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Effect of Asymmetric Functionalized Graphene Oxide (Janus GO) on Young's Modulus and Glass Transition Temperature of PSf Ultrafiltration Membrane

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Abstract

In this study, effect of asymmetric functionalized graphene oxide (Janus GO) on Young's modulus and glass transition temperature of Polysulfone (PSf) ultrafiltration membranes was investigated. The membranes were prepared via phase inversion method and GO nanosheets were dispersed in casting solution by sonication. Results showed that the Normalized Young's modulus (on the basis of neat PSf membrane Young's modulus) increased from 1 to 1.35 for neat PSf membrane compared to the membrane with 1% Janus GO nanosheets. This enhancement indicated the improvement of mechanical properties of modified membranes. Also, application of Janus GO nanosheets caused enhancement of thermal stability of modified membranes by increasing glass transition temperature to 182.97 °C compared to 180.1 °C for neat PSf membrane. These improvements were ascribed to the enhancement of dispersion and stability of Janus GO nanosheets in membranes matrix.

Keywords: *Janus graphene oxide, Ultrafiltration membrane, Young's modulus, Glass transition temperature.*

1. INRODUCTION

Filtration using polymeric membranes is one of the most widely used methods in membrane separation processes [1]. With increase in the application of filtration technique (especially ultrafiltration) in vari-ous fields such as food industry [2], water and waste water treatment [3, 4], medical production [5, 6], etc., new materials and also new modification methods are required to improve polymeric membranes prope-rties and performance. There are many methods used to enhance their properties such as blending with copolymers [7], grafting with monomers [8] and addition of nanoparticles [9]. Different nanoparticles such as SiO_2 [10], TiO_2 [11], Al_2O_3 [12] and GO [13] were used to enhance various prop-erties of polymeric membranes specially hydro-philiccity, permeate flux and anti-fouling properties. It should be considered that the application of nanoparticles for improving membrane's performance also affects its mechanical and thermal prope-rties. This issue is very important for some applications. Among nanomaterials, GO has received great attention in recent years because of its two-dimensional structure and excellent properties [14]. GO has many covalently attached groups such as

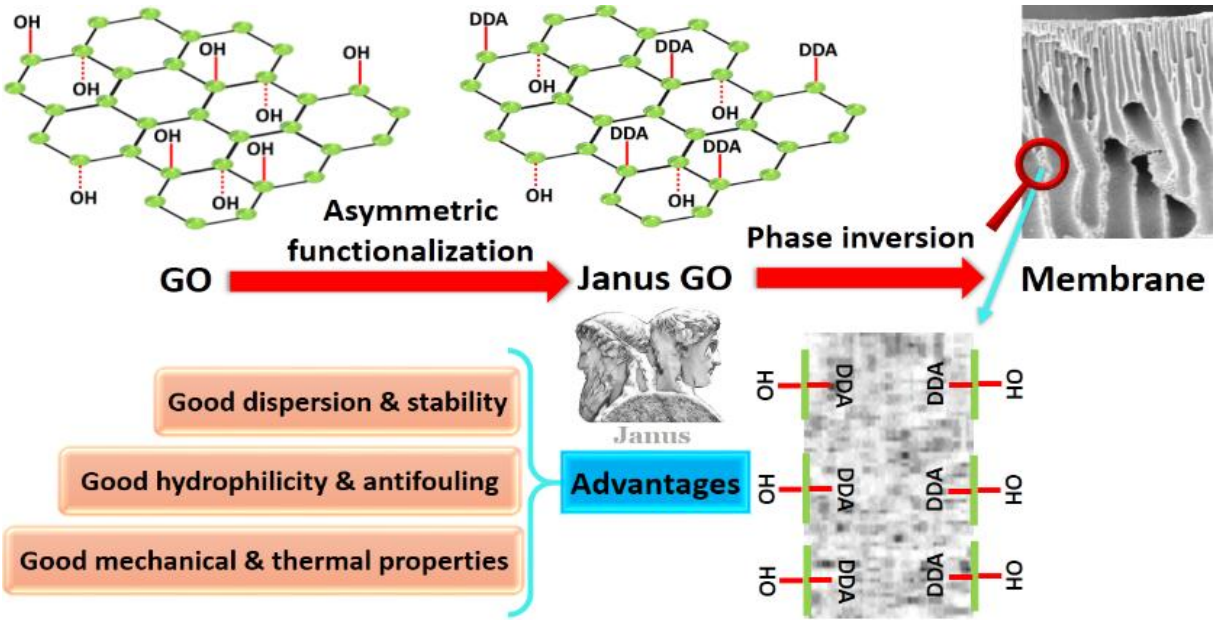
carb-oxyl, hydroxyl, epoxy and carbonyl groups that facilitate the processing and modi-fication [15]. Lee et al. [16] studied PSf me-mbranes with various concentrations of GO that were prepared via phase inversion method. Their result showed that Young's modulus of PSf membranes increased with increasing GO concentration up to 1.3 wt.% but for higher concentrations, Young's mo-dulus decreased because of agglomeration of GO at high concentrations. In another stu-dy, Ionita et al. [17] investigated mech-anical and thermal performances of PSf-GO membranes. They also observed that You-ng's modulus of the prepared membranes was enhanced up to 1 wt. % of GO but for higher concentrations, Young's modulus significantly decreased. Similar trends were observed for thermal properties of memb-ranes [17]. Poor performance of nanoco-mposites at the high concentration of GO was ascribed to the presence of GO agglo-meration, which reduced the GO rein-forcing effect because of poor interface interaction of GO and membrane matrix [18, 19]. Moreover, GO agglomerates caused harmful concentration of stress. Functionalization of GO is one of the proposed methods to reduce negative effects of GO agglomeration. Xu et al. [20] studied the effect of functionalization of GO with organosilane agent on mechanical properties of PVDF membranes. They compared mechanical properties of GO and functionalized GO mixed matrix memb-ranes with 1% concentration of nanofillers. They found that functionalized GO signif-icantly improved mechanical properties of the membrane while GO caused reduction of the mechanical strength of the membra-ne. They assigned this result to better inte-rfacial interaction between functionalized GO and membrane matrix as well as better dispersion (lower agglomeration) of functi-onalized GO. Ryu and Shanmugharaj [21] investigated the effect of GO modification by long chain alkylamines on crystallization and mechanical properties of isotactic poly-propylene nanocomposites. Their result showed that modified GO had better disper-sion and interfacial interactions with poly-mer that caused a significant enhancement in mechanical properties.

Since functionalization of hydrophilic nan-oparticles with hydrophobic functional gro-ups (for better dispersion and decreasing agglomeration problem) reduces their hydr-ophilicity, in our previous study [22], we used asymmetric functionalized GO (Janus GO) to overcome this problem. Janus GO has one hydrophilic side that contains car-boxyl, hydroxyl, epoxy and carbonyl grou-ps and also one hydrophobic side conta-ining mainly long chain alkyl groups. In phase inversion method (for membrane preparation), hydrophobic side of Janus GO helps better dispersion and stability of nanosheets in membrane matrix, while hyd-rophilic side of Janus GO increases the membrane surface hydrophilicity and impr-oves its anti-fouling properties (Figure 1). The good interaction of Janus GO with polymeric matrix not only helps to obtain better dispersion but also improves mechan-ical and thermal properties of the prepared membrane. Therefore, in this study, the effects of Janus GO on Young′s modulus and glass transition temperature of Janus GO blended PSf membranes were inves-tigated.

2. MATERIALS AND METHODS

2.1. Materials

Polysulfone (PSf, Udel® P-3500 LCD MB7, Mw=77,000–83,000, Mn=22,000) was procured from Solvay Specialty Polymers. Sulfuric acid (H_2SO_4), Nitric acid (HNO_3), Hydrochloric acid (HCl), Potassium permanganate (KMnO4), Hydrogen peroxide (H_2O_2, 30%), N-Methyl-2-pyrrolidinone (NMP), Paraffin (melting point=54-56oC), Dodecylamine (DDA), sodium hydroxide (NaOH) were procured from Merck. Bovine serum albumin (BSA, Mw=68,000 g/mol) and



graphite powder were purchased from Sigma Aldrich.

Figure 1. *Schematic of Janus GO synthesis and application in phase inversion method.*

2.2. GO Preparation

Hummers' method was used to prepare GO from graphite [23]. In brief, 7 g graphite were mixed with mixture of H2SO4/HNO3 (225 mL: 85 mL) at 0 °C for 1 h. Then 42 g of KMnO4 were added slowly in 2 h to the mixture under stirring condition. Tempera-ture of the mixture was raised to 36 °C and stirred for 2 days. After 2 days, the tempe-rature was increased to 97 ˚C in 15 min. Then 1120 mL distilled water was added to the mixture and the temperature was adjusted to 30˚C. After that, 100 mL of H2O2 was added slowly to the mixture and stirred for 1 h. The mixture was cooled to room temperature and filtered to obtain GO, then was washed with distilled water until neutral pH. Eventually the GO was put in vacuum oven at 50 ˚C for 24 h.

2.3. Asymmetric Functionalization of GO

Pickering emulsion template was used for preparation of asymmetric functionalized GO (Janus GO) as described in ref [24] with some modifications. In brief, a desired amount of GO was dispersed in distilled water by sonication for 30 min in an ultrasonic bath and then 1 h with probe ultrasonic to ensure complete dispersion. Then, the GO suspension and paraffin were put in 25 mL flask and heated to 70 °C on a heating plate and then emulsification was carried out with probe ultrasonic in pulse mode (100 W, 3 seconds on, 7 seconds off) for 1 min. The mixture was allowed to cool to room temperature and then filtered and GO-coated wax microspheres were obtain-ned. Microspheres were sonicated for 5 min in 50 ml of NaOH aqueous solution (pH=10) to remove weakly attached GO. Then, 10 g of microspheres and 0.1 g of DDA were mixed in 60 g of aqueous ethanol solution (1/1, v/v) at 30 °C for 12 h. During reaction time, DDA reacted only with one side of GO that faces aqueous phase. To obtain Janus GO, microspheres were dissolved in chloroform and centrif-uged. For further purification, Janus GO was transferred to separatory funnel and then 50 ml of distilled water was added and left for 3 days. Janus GO was collected from interface, washed with ethanol by centrif-ugation-sonication cycle and eventually dri-ed in a vacuum oven at 50°C for 1 day. For better comparison between GO and Janus GO, a same

procedure except reaction with DDA was used for some GO-coated mic-rospheres.

2.4. Membrane Preparation

Phase inversion method was used for membranes preparation. For all samples, amount of PSf and NMP were constant (in ratio of 3 to 17) and concentration of nano-sheets was determined based on the PSf. For example for GO-0.5 membrane 0.5% of PSf was added to solution. For membrane preparation, GO or Janus GO was dispersed in NMP by sonication for 1 h. Then, PSf was added and mixture was stirred with a magnetic stirrer (100 rpm) for 12 h. To remove the bubbles the solution was further sonicated (30 min) and vacuum dried in a desiccator (1 h). The solution was cast on a glass plate by a casting knife (thickn-ess=200 μm) and after 30 seconds the cast film was immersed into coagulation bath of water at room temperature.

2.5. Characterization of Nanosheets

FESEM (model: ZEISS VP) was used for observation of GO and GO-coated micro-spheres morphology. For obtaining better results, GO was dispersed in ethanol using sonication and then deposited on a lamel. GO-coated microspheres were diluted with distilled water and then dried on the lamel. For better observation of GO nanosheets, transmission electron microscopy (TEM) was also carried out by (TEM, Philips CM30 electron microscope). EDX analysis was used to confirm the functionalization of graphene oxide nanosheets. The analysis was carried out for two samples of GO and Janus GO with the trace of oxygen, carbon and nitrogen elements using the ZEISS VP model. XRD analysis (model: Siemens D5-000) was employed with Cu Kα radiation.

2.6. Characterization of Membrane

2.6.1. Morphology

The structure and cross-sectional morph-ology of the membranes were analyzed by SEM (model: ZeissDSM-960A). Samples were cut into small parts and submerged in liquid nitrogen and fractured after 30 secon-ds. To enhance conductivity of the membr-anes, the samples were sputter-coated with gold.

2.6.2. Mechanical Strength

The mechanical strength of the membranes was characterized by the tensile strength using a universal mechanical tester (Instron, USA). The membranes were cut into a rectangular shape (1 cm×10cm). All the tensile tests were carried out at a stepper motor speed of 10 mm min-1 at room temperature, and the average thickness of the samples was obtained from the SEM pictures. Young's modulus was calculated from the linear part of the stress-strain curve. The reported results are the averages of 3 samples.

2.6.3. Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) is related to rigidity of the polymer chain in the membrane. Tg was obtained by differ-rential scanning calorimetry (Mettler Tole-do DSC 1) at heating rate of 10 °C/min in the range of 100–300°C under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Characterization of Nanosheets

Figure 2 shows FESEM and TEM images of GO nanosheets. It can be observed that GO nanosheets has a layered and folded structure with a wrinkled surface.

Figure 3 exhibits XRD patterns of GO nanosheets. Graphene oxide's characteristic peak at 2θ~10˚ was determined that is in agreement with the literature [25, 26]. The lack of other peaks shows that there are no graphite and reduced graphene oxide [26]. The EDX analysis result of GO and Janus GO are shown in Figure 4 and Table 1.

According to the results, it can be seen that the amount of carbon and nitrogen in Janus GO, rather than GO, increases while

the amount of oxygen decreases. This is due to the addition of dodecylamine to the stru-cture of GO and also the elimination of hydroxyl group from its surface. These results together with FTIR result (in our previous study [22]) confirm the successful addition of dodecylamine to GO nanosh-eets.

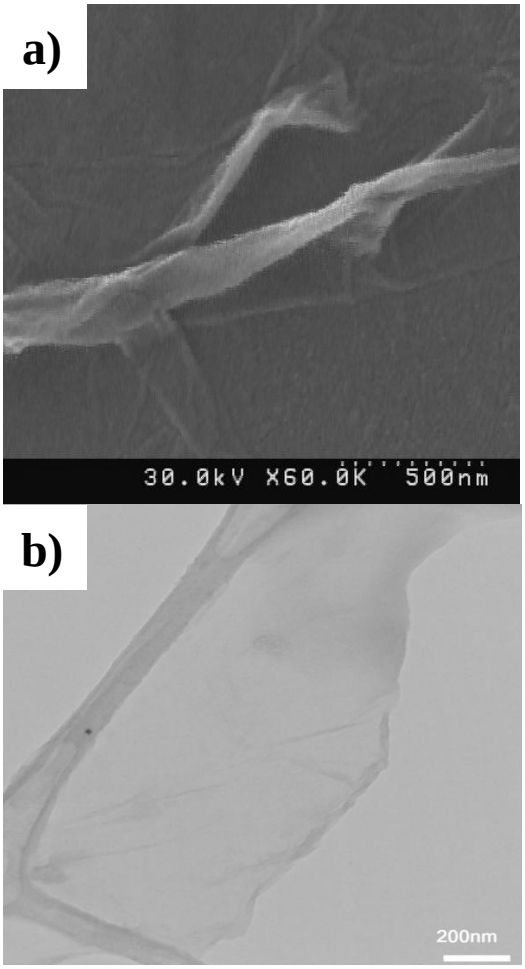


Figure 2. (a) FE-SEM and (b) TEM images of GO nanosheet.

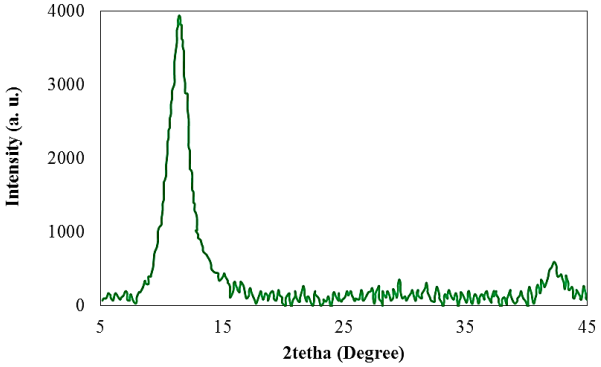


Figure 3. *XRD patterns of GO.*

Figure 5 a-c represent the photographs of various steps of GO-coated microspheres preparation. Figure 5 d shows FESEM ima-ge of GO-coated microspheres. As can be seen, GO nanosheets were successfully ads-orbed onto the microspheres surface and stabilized them.

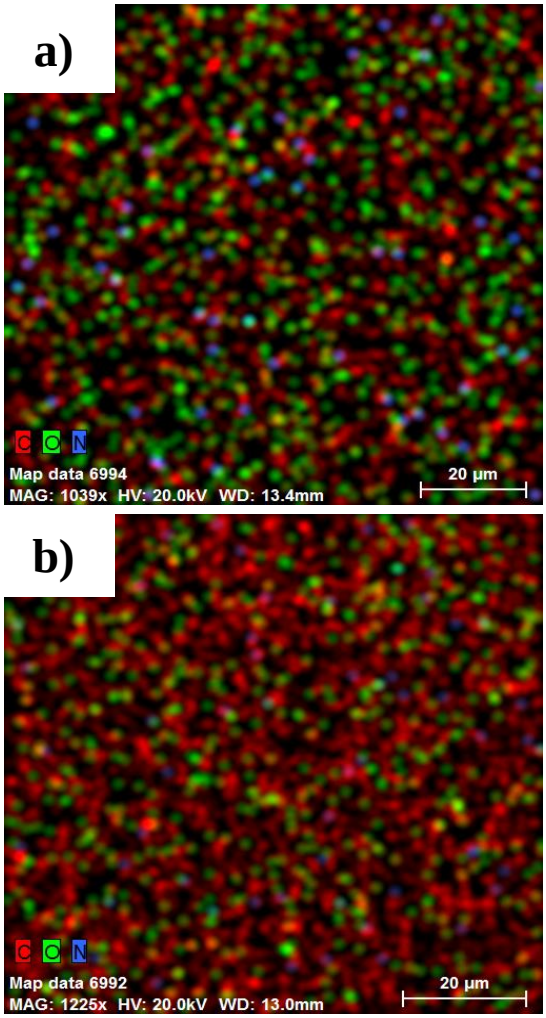


Figure 4. *EDX images of (a) GO and (b) Janus GO.*

3.2. Characterization of Membranes

3.2.1. Stability of GO and Janus GO Nanosheets in Casting Solution

Photographs of the casting solutions taken three months after their preparation are exhibited in Figure 9. It can be seen that GO nanosheets were precipitated at the bottom of the round bottom flask caused by their agglomeration but for Janus GO nanoshe-ets, precipitation is hardly observable. Different behavior of GO and Janus GO may be due to their

different thickness [27, 28] and steric stabilization of Janus GO (because of DDA).

3.2.2. Morphology of Membranes

Figure 7 shows a typical SEM image of the prepared membranes. It can be seen that the prepared membrane has a typical asymmetric porous structure with a dense skin layer and a support layer with a finger-like structure.

Table 1. Elemental analysis of GO and Janus GO.

Sample	Normalized atomic percentage			Normalized weight percentage		
	Nitrogen	Oxygen	Carbon	Nitrogen	Oxygen	Carbon
GO	2.52	36.34	61.14	2.62	43.03	54.35
Janus GO	5.78	21.24	72.98	6.24	20.26	67.56

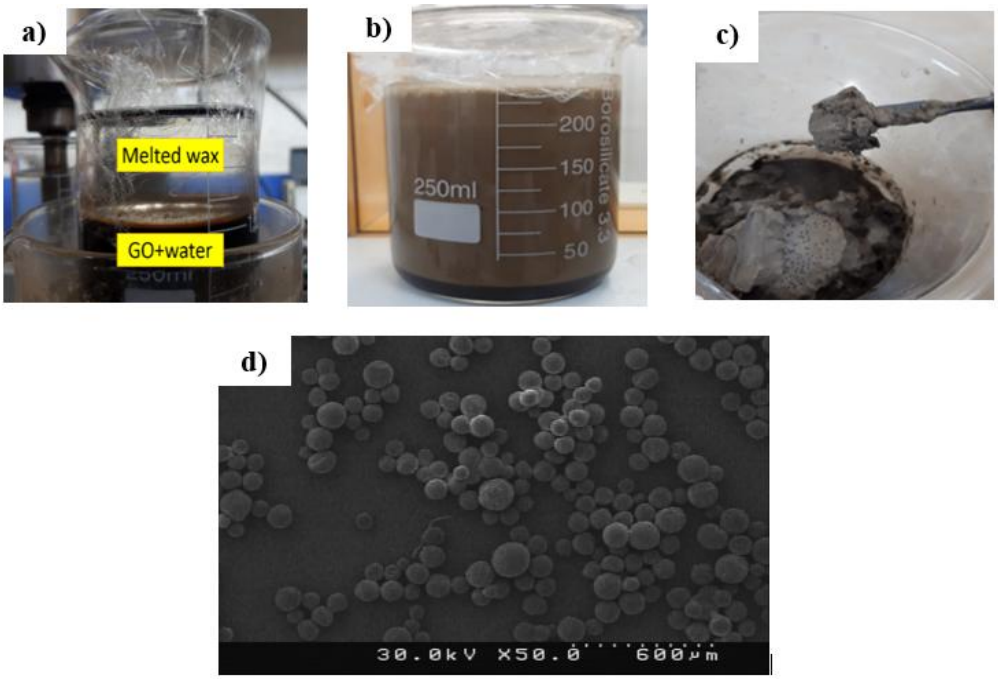


Figure 5. *Photograph of melted wax and GO dispersed water before sonication (a), photograph of melted wax and GO dispersed water after sonication (b), photograph of separated microspheres (c), FESEM image of GO-coated microspheres (d).*

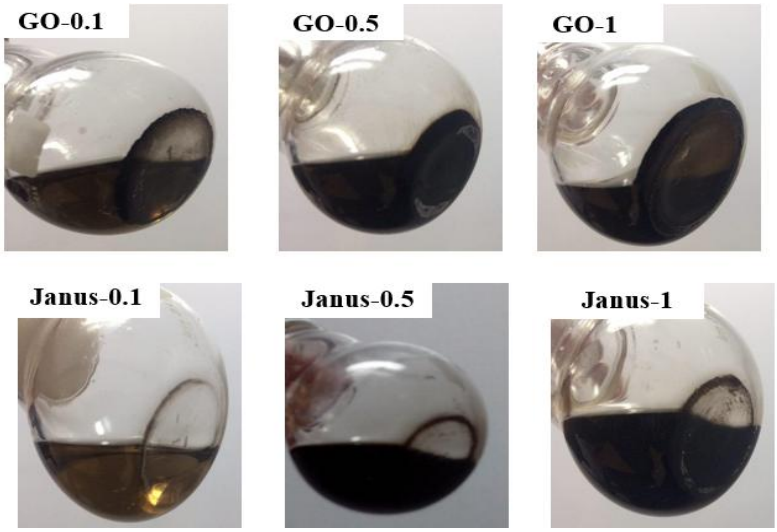


Figure 6. *Photographs of casting solutions after three months of their preparation.*

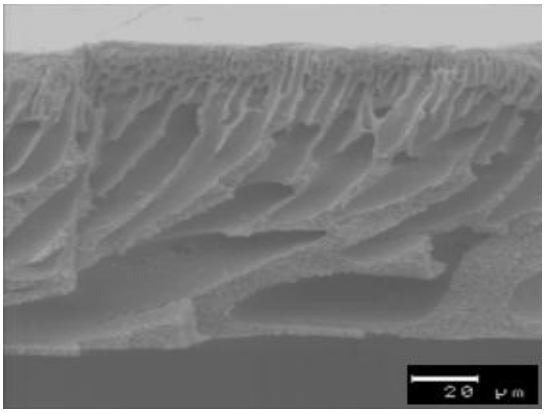


Figure 7. *Typical Cross sectional SEM image of prepared membranes.*

3.2.3. Mechanical Properties

Mechanical properties of blended membranes are very important for their applications [29]. Figure 8 shows the normalized Young′s modulus of the prepared memb-ranes. In the figure, normalized Young′s modulus of the GO membrane increases linearly from PSf to GO-0.5. This increm-ent can be related to the very high aspect ratio of GO nanosheets [16] and their acting as a bridge between two PSf polymer chains (30). However, further addition of GO to GO-1.0 reduced normalized Young's mod-ulus, caused by the agglomeration of GO nanoparticles. The observed trend is in agreement with the work of Lee et al. and Ionita et al. [16, 17]. On the other hand, Yo-ung's modulus of Janus GO incorporated membranes keeps increasing linearly as the Janus nanoparticle loading increases. This is again due to the better dispersion of Janus GO nanoparticles than GO nanoparticles.

3.2.4. DSC

DSC results of PSf, GO-0.5 and Janus-1 membranes are shown in Figure 9. The results demonstrate that glass transition tempe-ratures (Tg) of PSf, GO-0.5 and Janus-1 membranes are 180.1 °C, 181.51 °C and 182.97 °C, respectively. The strong additive-e-polymer interfacial interaction hinders the mobility of the surrounding polymer segments, leading to the increase in Tg [29]. Thus, the higher Tg of the Janus-1 membrane again implies the good Janus GO nanoparticle-polymer interaction, whi-ch also enabled the improvement in the dispersion of nanoparticles.

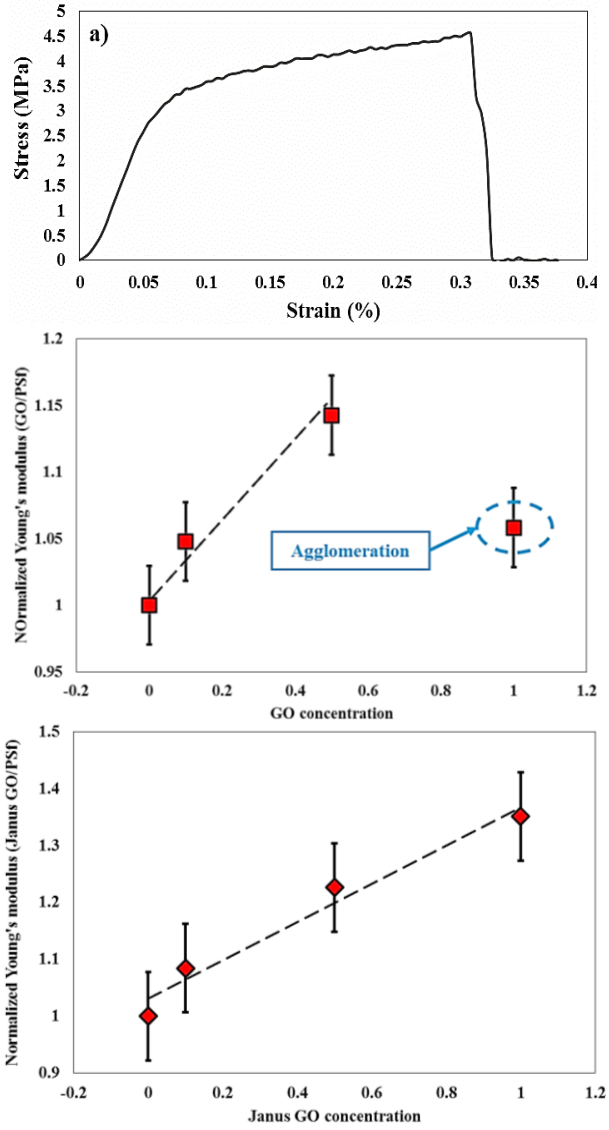


Figure 8. *(a) Typical stress–strain curves of prepared membranes, (b) Normalized Young's modulus of GO blended membranes, (c) normalized Young's modulus of Janus GO blended membranes.*

4. CONCLUSION

Effects of Janus GO on the Young's mod-ulus and Tg of PSf membranes

prepared via phase inversion method were investigated. The mechanical strength and thermal sta-bility of Janus-1 membrane were improved. Better mechanical and thermal properties of the modified membranes were ascribed to the better interaction of Janus GO and mem-brane matrix at interface and also better dispersion (more stability against agglome-ration) of Janus GO nanosheets.

5. ACKNOWLEDGEMENT

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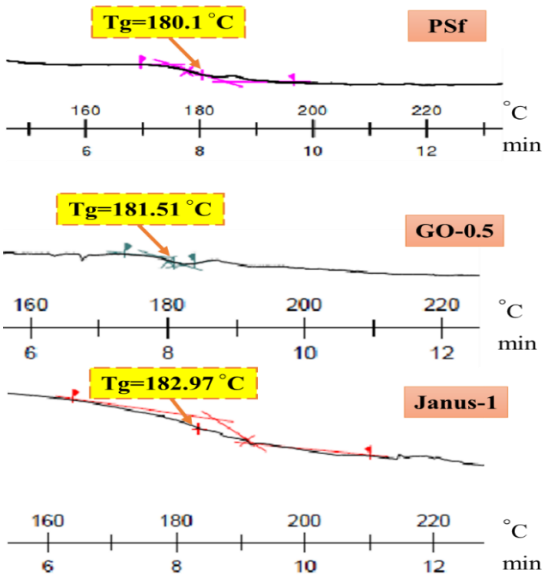

Figure 9. *DSC results of PSf, GO-0.5 and Janus-1.*

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