www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2013.4469

Spectroscopic and morphological analysis of graphene vinylester nanocomposites

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Received: 29 April 2013, Revised: 14 May 2013 and Accepted: 17 May 2013

ABSTRACT

This communication describes the development of graphene and graphene reinforced polyvinylester nanocomposites. Low concentration of graphene was incorporated in the polymer matrix with the help of two different solvents. The role of solvent in the nanocomposite was studied. The FTIR spectroscopy and electron microscopy have supported the presence of graphene in the nanocomposites. It was discovered that vehicular medium (i.e., solvent) plays a vital role in the properties of the ultimate nanocomposites. When dimethylacetamide was used as solvent, the morphological analysis suggested the increased toughness while in case when tetrahydrofuran was used as solvent, nanocomposite appeared brittle in nature. Copyright © 2013 VBRI press.

Keywords: Graphene; polyvinyl ester; nanocomposites; spectroscopy; morphology.

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Introduction

The composites containing nanoparticles display synergism in the physicochemical and physicomechanical properties yet the level of improvement maximizes up to a certain extent. Among engineering materials, vinyl ester resin (VE) is a relatively cheaper than other polymers of its class and possess properties that are intermediate between epoxy resin and polyester resin. It is worth mentioning that VE and polyester resin occupy approximately 75 % of the market share making them the one of the most valuable industrial polymers. Therefore, improvement in their properties without sacrificing the basic properties of the resin is highly desirable. Several attempts have been made to enhance the properties of VE resin by incorporating carbon nano-materials such as single and multiple walled carbon nanotubes (CNT) **[1-3]**. However, few serious concerns limit the use of such nanomaterials and foremost are the cost and scarce production of CNT. Moreover, CNT needs to be functionalized to achieve a uniform/homogenous dispersion in the polymer matrix. Also, half of the area of such CNT is not available for the reaction as it remains hidden and inaccessible inside the tube.

On the other hand, graphene (GR) could now be derived from relatively cheaper graphite that is naturally abundant and an anisotropic material. The GR has a layered structure of carbon atoms arranged in a hexagonal ring and attached through Sp^2 covalent bonds. These hexagonal rings possess high mechanical stiffness of approximately 1060 GPa **[4-6]**.

In order to solve the problems that arise in CNT based polymer nanocomposites, in this communication we report our studies on synthesis of reactive GR nanosheets and its incorporation in VE resin to make nanocomposites. The amount of GR was deliberately kept to lower concentration to visualize the effect of nanomaterial on the properties of ultimate nanocomposites. Recent studies have shown that the presence of GR in polymer nanocomposite tends to improve the mechanical properties of the polymers. Such nano-modified polymeric materials may find enormous applications in areas such as adhesives for wind turbine blades, EMI shielding, corrosion resistant, and fire resistant coatings etc. **[5]**. Unlike in other cases reported before on nanocomposites containing nanofillers, in this case, the quantity of GR is kept at low concentration value so that nanofiller do not agglomerate and degrade the basic properties of the resin. But, GR would provide additional strength to the ultimate composite material. Higher strength of such nanocomposites will allow the reduction of resin quantity in the fiber reinforced composites. The characterization and morphological investigations on GR and GR based nanocomposites are briefly described in this article.

Table 1. Properties of vinyl ester resin.

Color	Styrene content	Specific gravity @25^{o}C	VOC content	Physical state	Self life
Blue	43 wt%	1.04-1.12	486 gm/l	liquid	3-5 months @ 25 ^{o}C

Experimental

Materials

The graphite powder was provided by Asbury Carbon, USA. The concentrated sulfuric acid, potassium permanganate, hydrogen peroxide, hydrogen chloride, dimethylacetamide (DMAC) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. The chemicals were of analytical grades and used without further purification. Water used during the synthesis process was ultrapure with 18µ resistivity. The VE resin (**Fig. 1**) in styrene was purchased from Fiber Glass Hawaii LLC, Honolulu. The resin was formulated by Reichhold Inc. under the trade-name HYDREX 100 **[7-8]**. The following properties were mentioned by the manufacturer in their MSDS sheet:

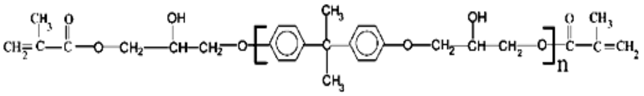

Fig. 1. Chemical structure of vinyl ester resin.

Synthesis of graphene

The GR was prepared following a patent pending procedure as described elsewhere **[9]**. In brief, the graphite powder was chemically treated with strong oxidizing agents followed by ultrasonication in a volatile solvent. The exfoliated graphene powder was obtained on inert atmosphere thermal shocking of the above obtained chemically treated graphite powder.

Preparation of nanocomposite

The nanocomposites were prepared following a patent pending procedure and briefly described here **[10]**. The nanoparticles (modifiers) were dispersed in the polymeric matrix with the help of solvents that dissolve the VE. It was necessary to verify the solubility of the VE in the desired solvent as the solvent acts as a vehicular medium for the uniform/homogenous distribution of the nanoparticles. The exfoliated GR powder was, therefore, ultrasonicated in 5 ml of either analytical grade (≥99%) DMAC or THF solvents for 16 h duration. The colloidal solution so obtained was then added to the polymer.

Preparation of vinylester and dimethylacetamide (VEGRDMAC) nanocomposites

The GR (0.2% w/w) was ultrasonicated in 5 mL of analytical grade DMAC for 16 h. The homogeneous solution of GR, in DMAC, was then added to 180 g of VE followed by vigorous mixing for 15 min with the help of homogenizer. Finally, 1.5 mL of industrial grade methylethylketoneperoxide (MEKP) is gently mixed with the above mixture and poured in the polypropylene molds (**Fig. 2**). The cured plates were taken out of the molds after 24 h and pressed between two aluminum plates for another 48 h.

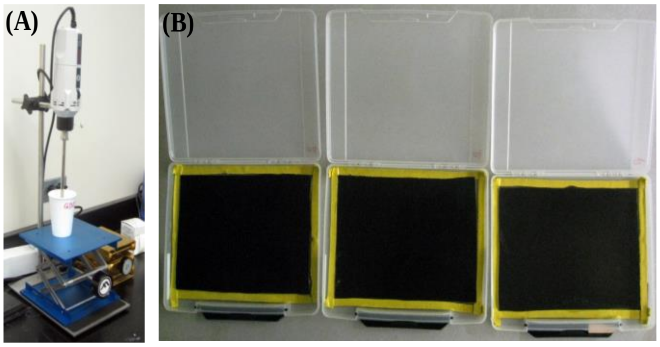

Fig. 2. Preparation of nanocomposites. (A) Homogenization of graphene in polymer matrix. (B) Casting and curing of nanocomposites.

Preparation of vinyester graphene (VEGRTHF) nanocomposites

The GR (0.2% w/w) was ultrasonicated in 5 mL of tetrahydrofuran (THF) for 16 h. The homogeneous solution of GR, in THF, was then added to 180 g of vinylester followed by vigorous mixing for 15 minutes with the help of homogenizer. Finally, 1.5 mL of MEKP is gently mixed with the above mixture and poured in the polypropylene molds (**Fig. 2**). The cured plates were taken out of the molds after 24 h and pressed between two aluminum plates for another 48 h.

Characterizations

The FTIR analysis was conducted on Thermo Nicolet FT-IR spectrometer using Easy Omnic software. The reactive GR or gel polymer nanocomposites were taken on KBr pellet and analyzed under the spectroscope. A minimum of 60 scans were acquired at a resolution of 4 cm^{-1}. A background spectrum was collected prior to collecting a spectrum of the sample. The baselines of the spectra were corrected using the Easy Omnic or Origin software. The FESEM analysis was performed on Hitachi S4800, and TEM analysis was performed on LEO912 Energy-Filtering Transmission Electron Microscope. The samples were thin coated with gold-palladium to prevent the charging during FESEM analyses.

Results and discussion

The nanoparticles have high surface to volume ratio that maximizes the interfacial contact between the nanoparticles and polymer matrix. Due to the increased surface area at the interface, there is a good adhesion between the matrix and the nano-size reinforcements. In such cases, the stress transfers efficiently from the matrix to the reinforcements. It is, therefore, crucial to understand the mode of interaction between the nanoparticles and polymeric medium. Studies based on FTIR and microscopic analysis could give valuable insight of the material.

Characterization of graphene and nanocomposites

The hardening process in VE resin was monitored using spectroscopic techniques. The material was sampled at various stages of the curing process to study the changes occurring in the resin system. The distribution of the GR in resin was studied using FESEM and TEM techniques.

The FTIR spectral assignment of GR provides little information. On close observation, it appears that C=C aromatic stretching can be seen at 1515 cm^{-1} and 1538 cm^{-1}. Similarly, C-OH stretching appears at 1224 cm^{-1} and C-O stretching at 1056 cm^{-1}. Vibration at 1628 cm^{-1} may be due to unoxidized graphite domains **[11]**. This suggests that GR was not entirely reduced on thermal shock treatment.

FTIR spectroscopy

As mentioned earlier, it is necessary to understand the effect of various constituents in the final resin compositions. Moreover, it also crucial to understand the role of solvent in the nanocomposite composition. The **Fig. 3** shows FTIR spectra of various ingredients used in the nanocomposite preparation. From **Fig. 3**, it appears difficult to identify a particular material or group in the final nanocomposite as the spectral band from different components overlapped.

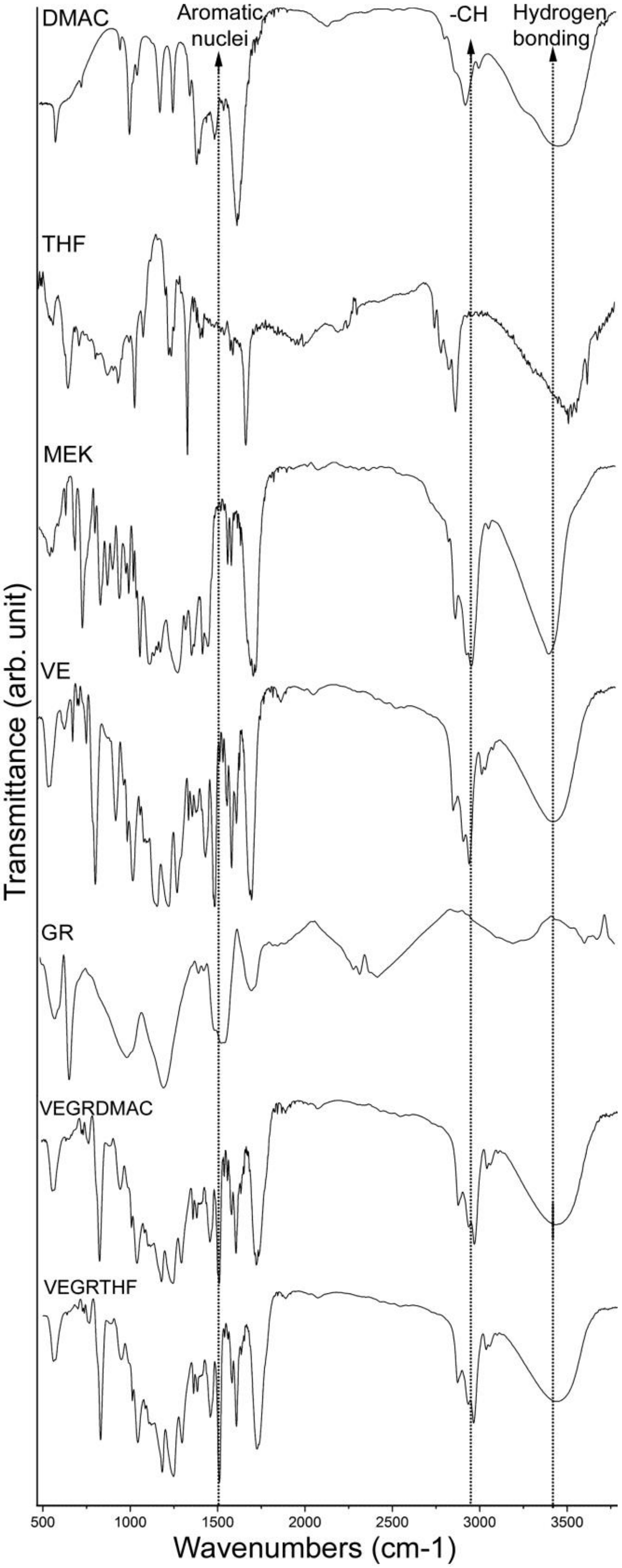

Fig. 3. FTIR analysis of the components in nanocomposites.

The FTIR spectra from different nanocomposites are also shown in **Fig. 3**. In case of pristine vinyl ester composite and nanocomposites (not shown), the peak appeared at 1624 cm^{-1} clearly suggested the presence of styrene double bond **[12]**. The peaks at 575, 830 and 891 cm^{-1} represents C-H out of plane bending vibrations. Similarly, the peaks position at 1115, 1249 and 1295 cm^{-1} are due to C-O stretching while peaks at 1401 and 1457 cm^{-1} are due to symmetric and asymmetric bending vibrations of the methyl group. Moreover, the peaks at 1511, 1582 and 1624 cm^{-1} are due to ring stretching vibrations of aromatic nuclei while additional peak appearing at 1721 cm^{-1} is due to ester carbonyl stretching. The three peaks at 2872 and 2933 cm^{-1} are due to symmetric and asymmetric –CH stretching while peak at 3036 cm^{-1} is from –CH of aromatic ring. A large hump displayed at 3400 cm^{-1} is due to hydrogen bonded –OH stretching **[13]**.

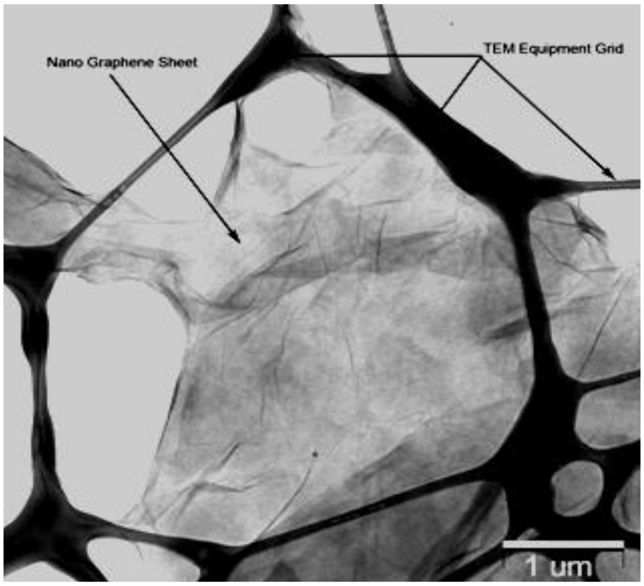

Fig. 4. TEM image of graphene sheets.

The FTIR spectra were also acquired at different time and temperatures (not shown). The spectra were recorded on the gel resin compositions at ambient condition, and after curing the resin compositions for 7 days. The spectra were also recorded on the compositions that were post cured at 70 ^{o}C (for 1 h) after 7 days of hardening. It was intriguing to note that spectral assignments were not affected by the presence of solvents in the nanocomposites compositions. Moreover, the spectra from different time and temperatures did not show much difference. This could be partially due to the overlapping of spectral assignments from different chemical ingredients. However, the two prominent peaks appearing at approximately 1600 cm^{-1} due to the aromatic ring stretching and at 1730 cm^{-1} due to carbonyl ester stretching changed the appearance with the increase in time and temperature. The splitting of peak occurred at approximately 1600 cm^{-1} is possibly due the benzene ring stretching that appears as the styrene evaporates with the passage of time and increase in temperature. Additional benzene ring stretching appearing at approximately 1600 cm^{-1} could be due to the presence of graphene in the nanocomposites as no such peak splitting was observed in the case of composites containing DMAC as a solvent. These peaks were initially masked due to the styrene stretching at 1624 cm^{-1}. Similarly, the components form stronger ester linkages as the styrene evaporates and the stretching can be clearly seen as splitting of band appearing at 1746 cm^{-1}.

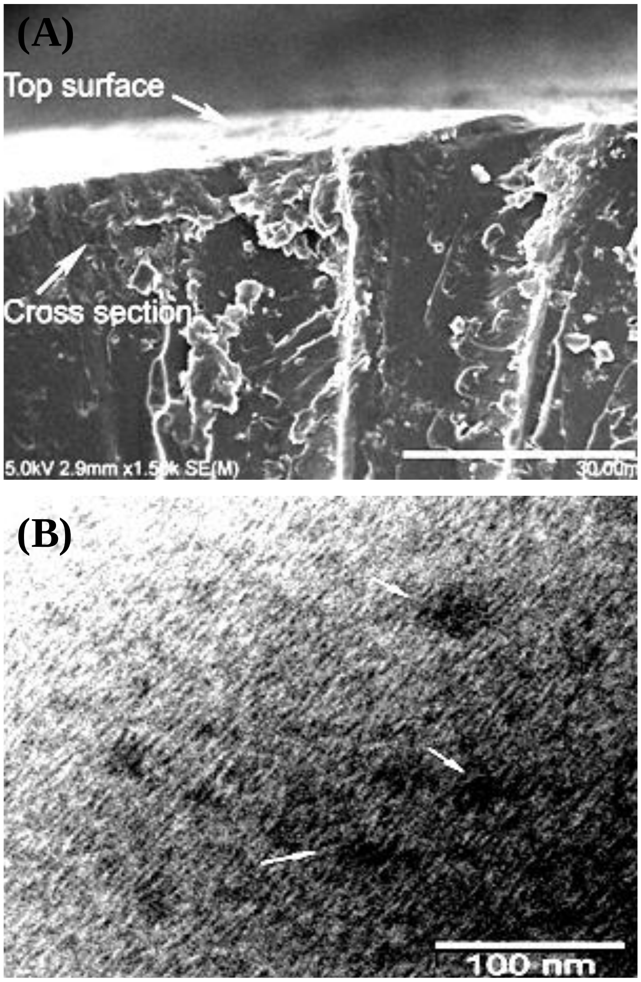

Fig. 5. Morphological investigation on VEGRDMAC. (A) FESEM image of the cross-section of the nanocomposite and (B) TEM images showing GR dispersion in VE.

Morphological investigation using TEM

The presence of solvent and incorporation of GR nano-sheets may alter the morphological appearance of a polymeric nanocomposite. The dispersion of foreign element in the continuous polymeric matrix may affect the overall packing arrangement of the polymeric chain leading to the pockets inherited with the possible defects or imperfections. The overall properties of the nanocomposite are adversely affected in cases that lead to the agglomeration of the nanomaterials in the polymeric matrix. It is, therefore, necessary to check the distribution of the graphene in the bulk of the nanocomposites.

Fig. 4 shows single sheet of graphene on the TEM grid. The estimated thickness of the reactive GR nano-sheet was approximately 4 to 7 nm suggesting that graphene sheets observed under the microscope were actually made of at least 3 to 10 layers. The top surface of the nanocomposite samples were analyzed using FESEM technique. The surface topography using FESEM method, however, did not reveal the insight of the material. The nanocomposite samples were then fractured in liquid nitrogen, and the cross section was analyzed using the FESEM and TEM techniques.

Fig. 5 (**A**) shows cross section FESEM of vinylester-graphene-DMAC (VEGRDMAC) nanocomposite. The dense top surface can be seen in the micrograph along with the densely packed cross section. There was no sign of cavitations, pinhole or any other type of defect in the area of the scan suggesting that the material was fully cured. Moreover, the presence of the minute amount of DMAC solvent limits scanning resolution to capture the presence of graphene. The TEM technique (**Fig. 5** (**B**)) was used to check the dispersion of graphene in the bulk of the material. The single layer of graphene is impossible to detect in the polymer composite due to the absence of contrast between the two hydrocarbons. However, there were few regimes that displayed the presence of graphene between the layers of nanocomposite.

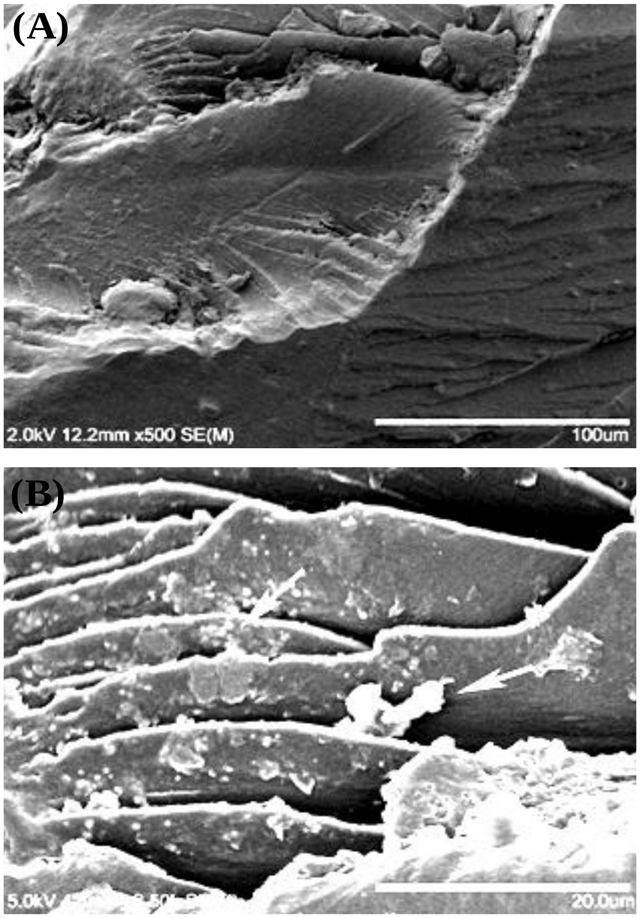

Fig. 6. Morphological investigation on VEGRTHF. (A) FESEM image of the nanocomposite surface; (B) Cross-section FESEM images showing GR dispersion in VE.

Fig. 6 shows the cross section FESEM images of vinylester-graphene-tetrahydrofuran (VEGRTHF) nanocomposite. In this case, THF was used as a solvent for the dispersion of GR. The uniqueness of this solvent is that it homogenously disperses GR in the polymeric matrix and evaporates at room temperature without leaving any residue. It helps in eliminating the effect of the solvent and to visualize the effect of GR nano-sheets in finally cured nanocomposites.

The VEGRTHF nanocomposite showed granulated textured morphology (**Fig. 6** (**A**)) that was different from the former case where DMAC was used as a vehicular media for the dispersion of GR. In this case, FESEM technique was unable to capture the presence of GR on the surface of the polymer. However, in cross-section, the agglomerated GR regimes can be clearly seen in the **Fig. 6** (**B**). It is worth mentioning that regions showing the presence of GR were not frequently noticed suggesting that the distribution of nano-sheets was relatively homogenous except in few sites where the agglomeration was observed.

Conclusion

The GR was homogeneously distributed in VE resin with the help of two different solvents (i.e. DMAC and THF). The nanocomposites were characterized using FTIR spectroscopy, and the effect of solvent on the development of nanocomposites was studied. No clear peaks were observed during the spectroscopic studies. However, splitting of few stretching bands suggested that GR was present in the nanocomposites. The high resolution electron microscopic studies confirmed the presence of GR in the nanocomposites.

Acknowledgement

Authors are thankful to the Department of Mechanical Engineering, Department of Chemistry, Biological Electron facilities of the University of Hawaii and particularly to Asbury Carbons for their help for this research.

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