigated by scanning electron microscopy (XL30 FESEM FEG, FEI Co.). The samples were fractured in liquid nitrogen, and the fracture surfaces were coated with gold before SEM observation. Thermogravimetric analysis (TGA) was performed with a Q600 thermal analyzer (TA Instruments, New Castle, DE, USA) from 25 to 800 °C at a heating rate of 10 K/min under nitrogen. The nitrogen purge flow was maintained at a rate of 100 mL/min. Differential scanning calorimetry (DSC) was recorded from 25 to 300 °C on a Mettler Toledo DSC STARe system at a heating rate of 10 K/min under nitrogen atmosphere. The tensile properties were measured on a WSM-20kN universal testing machine at room temperature. The crosshead speed was maintained at the rate of 20 mm/min and the dogbone-shaped specimens with dimensions of 20 mm  $\times$  4 mm  $\times$  0.12 mm were used. The exact dimensions of each specimen were measured before the test.

## RESULTS AND DISCUSSION

### Structure and Morphology of GO-MMT Hybrids

The morphology of the nanofiller was investigated by TEM technique. Figure 1 shows TEM images of GO, MMT and GO-MMT nanofillers. The size of GO sheets is about several micrometers, and the platelets of MMT can also be clearly seen with the length of several hundred nanometers. TEM images of GO-MMT hybrid show that the individual GO and MMT platelets were bound together, forming mixed filler. Although GO sheets and layered MMT may tend to re-stack, hydrogen bonding between GO and MMT can hold them together as a single unit after GO and MMT are mixed with sonication and stirred for a long time. Additionally the GO and MMT surfaces may become charged and  $\text{Na}^+$  ion acts as a linker between them<sup>[29]</sup>.

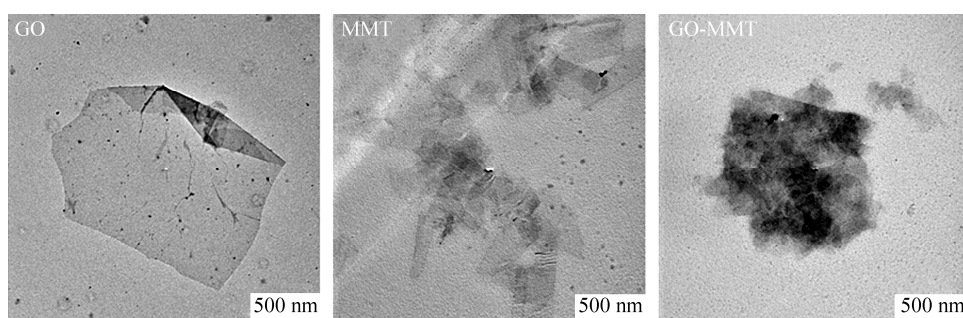


**Fig. 1** TEM images of GO, MMT and GO-MMT hybrid

Figure 2(a) shows the XRD patterns of GO, MMT and GO-MMT hybrid (1:3 by weight). For MMT, an obvious peak is found at  $2\theta = 7.90^\circ$ , which corresponds to  $d_{001}$ -spacing (1.12 nm). The relatively low  $d$ -spacing of MMT is a result of removal of water molecules from the nano-layers. The peak at  $2\theta = 19.6^\circ$  is assigned to the 100 and 020 reflections and other peak at  $2\theta = 29.1^\circ$  corresponds to  $(\text{Mg Fe})\text{SiO}_3$  salts<sup>[19, 34]</sup>. In the XRD profile of GO, a diffraction peak is found at  $2\theta = 9.3^\circ$  which is assigned as 001 reflection indicating the graphitic interlayer distance of about 0.95 nm. The XRD profile of GO-MMT nanoadditive clearly shows the two diffraction peaks at  $2\theta = 7.40^\circ$  (broadened peak) indicating 1.19 nm interlayer distance and  $2\theta = 28.90^\circ$  with the elimination of GO peak. A slight shift of 001 peak of MMT to lower  $2\theta$  values having broader shape indicates an increase in the inter-gallery distance as compared to pristine MMT, which shows that the MMT layers are incorporated fully with GO as there is no GO peak in the hybrid system.

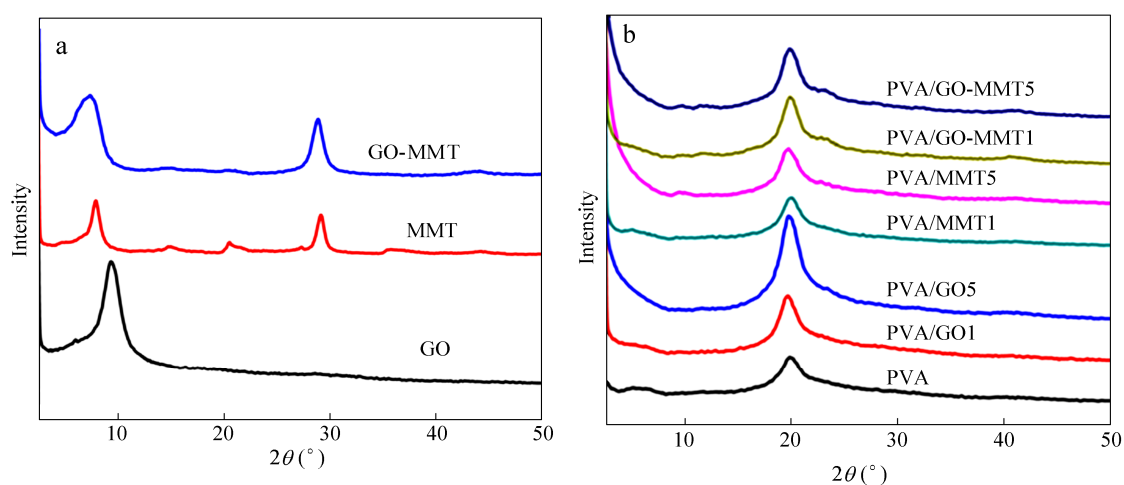


**Fig. 2** XRD patterns of (a) nanofillers and (b) PVA nanocomposites

### Structure and Morphology of PVA/GO-MMT Nanocomposites

Figure 2(b) shows the XRD patterns of pure PVA and PVA nanocomposites. It can be seen that the basal reflections (001) of the nanoadditives (for both MMT and GO) do not appear in the  $2\theta$  region of  $2^\circ$ – $15^\circ$  for all PVA nanocomposites, even in the case containing 5 wt% nanofillers. The peak at  $2\theta \approx 19.9^\circ$  is observed consistently in all the composite samples, which results from crystalline PVA. The absence of the basal diffraction peaks in the XRD profiles implies the formation of exfoliated structures in the final nanocomposites where the reinforcement phase has been well dispersed within the polymeric matrix<sup>[35]</sup>. In such nanocomposites, the improved dispersion of the layered nanoadditives increases the interaction of matrix with the nanoadditives on the layer surfaces of MMT and GO<sup>[1, 36, 37]</sup>. Further analysis shows that there is an obvious slope in the region below  $8^\circ$  in the XRD patterns of PVA nanocomposites with 5 wt% nanofillers, in spite of MMT, GO or GO-MMT as nanofillers. This phenomenon can be ascribed to the complex results from the structures with different interlayer distances, meaning that the nanofillers are not completely exfoliated structures.

Figure 3 shows the dispersion state of PVA nanocomposites with 5 wt% nanofillers in PVA matrix. The nanofillers are homogeneously dispersed in the PVA matrix. In the representative SEM images of PVA nanocomposites, it can be seen that the hybrid and pure nanofillers are well dispersed within the bulk polymer. The dispersion state of filler in a matrix is the key factor for the improvement in mechanical properties of the final material.

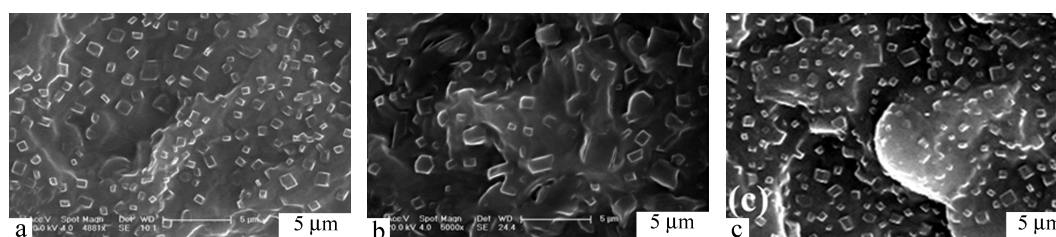


**Fig. 3** SEM images of PVA nanocomposites: (a) PVA/GO5, (b) PVA/MMT5 and (c) PVA/GO-MMT5

### Effect of Fillers on Glass Transition Temperature ( $T_g$ ) and Crystalline Properties of PVA

DSC measurements were performed to investigate the glass transition temperature ( $T_g$ ), melting point ( $T_m$ ) and crystalline behavior of PVA and PVA nanocomposites. The  $T_m$  and  $\Delta H_m$  (fusion heat) are measured from the maximum position of the endothermic peak and its area on the DSC curves, respectively. Figure 4 shows DSC heating curves of pure PVA and PVA nanocomposites. Pure PVA has a  $T_g$  at  $87.5^\circ\text{C}$ , and the  $T_g$  does not change noticeably in the PVA nanocomposites except for PVA/GO5, in which  $T_g$  increases to  $103.4^\circ\text{C}$  (curve (c) in Fig. 4). This rise is attributed to the presence of graphitic sheets in the matrix<sup>[38]</sup>. A melting peak is found at about  $190^\circ\text{C}$  for pure PVA. The position of this peak changes due to the addition of nanoadditives. However, this melting peak is diminished in the case of PVA/GO5. The possible reason can be that the signals are so weak or too broader to be measured. This phenomenon requires more investigations. The melting peak with the increased intensity for the PVA/GO1 shifts to  $215.2^\circ\text{C}$ . In the case of PVA/MMT composites, the melting peak shifts to lower temperature with the increase of MMT concentration (from  $176.6$  to  $170.6^\circ\text{C}$ ). For PVA/GO-MMT nanocomposites, the melting peaks are located at  $176.0^\circ\text{C}$  and  $192.1^\circ\text{C}$  for PVA/GO-MMT1 and PVA/GO-MMT5, respectively. The change in the melting peak of PVA suggests the strong interactions between PVA and the fillers. It is noted that the  $T_m$  of the nanocomposites containing MMT decreases by increasing the concentration of MMT within the PVA matrix, while the  $T_m$  is increased with increasing the concentration in the case of GO-MMT.

Although GO and MMT both have the similar structures (2-D geometry), their surface nature is quite different. For example, GO is much more hydrophilic than MMT, because GO possesses a large number of oxygen containing groups on its surface compared to that of MMT. These differences make GO more compatible to PVA matrix. So the dispersed state of GO in PVA matrix is much better than that of MMT. As a result, there

are more chances of forming hydrogen bonding between GO and PVA backbone and hence strong interaction compared to MMT<sup>[39]</sup>. At the same time, the hydrogen bonding among the PVA chains was reduced due to the presence of well-dispersed GO sheets. The mobility of PVA chains will increase if the content of GO is low (such as 1 wt%), so the thick crystalline lamella can be formed during crystallization. In addition, the presence of a small amount of GO showed a nucleation for the crystallization of PVA (Table 1). However, when the content of GO is high (such as 5 wt%), the strong interaction between well-dispersed GO sheets and PVA chains leads to the reduction of PVA mobility, which makes the difficulty of PVA crystallization. In contrast, the presence of MMT does not reduce the hydrogen bonding among the PVA chains due to poor interaction between MMT and PVA and poor dispersed state of MMT (compared to GO), so the mobility of PVA chains does not change (compared to pure PVA). Moreover, the presence of MMT blocks the crystallization of PVA to some extent (Table 1).

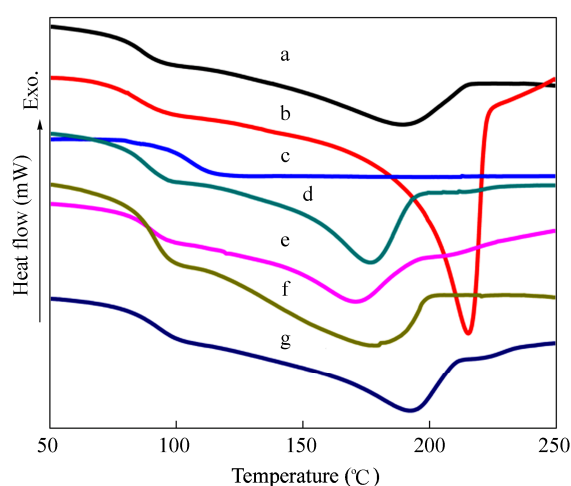


**Fig. 4** DSC curves (second heating) of PVA and its composites: (a) PVA, (b) PVA/GO1, (c) PVA/GO5, (d) PVA/MMT1, (e) PVA/MMT5, (f) PVA/GO-MMT1 and (g) PVA/GO-MMT5

**Table 1.** DSC data of PVA and PVA nanocomposites

| Sample      | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|-------------|------------|------------|------------|--------------------|-----------|
| PVA         | 87.5       | 189.7      | 165        | 15.6               | 11.2      |
| PVA/GO1     | 84.0       | 215.2      | 193        | 59.4               | 42.9      |
| PVA/GO5     | 103.4      | —          | —          | —                  | —         |
| PVA/MMT1    | 87.5       | 176.7      | 142        | 18.8               | 13.6      |
| PVA/MMT5    | 89.9       | 170.8      | 130        | 15.9               | 11.5      |
| PVA/GO-MMT1 | 90.8       | 178.7      | 157        | 19.1               | 13.8      |
| PVA/GO-MMT5 | 89.7       | 192.3      | 167        | 19.5               | 14.0      |

On the other hand, the  $\Delta H_m$  values are reduced by increasing the content of MMT, but it does not change by increasing the concentration of GO-MMT. In case of GO-MMT the values of  $\Delta H_m$  for all the nanocomposites are higher than that of pure PVA. This indicates that the total crystallinity of PVA is influenced by the presence of nanoadditives. The degree of crystallinity ( $X_c$ ) can be calculated by the following equation:

$$X_c = \Delta H_m / \Delta H_m^0 \quad (1)$$

where  $\Delta H_m^0$  is the melting heat of 100% crystalline PVA (about 138.6 J/g<sup>[40, 41]</sup>). The results about  $T_g$ ,  $T_m$ ,  $\Delta H_m$  and  $X_c$  are summarized in Table 1. The  $X_c$  of PVA nanocomposites exhibited an increasing trend compared to pure PVA. The possible reason is that the added nanofillers serves as nucleation sites promoting the crystallization of PVA, so the degree of crystallinity of the nanocomposites is higher than that of pure PVA<sup>[42–44]</sup>.

### Effect of Fillers on Thermal Stability of PVA

TGA was used to investigate thermal decomposition behaviors of neat PVA and PVA nanocomposites. Figure 5 shows TGA plots for pure PVA and PVA nanocomposites. The thermal decomposition behavior of all the materials studied presents three regions when they are heated from 25 to 800 °C. For pure PVA, the weight loss in the first stage, occurring in the temperature region of about 50–150 °C, is attributed to the loss of the absorbed solvent. The second stage, a big weight loss occurring at about 230–375 °C, is attributed to the degradation of PVA. The third stage for weight loss (at about 375–550 °C) is attributed to the further decomposition of the remainders. Table 2 also displays thermal degradation temperatures for 5 wt% mass loss ( $T_{5\%}$ ), 10 wt% mass loss ( $T_{10\%}$ ), the half weight loss ( $T_{50\%}$ ) and the char yield at 600 °C. The  $T_{5\%}$  and  $T_{10\%}$  of PVA composites are probably related to the cleavage of residual carboxylic acid, hydroxy and other oxygen containing groups on the surfaces of nanoadditive<sup>[29]</sup>. The value of  $T_{5\%}$  stays in the range of 134.5–142.6 °C for PVA/GO, 229.8–240 °C for PVA/MMT and 263.2–231.6 °C for PVA/GO-MMT with the contents of 1 wt%–5 wt% fillers. The maximum increase in  $T_{5\%}$  values is observed in the case of PVA/GO-MMT1, which is an increase of 170 K to that of pure PVA.  $T_{50\%}$  values of the nanocomposites are 39–102 K higher than that of pure PVA. The improvement in thermal stability is due to the presence of nanofillers, which acts as barriers for heat transfer and diffusion of volatile degradation products in the nanocomposites<sup>[45, 46]</sup>. The char yield at 600 °C for all the nanocomposites is found to be higher than that of pure PVA. The maximum char is produced by PVA/GO-MMT5 that is 8.2 wt% to the initial weight. The presence of the nanofillers effectively increased the weight residues of the nanocomposites. The increase in char formation is ascribed to the high heat resistance exerted by the nanofillers<sup>[47]</sup>. On the basis of the above mentioned results, it is clear that the thermal stability of PVA/GO (or MMT) nanocomposites is improved, which is further enhanced by the presence of the GO-MMT over that of pure PVA.

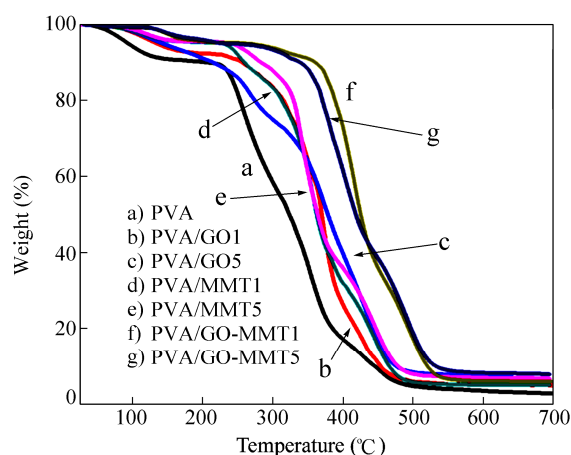


**Fig. 5** TGA curves of (a) PVA, (b) PVA/GO1, (c) PVA/GO5, (d) PVA/MMT1, (e) PVA/MMT5, (f) PVA/GO-MMT1 and (g) PVA/GO-MMT5 (under nitrogen)

**Table 2.** Summary of the TGA results for PVA and its nanocomposites

| Sample      | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{50\%}$ (°C) | Char yield at 600 °C (%) |
|-------------|----------------|-----------------|-----------------|--------------------------|
| PVA         | 93.2           | 206.5           | 323.5           | 3.4                      |
| PVA/GO1     | 134.5          | 256.4           | 369.8           | 5.1                      |
| PVA/GO5     | 142.6          | 215.1           | 378.5           | 7.5                      |
| PVA/MMT1    | 229.8          | 259.7           | 362.3           | 5.0                      |
| PVA/MMT5    | 240.0          | 283.6           | 363.9           | 6.9                      |
| PVA/GO-MMT1 | 263.2          | 361.0           | 425.5           | 6.0                      |
| PVA/GO-MMT5 | 231.6          | 339.6           | 418.3           | 8.2                      |

### Effect of Fillers on Mechanical Properties of PVA

The main objective incorporating nanofillers into PVA matrix is to improve mechanical properties and thermal stability. Figure 6 shows the stress-strain curves of neat PVA and its nanocomposites with 1 wt% and 5 wt% filler loadings. It can be seen that tensile properties of PVA are improved by the addition of nanofillers. Compared to neat PVA, the PVA/GO nanocomposites with GO loading of 1 wt% and 5 wt% show the increase of 65.2% and 84.1% in tensile strength, and 196.6% and 224.1% in elastic modulus, respectively. Similarly, the tensile strength of PVA is increased by 4.8% and 13.0%, the elastic modulus by 41.4% and 62.1% respectively, after loading 1 wt% and 5 wt% of MMT. The effect of GO-MMT hybrid on mechanical properties of PVA is more pronounced, compared to the cases containing GO or MMT alone. Tensile strength increases with increasing the contents of GO-MMT. PVA/GO-MMT1 shows 153% and 337.9% increment in tensile strength and elastic modulus, respectively, while PVA/GO-MMT5 shows 199% enhancement in tensile strength and 396.6% in elastic modulus as compared to neat PVA. From Table 3, it is clear that the elongation at break of PVA nanocomposites decreases with increasing the loading of fillers. The reason is attributed to strong interaction between fillers and the matrix and enhanced rigidity of the PVA chains caused by presence of GO, MMT and GO-MMT, which restrict the movement of the polymer chains<sup>[5, 48, 49]</sup>. From the above results, it is clear that the presence of GO-MMT nanoadditive enhances the ability of PVA to sustain mechanical stress. The improvements in tensile stress and elastic modulus result from efficient load transfer ability of PVA nanocomposites from matrix to filler due to better dispersion of the reinforcement phase<sup>[50]</sup>.

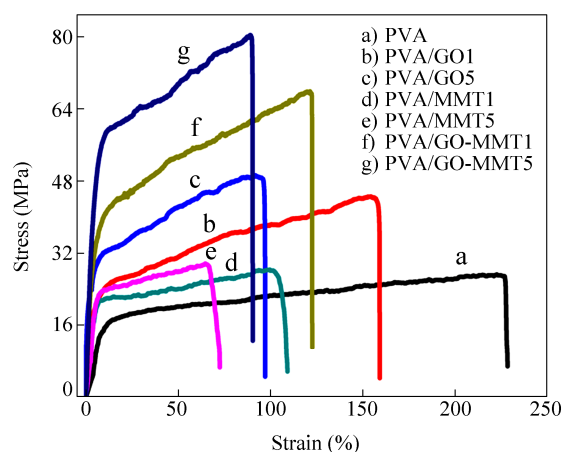


Fig. 6 Stress-strain curves of neat PVA and its nanocomposites at a crosshead speed of 20 mm·min<sup>-1</sup>

Table 3. Mechanical properties of PVA and PVA nanocomposites

| Sample      | Tensile strength (MPa) | Elastic modulus (GPa) | Elongation at break (%) |
|-------------|------------------------|-----------------------|-------------------------|
| PVA         | 27 ± 1.3               | 0.29 ± 0.16           | 227 ± 7                 |
| PVA/GO1     | 44.6 ± 1.9             | 0.86 ± 0.21           | 158 ± 6                 |
| PVA/GO5     | 49.7 ± 2.5             | 0.94 ± 0.25           | 95 ± 4                  |
| PVA/MMT1    | 28.3 ± 3.3             | 0.41 ± 0.16           | 103 ± 4                 |
| PVA/MMT5    | 30.5 ± 2.9             | 0.47 ± 0.18           | 67 ± 6                  |
| PVA/GO-MMT1 | 68.3 ± 1.7             | 1.27 ± 0.34           | 122 ± 8                 |
| PVA/GO-MMT5 | 80.7 ± 3.6             | 1.44 ± 0.42           | 90 ± 4                  |

The significant improvements in tensile strength and modulus in the final PVA nanocomposites by loading GO-MMT hybrid make it interesting to compare the mechanical properties of PVA/GO-MMT with PVA/GO and PVA/MMT composites. Generally the morphology of nanocomposites and interfacial interaction between nanofillers and PVA matrix have important effects on the mechanical properties. The key to comprehend the improved mechanical behavior of PVA/GO-MMT composites lies in examining the collective behavior of

stacked platelets along with PVA matrix. GO is more hydrophilic than MMT because GO has more oxygen containing polar functional groups, which can form hydrogen bonds with PVA. Thus GO-MMT hybrid is more compatible with PVA than MMT and less compatible than GO. On the other hand, it has been reported that MMT platelets are mechanically stronger than GO sheets<sup>[51–56]</sup>. The mechanical properties of GO-MMT hybrid are probably intermediate between GO and MMT. The combination of MMT platelets with GO sheets potentially forms a hybrid with high strength and rigidity. Polymer chains, adhered by strong physisorption forces onto the rigid GO-MMT nanolayers, become equally a portion of rigid material and exhibit higher tensile strength and elastic modulus. Thus the increase in the tensile strength and modulus results from strong interaction between PVA chains and layered GO-MMT as well as good mechanical properties of GO-MMT hybrid, compared to PVA/GO and PVA/MMT nanocomposites.

## CONCLUSIONS

GO-MMT nanohybrid was successfully synthesized and used as a new filler to prepare PVA nanocomposites. A synergistic effect between GO and MMT in the GO-MMT hybrid on improving thermal and mechanical properties of PVA is observed. Compared to pure PVA, the thermal and mechanical properties of PVA/GO-MMT system are greatly improved. The presence of nanofillers influences the crystalline properties and crystallization behavior, depending on the kind of nanofillers. Furthermore, compared to PVA/GO and PVA/MMT nanocomposites, the increments in tensile strength and elastic modulus in the PVA/GO-MMT nanocomposites are the highest. This phenomenon results from strong interaction between PVA chains and layered GO-MMT as well as good mechanical properties of GO-MMT hybrid.

## REFERENCES

- 1 Zhao, Y.Q., Lau, K.T., Wang, Z., Wang, Z.C., Cheung, H.Y., Yang, Z. and Li, H.L., *Polym. Compos.*, 2009, 30: 702
- 2 Yu, B., Wang, X., Xing, W.Y., Yang, H.Y., Song, L. and Hu, Y., *Ind. Eng. Chem. Res.*, 2012, 51: 14629
- 3 Yao, K., Wen, X., Tan, H.Y., Gong, J., Zheng, J., Zhao, W., Wang, Y., Cui, D.M., Na, H. and Tang, T., *Soft Matter*, 2013, 9: 10891
- 4 Zhang, C., Huang, S., Tjiu, W.W., Fan, W. and Liu, T.X., *J. Mater. Chem.*, 2012, 22: 2427
- 5 Zhao, X., Zhang, Q.H. and Chen, D.J., *Macromolecules*, 2010, 43: 2357
- 6 Liang, J.J., Huang, Y., Zhang, L., Wang, Y., Ma, Y.F., Guo, Y.T. and Chen, Y.S., *Adv. Funct. Mater.*, 2009, 19: 2297
- 7 Xu, Y. X., Hong, W.J., Bai, H., Li, C. and Shi, G.Q., *Carbon*, 2009, 47: 3538
- 8 Yang, X.M., Li, L., Shang, S.M. and Tao, M.X., *Polymer*, 2010, 51: 3431
- 9 Rafiee, A.M., Rafiee, J., Wang, Z., Song, H.H., Yu, Z.Z. and Koratkar, N., *ACS Nano*, 2009, 3: 884
- 10 Rafiee, A.M., Rafiee, J., Srivastava, I., Wang, Z., Song, H.H., Yu, Z.Z. and Koratkar, N., *Small*, 2010, 6: 179
- 11 Kuila, T., Bhadra, S., Yao, H.D., Kim, N.H., Bose, S. and Lee, J.H., *Prog. Polym. Sci.*, 2010, 35: 1350
- 12 Liang, L., Liu, J. and Gong, X.Y., *Langmuir*, 2000, 16: 9895
- 13 Strawhecker, K.E. and Manias, E., *Chem. Mater.*, 2000, 12: 2943
- 14 Feng, S.S., Mei, L., Anitha, P., Gan, C.W. and Zhou, W.Y., *Biomaterials*, 2009, 30: 3297
- 15 Kwon, Y.S., Cho, H.E., Kim, S.S. and Biomed, J., *Mater. Res. Part B: Appl. Biomater.* 2007, 83: 276
- 16 Bassner, S.L. and Klingenberg, E.H., *Am. Ceram. Soc. Bull.* June, 1998, 71
- 17 Kokabi, M., Sirousazar, M. and Hassan, Z.M., *Eur. Polym. J.*, 2007, 43: 773
- 18 Mansur, H.S., Sadahira, C.M., Souza, A.N. and Mansur, A.A.P., *Mater. Sci. Eng. C*, 2008, 28: 539
- 19 Zhang, W.D., Phang, I.Y. and Liu, T.X., *Adv. Mater.*, 2006, 18: 73
- 20 Wang, Z.C., Xu, C.L., Zhao, Y.Q., Zhao, D.D., Wang, Z., Li, H.L. and Lau, K.T., *Mater. Sci. Eng. A*, 2008, 490: 481
- 21 Cai, D.Y., Song, M. and Xu, C.X., *Adv. Mater.*, 2008, 20: 1706
- 22 Hsu, H.L. and Jehng, J.M., *Mater. Sci. Eng., C*, 2009, 29: 55

- 23 Wang, R.R., Sun, J., Gao, L., Xu, C.H., Zhang, J., and Liu, Y.Q., *Nanoscale*, 2011, 3: 904
- 24 Kim, Y.K., Na, H.K., Kwack, S.J., Ryoo, S.R., Lee, Y.M., Hong, S.H. and Min, D.H., *ACS Nano*, 2011, 5: 4550
- 25 Zhang, Q., Yang, S.J., Zhang, J., Zhang, L., Kang, P.L., Li, J.H. and Song, X.M., *Nanotechnology*, 2011, 22: 494010
- 26 Han, P.X., Yue, Y.H., Liu, Z.H., Xu, W., Zhang, L., Xu, H.X. and Cui, G.L., *Energy Environ. Sci.*, 2011, 4: 4710
- 27 Dong, X., Xing, G., Chan-Park, M.B., Shi, W., Xiao, N., Wang, J. and Chen, P., *Carbon*, 2011, 49: 5078
- 28 Wang, R.R., Sun, J., Gao, L., Xu, C. and Zhang, J., *Chem. Commun.*, 2011, 47: 8650
- 29 Zhang, C., Tjiu, W. W., Fan, W., Yang, Z., Huang, S. and Liu T.X., *J. Mater. Chem.*, 2011, 21: 18011
- 30 Li, Y.F., Liu, Y.Z., Yang, Y.G., Wang, M.Z. and Wen, Y.F., *Appl. Phys. A*, 2012, 108: 701
- 31 Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z.Z., Slesarev, A., Alemany, L.B. Lu, W. and Tour, J.M., *ACS Nano*, 2010, 4: 4806
- 32 Zhao, Y.F., Xu, Z.W., Shan, M.J., Min, C.Y., Zhou, B.M., Li, Y.L., Li, B.D., Liu, L.S. and Qian, X.M., *Sep. Purif. Tech.*, 2013, 103: 78
- 33 Etacheri, V., Yourey, J.E. and Bartlett, M.B., *ACS Nano*, 2014, 8: 1491
- 34 Carrador, K.A., *Appl. Clay Sci.*, 2000, 17: 1
- 35 Meng, X.Y., Wang Z., Yu, H.O., Du, X.H., Li, S.Y., Wang, Y.H., Jiang, Z.W., Wang, Q.Y. and Tang, T., *Polymer*, 2009, 50: 3997
- 36 Alla, S.G.A., El-Din, H.M.N. and El-Naggar, A.W.M., *J. Appl. Polym. Sci.*, 2006, 102: 1129
- 37 Enotiadis, A., Litina, K., Gournis, D., Rangou, S., Avgeropoulos, A., Xidas, P. and Triantafyllidis, K., *J. Phys. Chem. B*, 2013, 117: 907
- 38 Yang, Y.K., Xie, X.L., Wu, J.G. and Mai, Y.W. *J. Polym. Sci., Part A: Polym. Chem.*, 2006, 44: 3869
- 39 Bao, C., Guo, Y., Song, L. and Hu, Y., *J. Mater. Chem.*, 2011, 21: 3942
- 40 Cerezo, F.T., Preston, C.L.M. and Shanks, R.A., *Macromol. Mater. Eng.*, 2007, 292: 155
- 41 Su, J.X., Wang, Q., Su, R., Wang, K., Zhang, Q. and Fu, Q., *J. Appl. Polym. Sci.*, 2008, 107: 4070
- 42 Li, L.Y., Li, C.Y. and Ni, C.Y., *J. Am. Chem. Soc.*, 2006, 128: 1692
- 43 Laird, E.D. and Li, C.Y., *Macromolecules*, 2013, 46: 2877
- 44 Shaffer, M.S.P. and Windle, A.H., *Adv. Mater.*, 1999, 11: 937
- 45 Guo, J., Ren, L.L., Wang, R.Y., Zhang, C., Yang, Y. and Liu, T.X., *Composites Part B*, 2011, 42: 2130
- 46 Mallakpour, S. and Barati, A., *Prog. Org. Coat.*, 2011, 71: 391
- 47 Jung, Y.H., Bang, G.S., Park, B.J., Ham, S.K. and Chang, J.H., *J. Appl. Polym. Sci.*, 2006, 101: 591
- 48 Zhao, Y.S., Wang, K.J., Zhu, F.H., Xue, P. and Jia, M.Y., *Polym. Degrad. Stab.*, 2006, 91: 2874
- 49 Bartholome, C., Miaudet, P., Derré, A., Maugey, M., Roubeau, O., Zakri, C. and Poulin, P., *Comp. Sci. Tech.*, 2008, 68: 2568
- 50 Zhang, P.J. and Wang, Q.A., *Express Polym. Lett.*, 2009, 3: 302
- 51 Podsiadlo, P., Kaushik, A.K., Arruda, E.M., Waas, A.M., Shim, B.S., Xu, J.D., Nandivada, H., Pumphlin, B.G., Lahann, J., Ramamoorthy, A. and Kotov, N.A., *Science*, 2007, 318: 80
- 52 Podsiadlo, P., Kaushik, Shim, B.S., Agarwal, A., Tang, Z.Y., Waas, A.M., Arruda, E.M. and Kotov, N.A., *J. Phys. Chem. B*, 2008, 112: 14359
- 53 Huang, S., Chen, X., Peng, H.D., Guo, S.Z., Wang, W.Z. and Liu, T.X., *J. Phys. Chem. B*, 2009, 113: 15225
- 54 Medhekar, N.V., Ramasubramaniam, A., Ruoff, R.S. and Shenoy, V.B., *ACS Nano*, 2010, 4: 2300
- 55 Gao, Y., Liu, L.Q., Zu, S.Z., Peng, K., Zhou, D., Han, B.H. and Zhang, Z., *ACS Nano*, 2011, 5: 2134
- 56 Compton, O.C., Cranford, S.W., Putz, K.W., An, Z., Brinson, L.C., Buehler, M.J. and Nguyen, S.T., *ACS Nano*, 2012, 6: 2008