

Effect of MWCNTS on Spectroscopic and Thermal properties of PVB Nanocomposite films

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Research Article

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Abstract

In this paper, we demonstrate a simple fabrication process for polyvinyl butyral (PVB) based nanocomposite films reinforced with MWCNTS. The solution casting method was used to prepare pure PVB and composite films. XRD, FTIR, SEM and DSC methods were used to study the effect of multiwalled carbon nanotubes (MWCNTS) on the spectroscopic and thermal properties of polyvinyl butyral (PVB) composite films. The structural, spectroscopic and thermal properties of PVB based nanocomposite films were significantly altered after being reinforced with the MWCNTS. The chemical structure and crystalline phase of the composites were studied using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), respectively. The surface morphology (SEM) was characterized using scanning electron microscopy. The XRD patterns and SEM images show the MWCNTS are well dispersed in the PVB matrix. The glass transition temperature (T_g) and melting temperature (T_m) of PVB nanocomposite films were determined using DSC analysis (from 37 ° C to 250 ° C). With increasing MWCNTS weight percentage, the glass transition temperature and the melting point of composite films have been found to enhance.

1. Introduction

Polymer nanocomposites are made up of polymer or copolymer matrices that have nano-scale fillers added to them. This novel family of composite materials has been shown to effectively increase mechanical and physical properties, and it is of significant scientific and technological importance. Because of the increased specific surface area in these systems, the (mechanical, electrical, thermal, rheological, magnetic, electrochemical, and optical) characteristics of the resulting nanocomposites can be dramatically altered at lower loadings compared to micro composites [1]. Antistatic materials, supercapacitors, rechargeable batteries, biosensors, chemical sensors, electromagnetic shielding, organic solar cells, optical waveguides, and other fields use both conductive and non-conductive polymeric nanocomposites [2]. Lower loadings make processing easier and component weight lighter, making them more appealing to the industry. Every sector places a premium on using ecologically friendly materials. Polyvinyl butyral, which has good flexibility, adherence to diverse surfaces, better optical clarity, good water resistance, high compatibility with other polymers, and also very good processing possibilities, is becoming a priority material in the industry and meets many important requirements [1]. PVB is a non-toxic, odourless, and environmentally friendly polymer that is widely employed in the production of organic and inorganic composite materials [1, 5]. It is also utilized as an interlayer for laminated glass in coatings, paints, windshields for automobiles, optical windows for equipment, and emergency glass for structures due to its exceptional qualities such as strong radiation resistance and low-temperature impact strength [15]. Simultaneously, 90 per cent of the polyvinyl butyral is generated and available in the form of films for industrial purposes.

PVB's heat resistance is not one of its strongest qualities. This is because PVB has a low glass transition temperature (T_g). It is utilized in laminated safety glasses that must be improved at high temperatures [16]. The thermal characteristics of the PVB interlayer must be enhanced to correct this flaw. The major goal is to create high-performance polymer nanocomposites with excellent dispersion and uniform

distribution of nanoparticles inside the polymer matrix while maintaining the nanoparticles' distinctive features. Nanoparticle aggregation, which is influenced by interparticle forces, polymer–nanoparticle interactions, nanoparticle morphology, and the preparation technique [3, 18], obstructs this. Polymer nanocomposite films can be made in many ways. When the solvent (chloroform, acetone, alcohol, or water) is less harmful, solution casting is one of the best and easiest ways to make good nanocomposite films. This method can spread different numbers of nanoparticles due to the good interaction between the solvent and the polymer. By adding MWCNTS to PVB films, we were able to increase their spectroscopic and thermal properties. Adding a small amount of MWCNTS to pure PVB effectively modified its spectroscopic characteristics, glass transition temperature, and melting point.

2. Experimental Section

2.1 Materials (Table-1)

S. No	Material	Physical Parameters	Material Form/Colour	Supplier	Place
1	PVB	Molar Mass 300.395g/mol, Melting Point 90 to 120°C	Powder/ White	Rolex Chemical Industries	Bengaluru
2	MWCNTS	Length ~ 5µm, Average outer diameter 10-30nm, Purity > 99%, Surface area 110–350 m ² /g	Fluffy, very light powder/ Black	Shilpent	Nagpur
3	Chloroform	Molecular Wt. 119.38 g/mol, minimum Assay (GC) 99.5%	Liquid	Molychem Laboratories	Mumbai
4	Petri dishes	High-Quality PTFE 60mm Diameter	Solid white Dishes	Canfort Laboratory	USA

2.2 Fabrication of PVB-MWCNTS composite films

Pure PVB film: PVB film was made using a straightforward solution casting procedure. 3g polyvinyl butyral was dissolved in 30ml chloroform and stirred for 48 hours at room temperature using a magnetic stirrer at 600rpm. A Teflon Petri dish was used to transfer the uniform viscous fluid. The dish was allowed to cure at room temperature (27°C) for 30 days, resulting in a PVB film with a thickness of 0.33 mm [12]. For further characterization, the created film was withdrawn from the dish and sliced into the desired dimensions.

PVB-MWCNTS composite films: Using the above process obtained PVB-MWCNTS 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 MWCNTS 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 [15]. 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-2 indicate the wt.% of MWCNTS in the PVB nanocomposite films.

Table-2 Compositions

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

3. Characterization Techniques

Crystallographic, spectroscopic, and thermal characterization of pure PVB and composite film samples was performed in the analytical lab at room temperature. An X-ray diffractometer (SHIMADZU XRD-7000) was used to investigate the morphology-induced crystal formations in the scattering range of 2 of 10-80o. Bragg's formula ($2d\sin = n\lambda$) was used to calculate the interplanar distance (d), where d, n, and n are the Bragg's angle, order of spectrum, and wavelength (0.15406nm) of the target (CuK α) material, respectively. The Debye Scherrer formula was used to calculate the average particle size (D) of all composite films using X-ray line broadening analysis.

$$D = 0.9\lambda/\beta\cos\theta$$

Where is λ the X-ray wavelength, is β the value of the selected peak's full width half maximum (FWHM), and θ is Bragg's angle. Surface morphological pictures were obtained at 10 kV using an FEI Quanta-250 SEM with energy-dispersive X-ray detectors. The FTIR spectra of the produced films were scanned using SHIMADZU (FTIR - 8400S) spectrometer.

The films were subjected to DSC studies using a SHIMADZU DSC-60 calorimeter and also the following thermal protocol. The cooling/heating rate was always 10 degrees Celsius per minute. DSC was performed on a sample of mass 2.214 mg. The film samples were thoroughly dried at room temperature for 30 days before being stored in a nitrogen environment for DSC testing. The melting and glass transition temperatures of the films were determined using thermograms.

4. Results And Discussion

4.1 XRD analysis

X-ray diffraction studies were performed on pure PVB and PVB-MWCNTS composite films to study the effect of MWCNTS on polymer structure. Figure-2 illustrates typical X-Ray diffraction patterns for pure PVB and composite films including 1.0 and 2.0 weight percentages of MWCNTS, respectively. The pure PVB has a diffraction peak at $2\theta = 19.72^\circ$ with an interplanar distance of 0.45 nm, which can be attributed to the polymer's amorphous nature. After dispersing MWCNTS into the PVB matrix, the composite film's diffraction peaks shifted to 19.68° and 19.36° , respectively. At the 2θ position of 42° , the pure PVB and complexed films displayed another broad and low-intensity crystalline peak. Peak locations in the obtained composite films are comparable, confirming MWCNTS dispersion and homogenization inside the PVB. Because of the numerous hydroxyl groups present in its backbone, this may be seen in the successful creation of nanoparticle loaded composite films with slightly changed architectures [18]. This is commonly seen in the purity and success of MWCNTS-loaded composite film creation. The particle size (D) of composite films was calculated to be about 12nm on average.

It could also be observed that the XRD patterns show a relative rise in intensity with a 1.0 wt.% increase in nanotubes concentration while a decrease with a 2.0 wt.% increase in the peak because molecules of polymer pack closely together. This could be owing to the amorphous phase of PVB changing with the addition of MWCNTS. The intensity of the peak and the degree of crystallinity were found to be related by Hodge et al. [14]. The XRD peaks width of the prepared films was broadened by stepwise inclusion of nanoparticles quantity after incorporating MWCNTS [21].

4.2 FTIR analysis:

The FTIR spectra of pure PVB and PVB-MWCNTS composite films are given in Fig-3 and their corresponding peak assignments are listed in Table-3. A typical -O-H stretching band of the PVB functional group was observed at 3436 cm^{-1} in pure PVB and 3448 cm^{-1} in composites 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.% MWCNTS a decrease in intensity of this band, characterizing that part of the hydroxyl groups of the PVA was condensed into acetyl and butyral groups [1]. A -C-H asymmetric stretching vibrations of CH_2 showed an absorption band at $2,924\text{ cm}^{-1}$ in pure PVB and is slightly shifted in the 1.0 and 2.0 wt. % composite films of PVB [4]. The changes in peak troughs were observed in the Nanocomposite spectra, demonstrating the effect of MWCNTS incorporation with PVB bonding. The observed bands at 1630 cm^{-1} correspond to the acetyl C = O group and can be explained based on intra/ intermolecular hydrogen bonding with the adjacent O-H group [8]. The C-H vibrational bands were observed at 1383 cm^{-1} . A sharp band at $1,058\text{ cm}^{-1}$ corresponds to the C-O stretching of the acetyl group present in the PVB backbone. Compared with PVB, the intensity of composites with the range of $1105\text{--}980\text{ cm}^{-1}$ has weakened owing to the interaction between PVB and CNTS [7]. These results demonstrated that the PVB and MWCNTS had been compounded together excellently because hydrogen bonding was generated between PVB and MWCNTS in composite films.

Changes in the FTIR spectra show an increase in hydrogen bonding between the polymer and the nanotubes at higher weight percentage levels. Consequently, loading with MWCNTs enhances the unsaturated conjugated C = C double bonds in the polymer matrix. These observed changes in the FTIR spectra suggest that the addition of MWCNTS forms clustering. This affects the chemical structure of the composite films.

Table-3 FTIR peak assignments of pure PVB and PVB-MWCNTS composite films

S.NO	Peak position (cm ⁻¹)		Group	Compound Class	Appearance	Comments
	Pure PVB	Composite Films				
1	3436	3448	O-H Stretching	Alcohol	Strong/Broad	Intermolecular bonded
2	2924	2931	CH ₂ Stretching	Alkane	Medium	CH ₂ Asymmetric stretching
3	1630	1630	C = O Stretching	Acetyl	Medium	scissor bending vibrations of -CH ₃
4	1383	1382	C-H Bending	Alkynes	Medium	CH ₃ - Deformation
5	1058	1057	C-O Stretching	Carbonyl	Strong	The out of plane bending H bond

4.3 Morphological studies: SEM micrographs of pure PVB and composite films are shown in Figure- 4. The morphologies of these films are of the same kind, with varying degrees of roughness, observed in the films [10]. The smooth surface morphology of the pure PVB film may be seen in SEM images. PVB's semi-crystallinity is therefore expected to be microscopic. MWCNTS is equally distributed throughout the PVB matrix, according to SEM micrographs. In comparison to pure polymers, this determines the flexibility and strength of composites [6]. The presence and random dispersion of 1 wt. per cent and 2 wt. per cent, MWCNTs in the PVB matrix are shown in Figures 4(c) and 4(d). There were no cracks on the films, however, there were many small black patches on the upper surface. On the top surface of the membrane, the surface morphology of the composite film displayed aggregates or particle fragmentation. With increasing MWCNTS content in the composite films, this increase in particle cluster size is seen. On the other hand, the compatibility of MWCNTS and PVB polymer matrices stays isotropic and homogeneous. PVB polymer films mixed with different nanoparticles exhibited similar behaviour [11]. As a result, morphological studies look into phase separation. The colour of the films also changed from obviously transparent (pure PVB) to translucent under normal inspection.

4.4 DSC Analysis DSC is an analytical tool that helps to understand the thermal behaviour of polymer nanocomposites. This helps to determine the glass transition temperature (T_g) and melting point (T_m) of

polymers and their composites. PVB is amorphous and exhibits an easily observable transition to the free state. The effect of MWCNTs content on the glass transition temperature of PVB was studied in detail through the observations listed in Table-4 by changing the wt.% of MWCNTs nanoparticles. The T_g of pure PVB is 63.3°C [1], which is almost 64.8°C for films containing 1.0 wt.% MWCNT, whereas it is 84.8°C for PVB containing 2.0 wt.%. It can also be observed that adding only 2.0 wt.% MWCNTS to PVB increases the melting point to 121.6°C (compared to 90.5°C for pure PVB). When the content of MWCNT is 2.0 wt.%, the number of side groups and intermolecular force increase, and the glass transition temperature and melting point increase. These results showed that the addition of MWCNTS improved the thermal properties of PVB. A recent study showed a slight change in T_g in polymer nanocomposites regardless of the interaction of the polymer with the surface. This is explained by the fact that the DSC glass transition is only sensitive to the volume of the sample and not the interface [20].

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

(1). The presence of plasticizers in polymers increases the mobility of polymer chains [9]. (2). A significant departure from group addition due to the increased content of hydroxyl groups increases hydrogen bonding. three. Adding nanofillers can affect crystallinity in many ways. In general, the most important effect is the "nucleation effect".

(3). Crosslinking introduces restraint and stiffness in the polymer. It should also be noted that for the composite film, the height of the specific thermal step at T_g was significantly reduced compared to the pure PVB sample. This decrease indicates that the specific heat capacity of the increasing composite film in the glass state is comparable to that of pure PVB. Almost identical results were obtained for other nanocomposites characterized by relatively low loading in a previous study [12].

Table-4 Glass transition temperature and the melting point of pure PVB and PVB-MWCNTS composite films:

S.NO	Sample	X wt.%	T _g (°C)	T _m (°C)
1	PVB	0	63.3	90.5
2	PVB + X wt. % MWCNTS	1.0	64.8	119.7
3	PVB + X wt. % MWCNTS	2.0	84.8	121.6

5. Conclusions

The solution casting method has been used to successfully produce polyvinyl butyral (PVB) nanocomposite films. Experiments were conducted to study and discuss the influence of MWCNTS weight per cent on the chemical structure and thermal stability of pure PVB and nanocomposites. The following conclusions are drawn from the results. The loading of MWCNTS form clusters is evidenced by changes in the FTIR spectra. The chemical structure of the composite films is affected as a result of this.

PVB crystallinity reduces and amorphousness increases when MWCNTS is added. According to DSC results, incorporating MWCNTS into the PVB matrix raises the glass transition temperature and melting point. So, the fabricated composite films maintained remarkable heat-resistance qualities. So, the T_g and T_m values of the composite films are suitable for use in laminated safety glasses at high temperatures.

Declarations

6. ACKNOWLEDGMENTS

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Figures

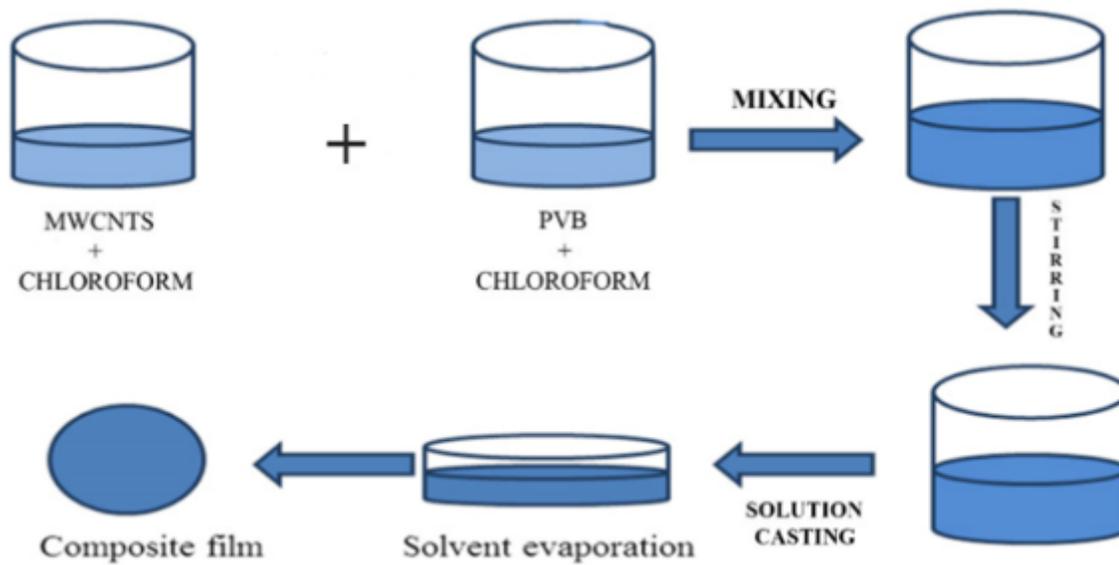


Figure 1

Fabrication process of PVB-MWCNTS composite films

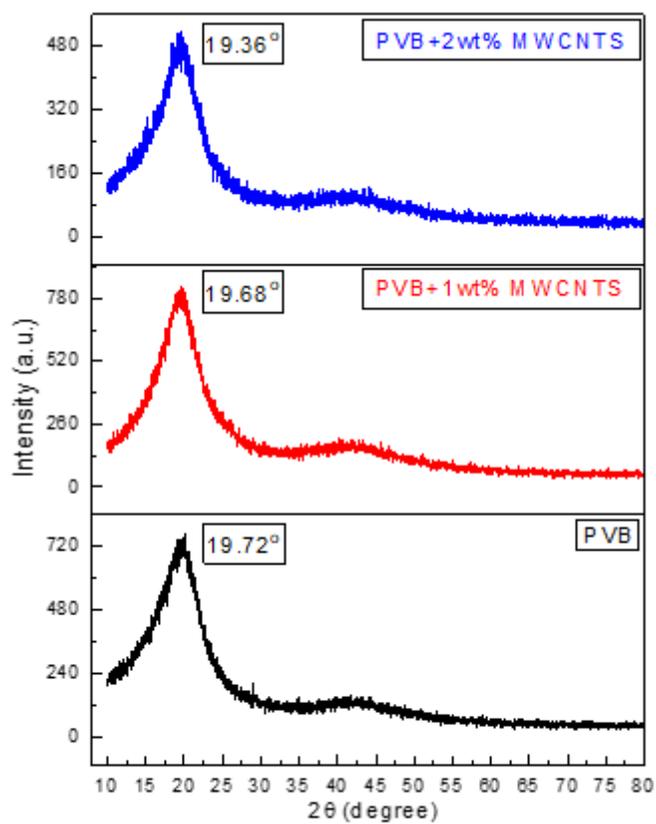


Fig.2 XRD fingerprints of pure PVB and PVB-MWCNTS composite films

Figure 2

See image above for figure legend.

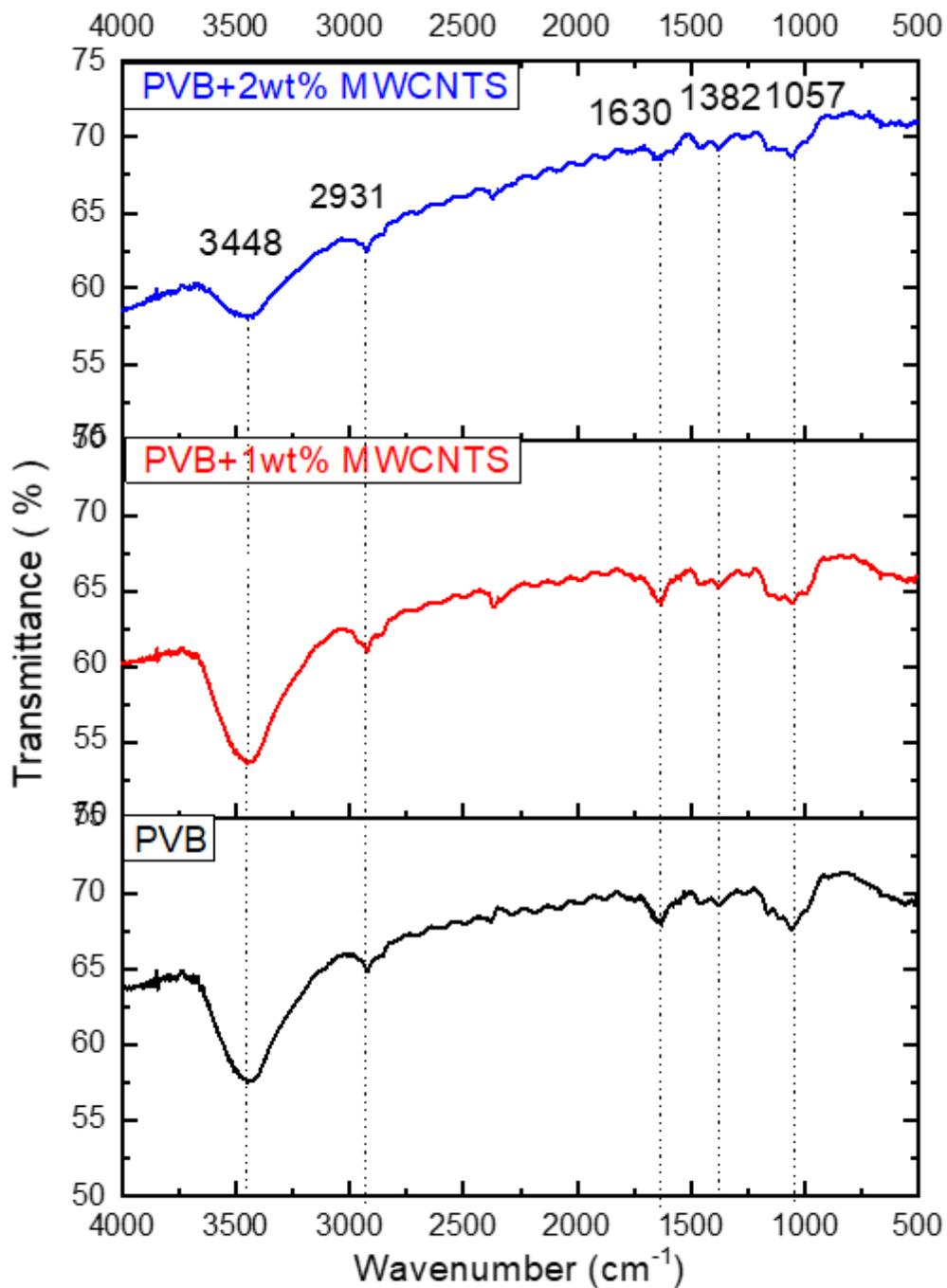


Fig.3 FTIR signatures of pure PVB and PVB-MWCNTS composite films

Figure 3

See image above for figure legend.

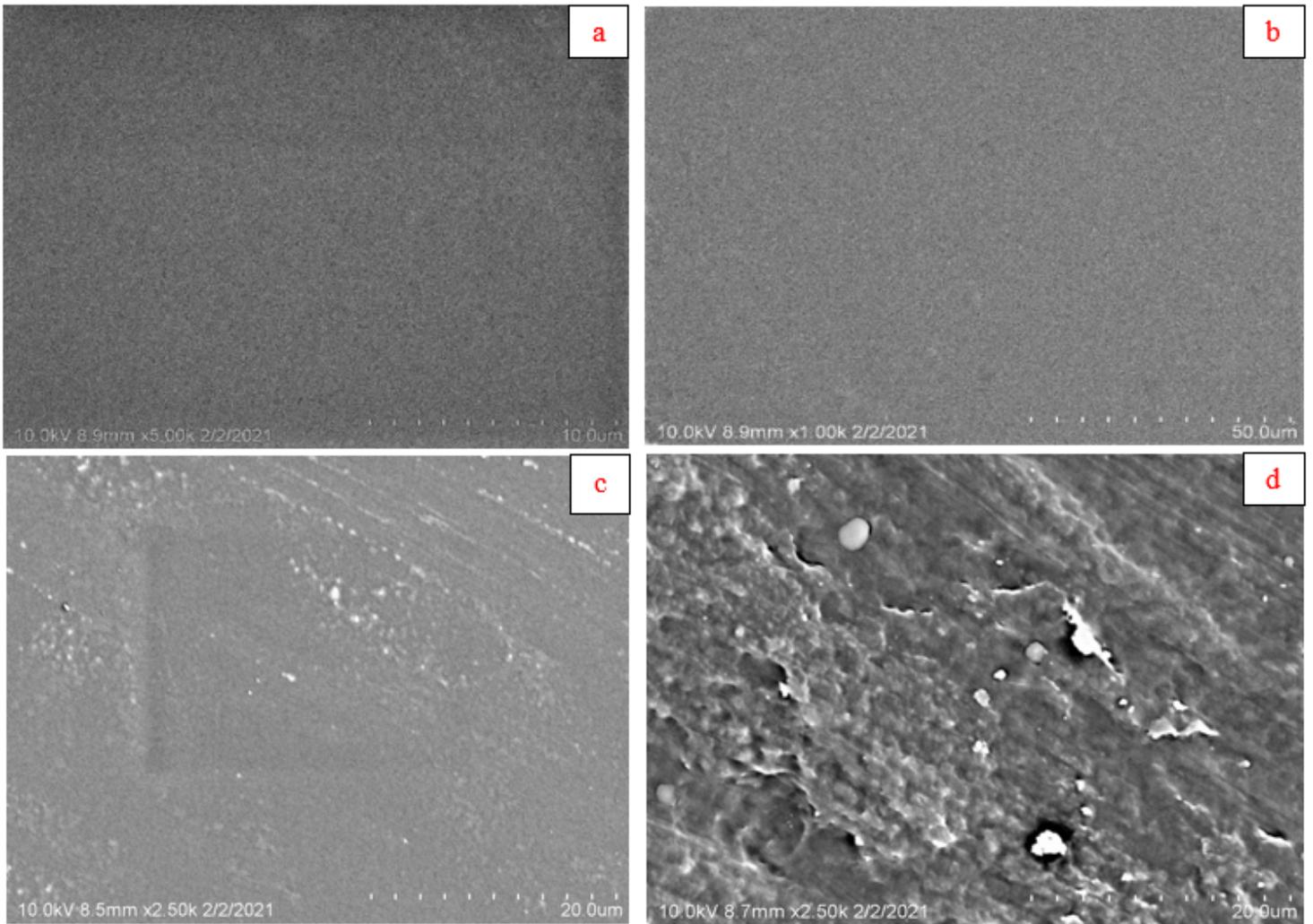


Figure 4

SEM micrographs of pure PVB and PVB-MWCNTS composite films

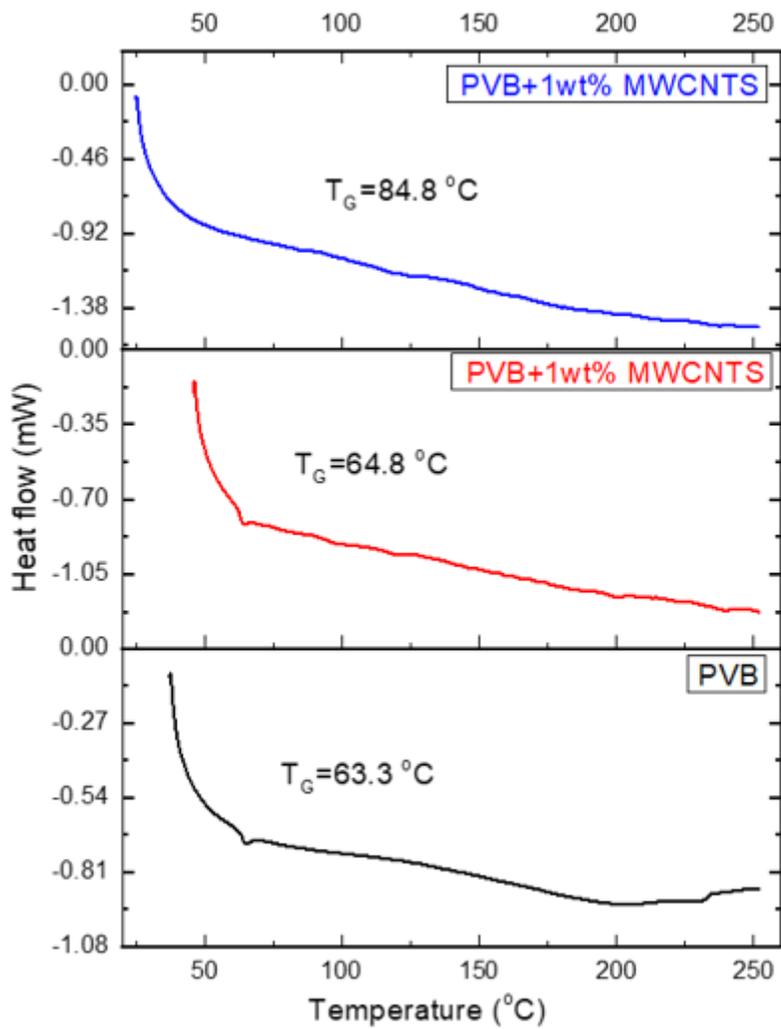


Fig.5 DSC thermograms of pure PVB and PVB-MWCNTS composite films

Figure 5

See image above for figure legend.