

Spectroscopic Properties of MWCNTS loaded PVB composite films

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Abstract

The pure Polyvinyl butyral (PVB) and Multiwall carbon nanotubes (MWCNTS) loaded PVB composite films were fabricated by using a simple method of solution casting. The effect of MWCNTS on spectroscopic properties of PVB composite films was carried out using XRD and UV-Visible techniques. The XRD patterns showed that MWCNTS are dispersed excellently in the PVB matrix. The UV-Visible studies were performed in the wavelength range of 190–1100 nm and the absorption edge, direct bandgap, indirect bandgap and Urbach energy values were evaluated. The loading with 2.0 wt.% of MWCNTS in PVB resulted in significant changes in direct bandgap from 4.62 eV to 1.72 eV, indirect bandgap from 4.90 eV to 2.49 eV and Urbach energy from 0.77 eV to 1.80 eV. The results showed that the spectroscopic properties of PVB nanocomposite films are modified considerably with small loadings of MWCNTS due to cross-linking formation between the nanotubes and polymer chains.

Keywords: PVB nanocomposite films, Multiwall carbon nanotubes, X-Ray diffraction, UV-Visible spectroscopy, Bandgap energy, Urbach energy.

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I. Introduction

Polymer nanocomposites consist a polymer or copolymer matrices reinforced with nano-scale fillers. This new class of composite materials has shown improved mechanical and physical properties and is of major scientific and technological interest. The properties of resultant nanocomposites may be remarkably changed at lower loadings compared to micro composites due to the larger specific surface area [1]. The polymer nanocomposites have a diversity of applications in various fields such as optical integrated circuits, automobile, energy storage and saving, building and military industries and medical devices, etc. [2]. They are scientifically and industrially very attractive because lower loadings of nanoparticle easily processing and reduce component weight.

The materials used for environmentally friendly area priority for every industry. Polyvinyl butyral (PVB) is an environment-friendly (Non-toxic and odourless) thermoplastic polymer that is widely used as a functional material in various fields for the fabrication of organic/inorganic hybrid composites [1,4]. It is one of the high priority materials in the industry and fulfils many essential aspects, because of good elasticity and water resistance, adhesion to various surfaces, sharp optical clarity, high compatibility with other polymers and very good processing options [1]. PVB is also used as the interlayer of laminated glass in automotive windshields, optical windows for equipment, and emergency glass for buildings due to its excellent properties such as high radiation resistance. The main goal is to produce high-performance polymer nanocomposites, which mainly depends on interparticle forces, polymer–nanoparticle interactions and nanoparticle shape, as well as on the preparation procedure [3,5]. Polymer nanocomposite films can be fabricated by various methods. Solution casting is one of the best methods when the solvent used is less toxic. This is the easiest method to obtain fine nanocomposite films. In this study, we aimed to improve the spectroscopic properties of PVB films by the addition of low wt.% Multiwall carbon nanotubes (MWCNTS).

II. Experimental Section

Materials

Poly (vinyl butyral) (molar mass 300.395 g/mol, melting point 90 to 120°C) powder purchased from Rolex chemical industries, Bengaluru. MWCNTS (Average diameter 10 to 15 nm, purity > 99%) purchased from Ad-Nano Technologies Pvt.Ltd, Shimoga. High-quality PTFE 60mm Petri dishes purchased from Canfort Laboratory Co.Ltd. USA. Chloroform was purchased from Molychem laboratory, Mumbai.

Preparation of PVB-MWCNTS composite films

The PVB-MWCNTS composite films were fabricated using the solution casting technique. Polyvinyl butyral 3g was dissolved in chloroform (30ml) and stirred using a magnetic stirrer at 600rpm for 48 h. at room temperature. The homogeneous viscous solution was transferred into Teflon Petri dishes. The Petri dishes were left for drying and allowed to dry slowly over 30 days to obtain ~0.33 mm thick PVB films. The prepared films were peeled off and cut into suitable dimensions for further analysis. The composite films with different weight percentages (wt.%) of nanotubes, the solution of MWCNTS dispersed in chloroform were taken as 1.0wt.% (0.03g) and 2.0 wt.%(0.06g) mixed in aqueous solution (30 ml) of PVB separately, after using the above process obtained ~0.34 mm thick PVB-MWCNTS nanocomposite films.

III. Characterization Techniques

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 (CuK α) material used, respectively). The spectrometer (UV-1800 series) in the 190–1100 nm range was used to get the absorption data.

IV. Results And Discussion

X-ray diffraction

The typical X-Ray diffraction patterns for pure PVB and PVB-MWCNTS composite films with 1.0 and 2.0wt.% samples were observed and shown in Fig-1. The XRD pattern of pure PVB exhibited a large specific diffraction peak observed at scattering angle ($19^\circ < 2\theta < 20^\circ$) represents the "d" spacing value of 0.45 nm, which is a typical result for high molecular-weight amorphous polymer [6]. This diagram shows a small and sharp peak displayed at $2\theta = 25.92^\circ$ and 25.74° for composite films respectively, this corresponds to peak diffraction associated with MWCNTS. The pure PVB and complexed films showed another broad and low-intensity crystalline peak at a 2θ position around $\sim 42^\circ$. After nanotubes were dispersed into the PVB matrix, the XRD of the resulted nanocomposites only showed the PVB diffraction peak. This demonstrates that nanotubes were homogenized in the PVB. There are no changes found in the structure of the PVB matrix after MWCNTS being mixed, due to the plenty of hydroxyl groups present in its backbone [5]. This is evident, for the purity and successful formation of MWCNTS loaded composite films.

It can be seen from Fig-1 that the broad peak of the PVB polymer becomes more broadened with increasing nanotubes concentration. This is evidence for the increase of the amorphous phase in composite films in comparison with the pure PVB film [6].

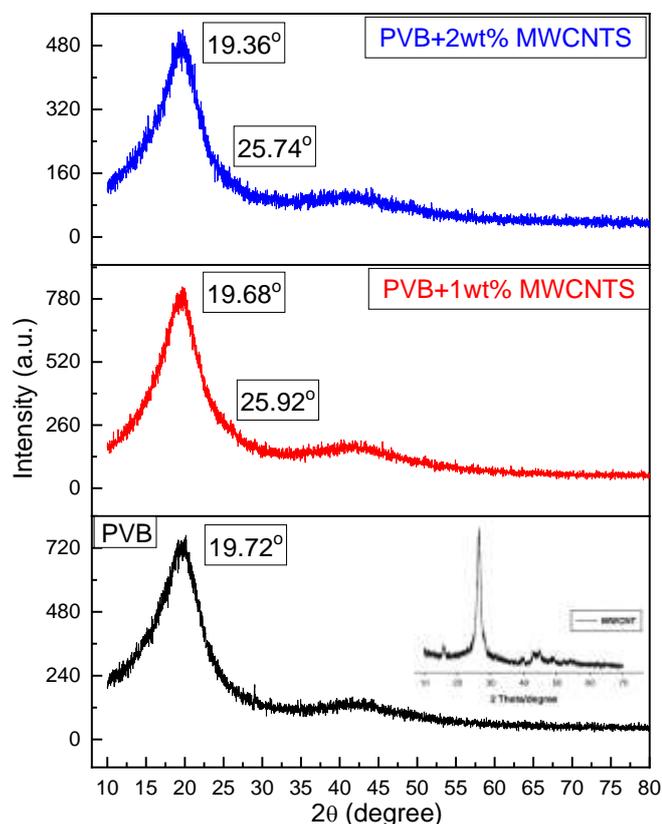


Fig.1 XRD fingerprints of pure PVB and PVB-MWCNTS composite films

Optical absorption

An optical absorption spectrum is an analytical tool used to determine the optical band constants, analyze complex mixtures, understanding the band structure and electronic properties of pure and composite polymers. The pure PVB film showed low absorption in the visible light range, while the composite films exhibited strong absorption starting from the visible to UV light range displayed in Fig-2. Also, as wavelength decreases, the absorption of the composite films increases remarkably. It can be seen that after nanotubes disperse homogeneously to PVB polymer, its characteristics of absorbing ultraviolet is brought into full play.

Besides, in 400 nm ~ 800 nm visible light, composite films have demonstrated higher transparency [7]. Therefore, the prepared composite films have the fine ultraviolet glossy shield characteristic; moreover, its transparency is fairly good in the visible light area. From the above results, it is clear that the prepared nanocomposite films had been absorbed a broad range of light.

The absorption edge of composite films was shifted from 258 nm (for pure PVB) to 543 nm. The absorption edge of the composite films moves towards longer wavelengths with the concentration of MWCNTS, which shows the amorphous nature of PVB and the formation of a new structure for the composite films. The shift in wavelength of the films indicated hydrogen bonding between nanotubes and -OH groups of PVB. The absorption spectra of composite films with 1wt.% showing absorption peaks at 295nm and 306nm, while for 2wt.% in the range of 407-430nm. The absorption bands are assigned to $n-\pi^*$ transition and $\pi-\pi^*$ transition, respectively [8]. These electronic transitions indicate the presence of unsaturated bonds, C=O or C=C mainly in the tail-head of pure PVB polymer. Also, the acetyl C=O and C-O-C cyclic electrons are present in the polymer backbone and all the functional groups involved in intramolecular and intermolecular hydrogen bonding [1].

Direct bandgap and indirect bandgap energy

The UV-Visible spectrum can be used to calculate the bandgaps of composite films using Tauc's equation [9].

$$\alpha = \frac{D}{h\nu} (h\nu - E_g)^n \text{-----(1)}$$
 Where α is the absorption coefficient, $h\nu$ is the energy of incident photons, D is the band tail constant, E_g is optical band gap energy and n is an exponent which is equal to $\frac{1}{2}$ for allowed direct bandgap transition and 2 for

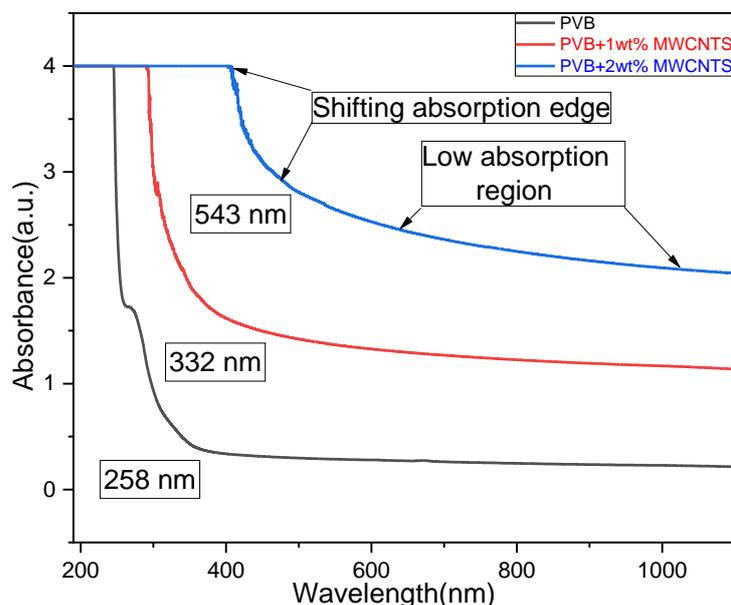


Fig. 2 Absorbance as a function of wavelength for pure PVB and PVB-MWCNTS composite films

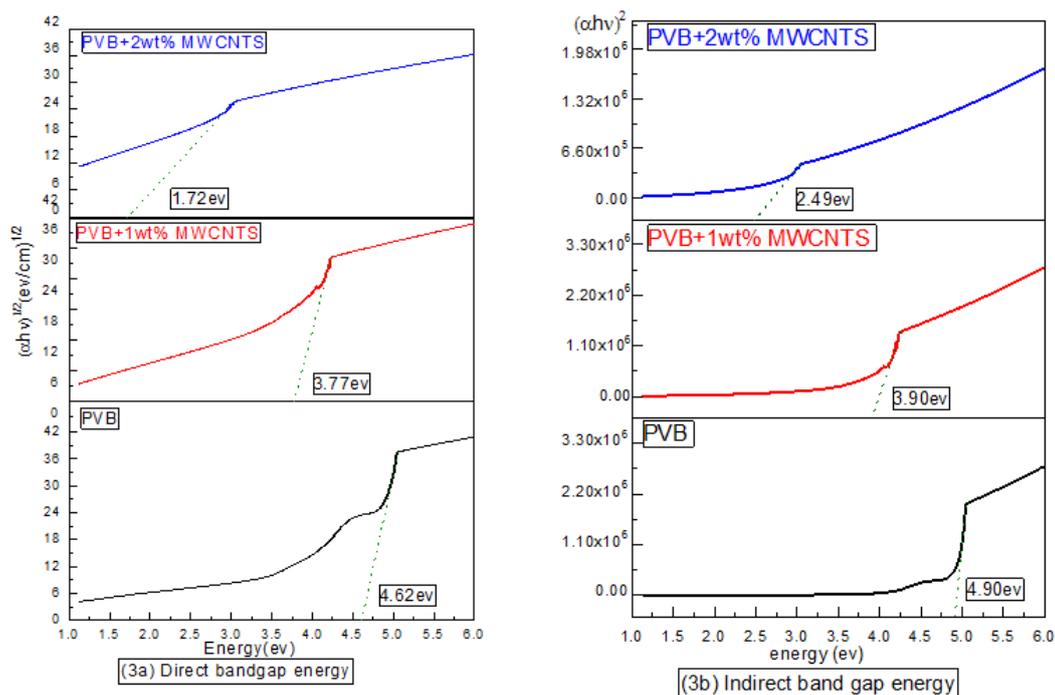


Fig.3 Bandgap energy plots for pure PVB and PVB-MWCNTS composite films

allowed indirect bandgap transition. A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ was drawn, and direct bandgap energy was calculated from the plot as shown in Fig-3(a). It could be observed that on adding just 2.0wt.% MWCNTS in the PVB, direct bandgap value was decreased from 4.62 eV (of pure PVB) to 1.72eV.

The indirect bandgap energy was estimated using $(\alpha h\nu)^2$ against $h\nu$ plot and is presented in Fig-3(b). The indirect bandgap energy reduced to 2.49eV from 4.90 eV (of pure PVB) and the bandgap energy values are listed in table-1.

Table-1 Absorption edge, Direct, Indirect bandgap and Urbach energy values of pure PVB and PVB-MWCNTS composite films:

S.NO	Composite	Absorption edge(eV)	Direct bandgap(eV)	Indirect bandgap(eV)	Urbach energy(eV)
1	Pure PVB	4.80	4.62	4.90	0.77
2	PVB+1.0wt.% MWCNTS	3.69	3.77	3.90	1.41
3	PVB+2.0wt.% MWCNTS	2.18	1.72	2.49	1.80

It could also be observed that on adding just a step up 1.0wt.% of MWCNTS in the PVB direct bandgap and indirect band gaps are shifted to lower values. The complex formation via interaction between nanotubes with the hydroxyl groups of the polymer modified the energy states of pure PVB [7]. The inclusion of MWCNTS into the polymer matrix creates additional localized defect states in the optical bandgap which can effectively influence the valence and conduction band edges. It could be the main reason for triggering a decreased bandgap in composite films.

Urbach energy

The bandtail energy of amorphous and semi-crystalline materials can be calculated by using Urbach's relation. It is influenced by the following factors: impurity level in the middle of optical bandgap, structure disorder, inhomogeneous strain and exact absorption. Urbach energy indicates the disorder of phonon states due to impurity level in the middle of the bandgap. The Urbach energy (E_u) has been evaluated using the relation given below [9].

$$\log \alpha = \log c + \frac{h\nu}{E_u} \text{-----(2)}$$

Where C is a constant. The band tail energy or Urbach energy (E_u) can be obtained from the slope of the straight line of plotting $\ln(\alpha)$ against the incident photon energy ($h\nu$). On loading with 2.0 wt.% MWCNTS contents, the E_u value decreased to 0.77 eV from 1.80 eV (of pure PVB) and E_u values are recorded in table-1. The values of Urbach energy increased with increasing the nanotubes concentration showing low crystallinity and disorder of phonon states in the polymer nanocomposites. As can be seen from the results, the variation of Urbach energy is inverse to the bandgap.

V. Conclusions

The XRD pattern reveals the increase in the amorphous nature of the film with the addition of MWCNTS. The absorption spectra were altered with increasing MWCNTS wt.%, where the absorption edge shifted to smaller photon energy sides up on the nanotube's inclusion to the PVB polymer. The UV-visible spectroscopy demonstrated that the obtained thin films show radiation dependent absorption properties. So, these composite films are suggested for excellent UV absorbers and are useful for the fabrication of Electrochemical cells. The bandgap values of the composite films are suitable for use in Solar cell fabrication, Optoelectronics and high-frequency applications.

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