IMPROVED ELECTRICAL, MECHANICAL AND EMI SHIELDING PROPERTIES OF PANI-VGCF-DBSA/DVB HYBRID NANOCOMPOSITE

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Abstract

A Polyaniline (PANI) based electrically conductive thermosetting hybrid nano-composite has been prepared by incorporating high apparent-density type vapor grown carbon fibers (VGCF-H) as additional conductive filler. The main conducting component of the matrix is PANI, protonated with a protonic acid, dodecylbenzenesulfonic acid (DBSA). Divinylbenzene (DVB) is used as a cross-linked thermosetting polymer. With addition of VGCF-H higher electrical conductivity and better mechanical properties have been achieved. Different weight percentages of VGCF-H in the PANI-DBSA/DVB matrix, were used and their effect on composite's properties have been investigated. Electrical conductivity up to 1.97 S/cm with the addition of 5 wt. % VGCF-H and flexural modulus of 1.71 GPa with 3 wt. % of VGCF-H have been achieved. Electromagnetic interference (EMI) shielding properties of composite with and without VGCF-H are measured in X-band frequencies and compared. Composite with 5 wt. % VGCF-H has shown EMI shielding effectiveness about 51 dB in X-band, which is higher than the composite without VGCF-H (around 22 dB). The morphologies of the composites were studied by SEM analysis. The effect of dispersion on electrical and mechanical properties also has been explained using SEM micrographs. The results of these studies confirmed that a polymer thermoset conductive composite with improved electrical, mechanical and EMI shielding effectiveness has been successfully prepared.

1. Introduction

In the recent years, aerospace industry has seen a gradual shift from metallic structures to the carbon fiber reinforced plastics (CFRPs) in structural applications. CFRPs has shown remarkable properties in many structural areas but still there are some issues which need to be addressed in near future, one of them is the loss of the electrical properties of the fibers in thickness and longitudinal direction in the epoxy based CFRPs. This loss of the conductivity of the composites can be attributed to the insulating behavior of the resin matrix. To improve the electrical properties of the composites many researchers have tried to add conductive filler into the insulating matrix. Adding CNT, carbon black, graphite, graphene etc. into the insulating matrices is the most common methodology [1-2]. However, using this

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methodology, very high electrical properties have not been realized yet. Recently researchers have tried many other alternative ways and have also shown great interest in conductive polymer based composites.

Since the discovery of intrinsically conductive polymers (ICPs), they have attracted tremendous attention of the researchers. Conductive polymer based composites have been researched extensively due to their outstanding properties and vast applications. Applications in the field of Electromagnetic interference (EMI) shielding, sensing, actuation, capacitor/battery and biomedical are just few to name [2-8]. Polypyrrole(PPY), ploy(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) are the most studied conductive polymers, specially PANI has been the center of the research due to its easy availability, ability to tune electrical conductivity and remarkable optical properties [9-11]. It is well known that, emeraldine base form of PANI can be rendered conductive by doping with a protonic acid. Dodecylebenzenesulfonic acid (DBSA), camphor sulfonic acid (CSA) and p-toulenesulfonic acid (PTSA) are some of the most common protonic acids used for doping with PANI [12-13]. We have chosen DBSA in the present work due to its surfactant properties which improves the solubility of the PANI-DBSA complex in most of the organic solvents. We demonstrated a unique one-step synthesis process of PANI-DBSA/DVB composite in our previous work while choosing divinylbenzene (DVB) as the resin system [14]. It was demonstrated that a PANI-DBSA/DVB composite has very high electrical and good mechanical properties. Effect of graphene oxide on the composite was also investigated by our group [15].

In the present work authors have tried to improve the electrical and mechanical properties of the PANI-DBSA/DVB system by adding additional filler namely vapor grown carbon fibers (VGCF-H). VGCF-H has been chosen due to its high electrical properties, easy handling, availability and ability to disperse easily. The idea of using VGCF-H is inspired by the hypothesis that PANI-DBSA agglomerates are the conductive islands in the insulating DVB matrix. Therefore, VGCF-H can be used as the connective conductive bridge between those islands and also improve the mechanical properties.

A highly conductive composite material with good mechanical properties is the demand of present industrial and academic fields. Therefore, authors have tried to prepare a thermoset conductive composite with high mechanical and electrical properties. The same composite also has shown remarkable EMI shielding behavior attributed to its conductive nature.

2. Experimental Details

2.1. Material

PANI in emerldine base (EB) form has been procured from Regulus Co. Ltd. DBSA was supplied by Kanto Chemical Co. Ltd. and DVB was obtained from Sigma-Aldrich Co. All of the materials were used as received without any further purification or modification. VGCF-H was supplied by Showa Denko, Japan and used as received.

2.2. Synthesis of PANI-DBSA-VGCF/DVB matrix

It has been reported in our previous work that undoped PANI-DBSA complex is very difficult to use directly to obtain an environmentally stable (longer curing time at room temperature) matrix using DVB cross-linked polymer due to the exothermic reaction between DBSA and DVB. Therefore we reported to use semi-doped PANI-DBSA complex to obtain an environmentally stable matrix by using roll-milling process [16]. Addition to that work, we propose that we can obtain a semi-doped PANI-DBSA complex even by mixing in centrifugal mixer by utilizing the heat generated during mixing.

In the present work we have used centrifugal mixing and optimized the mixing parameters to get a semi-doped PANI-DBSA complex due to heat generated after mixing VGCF-H. VGCF-H has high aspect ratio therefore, more heat is generated during centrifugal mixing with the addition of more amount of VGCF-H. To obtain a good dispersion of VGCF-H into the final composite, VGCF-H was first mix with DBSA to obtain the good homogenous DBSA-VGCF-H complex. PANI was further added to the DBSA-VGCF-H complex and mixed in a centrifugal mixer. Due to heat generated during

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the mixing procedure PANI got semi-doped and an environmentally stable PANI-DBSA-VGCF/DVB composite could be prepared. The matrix was further poured into mold and put in a hot-press machine for two hours at 120°C. In all of the samples, PANI-DBSA were kept in the ratio of 1:0.6 Molar ratio. DVB wt. % was fixed as 50 wt. % of the total composite. The hypothesis to use VGCF and manufacturing scheme has been shown in the figure 1.

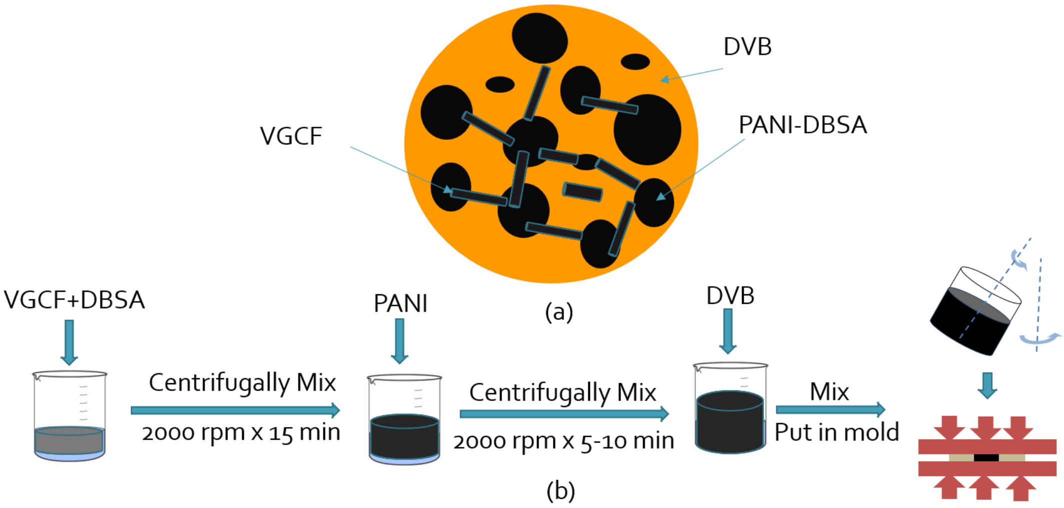
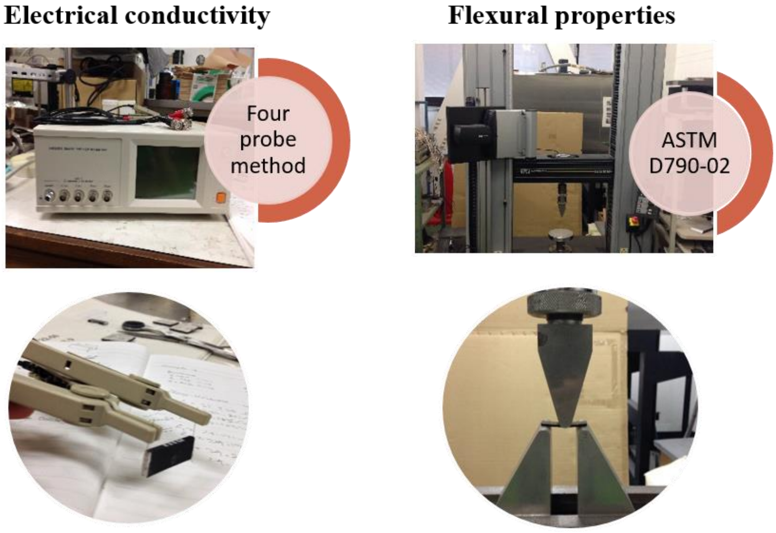


Figure 1. (a) Hypothesis (b) Scheme to prepare PANI-DBSA-VGCF/DVB composite.

2.3. Measurements

For electrical conductivity measurement samples with size thickness 2mm, width 12.7 mm and length 25 mm were prepared. Similarly for flexural properties measurement samples with size thickness 2mm, width 12.7 mm, length 50 mm were prepared. For electrical properties measurements, silver paint was applied in the perpendicular direction of the measurement. Electrical resistance was measured at DC frequency using LCR meter (3522-50 LCR HiTester, Hioki E.E. Corporation) as shown in Figure 2 (a). Conductivity was measured from the recorded resistance of the samples.



(a) (b)

Figure 2. (a) Electrical conductivity measurement by four-probe method (b) Flexural properties measurement using ASTM 790-02.

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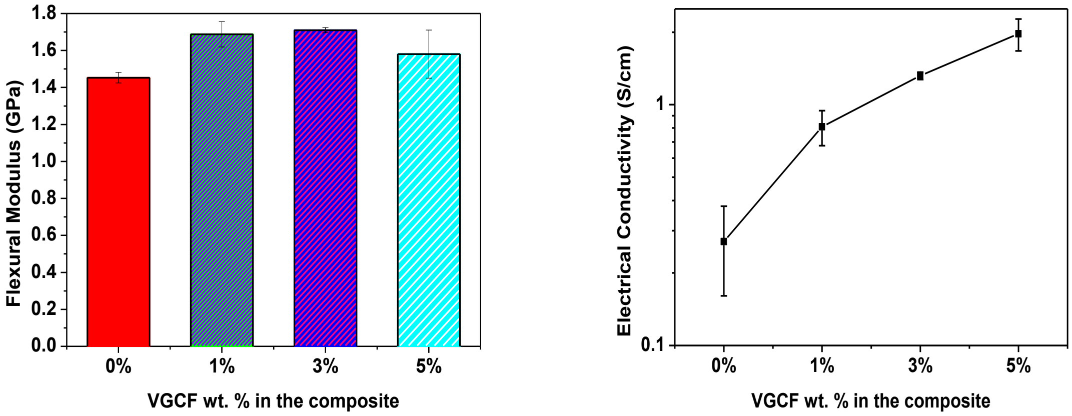
Flexural properties of the samples were measured by Universal Testing Machine (Instron-5582) by 3-point bending test. Load cell of 5 kN and testing speed of 1 mm/min were chosen. Radii of Supporting and loading nose was set to be 5 mm as per ASTM D790-02 [17]. Thickness to span ratio was 1:16. Morphologies were observed using SEM. EMI shielding effectiveness in X-band were measured using Vector Network Analyzer (VNA E8263BAgilent Technologies). For measuring EMI SE in X-band frequency, sample with size thickness 3mm. Different samples were prepared for different measurements.

3. Results and Discussions

3.1 Electrical and Mechanical Properties

Electrical properties of the composites w.r.t. the VGCF-H content was measured and compared with the neat PANI-DBSA/DVB composite. For comparison purpose 50% DVB was fixed and the VGCF-H amount was varied while making the composite samples. It has been found that with the increase in VGCF weight percentage in the composite there is a significant improvement in the electrical properties. With the 5 wt. % of the VGCF, electrical conductivity was 1.97 S/cm as compared to 0.27 S/cm in the composite without VGCF. Similarly, Flexural Modulus was also improved with the addition of VGCF in to the matrix. Increase in the flexural modulus was observed with the increase of VGCF-H content in the composite up to 3%. However, the modulus of the composite with 5 wt. % VGCF was decreased. This behavior could be attributed to the poor dispersion of the VGCF in the matrix. Agglomeration of VGCF-H could be the main reason for the decrement in the flexural modulus of the composite, which is also supported by the SEM investigation.



(a) (b)

Figure 3. (a) Flexural modulus (b) Electrical conductivity of PANI-DBSA-VGCF/DVB composite w.r.t VGCF wt. %.

3.2 SEM Morphologies

The morphologies of the PANI-DBSA-VGCF/DVB composite were studied and compared using SEM as shown in Figure 4. Connecting conductive networks can be seen clearly from the micrographs with the increase in the VGCF weight percentage, contributing to the improved electrical. However VGCF agglomerates are also very much visible in the composite with 5 wt. % of VGCF. As we have seen a decrement in the mechanical properties of the composite with 5% wt. % of VGCF-H, the SEM micrographs confirm our hypothesis that this reduction could be due to the formations of VGCF agglomerations. VGCF-H dispersion is one of the most important factor to improve overall properties of the composite. With the higher VGCF-H wt. % in the composite, the viscosity of the matrix increases substantially. Therefore composite with 3 wt. % of VGCF-H is optimum for better electrical and mechanical properties.

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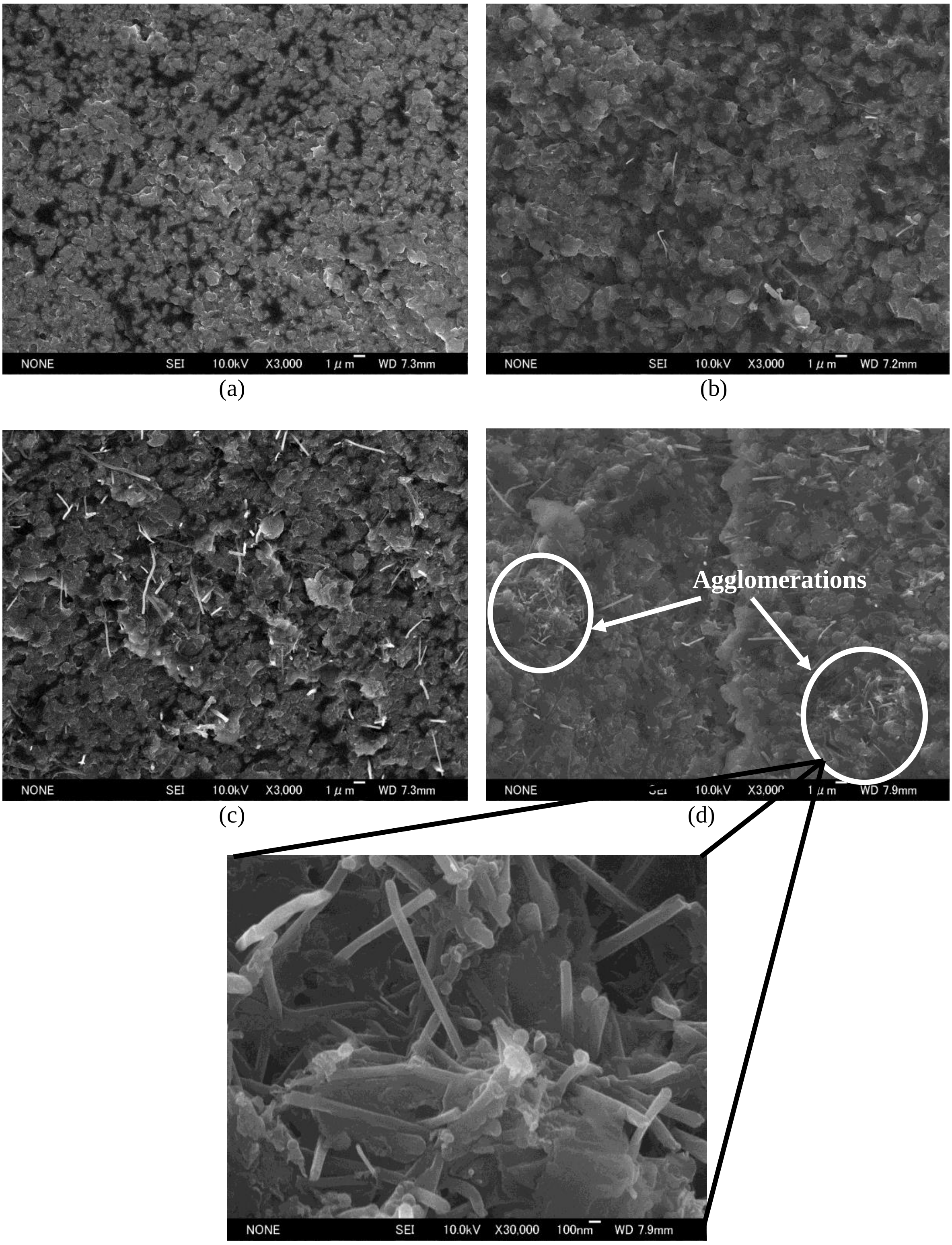

(a) (b)

(c) (d)

(e)

Figure 4. SEM micrographs of PANI-DBSA-VGCF/DVB composite w.r.t VGCF wt. % in the composite (a) 0% (b) 1 % (c) 3% (d) 5% (e) VGCF agglomeration.

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3.3 EMI Shielding effectiveness

The ability of the material to weaken the incoming electromagnetic waves is known as the electromagnetic interference (EMI) shielding of the material. EMI shielding effectiveness (SE) of PANI-DBSA/DVB composite with or without VGCF-H has been reported. For comparison purpose, composites with 5 wt. % of VGCF-H and without VGCF-H in 50 wt. % DVB are presented in figure 5. It has been found that composite with 5 wt. % of VGCF-H has shown remarkable improvement in the EMI SE of the composite compared to the composite without VGCF-H. Total EMI shielding effectiveness (SE_T) improved to 51 dB for PANI-DBSA-VGCF/DVB composite from 28 dB for PANI-DBSA/DVB composite (23 dB) at 12.4 GHz frequency. SE due to reflection (SE_R) and absorption (SE_A) were improved by 2.46 dB and 21.32 dB respectively at 12.4 GHz.. This means that these samples are capable to attenuate more than 99.99% of the incident electromagnetic waves.
The increase in the EMI SE can be attributed to the improved electrical conductivity of the composite by adding VGCF-H. The electrical conductivity of the composite with VGCF is more than ~ 7 times of the composite without VGCF-H. The intrinsic behavior of VGCF to absorb electromagnetic waves is also responsible for such remarkable improvement of EMI SE in the material.

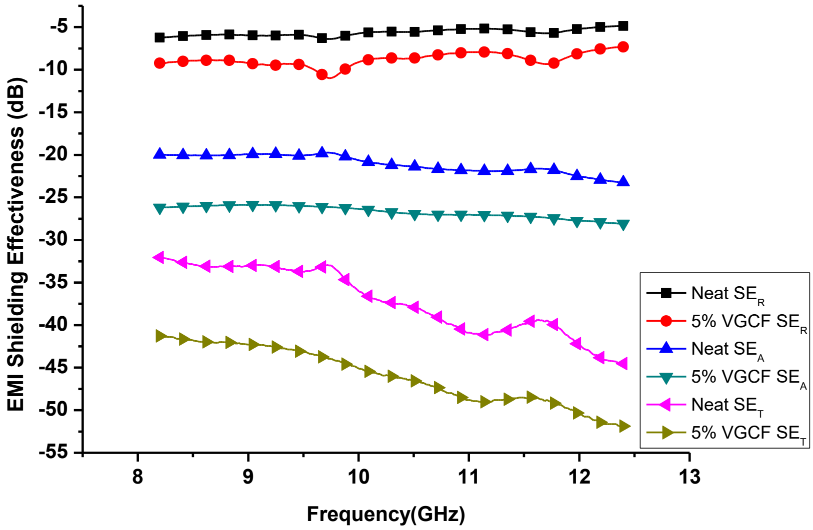

Figure 5. Shielding effectiveness of PANI-DBSA/DVB and PANI-DBSA-VGCF/DVB nanocomposites in X-band (8.2–12.4 GHz).

4. Conclusions

A highly conductive PANI-DBSA-VGCF/DVB hybrid nano-composite were prepared and analyzed. Electrical and mechanical properties of the composites improved significantly with the addition of the VGCF in PANI-DBSA/DVB composite. Flexural modulus of PANI-DBSA-VGCF/DVB hybrid nano-composite is improved to 1.71 GPa value at 3 wt. % loading of VGCF-H in to the composite from 1.45 GPa value for PANI-DBSA/DVB composite. Beyond 3 wt. % of loading, slight decrease in the flexural modulus is observed due to agglomerations, but it is still higher than the pure PANI-DBSA/DVB composite. The micrographs obtain by SEM has confirmed that VGCF-H acted as connecting bridge between the conductive PANI-DBSA islands in insulating DVB matrix. Composite with VGCF-H has shown great improvement in the EMI SE of the composite. This behavior can be assigned to the improved overall electrical conductivity of the PANI-DBSA/DVB composite as well as due to the good EMI shielding properties of VGCF-H itself. In this work, a thermoset composite has been reported with 51 dB of EMI shielding effectiveness in X-band, 1.97 S/cm of electrical conductivity and up to 1.71 of GPa flexural modulus.

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