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Fabrication and Characterization of PVA/PEO/CB Nanocomposite Films

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Abstract: We report the fabrication of polyvinyl alcohol (PVA) and polyethylene oxide (PEO) blended polymer nanocomposites (PNCs) films loaded with different percentages of carbon black (CB) using the stencil printing method. Effect of blend polymer composition, weight ratio and loading on the electrical and morphological properties of the PNC films were studied using a surface profilometer, SEM, and four-point probe method. SEM analysis showed homogenous dispersion of CBs in the blend matrix as well as the formation of CB agglomerations. An electrical conductivity of 0.417 S/m was achieved with 14wt% CB loading. In general, the CB-polymer composite films with improved morphological and electrical properties were fabricated and characterized for potential sensing applications.

Keywords: PNC; PEO; PVA; CB; Film

1. Introduction

Polymer nanocomposites (PNCs) have recently gained widespread attention owing to their intriguing mechanical, electrical and optical properties [1]. Exploring the structural and electrical properties of PNC materials have been the focus of many researchers due to their potential applications as sensing materials or layers in sensor devices [2,3].

Polymer nanocomposites typically comprise of polymers as a host matrix and nanoparticles as conductive fillers. A wide variety of polymers have been used as host matrices. However, in recent years, non-toxic and water-soluble polymers such as PVA and PEO are gaining attention due to their promising applications in humidity sensing devices [4,5]. As conductive fillers, carbon-based nanofillers [6,7], 2D-materials [8], metal oxides [9] and metal nanoparticles [4] have been widely used to synthesize PNCs. Among the carbon-based nanofillers, carbon black (CB) is a promising candidate for use in preparing PNCs because of its unique properties, including high electrical conductivity, high thermal stability, and desirable wetting characteristics [10]. CB based PNC films have been fabricated and utilized as sensing layers in sensor devices. For instance, [11] and [12] reported the potentials of CB based PNC films on efficiently sensing humidity and volatile organic compounds.

Nowadays, instead of using a pristine polymer as a host matrix, multiple polymers are blended to prepare a new host matrix by adapting the useful properties of the pristine polymers [13]. In this regard, PNC films based on a variety of polymer blends have been reported. For instance, PNC films based on PVA and polyvinylpyrrolidone (PVP) blended host matrices loaded with different weight ratio of alumina and zinc oxide have been fabricated, and the corresponding morphological, thermal, and electrical properties of the

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PNC films have been studied [14,15]. Similarly, PNC films based on PEO-PVP blend matrix loaded with gold nanoparticles were also demonstrated [16]. In general, polymer blends are doped with various kinds of nanofillers to prepare PNCs and advanced functional materials. Nevertheless, the topographical, morphological, and electrical properties of PNC films based on CB loaded PVA-PEO blend matrix are yet to be studied to confirm their suitability as potential sensing materials.

In this work we present the preparation and characterization of PNC films. The films were prepared from PEO-PVA blends loaded with different concentrations of CBs. Stencil printing method was used to print PNC films of different thicknesses. High-resolution scanning electron microscope (HRSEM) and four-point probe resistance measurement techniques were applied to characterize the morphological, structural, and electrical properties of the PNC films. The topographic properties such as the surface roughness and thickness of the PNC films were obtained using a surface profilometer. The findings indicated that the PNC films exhibited good structural, morphological, and electrical properties which make them suitable for various sensing applications.

2. Materials and Methods

2.1. Materials

PEO (molecular weight (MW) ≈ 600,000 g/mol) and PVA (MW ≈ 89000-98000 g/mol and 99+% hydrolyzed) powders were purchased from Sigma-Aldrich, USA. Vulcan XC72R carbon black was generously donated by Cobat inc. These reasonably high MW materials are appropriate to prepare polymer blends owing to their film forming characteristics. Different thicknesses of stencil sheets were utilized to create the desired microstructures. Glass was utilized as a substrate. DI water was used as a solvent.

2.2. Methods

2.2.1. Synthesis of PNC films

To prepare the PVA-PEO blend matrix, 10wt% PVA and 5wt% PEO polymers were used. The 10wt% PVA polymer was prepared by dissolving 1 g of PVA in 9 g of distilled water. To get a homogenized solution, first the PVA solution was stirred on a magnetic stirring plate at 500 rpm for 30 mins at room temperature. After 30 mins, the PVA solution was stirred at 90°C for 2 additional hours. Similarly, 5wt% PEO polymer was prepared by dissolving 0.5 g of PEO in 9.5 g of distilled water. The PEO solution was stirred for 3 hours at room temperature on a stirring plate at 500 rpm and then stirred at 55°C for an additional hour. During the PEO and PVA stirring process air bubbles were generated in the polymers. After the stirring process, the air bubbles were removed by exposing the polymers to the nitrogen gas for 10 mins.

The PVA-PEO polymer blends were prepared with different weight ratios of PVA t0 PEO, see Table 1. The polymer blends were then mixed for 10 mins in an AR-100 conditioning mixer. Blend polymer nanocomposites were prepared by adding 10wt% CB to the PVA-PEO polymer blend matrices. The PNCs were mixed for 15 mins in the AR-100 conditioning mixer to obtain homogeneous viscous solutions. In a similar way, with a fixed PVA-PEO polymer blend ratio of 1:1, various PNCs were prepared with different weight percentages of CBs.

Table 1. Different weight ratio of PVA-PEO loaded with CBs.

PVA:PEO ratio	CB (wt%)
1:1	x*
3.5:1	10
1:3.5	10

* Different wt% of CBs content.

Using the PNC solutions, the PNC films were fabricated on the surface of the substrates (7.5 cm×2.5 cm) as follows. To fabricate the PNC films in a rectangular shape, the stencils were engraved with the desired pattern using a CO_2 laser (Boss LS1416). Then, the conventional screen-printing technique was utilized to obtain the PNC films, illustrated in Figure 1.

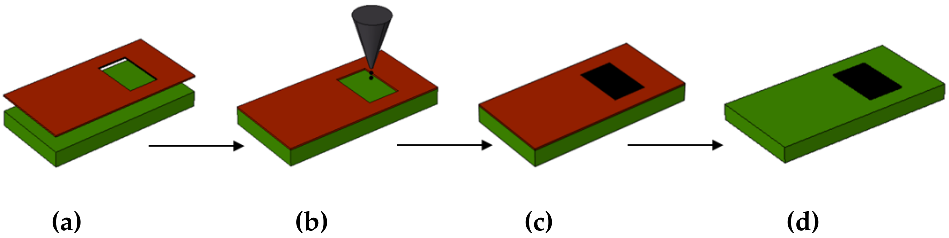


Figure 1. The conventional stencil-printing technique: (a) Placing of the stencil on the top of the substrate; (b) Pouring of the PNC solutions onto the opening of the stencil; (c) Spreading of the composites using a squeegee; (d) The resulting film obtained after curing.

2.2.2. Characterizations

Various characterization techniques were used to study the electrical, morphological, and structural properties of the films. The morphology and structure of films were analyzed using a HRSEM (Hitachi S-4800) and a surface profile (Dektak 6M). The HRSEM was carried out using two different accelerating voltages of 5 and 10 kV. The samples were mounted on the specimen stubs and coated on a carbon tape to obtain the SEM images. Surface profilometry was conducted to extract the topographical properties from the surface of the films. It provides quantitative data regarding the roughness of the surface of a film as well as the corresponding thickness by scanning the surface of the films as a diamond-tipped stylus moves from the substrate to and over the surface of the films.

The current-voltage (I-V) characteristics or electrical conductivity of the films were analyzed using a four-point probe resistance measurement method (Ossila) at room temperature. The measurements were performed by recording the current on application of voltage, and vice versa.

3. Results and Discussion

3.1. Effect of the weight ratio of PEO-PVA blends

PVA-PEO polymer blends loaded with a fixed 10 wt% of CBs were prepared with different weight ratios of the pristine polymers as presented in Table 1, followed by screen printing to fabricate the PNC films on glass substrates. Visual inspection was performed to observe the underlying physical properties. For instance, the formation of cracks on the surface of the films was observed on the PNC films which were prepared from 3.5:1 weight ratio, see Figure 2a. While the PNC films which were prepared from 1:3.5 weight ratio were peeled off from the substrates, see Figure 2b. It can be inferred that these weight ratios were not enough to form stable blend polymers (dual-phase), as the formation of the dual-phase is strongly influenced by the weight ratio of the parent polymers [17]. However, the formation of cracks and peeling off were not observed on the PNC films with a weight ratio of PVA to PEO of 1:1. The PNC films revealed a very good strength, rigidity, and toughness. This might be due to the formation of dual-phase in the polymer matrix. Henceforth, the 1:1 weight ratio was used to prepare the blended polymers.

(**a**) (**b**)

Figure 2. Effect of the weight ratios of PVA-PEO blends on the physical properties of the films: (**a**) 3.5:1; (**b**) 1:3.5.

3.2. Topographical analysis

Surface profilometry was carried out on the surface PNC films to obtain the topographical properties, such as thickness and the surface roughness parameters. For each surface profilometer scan, a z-axis which was perpendicular to the surface of the film was considered as the scanning axis, where $z = 0$ corresponded to a position on the surface of the substrate. Then, the z-direction values were recorded. All the scanning of the film surfaces were performed using a 12.5 μm diamond-tipped stylus for a scan length of 2000 μm scanned in 50 seconds. The surface profiles of the PNC films which contained 8, 10, 12 and 14wt% CB are shown in Figure 3. The surface roughness (R_A) and thickness (t) values of the films loaded with different weight percentages of CBs were summarized in Table 2.

Table 2. The R_A and t values for different wt5 of CBs.

CB Content (wt%)	**R_A (μm)**	**t (μm)**
0	0.2 ± 0.001	2 ± 0.11
8	1.9 ± 0.042	57 ± 0.24
10	1.5 ± 0.015	76 ± 0.02
12	1.2 ± 0.031	92 ± 0.05
14	1.2 ± 0.020	120 ± 0.32

From Table 2, it is evident that the thickness of the PNC film increased by increasing the wt% of the CB. This was expected because when the conductive filler wt% was increased in a polymer matrix, its dry thickness also increased. On the other hand, the R_A of the PNC films decreased with the increase of the wt% of CBs. For instance, when the CB concentration was increased from 8 to 14wt%, the R_A decreased from 1.9 to 1.2 μm. This might be due to change in the viscosity of the PNC solution caused by the increasing of the wt% of CBs. The R_A values indicated the flatness or regularity of the surface of the films.

3.3. Morphological analysis

The morphology of the PNC films was studied using the HRSEM. The topographic HRSEM images of PNC films which contain 12 and 10wt% CBs at different magnifications were shown in Figure 4. From Figure 4, it can be observed that the CB particles were uniformly dispersed in the PVA-PEO blend matrix. This indicated the presence of strong cohesion bond between the CBs and the blend matrices. The SEM images further revealed the presence of porous structures on the surface of the films. Apart from the pores, the formation of CB agglomerations in the PVA-PEO blend matrix was also observed, see Figure 4c. Due to this phenomenon, the increase in particle sizes was noticed. For instance, the smallest particle size detected for the cases of 12 wt% CB containing film was 41.7 nm, while the largest particle size detected was 437.2 nm. In general, a homogeneously dispersed conductive nanofillers in a blend matrix provides large surface area and greater

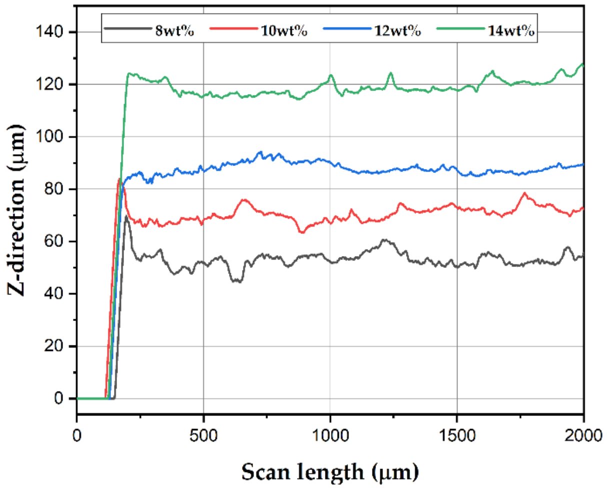


Figure 3. The surface profiles of the PNC films with different wt% of CBs content.

number of active sites which in turn plays an important role in improving the both mechanical strength and the sensing performance of the PNC films [15].

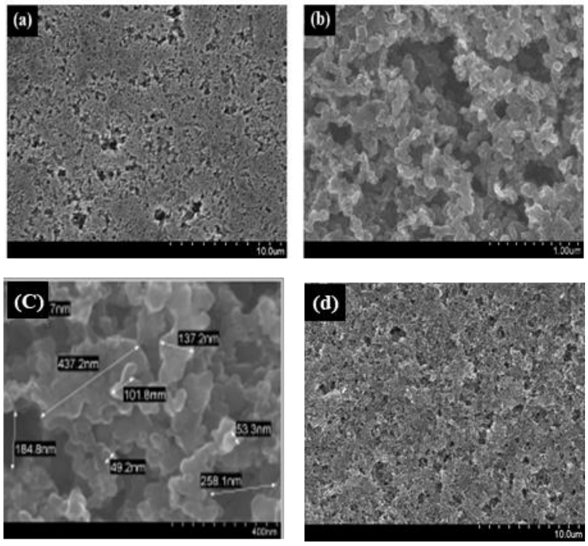
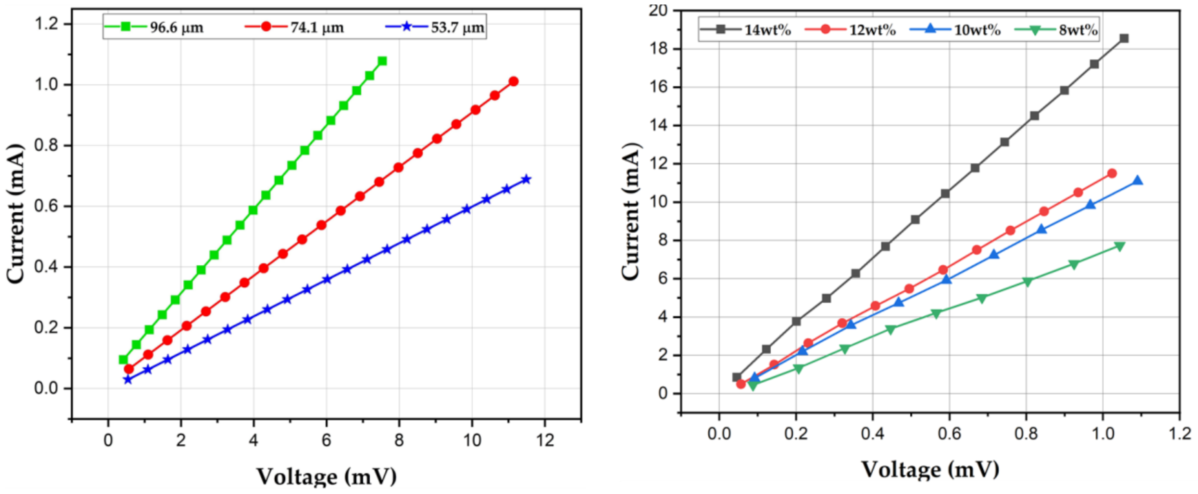


Figure 4. The SEM images of PNC films loaded with: (**a**) 12wt% CB at 10 µm; (**b**) 12wt% CB at 1 µm resolution; (**c**) CB agglomerations; (d) 10wt% CB at 10 µm.

3.4. Electrical properties

The I-V characteristics and the electrical conductivity of the PNC films were obtained using the four-point probe system at room temperature. The I-V characteristics were obtained for two different cases. In the first case, the CB content was fixed to 10wt%, and PNC films with different thicknesses were prepared by using 100, 150 and 200 µm thick stencils. The thicknesses of the films after curing were 53.7, 74.1, and 96.6 µm, respectively. Figure 5a illustrates the variation of the in-plane I-V characteristics of the films with the film thickness. From Figure 5a, it can be observed that the I-V curves were linear and the slope of the I-V curves increased with the increase of the film thicknesses. For instance, for the PNC films having thicknesses of 53.7, 74.1 and 96.6 µm, the corresponding slopes were 0.091, 0.132, and 0.167 A/V, respectively. In the second case, the CB content was varied from 8 to 14wt%, and the thickness of the films was fixed. Figure 5b shows the variation of the in-plane I-V characteristics of the films with wt% of CB contents. Here as well, the I-V curves were linear and the slope of the I-V curves increased with the increase of the CB contents. For instance, for the PNC films having CB contents of 8, 10, 12 and 14wt%, the corresponding slopes were 7.5, 10.2, 11.3 and 17.4 A/V, respectively.



(a) (b)

Figure 5. I-V characteristics of the PNC films showing the effect of: (**a**) Thickness; (**b**) CB contents variation.

The electrical conductivity of a PNC film can be calculated using the relation

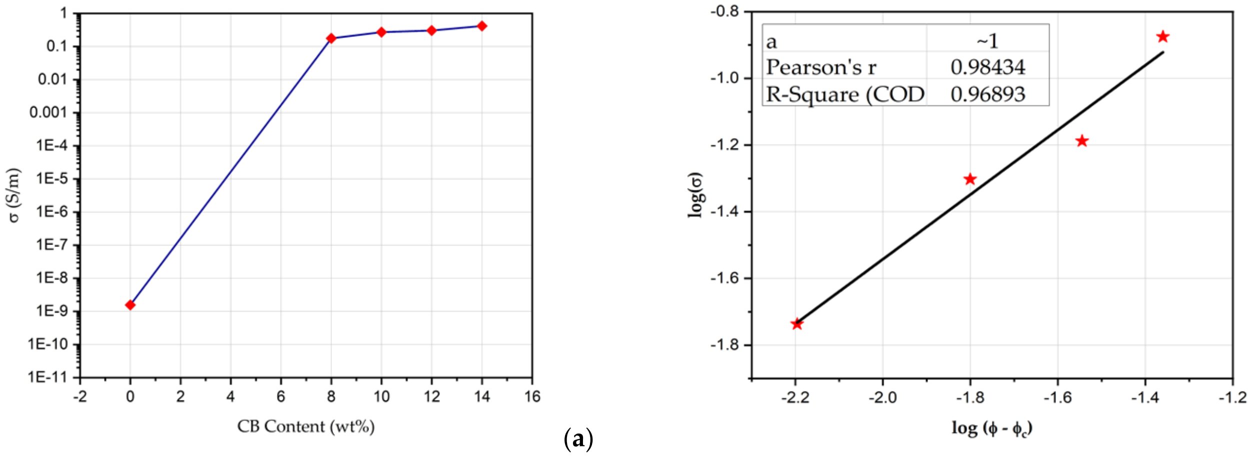
$$\sigma = 1/(R_s \times t), \tag{1}$$

where σ represents the electrical conductivity, R_s represents a sheet resistance which can be obtained by taking the inverse of the slope of the I-V characteristic curve, and t represents the thickness of the film. Figure 6a shows the effect of CB contents variation on the electrical conductivity of the PNC films. From Figure 6a, it can be observed that the electrical conductivity of the PNC films increased with the increasing CB contents. For instance, the electrical conductivity increased significantly from 1.56×10^{-9} to 0.176 S/m with the introduction of 8wt% of CBs. Then, the electrical conductivity of the films gradually increased and reached to 0.471 S/m as the CB contents increased from 8 to 14wt%. The change in the σ value of a PNC film might be attributed to the formation of charge transfer complexes (CTCs) in the polymer matrix after loading it with CBs. The CTCs reduce the interfacial barrier between the tapping sites and provide a conductive path through the amorphous regions of the PVA-PEO blend matrix thus enhancing the conductivity [18,19].

Further, the electrical conductivity behavior of conductive composites can be rationalized using the classical percolation theory [20]. The classical percolation theory equation can be expressed as:

$$\sigma = \sigma_o(\varphi - \varphi_c)^{\alpha}, \tag{2}$$

where φ is the volume fraction of the fillers, φ_c is the volume percolation threshold and α is the critical exponent which represents the dimension of the conductive network. For PNC films with CB contents and $\varphi > \varphi_c$, the linear fitting of log σ vs log (φ-φ_c) was performed to extract the percolation threshold and critical exponent by varying the value of φ_c until the best fit was obtained. Hence, based on the data in Figure 6b, the percolation threshold of PEO-PVA-CB nanocomposites was estimated and was around 0.2 vol% with R^2 of 0.98. As reported in literature, the percolation threshold of many composites with conductive nanofillers was in the range of 3 -15 wt% [21]. The result showed that the percolation threshold reported in the present study was comparable. Also, α value was estimated to be approximately 1, which indicated the presence of a two-dimensional conductive network [22].



(**a**) (**b**)

Figure 6. Effect of CB content on electrical conductivity: **(a)** The electrical conductivity as a function of CB content; **(b)** The linear fit of the films using the percolation theory.

4. Conclusions

The PNC films based on PEO-PVA blend loaded with different wt% of CB contents were prepared. The PNC films were characterized to obtain the topographical, morphological, and electrical properties. The weight ratio of PVA to PEO had an impact on the presence of dual-phase in the blend polymer matrices. The SEM images of the PNC films confirmed the uniform dispersion of CBs in the PVA-PEO blend matrices. The formation of CB agglomerations was also observed. The effect of the variation of CB content and thickness on the electrical properties of the PNC films was demonstrated. The PNC film changed from being as an insulator to a conductive with addition of 8wt% of CBs which in turn helps the formation of CTCs in polymer matrix. The critical exponent value indicates the existence of a 2D conductive network. An enhancement was observed in both morphological and electrical properties of the films. In general, the method reported herein opens a route to fabricate blend polymer-CBs based PNC films and their suitability for future sensor applications, including humidity and voc sensors.

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