



High-Performance Starch-Modified Graphene Oxide/Epoxy Nanocomposite Coatings: A glimpse at Cure Kinetics and Fracture Behavior

E. Yarahmadi¹, K. Didehban¹, M. Shabani², M. R. Saeb^{3,*}

¹ Department of Chemistry, Payame Noor University, P.O. Box: 19395-3697, Tehran, Iran.

² Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), P.O. Box: 31745-139, Karaj, Iran.

³ Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

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ABSTRACT

Epoxy is a versatile resin used in different fields such as coatings, colors, colorants, and composites. Adding nano-scale fillers/additives to the epoxy has valued epoxy coatings for engineering applications, and opened the time of advanced epoxy-based nanocomposite coatings. In the present work, graphene oxide (GO) was chemically functionalized with starch, as a natural polymer, and added to the epoxy/amine system. Differential scanning calorimetry was utilized to assess the cure kinetics of neat epoxy and its composites containing pristine and starch-functionalized GO (GO-St). Cryofractured surfaces of epoxy/GO and epoxy/GO-St nanocomposites are detected by scanning electron microscopy. Overall, the results are indicative of appropriateness of surface functionalization of GO by starch for high-performance coating applications. Hindered cure observed in the case of epoxy/GO was conquered by the attachment of starch to GO; moreover, tree-like fracture was responsible for higher fracture resistance due to starch. Prog. Color Colorants Coat. 11 (2018), 55-62 © Institute for Color Science and Technology.

1. Introduction

High Young's modulus, yield strength, fracture toughness, melting point, and thermal/electrical conductivity are all credits given to the graphene [1-4]. In recent years, graphene and its derivatives, particularly graphene oxide, have been the choice of both engineers and scientists for many applications such as biosensors, super capacitors, and drug delivery systems [2, 5-7]. In a similar fashion, graphite- and graphene- and graphene oxide (GO)-based polymer

nanocomposites have attracted much attention for coating applications [8-12].

The properness of the graphene oxide dispersion in polymer matrices depends on the extent to which exfoliation of GO flakes into individual sheets is achieved [13, 14]. The considerable hydrophobicity associated with graphene nanosheets brings about significant immiscibility with polymers having polar chains. On the other hand, reactive groups attached to the surface of GO having mutual tendency acts as a driving force towards larger multilayer stacks [15].

*Corresponding author: saeb-mr@icrc.ac.ir; mrsaeb2008@gmail.com

Thus, success in achieving high-performance GO/polymer composites is pertinent to the state of GO exfoliation [16-18]. Chemical functionalization of GO prevents agglomeration and restacking of the GO flakes in the thermosetting composites [19, 20].

In this sense, we used starch biopolymer here for surface modification of GO flakes, because of its abundance in the nature, reasonable price, and hydroxyl groups in its structure which was believed to catalyze epoxy/amine crosslinking kinetics. Starting from graphite, GO was synthesized from Modified Hummer method [21-23]. The use of such a chemical method facilitates attachment of hydroxyl, ketone, epoxide, and carboxyl functional groups to the GO surface/edges making GO very active towards epoxy.

Fourier-transform infrared (FT-IR) spectroscopy was used for assessing the attachment of starch to the GO flakes. Low-concentration epoxy nanocomposites comprising GO and starch-functionalized GO (GO-St) prepared and their nonisothermal behavior was assessed by curing nanocomposites during differential scanning calorimetry (DSC). Morphology of cryofractured surfaces was studied by scanning electron microscopy (SEM) to investigate fracture resistance improvement caused by attachment of starch to the GO nanosheets.

2. Experimental

2.1. Materials

A bisphenol A-based epoxy resin with epoxide equivalent weight of 174 g/eq, viscosity of 40-100 poise (25 °C), and density of 1.169 g/mL (25 °C) was used together with a triethylenetetramine curing agent, both provided by Sigma Aldrich (Italy). The synthesis of GO was exactly the same as a reliable protocol depicted from the literature [21]. Starch having a bulk density of 0.3 g/cm³, the solubility of 30 g/L and the pH of 6-7.5 was provided by the Merck Co. (Germany). Acids, oxidants, and solvents employed in GO synthesis and surface modification with starch, i.e. epichlorohydrin (ECH), sodium hydroxide (NaOH) and acetone were all purchased from Merck Co. (Germany) and used as received.

2.2. Surface modification of GO by starch

Thanks to its bulky character, starch could be a good choice for surface modification of nanofillers and facilitating nanofiller dispersion within epoxy [24]. In

the case of GO, it was expected that exfoliation of nanolayers could be facilitated by attachment of starch to the nanosheets. Moreover, the presence of hydroxyl end-groups in the structure of starch can catalyze epoxy ring opening, as we observed in a previous work [24]. The synthesized GO of about 2 g was dispersed into 70 mL in H₂O, followed by addition of 5N NaOH solution to increase pH to ca. 12. Then, 4 mL ECH was added drop-wise to the mixture and stirred for 12 hours 25 °C. Then, 35 g starch was added to the mixture under stirring for another 6 hours at 85 °C. The resulting precipitate was fractionated by centrifugation and then washed consecutively with hot distilled water and acetone. The obtained powder was dried at temperature of 75 °C to collect GO-St.

2.3. Preparation of epoxy/GO nanocomposites

Epoxy and its nanocomposites containing GO and GO-St were prepared through solvent exchange method. Firstly, the nanofillers (0.1 wt.% GO or GO-St) with respect to the weight of epoxy were dispersed in 20 mL of tetrahydrofuran *via* ultrasonic probe (Vibracel 75043 tip sonicator). Low amplitude of ultrasound wave (10%) and short times were selected for dispersion of fillers into the epoxy to avoid structural damage. The dispersion of nanofillers in tetrahydrofuran was poured into the uncured epoxy under stirring. The removal of solvent was then accomplished using a hot plate at 70 °C until the stoichiometric amount of curing agent (14 phr of hardener based on 100 parts by weight of epoxy) was added to the epoxy dispersion and kept frozen for thermal analysis (Figure 1).

2.4. Characterization methods

Fourier transform infrared (FT-IR) spectroscopy was performed on a Jasco FT-IR 615 (Jasco Inc, USA) working in the wavenumber range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹ to proof successive surface modification of GO with starch and also to probe into the covalent bonding of starch with active centers on the surface of GO. For doing this test, 1 wt.% of GO and GO-St powders were added to KBr and pressed into tablet.

Cure kinetics of epoxy and its nanocomposites containing GO and GO-St was studied nonisothermally on a calorimeter (Mettler Toledo 822e, Mettler-Toledo S.p.A, Italy) under nitrogen atmosphere varying the

heating rate (2.5, 5, 7.5, and 10 °C/ min). The temperature was varied from 25 to 250 °C.

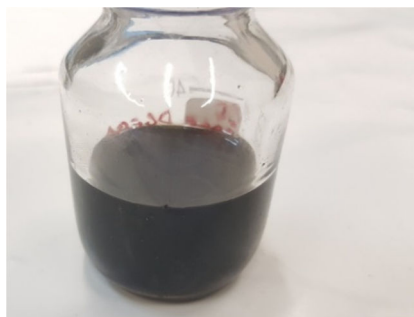
The cryofractured surfaces of epoxy/GO and

epoxy/GO nanocomposites were observed using a Field Emission Scanning Electron Microscope (FE-SEM), Zeiss model Supra 25.

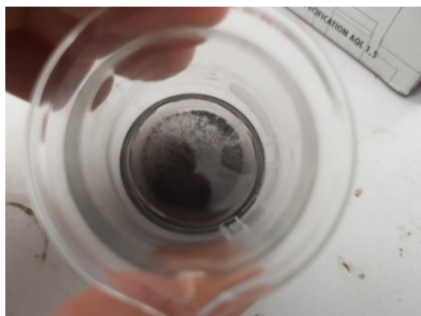
GO BARE after sonication in THF for 5 minutes (Amplitude 20%)



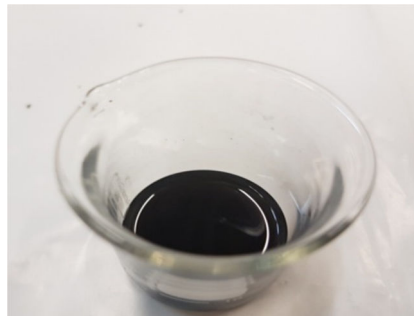
GO BARE + THF in epoxy



GO + STARCH after sonication in THF for 5 minutes (Amplitude 20%)



GO + STARCH after sonication in THF for 10 minutes (Amplitude 40%)



GO+STARCH+THF in epoxy



Figure 1: Schematic illustration of GO and GO-St-dispersion in the epoxy resin.

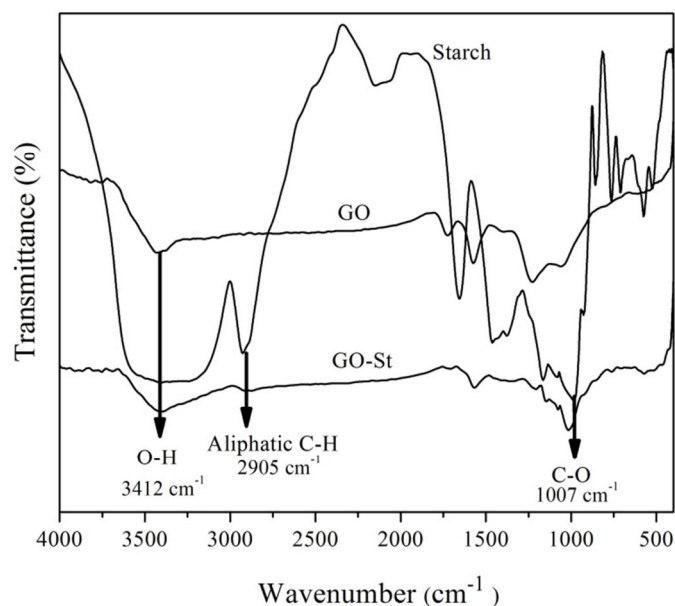


Figure 2: FT-IR spectra of the starch, GO, and GO-St.

3. Results and Discussions

3.1. Surface functionalization assessment

FT-IR spectra of the starch, GO, and GO-St are compared in Figure 2. The FT-IR spectrum of GO shows notable bands at 3200 cm^{-1} , 1715 cm^{-1} , 1642 cm^{-1} and 1600 cm^{-1} , which are assigned to the O-H stretching, C=O stretching, O-H bending and C=C stretching vibrations, respectively. The FT-IR spectrum of starch revealed a characteristic absorption band at 3412 cm^{-1} corroborating the O-H stretching vibration, a band at 2918 cm^{-1} attributed to the aliphatic C-H, and a broad peak at about 1007 cm^{-1} signifying C-O stretching of starch. FT-IR spectrum of the GO-St shows absorption bands of GO structure together with that of starch. A broad band at ca. 3087 to 3629 cm^{-1} showing sharp absorption at 3412 cm^{-1} confirms the presence the O-H starching bands attributed to GO and starch. Another peak at 2905 cm^{-1} can be ascribed to the aliphatic C-H contributed from starch, together with a broad band that lies in between 953 and 1080 cm^{-1} attributed to the C-O stretching of starch.

3.2. Cure kinetics study

Investigation on cure kinetics of thermosetting resins gives insights into the potential of system for achieving appropriate properties. In the other word, in order to predict the properties of thermosetting systems, there is a need for understanding network formation, which

helps to attain structure-property relationship. It should be added that the presence of fillers of different type (with or without surface treatment) may affects in different ways network formation and cure kinetics of epoxy systems, as we studied before epoxy systems containing carbon nanotubes [25-29], Fe_3O_4 [30, 31], calcium carbonate and eggshell [32], and layered double hydroxide [33]. In such systems, study of cure kinetics has been thoroughly discussed and the effect of each kind of filler on the crosslinking kinetics has been highlights. As a proper study based on nonisothermal calorimetric analyses, see this work [34]. After modeling the cure phenomenon, ariation of activation energy of the studied epoxy nanocomposites containing GO and GO-St in terms of the extent of cure reaction is plotted in Figure 3. As can be seen in the figure, activation energy of epoxy/amine system in the absence of filler follows a relatively sharp ascending trend because of transformation of the system from liquid to gel-like, and then solid-like phase behavior at late stages of crosslinking. By the progress in the extent of crosslinking or curing reaction, low-molecular-weight reactants experience chain polymerization and the reaction infinitesimally progresses towards gel point, the state at which the reaction changes from chemical-control to diffusion-control state [31]. At such a situation, the potential of system for curing is confined because of the collision getting sluggish. The presence of GO in the system

causes an average two-fold rise in the values of activation energy regardless of conversion. This is possibly because of the fact that GO large platelets act like big obstacles against epoxy and curing agent that hardens collision. The attachment of starch onto the GO can catalyze the curing reaction because of the presence of hydroxyl groups in the structure of starch biopolymer. Such an effect has been detected by a considerable fall in the values of activation energy in Figure 3, demonstrating facilitation of crosslinking and its independency on the extent of cure

3.3. Investigation of Fracture behavior

Figure 4 shows SEM micrographs provided from cryofractured surfaces of epoxy/GO and epoxy/GO-St nanocomposites. The smooth surface observed in the

case of epoxy/GO system (SEM in the left side in Figure 4) is indicative of a brittle fracture because of inadequate bonding between the filler and polymer matrix. As can be seen, fracture lines are signifying a progression in crack. On the other hand, attachment of starch to the GO platelets in the epoxy/amine system (SEM in the right side in Figure 4), suggests that fracture lines are short and multi-branched illustrating very higher interactions between GO-St and epoxy that hardens fracture. It should be also added that bulky groups of starch facilitate exfoliation of GO platelets leading to a well-GO-distributed network making possible resistance against fracture. Thus, the formation of a nanocomposite coatings having higher fracture resistance on the case of epoxy/GO-St can be recognized.

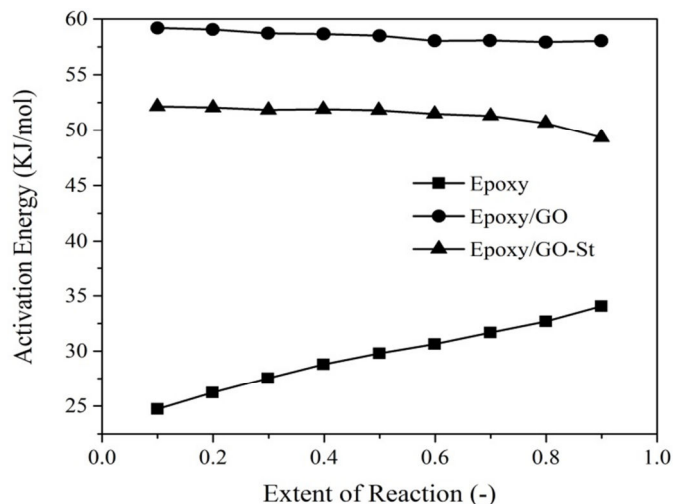


Figure 3: Activation energy as a function of the extent of reaction for epoxy and its nanocomposites obtained by modeling based on Kissinger–Akahira–Sunose approach.

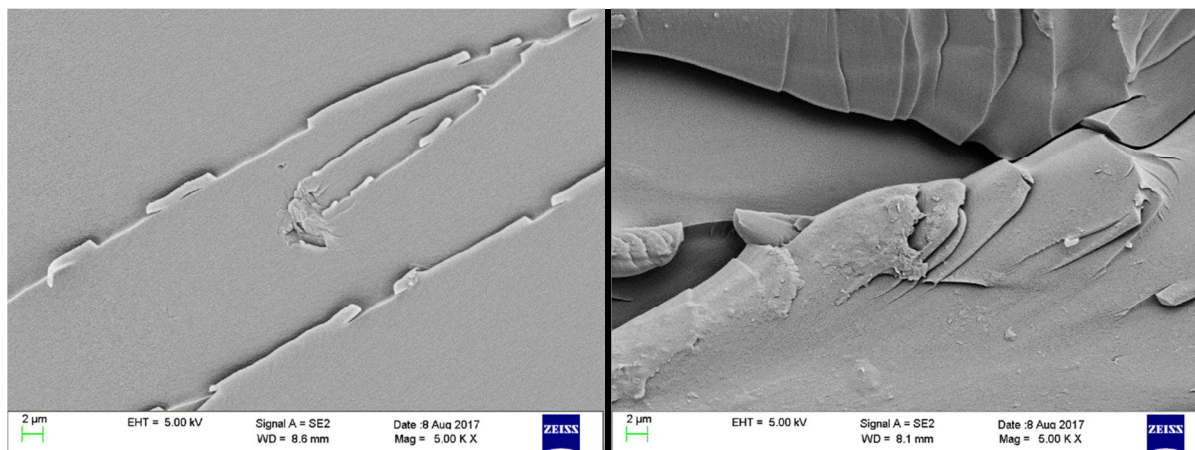


Figure 4: SEM micrograph taken from cryofractured surfaces of epoxy/GO (left) and epoxy/GO-St (right) nanocomposites

4. Conclusion

Epoxy/amine composites comprising GO and GO-St flakes are prepared and tested for cure kinetics and fracture resistance. Pristine GO was synthesized based on modified Hummer's method, then GO flakes were covalently surface functionalized by starch. FT-IR technique is used for assessing the attachment of starch to the GO, and appeared successful. Cure kinetics study revealed gradual hardening of curing over the extent of reaction because of changing the mechanism of curing from chemical-control to diffusion-control state, as appeared by a sharp increase in activation energy over conversion increment. Addition of GO considerable hardened the curing or crosslinking because of constrained collision, while starch functionalization of GO lowered activation energy compared with the epoxy/GO system. Such a

facilitated cure was corroborated on account of contribution of hydroxyl groups of starch to crosslinking, that catalyzed the reaction. Fracture behavior analysis revealed smooth fracture in the case of epoxy/GO system, but a relatively rough cryofractured surface was observed in the case of epoxy/GO-St, as per SEM analyses. The enhanced interaction between starch biopolymer and curing reactants was the reason behind rough fracture in the case of epoxy/GO-St system as compared with epoxy/GO.

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