MOISTURE EFFECT ON MECHANICAL PROPERTIES OF GRAPHENE/EPOXY NANOCOMPOSITES

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ABSTRACT

2-D graphene nanosheets (GNS) not only have superior mechanical properties, but stacking of GNS in composites is expected to inhibit moisture absorption. In this paper, moisture effect on tensile strength of graphene/epoxy nanocomposites is investigated. Two kinds of graphene reinforcements are used including graphene oxide (GO) and reduced graphene oxide (RGO) with reinforcement weight fraction WGO or WRGO in the range of 0.5 to 3.0wt%. A dispersion agent acetone is added in nanocomposites to enhance graphene dispersion. To evaluate moisture influence, those nanocomposites are soaked in two kinds of liquid including deionized water (DIW) and salt water (saline solution) for seven kinds of soaking periods of time including 24, 48, 72, 100, 400 hours, 30 days, and 60 days. After soaking test, diffusion coefficients of various composites are evaluated; besides tensile strengths of composites are measured by microforce testing machine. In order to correlate the strength with microstructure evolution, several techniques are adopted to analyze morphologies and functionalities of reinforcements and fracture surface of composites. They include Raman spectroscope, X-ray photoelectron spectroscope, and SEM. 2-D GNS are found to effectively enhance nanocomposites by moisture attack, and their corresponding reinforcing mechanisms are proposed.

Keywords: Nanocomposite, Moisture, Diffusion, Functionalities.

1. INTRODUCTION

Nanocomposite materials with nanoscale reinforcements have emerged in the past decades as a promising novel class of materials, which take advantage of greatly increased specific interfacial area, higher attainable loads, controlled interfacial interactions, and higher total compliance. Various graphene materials have very recently emerged as a new class of potential components for advanced nanocomposites with intriguing new opportunities for the integration into polymer matrices. Graphene nanocomposites show not only superior mechanical properties but also impressive functional properties, such as electrical conductivity, unique photonic/optical transportation, anisotropic transport, and low permeability. The most important material characteristics for graphene are [1-4]: The highest elastic modulus of 1TPa, very high thermal conductivity of 5.1×10^3W $m^{-1}K^{-1}$, and the highest known intrinsic electrical conductivity of 6×10^5S m^{-1}. It is noteworthy that thickness of individual graphene sheets of 0.34nm is the thinnest 2D nanofiller known to date [5].

Graphene oxide (GO) is an oxidized graphene-derived products, which can be widely used as an alternative for graphene materials due to its high dispersibility and processibility in aqueous environment [6-8]. GO can be produced from mineral graphite flakes by thermal oxidation method invented by Hummers [9]. The achieved single atomic layer graphene-like material possesses high density of epoxide and hydroxyl functional groups (functionalities) on both sides of the basal carbon plane and carboxyl groups around their edges [10]. GO can be reduced to graphene-like structures, named reduced graphene oxide (RGO), with similar mechanical and conductive properties but less functionalities by chemical, electrochemical, thermal, hydrothermal, and photothermal reducing techniques

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[11,12].

The fabrication methods control the fine morphology and physical/chemical properties of graphene-based polymer nanocomposites. For various graphene-polymer nanocomposites known to date, the extent of dispersion and exfoliation of graphitic layers is controlled by the applied shear force, temperature, and solvent polarity. Generally, traditional fabrication routines of the nanocomposites include solution-based processing [1,13] and melt-based processing [1,14]. Solution processing maximizes filler dispersion in polymer matrix by using pre-suspended single layered graphene sheets. Aqueous or organic solvents can be used to dissolve graphene materials, including GO and RGO. Advantages of this approach include high dispersion efficiency, simple and fast fabrication step, and a high level of control on component behavior; disadvantages include challenges in finding common solvents, toxic solvent utilization, thin-film limitation, difficulties in solvent removal, and common aggregation issues during mixing and solvent evaporation stages [15]. On the other hand, melt-based processing is a solvent-free process in which applied mechanical shear force distributes the fillers in the polymer matrix using a screw extruder or a blending mixer [14]. This method allows stacked GO or RGO sheets to be exfoliated into a viscous polymer melt by suppressing unfavorable interactions and inducing component dispersion. However, thermal heating and high local mechanical stresses can affect the stability of components, flake shapes, and the reduction state of graphene oxide sheets. Tseng *et al*. [16] synthesized PI/GO nanocomposites with excellent optical transmittance; furthermore, GO forms a moisture barrier that the PI/GO nanocomposite exhibits improved resistance to water vapor. Therefore the nanocomposites can be applied to the substrates of advanced touch panel or flexible display. Huang *et al*. [17] presented high barrier graphene oxide nanosheet (GONS)/poly(vinyl alcohol) (PVA) nanocomposite films and it will dramatically promote the application of this composite film in the packaging industry. Kim *et al*. [18] presented good moisture barrier composites made of non-oxidized graphene flakes (NOGFs) because they want to develop flexible encapsulation that can be applied in flexible electronics. Their fabrication procedure can increase average lateral size of NOGFs from nanometer-scale to micrometer scale, with extremely low defect ratios, low oxygen contents, and strong hydrophobicity. Yousefi *et al*. [19] found that the moisture permeability of the nanocomposites presents a systematic decrease with increasing graphene content due to high aspect ratio and horizontal alignment of the graphene sheets.

Based on the previous literature review, most researchers focused on the results that graphene can enhance moisture barrier effect; however, few are interested in finding the correlation between residual strength and the barrier effect of nanocomposites after long term moisture attack. The reliability study of graphene nanocomposites should be very important for their extensive applications. This paper is aimed at clarifying reinforcement mechanisms of GO and RGO on epoxy matrix subjected to liquid soaking. Two kinds of liquid are adopted in this paper including deionized and salt water. The soaking time is designed from 24 hours to 60 days; besides, acetone is used as dispersion agent for graphenes and its effect on moisture resistance is also studied. Micro tensile tests are adopted to evaluate mechanical properties of GO/epoxy and RGO/epoxy nanocomposites after liquid soaking. Raman spectroscope, and X-ray photoelectron spectroscope are used to study morphologies of GO and RGO. Correlation between mechanical properties and tensile fracture morphologies is analyzed by SEM in order to figure out the failure mechanism.

2. EXPERIMENTAL PROCEDURES

2.1 Fabrication of Graphene Nanocomposites

Graphene oxide (GO) is fabricated by modified Hummers method. First, 10 gram potassium persulfate $K_2S_2O_8$ and 10 gram phosphorus pentoxide P_2O_5 are added to 50 ml Sulfuric acid H_2SO_4 and kept stirring to achieve the solvent. Then 12 gram graphite powders are added to the solvent and the solution are heated to 85°C and stirred for 4.5 hours. The solution is poured into 2 liter deionized water and kept still for 12 hours. The solution is then vacuum filtered by a filter paper with 0.2μm pores and followed by dried in oven at 90°C for 2 hours in order to achieve the pretreated graphite powders. The powders are added to 460 ml H_2SO_4 and the solution is stirred in an ice bath. Later, 60 gram $KMnO_4$ are slowly added to the solution and heated to 35°C and stirred for 2 hours. Then 920 ml deionized water is slowly added the solution and the temperature has to be kept under 50°C. The solution is further diluted in 2800 ml deionized water, and then 50 ml 30% concentration H_2O_2 is added. The solution stands still for 24 hours. The solution is initially set in centrifuge by revolution of 6000rpm for 1 hour to separate solute and solvent. The solute is further purified as GO by the addition of mixture of water and methanol. The centrifuge and purification processes are repeated for several cycles.

To achieve the reduced graphene oxide (RGO), hexamethyl-enetetramine (HMTA) is used as reduction agent. HMTA is added to the water solution of GO, and weight ratio of HMTA to GO is 1.3 to 3.0. The reduced solution is kept stirring at 95°C for 12 hours without evaporation. By the centrifuge process similar to that of GO, RGO can be successfully achieved.

To fabricate GO/epoxy or RGO/epoxy nanocomposites, GO or RGO is first mixed with epoxy resin in a container by a stirrer and put on a hot plate at 80°C for 1 hour. Weight fraction of GO or RGO, denoted as W_{GO} or W_{RGO}, versus epoxy is controlled as 0.5, 1.0, 1.5, 2.0, 3.0wt%. The mixture is then subjected to ultrasonication for 1 hour in order to uniformly disperse GO or RGO in the epoxy resin. Curing agent is then added into GO/epoxy or RGO/epoxy resin mixture and weight ratio of resin versus curing agent is 5:3. The composite mixture is again uniformly mixed by stirrer.

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This composite mixture is then put on a glass substrate with PET release film, and a doctor blade is adopted to transfer the composite mixture as a composite film with blade gap of 600μm. The composite film is then put in an oven at 70°C for 1 hour for curing.

Another fabrication procedure uses acetone as dispersion agent. The procedure is similar to that in the previous section. Initially, acetone is added to the mixture of GO or RGO/epoxy resin mixture with the proportion of 0.5wt% GO or RGO versus 1 cm^3 acetone addition. The following procedure is the same as that without acetone.

2.2 Soaking and Tensile Tests

The cured thin film nanocomposite is cut as tensile testing specimen with length × width as 50mm × 5mm. To evaluate the moisture effect on mechanical properties of nanocomposites, soaking test of specimens is conducted. Two kinds of soaking liquids are used including deionized water (DIW) and salt water (saline solution). Composite specimens are fully soaked into these two kinds of liquid for seven kinds of periods including 24, 48, 72, 100, 400 hours, 30 days, and 60 days. For each kind of soaking period, increase of specimen weight is measured and recorded in order to calculate weight gain percentage and diffusion coefficient of specimen. After soaking, tensile testing of specimen is conducted by MTS Tytron 250 micro force testing machine. Both ends of the specimen with length of 10mm are clamped by fixtures that connect to the machine. The actuator of the machine is set up in monotonic type that pulls the specimen by a constant crosshead speed of 6mm/min until the specimen breakage. During the testing, the associated computer can record force, displacement, and time. Those data are then used to calculate strength of the nanocomposite. Each valid strength data is calculated by the average of results of five same specimens subjected to same testing parameter.

2.3 Characterization

Mechanical properties of graphene nanocomposites are closely related to the microstructure. Therefore, several analysis techniques are adopted to find the correlation. In order to clarify reinforcement mechanisms of GO and RGO on epoxy, microstructure of GO and RGO are distinguished by T6400 Triple Stage Raman Spectrometer (Horiba Scientific Inc.). Further, X-ray photoelectron spectra (XPS) measurements were performed by an ESCALAB 250Xi X-ray Photoelectron Spectrometer Microprobe (Thermo Scientific Inc.). Fracture morphologies of nanocomposites are then carefully examined by SEM and effect of moisture absorption on strength of nanocomposites is evaluated. The extent of moisture absorption of composites is evaluated by diffusion coefficient D which can be achieved by the slope of initial linear portion of water gain percentage M (ordinate axis) versus square root of soaking time (abscissa axis) curve as follows.

$$M = \frac{W_2 - W_3}{W_1} \tag{1}$$

$$D = \frac{\pi}{16}\left(\frac{h}{M_m}\right)^2 \left(\frac{M_{t_2} - M_{t_1}}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{2}$$

where W_1 is initial composite specimen weight, W_2 is specimen weight after soaking, W_3 is specimen weight after drying, h is thickness of specimen, M_m is maximum water gain percentage, M_{t_2} is water gain percentage at time t_2, M_{t_1} is maximum water gain percentage at time t_1, and t_1 and t_2 are two different times located at initial linear portion in the water gain percentage versus square root of soaking time curve.

3. RESULTS AND DISCUSSION

3.1 Microstructure and Morphology of GO and RGO

Fabricated by modified Hummers method, graphene oxide (GO) and reduced graphene oxide (RGO) may have specific microstructure and their Raman spectra are shown in Fig. 1. RGO is achieved by the reduction of GO using reducing agent HMTA. On the left hand side of the figure, spectrum of GO is depicted by red curve with lower double peaks, while spectra of RGO are depicted by the other three curves with gradually higher double peaks. RGOs depicted by number 1, 2, and 3 curves are respectively achieved via the reduction of GO by 300mg, 900mg, and 1500mg HMTA. With higher addition of HMTA, RGO number 3 shows higher I_G/I_D ratio (intensity of G peak/intensity of D peak) and higher 2D and S3 peaks, indicating microstructure similar to graphene [20]. Meanings of those bands are explained as follows. G band at 1575cm^{-1} is in-phase vibration of the graphite lattice, E_{2g} mode; weak D band around 1350cm^{-1} indicates defects inherent in the graphite and the edge effect of graphite, A_{1g} mode; 2D band indicates double resonance of graphite lattice, and width of 2D band is proportional to layer number of graphene. These data prove that more addition of HMTA can better reduce GO as RGO. Although position and FWHM (full width and half maximum) of the G and 2D peaks confirm the presence of single-layer graphene (GO and RGO), the relatively flat 2D peak indicates that part of graphenes may be multilayers.

Figures 2(a) and 2(b) respectively shows *x*-ray photoelectron spectra (XPS) of GO and RGO. Since the reduction process from GO to RGO can remove the oxygen-containing groups, peaks for epoxide group C-O and carbonyl group C = O become more flat in Fig. Fig. 2(b) for RGO. This demonstrates that GO is successfully reduced as RGO by HMTA, graphene-like structures [1]. Figures 3(a) and 3(b) respectively show micrographs of GO and RGO fabricated by modified Hummers method. It can be seen that morphologies of both materials show lamination structure; however, RGOs depict wavy graphene laminas that may cause

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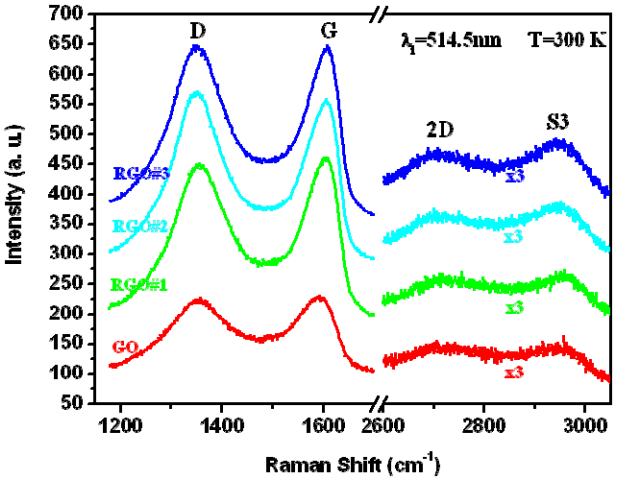
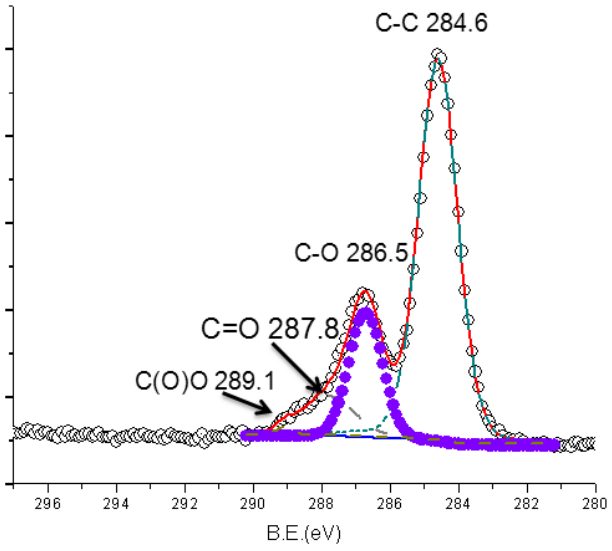
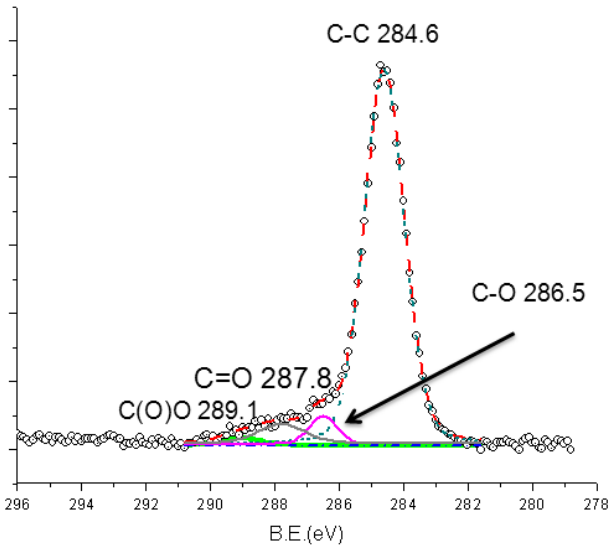


Fig. 1 Raman spectra of graphene oxide (GO) and reduced graphene oxide (RGO).

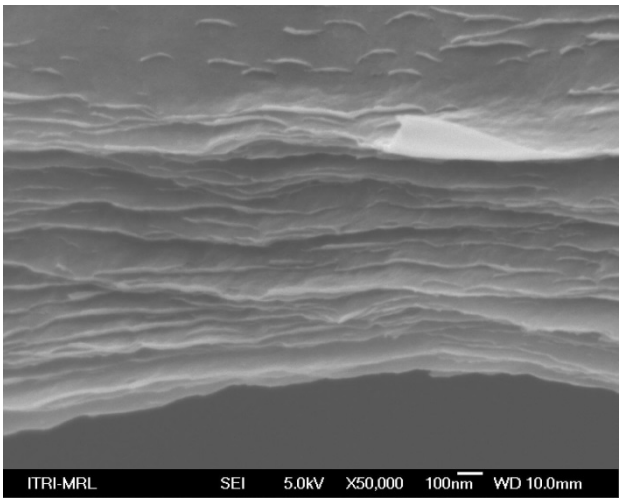


(a)

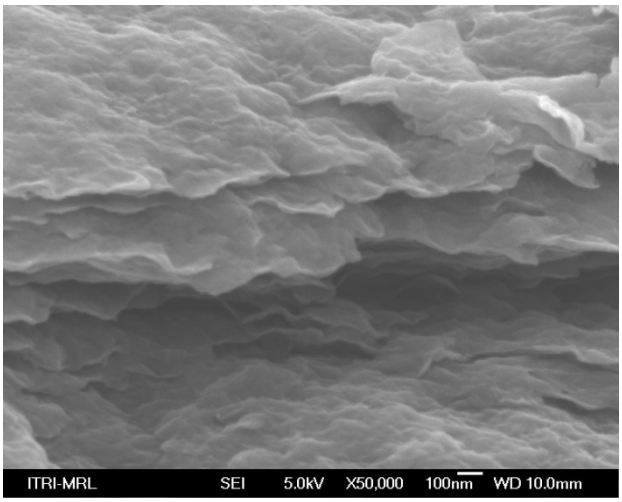


(b)

Fig. 2 X-ray photoelectron spectra of (a) GO and (b) RGO.



(a)



(b)

Fig. 3 Micrographs of (a) GO and (b) RGO fabricated by modified Hummers method.

larger interlaminar spacing. Graphene oxide possesses rich oxygen-containing polar functionalities, such as epoxide, carbonyl, hydroxyl, and carboxyl groups. By contrast, RGO removes the oxygen-containing groups such as carbonyl and epoxide. Some hydroxyl and carboxyl groups may still attach to the carbons which results in the wavy microstructure.

3.2 Diffusion Coefficient

Figures 4(a) and 4(b) shows the relationships between water gain percentage versus square root of soaking time in DIW for GO/epoxy and RGO/epoxy composites, and slopes of initial linear portion of the curve are used to calculate diffusion coefficients as shown repectively in Figs. 4(c) and 4(d). In Figs. 4(a) and 4(b), the saturation soaking time of the epoxy and nanocomposites is defined as the turning point of each curve. It can be observed that saturation soaking time is all around 100 hours. Figure 4(c) shows effect of W_{GO} on diffusion coefficient of GO/epoxy nanocomposites, and diffusion coefficient decreases as W_{GO} increases by an exponential function. For pure epoxy,

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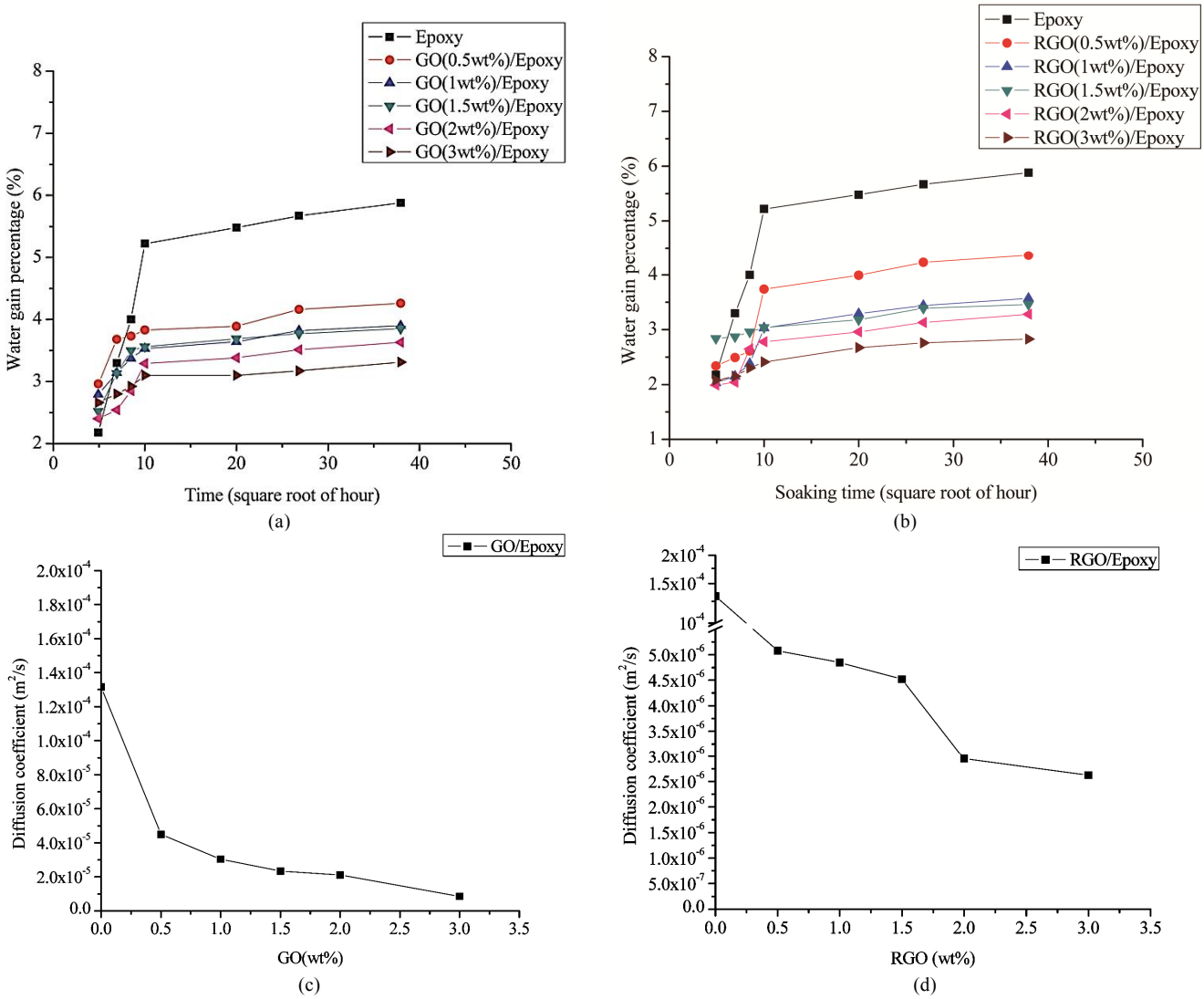


Fig. 4 The relationships between water gain percentage M versus square root of soaking time in DIW for (a) GO/epoxy composites or (b) RGO/epoxy composites, and effect of (c) W_{GO} or (d) W_{RGO} on diffusion coefficient D of graphene/epoxy nanocomposites.

diffusion coefficient is $1.32 \times 10^{-4}m^2/s$; while for GO/epoxy nanocomposites, diffusion coefficients are all one order of magnitude smaller than that of epoxy, and smallest value is $8.47 \times 10^{-6}m^2/s$ for the GO (3.0wt%)/epoxy nanocomposite. Results indicate that incorporation of GO in the epoxy matrix effectively inhibits the diffusion of water moisture into the nanocomposite. Similar results are found in Fig. 4(d) for RGO/epoxy nanocomposites. In Fig. 4(d), a significant drop at $W_{RGO} = 1.7\%$ is probably due to different dispersion extent of RGOs in the matrix for various W_{RGO}. Dispersion extent at W_{RGO} of 2.0wt% is better than that at W_{RGO} of 1.5wt%; therefore, this leads to significant lower diffusion coefficient at W_{RGO} of 2.0wt% as well as drop at $W_{RGO} = 1.7\%$. Further, diffusion coefficients of RGO/epoxy are almost one order of magnitude smaller than those of GO/epoxy, and their values are in the range of $5.08 \times 10^{-6}m^2/s$ to $2.62 \times 10^{-6}m^2/s$. This indicates that stacking of RGOs has better effect to inhibit diffusion due to their more tortuous diffusion paths caused by stacking of wavy laminas.

3.3 Effect of Soaking Conditions on Composite Properties

(1) Soaking time

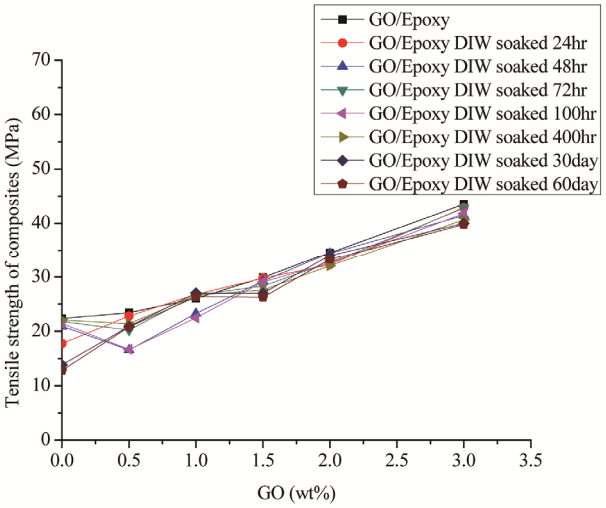
Figure 5(a) shows the effect of soaking time in deionized water (DIW) on tensile strengths of GO/epoxy nanocomposites. Seven kinds of soaking periods are in the range from 24 hours to 60 days. Major trend is that tensile strength decreases with the increase of soaking time and this is clearly indicated by sequentially downward data points in Fig. 5(a) for W_{GO} of 0, and larger than 1.5wt%. Another trend shows that composite strength increases with the increase of W_{GO} or W_{RGO}. Data in Table 1 also prove this trend. As compared in Figs. 3(a) and 3(b), RGOs have wavy morphology but not for GOs. This special morphology suggests that epoxy resin can better infiltrate interspacings of RGOs and results in higher interfacial and tensile strengths for unsoaked RGO (3.0wt%)/epoxy than for unsoaked GO (3.0wt%)/epoxy, as shown in Table 1. For epoxy soaked in DIW for 60 days, its strength of 12.80MPa is lowest among epoxies

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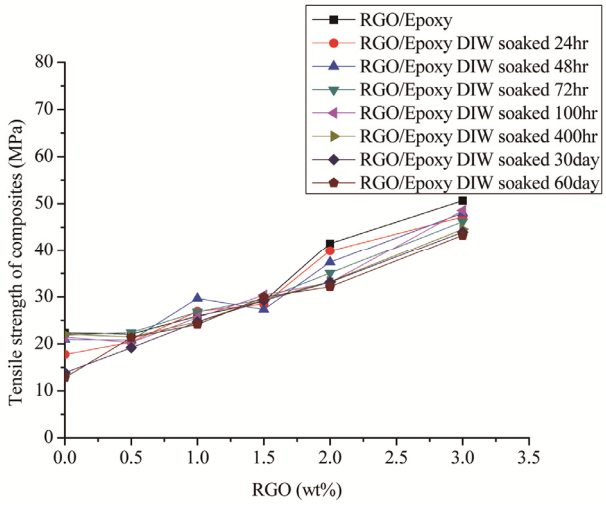
Table 1 Typical composite tensile strength and failure strain as a function of soaking liquid and time.

Soaking liquid and time	Composite type				
	Epoxy	GO(3.0wt%)/epoxy	RGO(3.0wt%)/epoxy	Acetone/GO(3.0wt%)/epoxy	Acetone/RGO(3.0wt%)/epoxy
DIW, 0 hour	22.35MPa σ = 1.55MPa ε_f = 0.04	43.54MPa σ = 1.75MPa ε_f = 0.034	50.65MPa σ = 1.87MPa ε_f = 0.031	47.26MPa σ = 1.94MPa ε_f = 0.034	56.83MPa σ = 2.35MPa ε_f = 0.035
DIW, 60 days	12.80MPa σ = 1.46MPa ε_f = 0.027	39.80MPa σ = 2.18MPa ε_f = 0.033	43.30MPa σ = 1.59MPa ε_f = 0.03	33.65MPa σ = 1.34MPa ε_f = 0.037	36.29MPa σ = 1.76MPa ε_f = 0.033
Salt water, 0 hour	22.35MPa σ = 1.55MPa ε_f = 0.04	43.54MPa σ = 1.75MPa ε_f = 0.034	50.65MPa σ = 1.87MPa ε_f = 0.031	47.26MPa σ = 1.94MPa ε_f = 0.034	56.83MPa σ = 2.35MPa ε_f = 0.035
Salt water, 60 days	11.76MPa σ = 1.44MPa ε_f = 0.03	37.89MPa σ = 2.25MPa ε_f = 0.031	43.98MPa σ = 2.50MPa ε_f = 0.028	33.77MPa σ = 1.23MPa ε_f = 0.025	38.12MPa σ = 1.38MPa ε_f = 0.027

σ: standard deviation of strength; ε_f: failure strain



(a)



(b)

Fig. 5 Effect of deionized water soaking time on strength of (a) GO/epoxy and (b) RGO/epoxy nanocomposites.

subjected to seven soaking periods, which is 42.7% lower than 22.35MPa of epoxy without soaking. Similarly, for GO(3.0wt%)/epoxy soaked in DIW by seven kinds of soaking periods, 60 day soaking leads to its lowest strength of 39.80MPa, which is 8.6% lower than 43.54MPa of the one without soaking. Smaller strength reduction of composites demonstrates that GO/epoxy can better retain strength than epoxy subjected to long term moisture attack. For the nanocomposite with highest W_{GO} of 3.0wt% soaked in DIW, it has lowest diffusion coefficient according to Fig. 4(a). Due to less moisture absorption, this composite can retain better strength compared with counterparts with lower W_{GO}. However, some deviations from the major trend are found at W_{GO} lower than 1.0wt% as shown in Fig. 5(a). For example, at W_{GO} of 0.5wt% 100-hour instead of 60 day soaking time results in lowest composite strength. This is probably due to very uneven graphene distribution in this 100-hour soaked specimen and moisture seriously attacks resin rich region in the composite.

Figure 5(b) shows the effect of soaking time in DIW on tensile strength of RGO/epoxy nanocomposites. Compared with GO/epoxy at W_{GO} of 3.0wt%, soaking time seems to show more significant effect on tensile strength of the composite with W_{RGO} of 3.0wt% because curves corresponding to different soaking periods of time spreading wider than those for GO/epoxy in Fig. 5(a). Table 1 also supports that 60 day soaking time in DIW leads to lowest strength 43.30MPa of RGO (3.0wt%)/epoxy, which is 14.5% lower than 50.65MPa of the counterpart without soaking. This strength reduction percentage is higher than 8.6% of GO (3.0wt%)/epoxy subjected to same soaking time in DIW; however, the former has lower diffusion coefficient than that of the latter and this indicates that less moisture has diffused into RGO (3.0wt%)/epoxy. There must be another factor that leads to the result. Molecular simulations have shown that the bonding energy and shear strength have been significantly improved by inducing the surface and edge functionalities on graphene nanosheets [21]. XPS analysis in section 3.1 reveals that epoxide and carbonyl functionalities are significantly reduced in RGO, this is likely to further decrease bonding strength of RGO (3.0wt%)/epoxy. Therefore, the weak bonding strength results in lower tensile strength of the composite after long term DIW soaking. Regarding the moduli associated with dif-

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ferent moisture conditions, failure strain data shown in Table 1 may be used to infer the relationship. According to our studies on stress-strain behavior of graphene composites without moisture condition, the stress-strain curve is quasi-linear. If we assume that the curve is linear, the ratio of strength to failure strain is a good approximation of tensile modulus. The ratio data infer that tensile moduli decrease as the soaking time increases.

(2) Soaking liquid

Figure 6(a) shows the effect of soaking time in salt water on tensile strengths of GO/epoxy nanocomposites. Figure 6(b) shows the effect of soaking time in salt water on tensile strengths of RGO/epoxy nanocomposites. Both figures depict two trends: Composite strength decreases with the increase of soaking time and increases with the increase of W_{GO} or W_{RGO}. Compared with soaking in DIW, soaking in salt water may have more significant effect on GO/epoxy than on RGO/epoxy. This is supported by data in Table 1. For GO/epoxy, 60 day soaking time in salt water leads to strength of 37.89MPa, which is slightly lower than 39.80MPa of the counterpart soaked in DIW. However, RGO/epoxy soaked in either DIW or salt water for 60 days has comparable strength of 43.30 or 43.98MPa. The result suggests that sodium ion in salt water may react with functional groups on GO such as hydroxyl group (OH). Besides, water molecules might also generate the hydrogen bonds with the functional groups on the graphene surface. Therefore both mechanisms reduce GO/epoxy interfacial bonding. On the other hand, due to reduction process RGO has few amounts of functional groups so that the ion does not influence the interfacial bonding.

(3) Acetone addition

Figure 7(a) shows effect of DIW soaking time on strength of acetone/GO/epoxy nanocomposites. For zero soaking time, acetone seems to have better dispersion effect of graphene in matrix [22] and leads to higher strength of acetone/GO(3.0wt%)/epoxy (47.26GPa) than that of GO(3.0wt%)/epoxy (43.54GPa) as compared with Fig. 5(a). The strength data in parentheses are quoted from Table 1. Another feature shown in Fig. 7(a) is that curves spread wider than those in Fig. 5(a), which indicates more significant influence of increasing DIW soaking time on strength of acetone/GO/epoxy than GO/epoxy. As shown in Table 1, 60 day DIW soaking leads to 29% strength reduction of acetone/GO(3.0wt%)/epoxy but only 9% strength reduction of GO(3.0wt%)/epoxy. Similar results are also found by the comparison of Fig. 7(b) with Fig. 5(b). 60 day DIW soaking also leads to 36% strength reduction of acetone/RGO(3.0wt%)/epoxy but only 15% strength reduction of RGO(3.0wt%)/epoxy. Higher strength reduction of acetone/GO/epoxy and acetone/RGO/epoxy by DIW soaking may be due to following factors. Initially acetone is a good solvent for epoxy resin that increases the resin flowability and enhances the dispersion of graphene. As cured, acetone may escape the composite due to its high volatility and leave some voids at interface. Later, when the

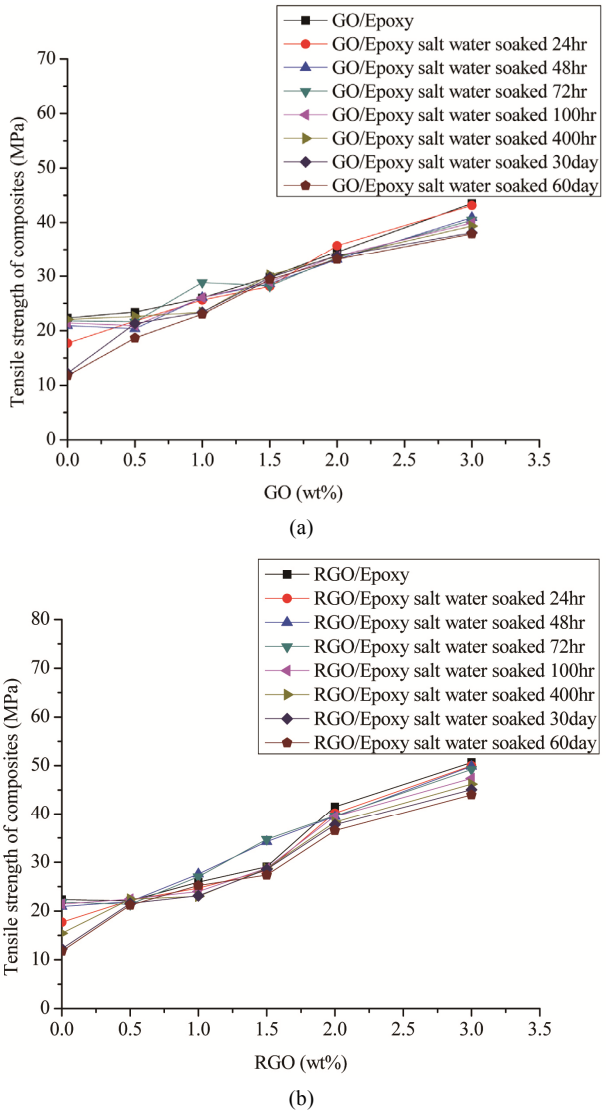


Fig. 6 Effect of salt water soaking time on strength of (a) GO/epoxy and (b) RGO/epoxy nanocomposites.

composite is soaked in DIW moisture may infiltrate those voids and react with GO or RGO. This behavior weakens the interface and significantly reduces composite strength.

Figures 8(a) and 8(b) show effect of salt water soaking time on strength of acetone/GO/epoxy and acetone/RGO/epoxy nanocomposites respectively. Compared Fig. 8 with Fig. 7 and referred data from Table 1, the strength reduction extent of composites by salt water soaking is similar to that by DIW soaking.

3.4 Microstructure Evolution

Tensile fracture morphologies of as fabricated and soaked composites are examined in this section by SEM in order to correlate with their tensile strengths. Figure 9(a) shows unsoaked acetone/GO(3wt%)/epoxy indicating good interface bonding on tensile fracture surface. However, in Fig. 9(b) the counterpart, acetone/GO(3wt%)/epoxy soaked in DIW for 400 hours depicts debonding at interface. Besides, central area

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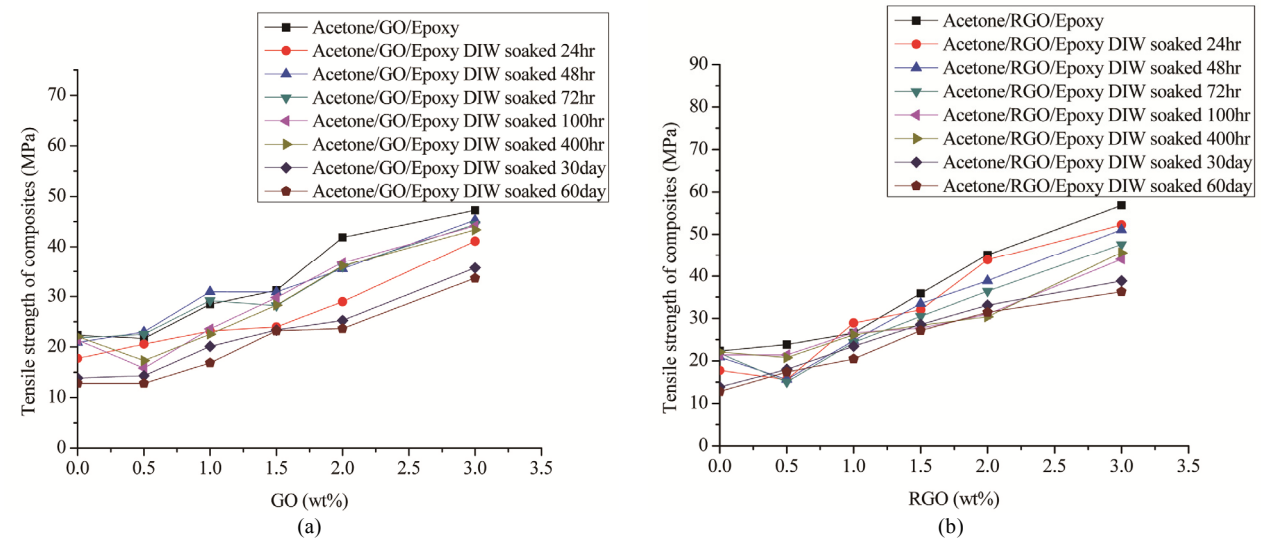


Fig. 7 Effect of deionized water soaking time on strength of (a) acetone/GO/epoxy and (b) acetone/RGO/epoxy nanocomposites.

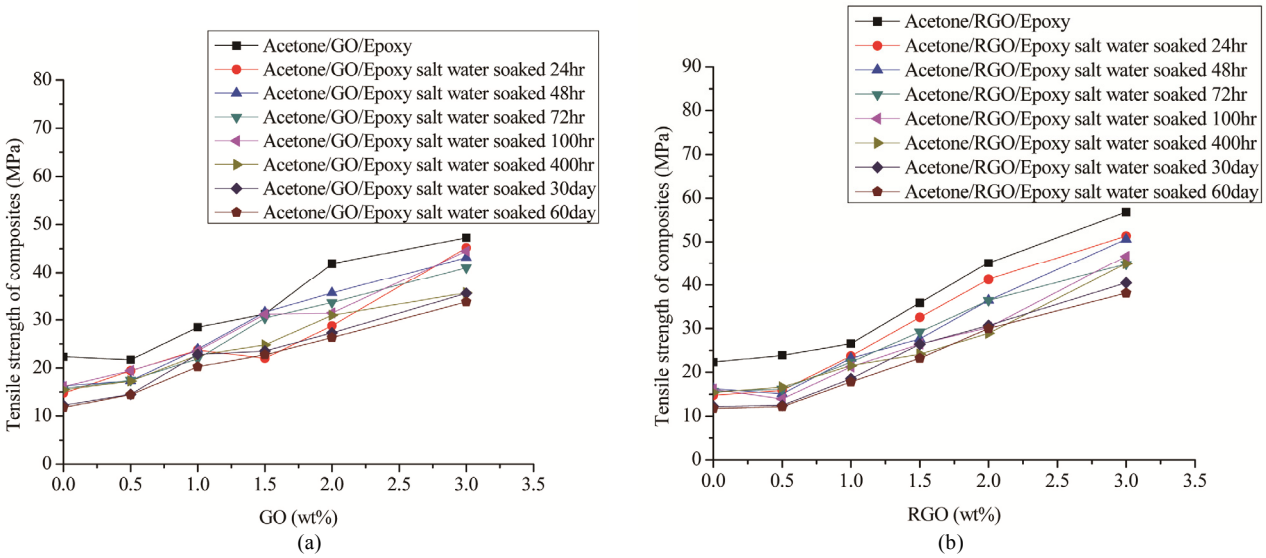


Fig. 8 Effect of salt water soaking time on strength of (a) acetone/GO/epoxy and (b) acetone/RGO/epoxy nanocomposites

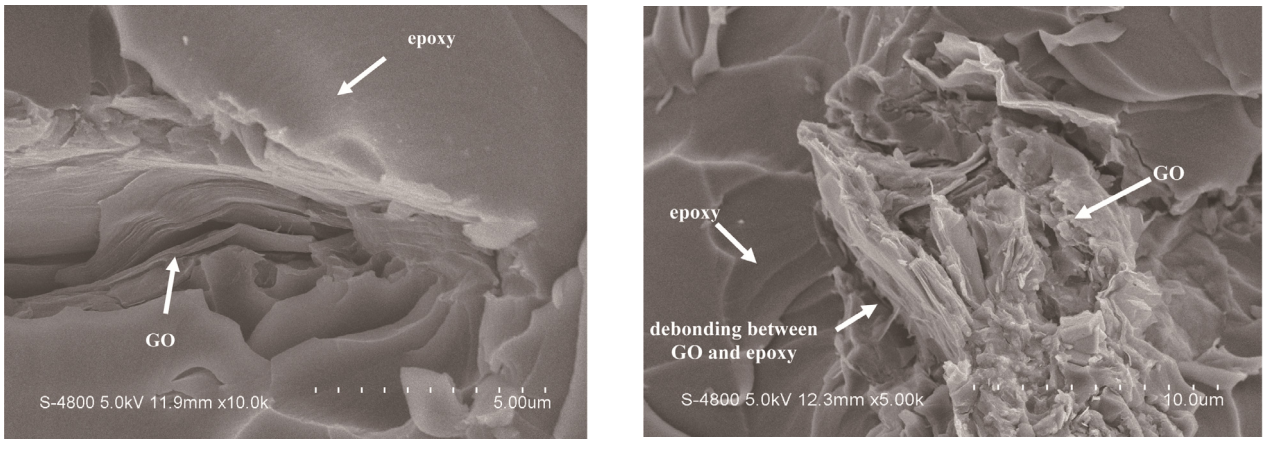
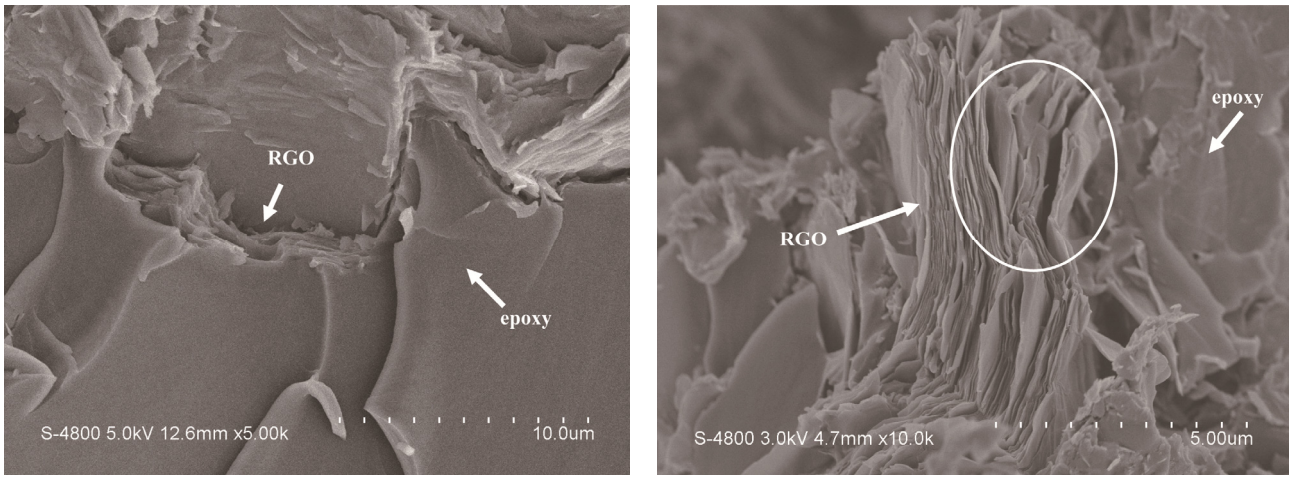


Fig. 9 (a) Unsoaked acetone/GO(3wt%)/epoxy showing good interface bonding on tensile fracture surface, (b) acetone/GO(3wt%)/epoxy soaked in deionized water for 400 hours showing debonding.

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(a) (b)

Fig. 10 (a) Unsoaked acetone/RGO(3wt%)/epoxy showing good interface bonding, (b) acetone/RGO(3wt%)/epoxy soaked in deionized water for 60 days showing graphene pull-out.

of the figure shows broken morphology which suggests that initially GOs have good dispersion due to acetone but interact with moisture by long term soaking. This mechanism weakens interfacial bonding as well as tensile strength. Similar comparison exists between Fig. 10(a) for unsoaked acetone/RGO(3wt%)/epoxy and Fig. 10(b) for acetone/RGO(3wt%)/epoxy soaked in DIW for 60 days. Good interface bonding is found in Fig. 10(a), while due to poor bonding RGOs bundle pull-out is found in Fig. 10(b). In Fig. 10(b), inter spacings are even found among RGO nanosheets inside white circle suggesting that better dispersion effect caused by acetone and poor interfacial bonding due to moisture infiltration.

4. CONCLUSIONS

Moisture effect on tensile strengths and moduli of GO/epoxy and RGO/epoxy nanocomposites is investigated in this paper. RGO/epoxy nanocomposites are found to have lower diffusion coefficients than those of GO/epoxy nanocomposites due to stacking of wavy RGO laminas. Diffusion coefficient decreases as W_{GO} or W_{RGO} increases by an exponential function. Lowest diffusion coefficient is $2.624 \times 10^{-6} m^2/s$ for RGO(3.0wt%)/epoxy, which is lower than $8.473 \times 10^{-6} m^2/s$ of GO(3.0wt%)/epoxy. For composites with higher W_{GO} or W_{RGO} soaked in either DIW or salt water for different periods of time, tensile strength and modulus decreases with increasing time. Although RGO(3.0wt%)/epoxy has lower diffusion coefficient than that of GO(3.0wt%)/epoxy, the former has higher strength reduction of 14.5% than 9.0% of the latter by soaked in DIW for 60 days. This result suggests that GO(3.0wt%)/epoxy can better retain its strength by more moisture attack due to better interfacial bonding caused by functionalities on GO.

With acetone as dispersion agent, composites do have higher strength due to better dispersion of graphenes. Acetone/RGO(3.0wt%)/epoxy has highest strength of 56.83MPa among all kinds of nanocomposites. However, when soaked in DIW for 60 days strength reduction is even higher for acetone/GO(3.0wt%)/epoxy and acetone/RGO(3.0wt%)/epoxy, 28.8% for the former and 36.1% for the latter, than for composites without acetone. DIW moisture infiltrates the voids left by the escape of acetone and react with GO or RGO. This behavior weakens the interface and significantly reduces composite strength. Soaking in salt water has similar effect to DIW on strength reduction of composites. Microstructure evolution indicates that debonding and graphene pull-out are two major failure modes for nanocomposites with acetone addition for soaked more than 400 hours. To sum up, graphene nanocomposites can better retain their strength by long term liquid soaking due to two mechanisms: Reduction of diffusion coefficient by stacking of GNS, and enhancement of interfacial bonding by graphene's functionalities.

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