POLY (VINYL ALCOHOL)/MULTILAYER GRAPHENE COMPOSITE STRUCTURES VIA ADDITIONAL MANUFACTURING ROUTE FOR EFFECTIVE EMI SHIELDING SOLUTIONS: STUDY OF MECHANICAL, THERMAL AND ELECTRICAL PROPERTIES

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Abstract
Polyvinyl Alcohol (PVA)/Multilayered graphene (MLG) composite structures with varying graphene weight percentages (5, 10, 15, 20 wt.%) were prepared by hot compression of solvent cast films and were investigated for their electromagnetic interference shielding effectiveness (EMI SE). At X band frequency range (8.2 – 12.4 GHz), 2mm thick structure with 20 wt. % graphene loading could achieve a shielding effectiveness of 23dB. As the graphene weight percentage increases, absorption contributes more to the shielding effectiveness than reflection. XRD, Raman spectroscopy, FESEM and TEM studies were carried out for the morphological and microstructural characterization of the composites. Differential thermal analysis of the composites shows significant improvement in thermal stability with an increase in graphene filler content. The tensile strength and Young's modulus of the composites were found to be better than or comparable with that of pure polymer. The composite films prepared meet the mechanical, thermal and electrical conductivity requirements of lightweight EMI shielding solutions. Composite structures tailor-made with proper selection of the number of layers and graphene loading percentage can be employed as effective EMI shielding solutions for a wide range of applications.

1. Introduction

Advanced telecommunication devices now in common use have raised the levels of electromagnetic pollution around us demanding effective electromagnetic interference (EMI) shielding solutions.EMI shielding protects sensitive electronic equipments as well as living tissues from stray electromagnetic emissions. EMI shielding is a necessity for industrial and laboratory use electronic instruments, antenna systems and military devices. Proper shielding enables electronic products to comply with acceptable electromagnetic radiation levels as per standards. EMI shielding works either by reflection and/or by absorption. Advances in conducting polymer composites offer a flexible, corrosion resistant alternative to the conventional metal sheets [1]. The contribution of reflection and absorption to the total shielding effectiveness depends on the type, composition and dispersion of fillers in the polymer matrix. Carbon nanoparticles, metallic fibers/powders and intrinsically conducting polymers have added successfully to thermoplastic as well as thermosetting polymer matrices for preparing effective EMI shielding CPCs [2,3]. Thermoplastic CPCs have the additional advantage of getting recycled, re-formed and reused. Graphene, carbon nanotubes and carbon nanofibers are the widely used carbonaceous fillers for EMI shielding CPCs. CPCs with graphene or CNTs achieve the percolation threshold with a lower weight percentage of fillers when compared to those with metallic fillers. This significantly reduces the net weight of the shielding material. Multilayered composite structures are more effective than bulk composite in EMI shielding applications. Multiple reflections within the structure result in an increased shielding effectiveness for such systems [4 -8]. Shielding effectiveness increases with number of layers in the structure [4,5]. Gradient multilayer structure results in reduced reflection, increased multiple internal reflections and increased absorption [6]. Multilayered gradient CPC has a higher contribution of absorption in total shielding effect when compared to a bulk sample with equivalent weight percentage of conducting filler [7].

PVA is a biodegradable, water soluble polymer with good adhesive properties. PVA/GNs/MWNT composite structure was prepared by hot pressing solvent cast as well as melt compounded films. The synergistic effect of MWCNTs and graphene nanosheets enhance the tensile properties, thermal stability, electrical conductivity, and EMI SE of composites [8]. It is proved that the solution mixing method outperforms the melt compounding method in terms of mechanical properties, dispersion, thermal stability, and EMI SE [8,9]. SWNT–PVA composite has been found suitable for low-bandpass THz filters [10]. In this study, we prepare highly filled PVA/MLG composite films by solvent casting technique and prepare a multilayered structure out of them by hot pressing. Electrical, thermal, mechanical and EMI shielding properties of the composites are studied.

For a transverse EM wave propagating into a sample with negligible magnetic interaction, the total SE of the sample is expressed by

$$SE_{total} = 10\log\frac{P_i}{P_o} = SE_R + SE_A + SE_{MIR} \tag{1}$$

where P_{in} and P_{out} are the power incident on and transmitted through a shielding material, SE_A, SE_R *and* SE_{MIR} are the absorption, reflection and multiple internal reflection shielding effectiveness.
When SE_{MIR} is negligible,

$$SE_{total} = SE_R + SE_A \tag{2}$$

The scattering parameters S_{11}, S_{22}, S_{12} and S_{21}obtained using a vector network analyser are used to calculate the shielding effectiveness.

$$SE_{total} = 10\log\frac{1}{|s_{12}|^2}\ \text{dB} = 10\log\frac{1}{|s_{21}|^2}\ \text{dB} \tag{3}$$

S_{12} and S_{21} are scattering parameters corresponding to transmission.

$$SE_R = 10\log\left(\frac{1}{1-s_{11}{}^2}\right)\ \text{dB} = 10\log\left(\frac{1}{1-s_{22}{}^2}\right)\ \text{dB} \tag{4}$$

S_{11} and S_{22} are scattering parameters corresponding to reflection.

$$SE_A = 10\log\left(\frac{1-s_{11}{}^2}{s_{12}{}^2}\right) \tag{5}$$

2. Experimental

2.1. Materials

PVA (86-89% hydrolysed and low molecular weight) was purchased from Alfa Aesar, Haverhill, MA, USA. MLG sheets obtained from United Nanotech Innovation Pvt. Ltd. have an average dimension in

X and Y direction: 10–20 μm, average thickness: 3–6 nm, average number of layers: 6–10, tensile modulus parallel to the surface: >1000GPa and tensile strength: >5GPa.

2.2. Composite preparation

PVA is dissolved in deionised water by hot stirring at 80°C for 4 hours. Graphene is added to the solution and stirred for 4 hours at 80°C. The mixture is then kept in ultrasonic bath for 90 minutes for further dispersion. The final solution is poured into a Teflon dish and kept for drying at 60°C in a vacuum oven for 24 hours. PVA/MLG composite films (~0.25mm thick) thus obtained were hot pressed at a temperature of 160°C and pressure of 10MPa to get 2mm thick multilayered structures.

2.3. Tests

XRD, Raman spectroscopy, FESEM and TEM studies were carried out for the morphological and microstructural characterization of the composites. Differential thermal analysis of the composites was carried out in nitrogen atmosphere to study the effect of graphene filler content on its thermal stability. Tensile test of composite films was performed with a Tinius Olsen UTM with 1 kN load cell at a grip separation rate of 12.5 mm/min. to evaluate the mechanical strength of the composites. Electrical conductivity of the composites was measured by two probe technique with the help of an impedance analyser. EMI shielding effectiveness of the composites was measured with the help of Agilent Vector Network Analyser in X band frequency range. Dynamic mechanical analyses of samples were done in tension mode in NETZCH DMA machine. 2mm thick samples were used for the purpose with a mixed stress-strain control mode in air atmosphere. A maximum dynamic load of 2N and static load of 0.5 N was applied during the process and maximum amplitude limited to 240 microns.

3. Results and discussion

Presence of multilayered graphene without much stressed condition in the polymer matrix was confirmed by the D, G and 2D peaks of graphene in the Raman spectra as shown in Fig. 1(a).

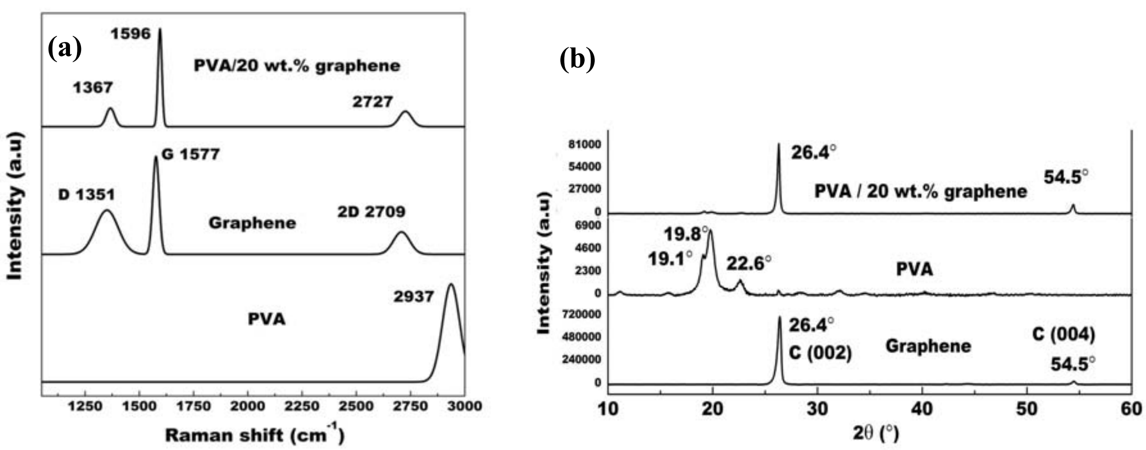

Figure 1. (a) Raman Spectra of PVA, MLG AND PVA/MLG composites (b) X-ray diffractograms of MLG, PVA and PVA/MLG composites

Almost identical I_D/I_G intensity ratio for graphene and polymer/graphene composites clearly indicates that no further damage is happening to the graphene sheets during the preparation and processing of the polymer composite films.

XRD diffractograms Fig. 1(b) shows the graphitic peaks which are evident in the polymer matrix. Crystalline peak of PVA becomes suppressed with the high intensity graphene peaks in the composite. SEM image of tensile fractured surfaces of 20 wt. % graphene – PVA composites (Fig. 2(a)) shows well dispersed graphene in PVA matrix with good interfacial adhesion between filler particles and the matrix. Fig. 2(b) shows the transmission electron micrograph of MLG in PVA matrix.

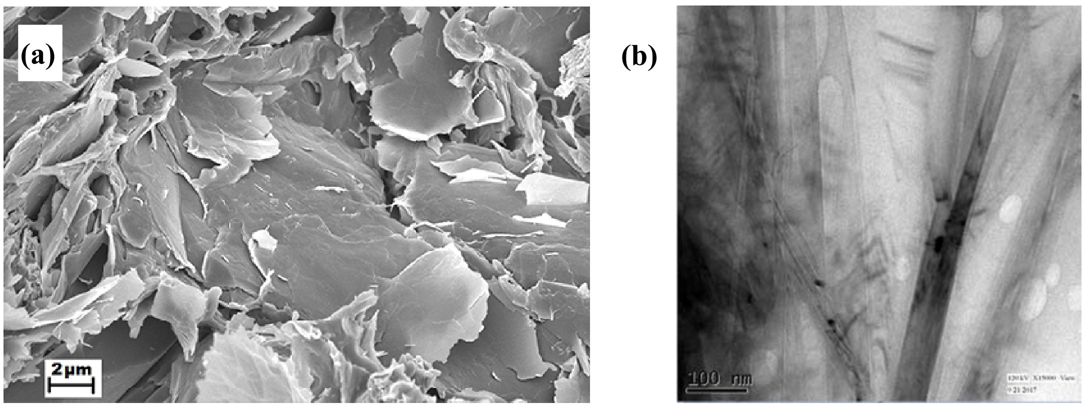

Figure 2. (a) SEM image of fractured surface of PVA-20 wt. % MLG (b) TEM image of PVA/MLG composite

Electrical conductivity and EMI SE increases with increase in graphene content as shown in Fig. 3(a). A comparatively good shielding effectiveness of ~22dB was obtained with PVA – 20 wt.% MLG composites. As shown in Fig. 3(b), the major contribution to total shielding effectiveness comes from absorption. Contribution of reflection is comparatively less at lower filler content because of the low electrical conductivity.

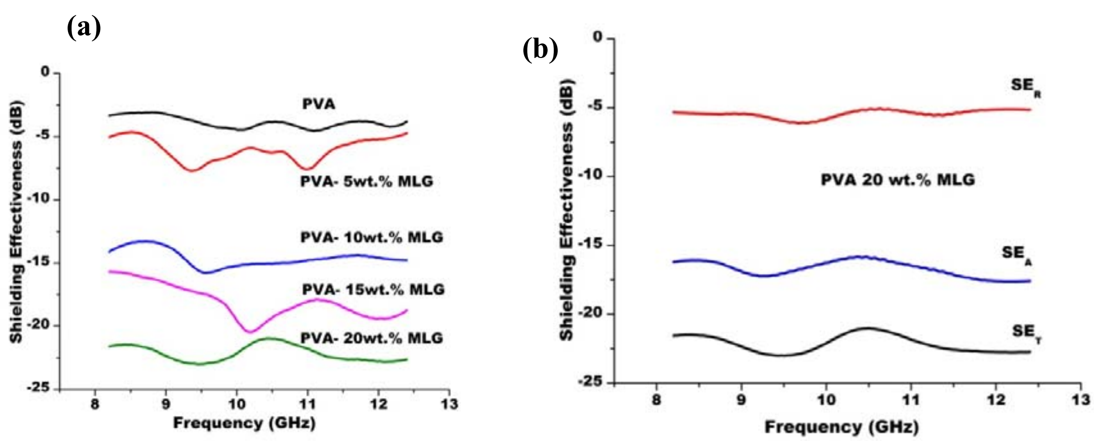

Figure 3. (a) EMI SE of PVA/MLG composites in X band frequency (b) Contribution of reflection and absorption to the total EMI SE of PVA-20 wt.% MLG composite

Thermal stability of the composites increases with increase in graphene filler content. As shown in Fig. 4, There is no considerable impact on thermal stability with low filler percentages. But with higher filler percentages (15 and 20 wt.%), there is a significant improvement in the thermal stability of the composite.

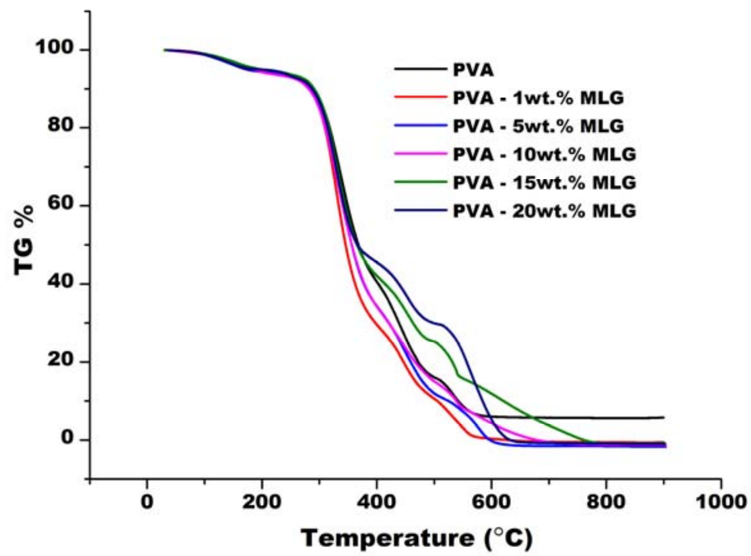

Figure 4. Thermal stability of PVA/MLG composite from TGA

Changes in the viscoelastic nature of the composites with varying filler content are clearly evident from the storage modulus curves and tan delta peaks obtained from DMA analysis. Effect of MLG particles on the sliding movement of polymer chains contribute to these changes in the viscoelasticity.

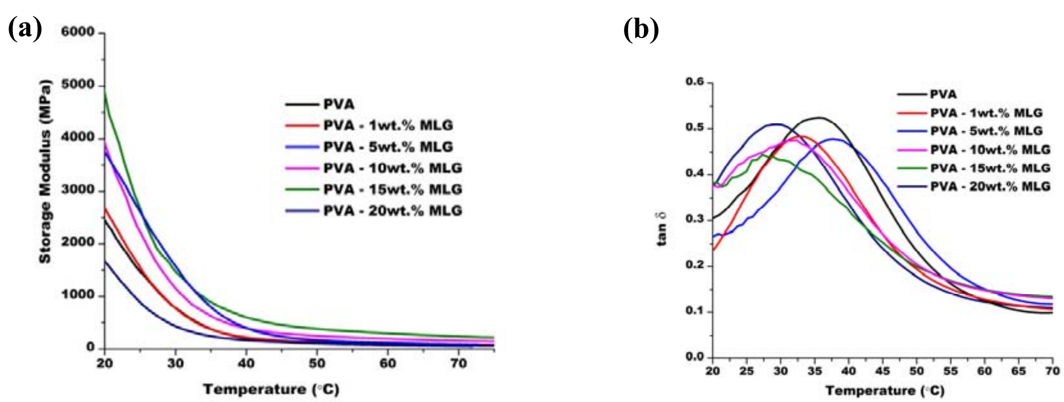

Figure 5. (a) Storage modulus of PVA/MLG composites from DMA (b) tan delta curves for PVA/MLG composites from DMA

There is a significant improvement in the Youngs modulus of the composites with increase in filler content. With 20 wt.% MLG content, the composites have approximately 200% increase in Youngs modulus value when compared to that of the base polymer. Tensile strength remains almost same for composites with different filler contents. Tan delta peaks broaden with increase in filler content. Peak position further depends on whether the added filler content is aiding or restricting the sliding of polymer chains.

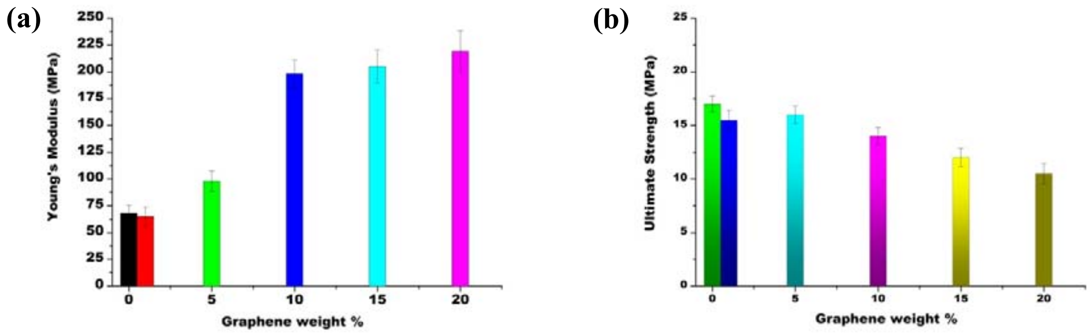

Figure 6. (a) Youngs modulus of PVA/MLG composites from tensile test (b) Ultimate tensile strength of PVA/MLG composites

4. Conclusions

PVA/MLG composites with 15 to 20 wt.% MLG content have good EMI shielding effectiveness. Mechanical strength and thermal stability of these composites are also favourable for their use in EMI shielding solutions. Tailor made EMI shielding solutions can be prepared by controlling the number of layers and the filler content. The relative contribution of absorption and reflection also can be designed as per requirement with the help of this additive manufacturing technique.

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