

Preparation and Characterization of RGO incorporated Polyvinyl Butyral Nanocomposite films

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ABSTRACT

The effect of incorporation of Reduced Graphene Oxide nanoparticles (RGONPs) on morphological, spectroscopic and thermal properties of Polyvinyl butyral (PVB) composite films was carried out using XRD, SEM, FTIR and DSC techniques. The pure PVB and RGO nanoparticles reinforced composite films were fabricated using solution casting method. A small loading with RGO nanoparticles resulted in prominent modifications of structural, spectroscopic and thermal properties of PVB. X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR) techniques were used to analyse the chemical structure and crystalline phase of the composites respectively. Surface morphology was studied using Scanning Electron Microscope (SEM). SEM studies show that the increase in roughness of the surface of the composite films and uniform dispersion of nanofillers in the polymer matrix. Differential scanning calorimetric (DSC) analysis was performed (from 37 °C to 250 °C) and to obtain glass transition temperature (T_g) and melting temperature (T_m) of the PVB Nanocomposite films. The glass transition temperature of the composite films was found to decrease with the increase of RGONPs weight percentage.

KEYWORDS: Polyvinyl Butyral, RGONPs, Nanocomposite, Crystallinity and Glass transition temperature.

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I. INTRODUCTION: -

The development of innovative polymeric composite materials has been a huge interest in the past decades, in particular, reduced graphene oxide incorporated polymer matrix Nanocomposite materials have been extensively studied and adopted for many engineering applications [1-5]. Studies on spectroscopic and thermal properties of these polymer Nanocomposite materials have been attracted much attention because of their applications in electronic and optical devices like electrochromic display devices, supercapacitors, fuel cells, gas sensors, solid-state batteries and acoustic properties [6-9].

Graphene is composed of a single layer of carbon atoms arranged hexagonally in a 2-D sheet of a crystal lattice. Two-dimensional graphene sheets are known as the strongest materials developed so far. Because of its very low density and good mechanical properties, it has often been used as reinforcement material in polymer Nanocomposites. Other important factors that make graphemes so special are small C-C bond length, very low band gaps, high electrical conductivity, thermal conductivity [1-5] etc. All these factors working together make Graphene a special material and create its demand in various fields like composite materials, bioengineering, nanotechnology, energy technology and so on. Due to high thermal and electrical conductivity as well as high tensile strength and modulus [2], it has also been used for many applications.

Nanocomposites made with reduced graphene oxide (RGO) are applicable in various fields, for example, in microwave absorbers, belts, hoses, flooring, aerospace, inner tubes, sensors, and dampers. Now, they are trying to apply it in solar cells, fuel cells, conductive inks, gaskets, artificial muscles, and electronics on a larger manufacturing scale [3]. One of the polymer Nanocomposites that have been produced is based on poly(vinyl butyral) (PVB) with the addition of RGO to improve the spectroscopic and thermal properties of the PVB material. This paper focuses on the studies of polyvinyl butyral (PVB) nanocomposites modified via the incorporation of reduced graphene oxide. By modifying the polymeric matrix with even a small amount of graphene, we can obtain PVB composite films with unique spectroscopic and thermal properties.

II. EXPERIMENTAL SECTION: -

Materials: -

Polyvinyl butyral (molar mass 300.395g/mol, melting point 90 to 120°C) powder purchased from Rolex chemical industries, Bengaluru, India. RGO nanoparticles (Average diameter 20 nm, purity > 99%, Number of layers 3-6) purchased from Shilpent Technologies Pvt. Ltd, Nagpur, India. High-quality PTFE 60mm Petri dishes purchased from Canfort Laboratory Co.Ltd. USA. Chloroform was purchased from the Molychem laboratory, Mumbai, India.

Fabrication of PVB-RGO Nanocomposite films: -

Pure PVB film: A simple method of solution casting was used in the fabrication of PVB film. Polyvinyl butyral 3g was dissolved in chloroform (30ml) and stirred using a magnetic stirrer with 600rpm at room temperature for 48h. The homogenous viscous solution was transferred into Teflon Petri dishes. The Petri dishes were left to dry at room temperature (27°C) and allowed to dry slowly over 30 days to obtain ~ 0.33 mm thick PVB films [11]. The prepared films were peeled off from the dishes and cut into the required dimensions for further characterization.



Figure-1 Fabrication process of PVB-RGO composite films

PVB-RGO composite films: Using the above process obtained PVB-RGO Nanocomposite films. The different weight percentages of nanoparticles were added to chloroform (30ml) and magnetically stirred vigorously for 2 hours at room temperature. The mixture was mixed with the PVB solution and magnetically stirred for 48 hours. The solution of PVB with RGO dispersed mixture is transferred into Teflon Petri dishes, air bubbles were removed by blowing air and shaking. The Petri dishes were left to dry for 30 days and the solvent is allowed to evaporate in the atmosphere at room temperature [14]. This procedure was repeated to make 1 Wt.% and 2 Wt.% composite films. The films were about 0.34 mm in average thickness. The same quantity of total materials and same Teflon Petri dishes were used to control the thickness of the prepared films. The dried films were peeled off from the Petri dish and used for further analysis. The data are given in Table-I indicate the wt.% of RGO nanoparticles in the PVB Nanocomposite films.

Table-I Compositions

S.No.	Sample	Composition	Contents of PVB (gm)	Contents of X Wt.%	Contents of RGO (gm)
1	Sample-1 (Matrix)	PVB	3.0	0	0
2	Sample-2	PVB+XWt.%RGO	3.0	1.0	0.03
3	Sample-3	PVB+XWt.%RGO	3.0	2.0	0.06

CHARACTERIZATION: -

Crystallographic, spectroscopic and thermal characterization of different film samples was performed in the analytical lab at room temperature. The morphology induced crystal structures were studied by using an X-ray diffractometer (SHIMADZU XRD-7000) in the scattering range of 2θ of 10-80°. The interplanar distance (d) was determined by applying Bragg's formula ($2d\sin\theta=n\lambda$), where θ , n and λ are Bragg's angle, order of spectrum and wavelength (0.15406nm) of the target ($\text{CuK}\alpha$) material used, respectively. The particle size (D) in composite films was determined by using Debye Scherrer formula as $t = 0.9\lambda/\beta\cos\theta$, where β is the half peak width of the selected peak [6]. The surface morphological images were obtained using FEI Quanta-250 SEM coupled with energy-dispersive X-ray detectors at 10 kV. A SHIMADZU (FTIR -8400S) spectrometer was used to scan FTIR spectra of the prepared films.

DSC experiments were performed on the films using SHIMADZU DSC-60 calorimeter with the following thermal protocol: The cooling/heating rate was always $10^{\circ}\text{C}/\text{min}$. The sample amount used for DSC was ~ 2.214 mg. Before the DSC measurements, the samples were carefully dried at room temperature for 30 days and afterwards kept under a nitrogen atmosphere. The glass transition temperature and melting point of the films was determined using thermograms.

III. RESULTS AND DISCUSSION

XRD analysis

To investigate the influence of RGO nanoparticles on polymer structure, X-ray diffraction studies were performed for pure PVB and PVB-RGO Nanocomposite films. Figure-2 shows the typical X-Ray diffraction patterns for pure PVB and composite films with 1.0 and 2.0 wt.% samples respectively. A major broad and intense diffraction peak of pure PVB is located at $2\theta=19.29^{\circ}$ with an interplanar distance of 0.45 nm. In the XRD pattern of pure PVB, there is no crystalline peak which reveals PVB as completely amorphous in nature. After RGO nanoparticles were dispersed into the PVB matrix the diffraction peaks of resulted composite films shifted to 19.46° and 19.87° respectively. A small and sharp RGO peak appears in the XRD pattern of composite films at $2\theta=26.62^{\circ}$ and 26.22° respectively [7, 13]. The pure PVB and complexed films showed other broad and low-intensity crystalline peaks at a 2θ position between 41° - 42° . The location of peaks in all the prepared composite films is similar, showing the good dispersion of RGO and homogenized in the PVB [11]. This is evident for the successful formation of RGO nanoparticles loaded composite films with slightly modified structures.

There are no changes with the crystal structure after RGO nanoparticles are mixed with the PVB matrix, due to a large number of hydroxyl groups present in its backbone [8]. The interaction between PVB chains and RGO nanoparticles decrease the intermolecular interaction of PVB chains, due to this interaction the degree of crystallinity of PVB decreases with RGO content. The average value of the grain size (D) of composite films was calculated around 2.02nm using the Debye Scherrer equation [13]. It could also be observed from the XRD patterns there is a relative decrease in the intensity with the increase of RGO concentration of the peak. The relative intensity of the peaks varied with the weight percentage of nanoparticles and dispersion in the samples, it indicates the change of crystallinity of the composite films [12]. As shown in figure-II, it may be observed that the width of the XRD peaks of the films was expanded with the increase of nanoparticles quantity [14]. This may be due to the change of the amorphous nature of the PVB with the addition of RGO nanoparticles.

FTIR analysis: -

The FTIR spectra of pure PVB and PVB-RGO composite films are given in Figure-I and their corresponding peak assignments are listed in Table-II. A typical -O-H stretching band of the PVB functional group was observed at 3431 cm^{-1} in pure PVB and 3450 cm^{-1} in composite films which are strong broader peaks deviating from its normal value $\sim 3600\text{ cm}^{-1}$ to show the presence of intermolecular hydrogen bonding. However, for PVB+2.0 wt.% RGO a decrease in intensity of this band, characterizing that part of the hydroxyl groups of the PVA was condensed into acetyl and butyral groups [8]. A -C-H asymmetric stretching vibrations of CH_2 showed an absorption band at 2924 cm^{-1} in pure PVB and is slightly shifted in the 1.0 and 2.0 wt. % composite films of PVB [10]. The changes in peak troughs were observed in the Nanocomposite spectra, demonstrating the effect of RGO incorporation with PVB bonding. The observed bands at 1631 cm^{-1} correspond

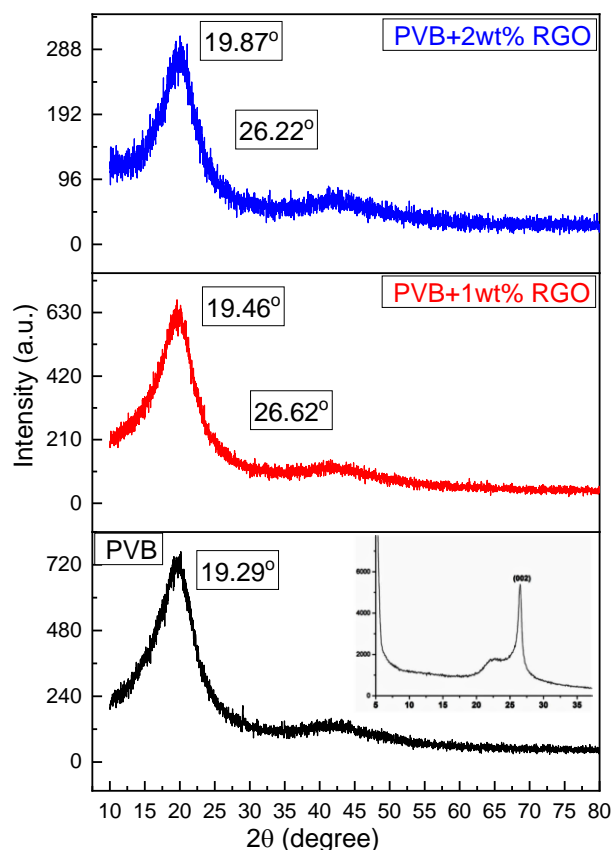


Figure-2 XRD fingerprints of pure PVB and PVB-RGO composite films

to the acetyl C=O group and can be explained based on intra/ intermolecular hydrogen bonding with the adjacent O-H group [14]. The C-H vibration bands were observed at 1380 cm⁻¹. A sharp band at 1059 cm⁻¹ corresponds to the C-O stretching of the acetyl group present in the PVB backbone and it is shifted to 1052 cm⁻¹ in composite films. Compared with PVB, the intensity of composites with the range of 1105–980 cm⁻¹ has weakened owing to the interaction between PVB and RGO nanoparticles [13]. These results demonstrated that the PVB and RGO nanoparticles had been compounded together excellently because hydrogen bonding was generated between PVB and RGO nanoparticles in composite films.

The changes in the FTIR spectra showing that there is an increase in hydrogen bonding between polymer and the nanoparticles at a higher weight percentage. Therefore, the addition of RGO nanoparticles enhances the unsaturated conjugated double bonds C=C within the polymer matrix. These observed modifications in the FTIR spectra suggest that the addition forms clustering of RGO nanoparticles. This affects the chemical structure of the composite films. A lot of oxygen-containing functional groups like hydroxyl (3431 and 3450 cm⁻¹), epoxy group (1380 cm⁻¹) and ether bond (1059 and 1052 cm⁻¹), etc. exist in the molecular structure of RGO and PVB excellent reactivity [4,7]. All of the above evidence interpreted the successful cross-linking and preparation of PVB-RGO Nanocomposite films.

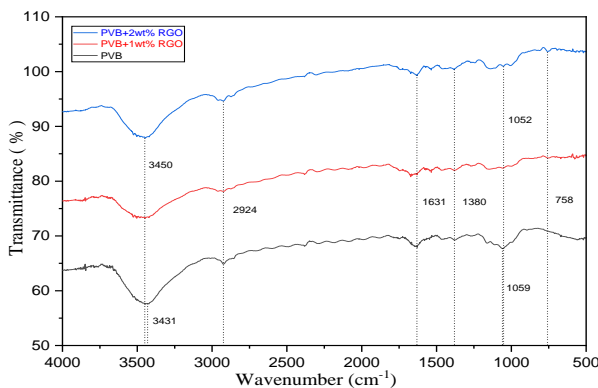


Figure-3 FTIR signatures of pure PVB and PVB-RGO composite films

Table-II FTIR Peak assignments of pure PVB and PVB-RGO composite films

S.NO	Peak position (cm ⁻¹)		Group	Compound Class	Appearance	Comments
	Pure PVB	Composite Films				
1	3431	3450	O-H Stretching	Alcohol	Strong/Broad	Intermolecular bonded
2	2924	2924	CH ₂ Stretching	Alkane	Medium	Asymmetric stretching
3	1631	1631	C=O Stretching	Acetyl	Medium	scissor bending vibrations of -CH ₃
4	1380	1380	C-H Bending	Alkynes	Medium	CH ₃ - Deformation
5	1059	1052	C-O Stretching	Carbonyl	Strong	The out of plane bending H bond

SEM images of the pure and composite films: -

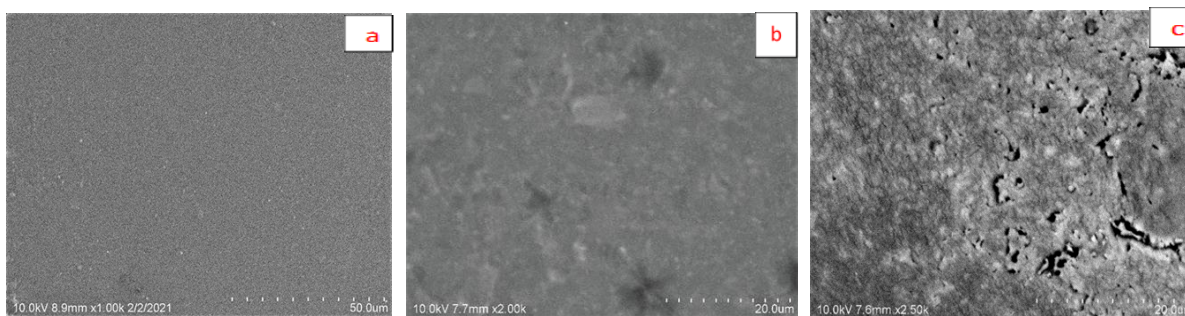


Figure-4 SEM micrographs of (a) pure PVB (b) PVB+1Wt.% RGO (c) PVB+2Wt.% composite films

Figure-4 shows the SEM micrographs for pure PVB and composite films. It is clear from the figures that the morphology of these films is a uniform type, with different degrees of roughness [17]. The SEM images of pure PVB films are showing smooth surface morphology. So, the semi crystallinity of PVB is likely to be submicroscopic. It is observed that from SEM micrographs the low content of RGO nanoparticles showed an

excellent and uniformly distributed in the PVB matrix. It causes flexibility and strength of the composites relative to the pure polymer [13]. Figures 4(b) and 4(c) show the presence and random dispersion of 1wt.% and 2wt.% of RGO nanoparticles in the PVB matrix.

There were no cracks found in the films, but a few small black patches were observed on the top surface of the films. It can be seen that the surface morphology of composite films shows RGO particles tended to aggregate together and formed thicker sheets with the growth of RGO fillers in the composite films. It is also observed that these particle cluster size found in the form of flakes increases in the composite films with RGO concentration. But as a whole, the compatibility of the PVB polymer matrix with RGO nanoparticles is still uniform and homogeneous. Therefore, morphological studies explore phase isolation. Further, when we observe normally, the colour of the samples changed from clearly transparent (pure PVB) to semi-transparent. These results indicated that RGO can be a good candidate to assist the dispersion of other nanoparticles.

DSC Analysis: -

DSC is an analytical tool that helps to understand the thermal behaviour of polymer nanocomposites. It helps in finding the glass transition temperature (T_g) and melting point (T_m) of polymers and their composites. PVB is amorphous and displays an easily observable glass transition. The effect of the RGO nanoparticles content on the glass transition temperature of PVB has been studied in detail by varying the Wt.% of RGO nanoparticles and the observations listed in table-III. It was found that the glass transition temperature decreased with increasing the weight percentage of nanoparticles. The T_g of pure PVB is 64.7°C [8] and 1.0 wt.% RGO nanoparticles loaded films are nearly 53.3°C , whereas that of PVB with 2.0 wt.% is 47.3°C . The decrease in T_g indicates weak hydrogen bonding between RGO and PVB matrix [18]. The degree of cross-links and intermolecular forces decreased with RGO nanoparticles content decrease the glass transition temperature. These results showed that the addition of RGO nanoparticles reduces the thermal stability of PVB. The recent investigations have shown negligible changes in T_g in polymeric nanocomposites, regardless of the polymer-surface interactions, which have been explained by considering that the DSC glass transition is sensitive only to the bulk of the sample and not to the interface [17].

The following factors may increase the glass transition temperature of composite films in this study

1. The presence of a plasticizer in a polymer increases the mobility of the polymer chains [15].
2. A significant departure from group additivity due to the increase in the content of hydroxyl groups gives rise to an increase in hydrogen bonding.
3. The addition of the nanofillers may affect the crystallinity in various ways. Usually, the most important effect is the "Nucleation effect".
4. The cross-linking introduces restriction and stiffness in the polymer.

In addition, one should notice that for composite films, the height of the specific heat capacity step at T_g was significantly increased, compared to that of the pure PVB sample. This increase is indicating that the specific heat of the composite films diminishing in the glassy state is comparable to that of pure PVB. The previous studies reported almost the same results on the other nanocomposites characterized by relatively low loadings [19,20]. It could also be observed that on adding just 2.0wt.% RGO nanoparticles in the PVB, melting point was increased to 324.3°C (from 225.2°C of pure PVB).

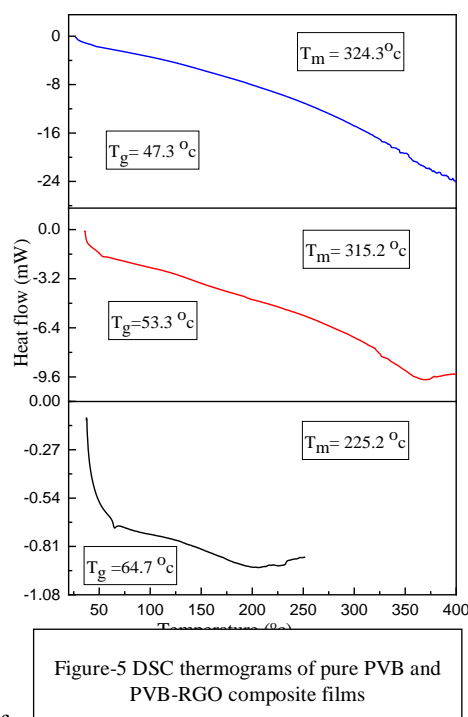


Figure-5 DSC thermograms of pure PVB and PVB-RGO composite films

Table-III Glass transition temperature and the melting point of pure PVB and PVB-RGO composite films

S.NO	Sample	X wt. %	T_g ($^{\circ}C$)	T_m ($^{\circ}C$)
1	PVB	0	64.7	225.2
2	PVB+X wt. % RGO	1.0	53.3	315.2
3	PVB+X wt. % RGO	2.0	47.3	324.3

IV. CONCLUSIONS

The polyvinyl butyral (PVB) composite films were successfully synthesised using the solution casting method. The detailed study about the influence of RGO nanoparticles wt.% on chemical structure and thermal stability of pure PVB and nanocomposites have been experimentally investigated and discussed. From the results, the following conclusions are summarized.

The addition of RGO nanoparticles attributed (XRD Spectrum) to a decrease in the degree of crystallinity and an increase in the amorphousness. X-ray diffraction analysis indicates that PVB-RGO nanocomposites are amorphous and the long-chain structure macromolecule still exists. The modifications in the FTIR spectra suggest that the addition of nanoparticles forms the clustering of RGO. This affects the chemical structure of the composite films. The thermal analysis confirms that an increase in the content of RGO nanoparticles reinforcement in the PVB matrix decreases glass transition temperature and increases melting point. The prepared composite films preserve remarkable properties of good thermal stability. The T_g and T_m values of the composite films showed that they are suitable for use in laminated safety glasses at low-temperature applications.

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