

FACILE REGULATION OF GLUTARALDEHYDE-MODIFIED GRAPHENE OXIDE FOR PREPARING FREE-STANDING PAPERS AND NANOCOMPOSITE FILMS*

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Abstract Colloidal suspensions of glutaraldehyde (GA) crosslinked or grafted graphene oxide (GO) sheets were fabricated by simply tailoring the feed sequence. The different structures were confirmed by Fourier transform infrared spectra and X-ray diffraction. As demonstration of the utilities, the different colloidal suspensions were used to prepare free-standing papers by flow-directed filtration and poly(vinyl alcohol) (PVA)-based nanocomposite films by casting. Free-standing papers from GA crosslinked GO sheets exhibited better mechanical properties than unmodified GO paper, while nanocomposite films from GA grafted GO exhibit higher tensile strength and Young's modulus.

Keywords: Graphene oxide paper; Glutaraldehyde; Mechanical properties; Nanocomposites; Crystallization behavior.

INTRODUCTION

Graphene has emerged as a subject of scientific interest owing to its extraordinary physical properties. Particularly, the remarkable mechanical properties make it envisioned as novel nanoscale building blocks for fabricating papers and polymer-based nanocomposites^[1–3]. Graphene oxide (GO), as an important derivative of graphene, could be readily exfoliated and functionalized to yield well-dispersed suspensions in both water and organic solvents^[4, 5]. The planar geometry of a GO sheet makes it easy to assemble into free-standing papers with excellent mechanical stiffness and strength surpassing most of carbon-based papers^[6]. Nevertheless, it is still a big challenge to further improve strength of GO papers, which is still far below the theoretical value of graphene nanosheets^[7]. Chemical crosslinking using divalent alkaline earth metal ions (Mg^{2+} and Ca^{2+})^[8], benzene-1,4-diboronic acid^[9], polyallylamine^[10] and glutaraldehyde (GA)^[7] has been used to enhance mechanical strength of GO papers. GA is not only an efficient crosslinking agent for GO papers for covalently bonding the neighboring GO nanosheets but also a disinfectant of high efficiency and low toxicity providing more possibilities for applications of GO papers in medical and biological fields. Crosslinked GO papers can be made by exposing the premade papers to GA vapors^[7], which, however, usually leads to an inhomogeneous crosslinking structure and causes loss of reproducibility of the paper.

Aqueous phase reaction between GA and GO sheets can produce homogeneous colloidal suspensions of either GA crosslinked or grafted GO nanosheets (GA-c-GO or GA-g-GO). The modified GO suspensions are used to prepare papers in this article. Given that GA is also a highly efficient crosslinking agent for water-soluble polymers such as poly(vinyl alcohol) (PVA), GA-g-GO with free aldehyde groups on the surface of the

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nanosheets could create interfacial links thus enhance mechanical properties of polymer-based nanocomposites (PNCs). Here, we report a favorable method for preparing colloidal suspensions of GA-*c*-GO or GA-*g*-GO nanosheets. Fourier transform infrared (FT-IR) spectra and X-ray diffraction (XRD) patterns are employed to clarify the GA-modified GO sheet structure, which is further confirmed by the investigation of mechanical properties of GO papers by flow-directed filtration and PVA-based PNCs.

EXPERIMENTAL

Materials

Graphite (99.8%) with an average particle size of 45 μm was obtained from Alfa Aesar Co. Ltd., UK. Concentrated sulfuric acid (H_2SO_4), concentrated hydrochloric acid (HCl), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), phosphorus pentoxide (P_2O_5), potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), hydrogen peroxide (H_2O_2 , 30%) and GA (25%) were purchased from Shanghai Chem. Reagent Co. Ltd., China. PVA (average polymerization degree 1700, degree of hydrolysis 88%) was purchased from Aladdin Chem. Reagent Co. Ltd., China. All the materials were used without further purification.

Sample Preparation

Graphite oxide (GO) was synthesized from natural graphite powder using a modified Hummers' method^[11, 12], including two steps of oxidation. In the pre-oxidation step, $\text{K}_2\text{S}_2\text{O}_8$ (8.4 g) and P_2O_5 (8.4 g) were dissolved in concentrated H_2SO_4 (40 mL) at 80°C, followed by slow addition of graphite powder (10 g). The oxidation reaction was conducted at 80°C for 4.5 h. After cooling down to room temperature, the suspension was diluted with deionized water and laid overnight. The mixture was then vacuum-filtered and washed with deionized water (1.5 L) using a 0.22 μm PC membrane. The product obtained was dried in air at room temperature. In the second oxidation step, the pretreated graphite powder was poured into concentrated H_2SO_4 (230 mL) in an ice bath and stirred until the temperature dropped to 0–3°C. KMnO_4 (60 g) was added gradually under continuous stirring, and the temperature was kept below 10°C. The mixture was then heated to 35°C and stirred for 2 h, followed by diluting with deionized water (0.5 L) and further stirring for 30 min. The reaction was terminated by adding deionized water (1.5 L) and 30% H_2O_2 (25 mL). The mixture was left undisturbed for 2 days and the nearly clear supernatant was decanted. The lower precipitate was filtered and washed with 1 mol/L HCl solution to remove residual metal oxides. The products were subjected to cycles of water-washing and separation *via* centrifugation until pH value of the decantate reached 6. The sample of GO was obtained after freeze-dehydration for 2 days. Colloidal dispersions of individual GO sheets in deionized water (1 mg GO/1 mL H_2O) were prepared under ultrasounding. The homogeneous GA-*c*-GO suspension was fabricated by dropping GA solution (10 mL, 25%) into the as-prepared GO dispersion at a dropping speed of 1 mL/10 min under agitation at 70°C; the homogeneous GA-*g*-GO suspension was fabricated by dropping the GO dispersion into the GA solution with the same dropping speed at 70°C. The products were dialysed in deionized water for two weeks at room temperature to remove unreacted GA. GA-*c*-GO and GA-*g*-GO papers of 30–50 μm in thickness were made by filtration of the resultant suspensions through a cellulose membrane filter (47 mm in diameter, 0.22 μm pore size), followed by air drying and peeling from the filter. A reference paper sample was prepared from the dispersion of unmodified GO. On the other hand, the suspensions were gradually added to a pre-dissolved PVA solution ($c = 10 \text{ wt}\%$) under magnetic agitation at 70°C and were sonicated for 30 min to obtain suspensions with 1 wt% nanosheet with respect to PVA content. The suspensions were poured into a glass plate and kept at 60°C for film formation until constant weights.

Characterization

Atomic force microscopy (AFM) tapping-mode images were taken on an NSK SPI3800 instrument (NSK Co. Ltd., Japan). Scanning electron microscope (SEM, S4800, Hitachi, Japan) was used to observe fractured surfaces of the papers at an acceleration voltage of 10 kV. FT-IR spectra were recorded with a spectrometer (Vector 22, Bruker, Germany) using KBr pellet technique. XRD was carried out using a Rigaku X-ray generator equipped with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) (Rigaku Co. Ltd., Japan). Tensile tests at a crosshead speed 1.5 mm min⁻¹

were conducted with a universal testing machine (CMT-4204, SANS Group, China) at 20°C and 50% relative humidity. The gauge length was 20 mm. More than five samples were tested and the mean value and standard deviation were reported for mechanical properties. Thermograms were recorded using a modulated differential scanning calorimeter (MDSC, Q100, TA, USA), which was calibrated using indium. The samples were heated to 100°C and held for 5 min to unify the heat history of different samples. Subsequently, the samples were heated from −30°C to 240°C at 3 K min^{−1} with an amplitude of 1 K and a period of 60 s. The transition temperatures and melting enthalpies were determined by the software of TA.

RESULTS AND DISCUSSION

Hydrophilic GO is readily dispersed in water at the level of individual nanosheets, which is confirmed by AFM images of the GO dispersions deposited onto a mica substrate. As shown in Fig. 1(A), most GO sheets have an average height of 0.9 nm, which is characteristic of a fully exfoliated GO nanosheet^[13, 14]. SEM images of cross section of the GO papers prepared by the flow-directed filtration (Fig. 1B) reveal a well-packed layer-structure similar to other graphene papers generated from colloidal suspensions^[15]. It is noteworthy that the GA-*c*-GO paper exhibits the more compact stacked-structure judged by absence of legible edges of nanosheets and apparent interspace^[10], which is ascribed to the crosslinking between adjacent GO sheets. In addition, photographs in insets of Fig. 1(B) demonstrate excellent toughness and self-supporting characteristics of the papers especially for the strip specimen of GA-*c*-GO.

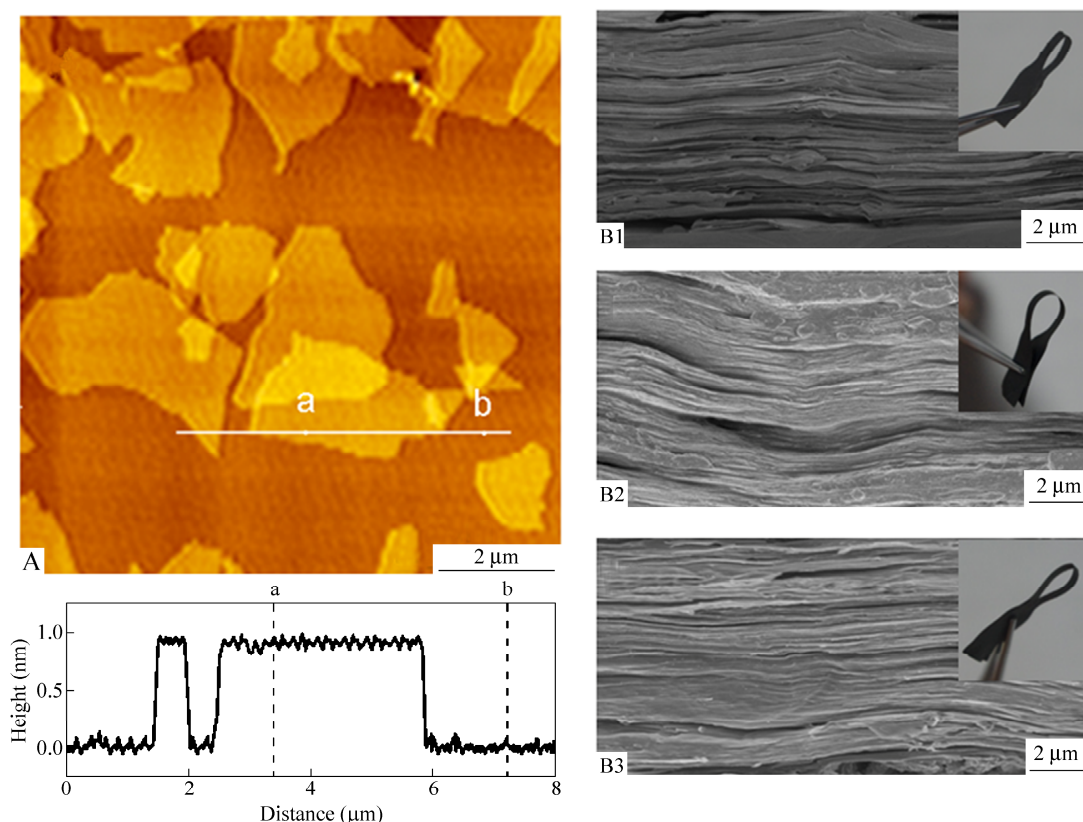


Fig. 1 (A) AFM ichnography and cross-section contour of GO on mica deposited from aqueous suspension; (B) SEM micrographs of the fracture edges of unmodified GO (B1), GA-*c*-GO (B2) and GA-g-GO papers (B3) Insets in B show photographs of strip specimens for tensile test.

Ortho-position or meta-position hydroxyl groups on the surface of GO sheets readily react with aldehyde groups of GA through intermolecular acetalization^[16]. During preparation of GA-*c*-GO suspension, GA is dropped gradually into GO suspension. Both of the two terminal aldehyde groups of GA could both covalently bond the neighboring GO nanosheets to strengthen the interlayer adhesion due to the excess of hydroxyl groups of GO sheets. The proposed schematic structure of GA-*c*-GO is shown in Fig. 2(a), most GO sheets have an average height of 0.9 nm, which is characteristic of a fully exfoliated GO nanosheet. GA molecular chains act as cross-linkers to increase interlayer spacing of GO nanosheets. On the contrary, when GO dispersions are dropped into the GA solutions at a slow enough speed, the most probable situation is that only one of the two terminal aldehyde of GA can react with hydroxyl groups of GO nanosheets owing to the excess of GA molecules and steric hinderance effect of adjacent GO nanosheets, shown in Fig. 2(b).

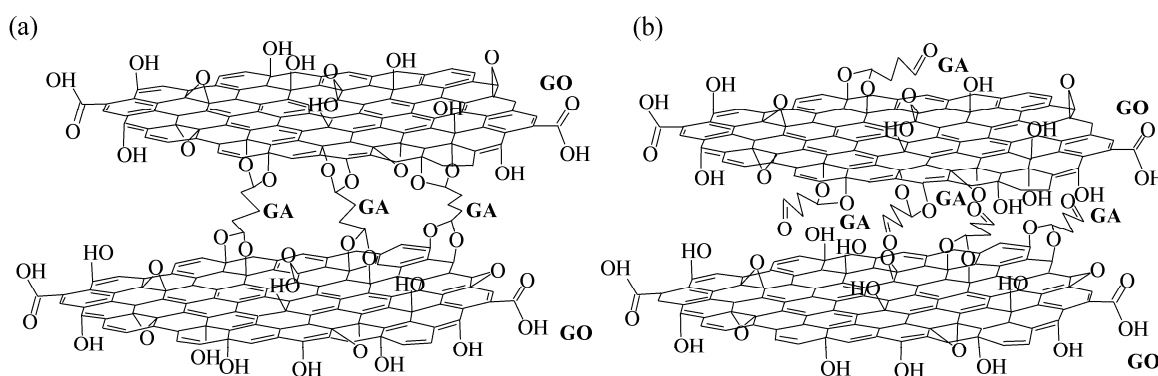


Fig. 2 Schematic illustration of the structure of GA-*c*-GO (a) and GA-*g*-GO (b)

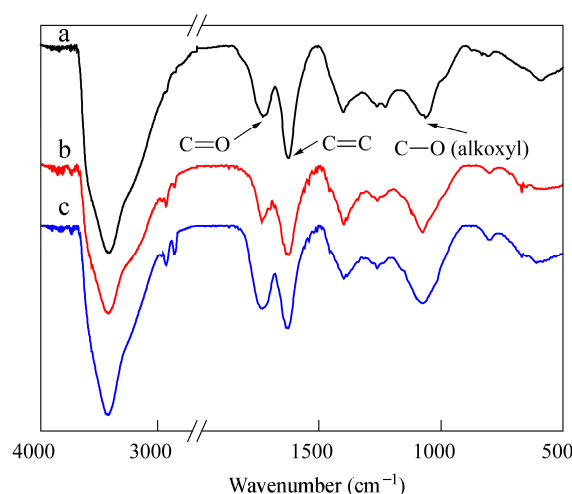


Fig. 3 FT-IR spectra of freeze-dehydrated GO (a), GA-*c*-GO (b) and GA-*g*-GO (c) powders

The different structure of GA-*c*-GO and GA-*g*-GO could be verified by FT-IR spectra and XRD. FT-IR spectra of freeze-dehydrated GO, GA-*c*-GO and GA-*g*-GO are shown in Fig. 3. Relative absorbance with respect to the invariable C=C peak at around 1622 cm⁻¹ is used to semiquantitatively analyze structural variations due to GA-modification^[17]. The peaks at around 2800–3000 cm⁻¹ in the modified GO are assigned to the C–H stretching of the GA molecules, and the relative absorbance (0.64) for GA-*c*-GO closely resembles that (0.66) for GA-*g*-GO, showing the similar amount of GA molecules reacted with GO. The relative absorbance of alkoxy C–O stretching at around 1100 cm⁻¹ is determined as 0.73, 0.68 and 0.60 for GA-*c*-GO, GA-*g*-GO and unmodified GO, respectively, implying the covalent linkage of GA molecules with GO nanosheets by

acetalization. Relative absorbance of C=O stretching of GA-g-GO (0.79) at around 1724 cm^{-1} is obviously higher than that of GA-c-GO (0.61) and unmodified GO (0.59), demonstrating that GA-g-GO possesses many unreacted aldehyde groups while GA-c-GO lacks of unreacted aldehyde groups.

Figure 4 shows the XRD patterns of GO, GA-c-GO and GA-g-GO papers. Unmodified GO paper exhibits a sharp diffraction peak at $2\theta = 12.3^\circ$ corresponding to a layer-to-layer distance (d -spacing) of 0.72 nm according to Bragg's law. The d -spacing of GA-c-GO paper visibly increases to *ca.* 0.92 nm because GA chains as cross-linkers are likely to stretch along the normal direction of GO sheets to intercalate into the gallery spaces (schematically depicted in Fig. 2a). Meanwhile d -spacing of GA-g-GO paper slightly increases to *ca.* 0.78 nm representing a weak intercalation of one end grafting GA molecules stretching along the lamellar plane (shown in Fig. 2b).

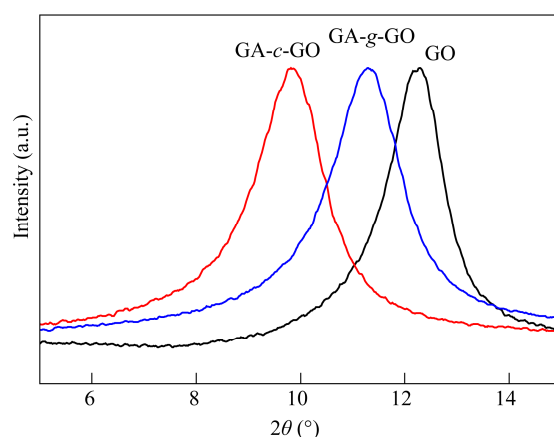


Fig. 4 XRD patterns of GO, GA-c-GO and GA-g-GO papers

GA-modification obviously influences the mechanical properties of GO papers and PNCs. Figure 5 shows stress-strain curves of GO, GA-c-GO and GA-g-GO papers, and the corresponding tensile strength σ_b , Young's modulus E and strain at break ϵ_b are listed in Table 1. The GO paper has $\sigma_b = 41.9\text{ MPa}$ and $E = 2.4\text{ GPa}$. The GA-c-GO paper exhibits better mechanical properties with σ_b and E increased by 116% and 238%, respectively, in comparison with the GO paper. The GA-g-GO paper also demonstrates σ_b and E higher than those of the GO paper. The significant enhancements of both stiffness and strength arise from the improved load-bearing capabilities of the GO nanosheets as a consequence of better interlayer adhesions.

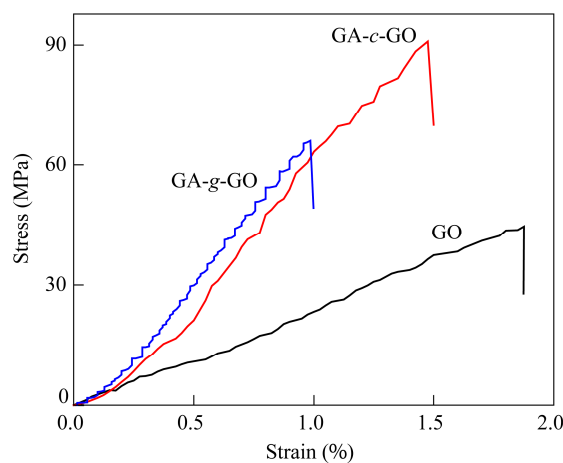


Fig. 5 Stress-strain curves of GO, GA-c-GO and GA-g-GO papers

Table 1. Mechanical properties of GO papers and PNCs

Materials		σ_b (MPa)	E (GPa)	ε_b (%)
Free-standing papers	GO	41.9 ± 0.7	2.4 ± 0.2	1.8 ± 0.3
	GA-c-GO	90.8 ± 1.2	8.1 ± 0.3	1.5 ± 0.2
	GA-g-GO	66.1 ± 0.5	7.6 ± 0.4	1.0 ± 0.1
PNC films	PVA	88.5 ± 1.7	2.6 ± 0.2	13.4 ± 0.5
	GO/PVA	120.0 ± 1.8	3.1 ± 0.2	8.7 ± 0.3
	GA-c-GO/PVA	109.2 ± 2.1	3.0 ± 0.1	8.1 ± 0.4
	GA-g-GO/PVA	132.6 ± 1.5	4.0 ± 0.3	7.4 ± 0.3

Mechanical performance of the PNCs is determined by the interfacial adhesion between the nanosheets and the PVA matrix. As the colloidal suspensions have been dialysed in deionized water for a long time, influence of free GA on mechanical properties of the PNC films can be ignored^[17]. In the light of the sufficiently high experimental-temperature, the unreacted aldehyde groups of GA-g-GO can further react with hydroxyls of PVA to form covalent acetal bridges, increasing interfacial adhesion between GO nanosheets and PVA chains. The GA-g-GO PNC thereby exhibits excellent mechanical properties as shown in Fig. 6 and Table 1. The transparent yellow-brown color of all the PNC films shown in the insets of Fig. 6 indicates that GO sheets are homogeneously dispersed in PVA matrix^[18]. σ_b and E of GA-g-GO PNC are 132.6 MPa and 4.0 GPa, respectively, being by 50% and 54% higher than those of pure PVA (88.5 MPa and 2.6 GPa) and also exceeding the GO PNC. However, mechanical property of GA-c-GO PNC is even worse than that of the GO PNC, which is ascribed to the existence of small agglomerates consisting of crosslinked GO sheets and poor interfacial adhesion between the GO sheet and the PVA matrix.

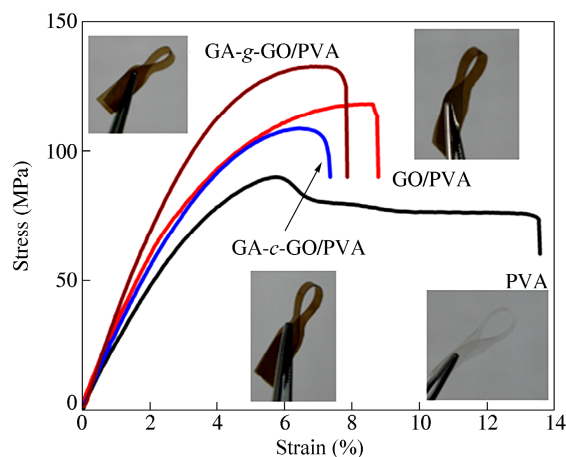


Fig. 6 Stress-strain curves of PVA and its PNC films containing 1.0 wt% GO, GA-c-GO and GA-g-GO. Insets show photographs of tensile samples.

Meanwhile, the crystallization behavior of the PNC films is closely related to the mechanical properties, which can be effectively characterized by MDSC. Figure 7 shows MDSC thermograms of PVA and its PNC films. The parameters derived from the experimental MDSC curves are summarized in Table 2. The endotherm assigned as the melting temperature (T_m) of pure PVA (around 186°C) was clearly observed. T_m of the PNC films with various GO structures was almost the same as that of pure PVA. The crystallinity (X_c) of PVA and its PNC films can be accurately determined from the reversing heat flow diagrams due to the elimination of the interference of kinetic component^[19], which can be expressed by $X_c = \Delta H_m / (1 - \phi) \Delta H_u$, where ϕ is filler loading, ΔH_m is melting enthalpy taken from the area of the fusion peak and ΔH_u is enthalpy of 100% crystallinity of PVA (161.6 J g⁻¹)^[19]. The decrease of X_c of PVA in all the PNC films demonstrates the existence of some interaction between the polymer and the filler to the detriment of interactions among polymer chain^[19], and the

largest decrease comes from GA-g-GO PNC due to strong interfacial adhesion. However, it is noteworthy that all the decrease of X_c within 10% could hardly affect mechanical properties of PNC films. So in the light of elimination of the interference of X_c we can confirm that the excellent mechanical performance of GA-g-GO PNC is ascribed to strong interfacial adhesion between modified GO nanosheets and PVA chains. In addition, the glass transition temperature (T_g) of PVA can also reflect the strength of interfacial adhesion^[20]. T_g of GA-g-GO PNC (67.8°C) is obviously higher than that of PVA (61.5°C) representing stronger interfacial adhesion between GO nanosheets and PVA chains which may suppress the molecular motion.

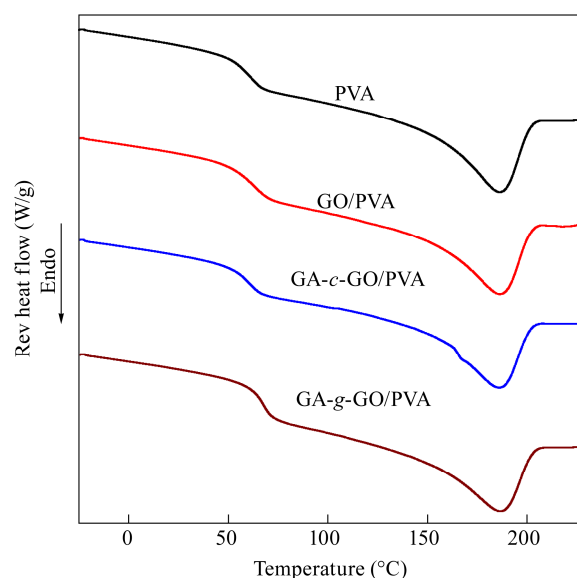


Fig. 7 MDSC reversing heat flow curves of PVA and its PNC films containing 1.0 wt% GO, GA-c-GO and GA-g-GO

Table 2. MDSC parameters of PNCs

PNC films	T_g (°C)	T_m (°C)	X_c (%)
PVA	61.5 ± 1.2	186.4 ± 0.8	22.2 ± 0.3
GO/PVA	63.9 ± 1.5	186.3 ± 1.0	20.7 ± 0.6
GA-c-GO/PVA	61.0 ± 1.8	186.3 ± 0.6	21.2 ± 0.5
GA-g-GO/PVA	67.8 ± 2.0	186.8 ± 1.2	19.9 ± 0.5

CONCLUSIONS

Colloidal suspensions of GA crosslinked or grafted GO were successfully generated by simply tailoring the feed sequence. The proposed schematic structures of GA-c-GO and GA-g-GO were verified by FT-IR spectra and XRD. The GA-c-GO paper fabricated through simple filtration exhibited better mechanical properties in comparison with GA-g-GO and unmodified GO papers, arising from the improved load-bearing capabilities of the GO nanosheets as a consequence of better interlayer adhesions. Meanwhile both σ_b and E of GA-g-GO PNC showed significant improvement over those of the PVA matrix and the GO and GA-c-GO PNCs. The incorporation of GO with various structures had weak enough impact on the crystallization behavior of the PNC films, determined by MDSC. The excellent mechanical performance of GA-g-GO PNC was ascribed to strong interfacial adhesion between modified GO nanosheets and PVA chains. Although the chemical structure and conformation of GA modified GO sheets and regulation mechanism for different structures still need to be deeply investigated, the approach for producing colloidal suspensions of cross-linked or grafted GO could be extremely convenient and useful for the large scale fabrication of PNCs and free-standing papers with excellent mechanical performance.

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