

Preparation and Properties of Poly(vinyl alcohol)/Chitosan Blend Bio-nanocomposites Reinforced by Cellulose Nanocrystals*

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Abstract The aim of this paper is to report the effect of the addition of cellulose nanocrystals (CNCs) on the mechanical, thermal and barrier properties of poly(vinyl alcohol)/chitosan (PVA/Cs) bio-nanocomposites films prepared through the solvent casting process. The characterizations of PVA/Cs/CNCs films were carried out in terms of X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA and DTG), oxygen transmission rate (OTR), and tensile tests. TEM and SEM results showed that at low loading levels, CNCs were dispersed homogeneously in the PVA/Cs matrix. The tensile strength and modulus in films increased from 55.1 MPa to 98.4 MPa and from 395 MPa to 690 MPa respectively, when CNCs content went from 0 wt% to 1.0 wt%. The thermal stability and oxygen barrier properties of PVA/Cs matrix were best enhanced at 1.0 wt% of CNCs loading. The enhanced properties attained by incorporating CNCs can be beneficial in various applications.

Keywords: Bio-nanocomposite; Poly(vinyl alcohol)/chitosan; Cellulose nanocrystals; Mechanical properties; Thermal properties.

INTRODUCTION

Currently, fabrication of advanced “green materials” derived from natural sources is one of the essential points of attention in the academic and industrial areas of material research^[1]. In recent years studies based on bio-nanocomposites using different reinforcements for poly (vinyl alcohol)/chitosan, have been reported by some research groups^[2–5]. PVA is a non-toxic, water-soluble synthetic polymer and has good physical and chemical properties and film-forming ability^[6]. The use of this polymer is important in many applications such as controlled drug delivery systems, membrane preparation, recycling of polymers and packaging. Nevertheless, PVA has low biodegradation rate and poor moisture barrier properties. To enhance its eco-friendliness, and performance, PVA is often treated with other polymers and nanoparticles^[7].

Strong research attempts have been focused on the use of natural fillers as reinforcing materials for polymer composites, because natural fillers are renewable, sustainable and have low abrasive nature in comparison with mechanically robust nano-sized reinforcements^[8]. Cellulose nanocrystals with one dimension in nano-range have

* This work was financially supported by Universiti Putra Malaysia (research grant RUGS 9199840), and the authors are grateful to staff of the Department of Chemistry UPM for their technical assistance.

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Received March 5, 2014; Revised May 15, 2014; Accepted May 29, 2014

doi: 10.1007/s10118-014-1548-0

more potential as reinforcements in polymer hosts because of their good mechanical properties with very high strength and stiffness^[9–11]. In the last decade, cellulose nanocrystals have merited substantial attention as potential nano-sized filler in blending with different polymers^[10, 12]. Cellulose nanocrystals are typically rod-formed monocystals, 2 to 20 nm in diameter and from tens to hundreds of nanometers in length, and extracted after acid hydrolysis of various natural cellulose fibers such as cotton, cellulose fibers from lignocellulosic materials, and marine animal tunicate^[13, 14]. Cellulose nanocrystals as a reinforcing phase have several advantages over other types of nano-sized fillers, such as high aspect ratio, large surface area ($\sim 150 \text{ m}^2 \cdot \text{g}^{-1}$), low density, outstanding mechanical properties (138 GPa of Young's modulus and 1.7 GPa of tensile strength), renewability, and bio-compatibility^[15, 16]. The hydrophilic surface of CNCs allows proper blending with water based host polymer matrices. Cellulose nanocrystals have been successfully used in reinforcing the silk fibroin^[17], cellulose acetate butyrate^[18], starch^[19], poly(lactic acid)^[20], poly(vinyl alcohol)^[21] and other plastics^[22]. However, such nano-sized filler have to overcome many obstacles against industrial practices because of time consuming extraction process with low yield, extremely hydrophilic surface, commercially unavailability, poor dispersion owing to higher aggregation trend, low thermal stability and most notably, generally, relative higher price through expensive source^[23].

A new approach in the nanocomposites studies consists in nanocomposites based on blends of two or more polymers. Polymer blend nanocomposites have combined properties of polymer blends and advantages of polymer nanocomposites. In the previous studies, nanocomposites based on polymer blends could represent a promising route to produce new materials with high performance^[24, 25]. PVA/Cs is an important biopolymer blend with suitable mechanical and chemical properties. The PVA/Cs polymer blend is being studied extensively in the fields of packaging, membrane filtration, dye adsorption, and biomedicine^[26, 27]. The improved physical and chemical properties of PVA/Cs are valuable. In this study, CNCs originated from the acid hydrolysis of cotton were incorporated into PVA/Cs matrices to improve the mechanical, thermal and oxygen barrier properties of PVA/Cs/CNCs bio-nanocomposite films. Although many papers have reported different single polymer hosts reinforced with CNCs, the literatures regarding polymer blends/cellulose nanocrystals nanocomposites have not yet been investigated.

EXPERIMENTAL

Materials

All the chemicals were analytical grade and used as received without more purification. Cotton cellulose from filter paper (Q1, Whatman) was supplied by Fisher Scientific (Pittsburgh, PA, USA). Sulfuric acid (95%–98%, reagent grade) was purchased from Scharlau (Barcelona, Spain). Chitosan with a 85% degree of deacetylation and $345500 \text{ g} \cdot \text{mol}^{-1}$ average molecular weight was obtained from the Malaysian Nuclear Agency. PVA (99% of degree of hydrolysis, average molecular weight of $89000 \text{ g} \cdot \text{mol}^{-1}$) was purchased from Sigma Aldrich.

Extraction of CNCs

Extraction of the CNCs was carried out according to a previous work^[28]. The cellulose powder harvested from one piece of filter paper (2 g) was hydrolyzed with a sulfuric acid solution (20 mL, 64 wt%) at 45 °C for 60 min. The resultant suspension was diluted 10-fold with cold water (4 °C) followed by centrifugation and dialysis until a neutral pH was reached. Finally, the sample was freeze-dried.

Preparation of Bio-nanocomposites

The PVA/Cs blend was prepared as a described work^[29]. Briefly, specific quantity of PVA (5.0 W/V%) hydrogel solutions was added into the 1.0 W/V% chitosan solution to obtain PVA/Cs molar ratio of (3:1). The mixture was kept under stirring for 30 min until the PVA and chitosan completely formed a clear solution. Then CNCs were dispersed in a solution of distilled water (100 mL) and ultrasonicated for 30 min. The CNCs filler loading level (0 wt%, 0.5 wt%, 1 wt%, 3 wt% or 5 wt%) was based on the amount of PVA/Cs blend. The above suspensions were added into 100 mL of the PVA/Cs solution under strong string for 2 h at 70 °C. The mixtures were cast in glass petri dishes and then dried at ambient temperature to obtain the composite films. The dried composite films

were roasted at 45 °C for 6 h. Finally, a series of nanocomposite films with a thickness of ~0.2 mm were prepared.

Characterization

The X-ray analysis was carried out using an XPERT-PRO diffractometer. The X-ray beam was nickel-filtered Cu ($\lambda = 0.1542$ nm) and the instrument was operated at 40 kV and 30 mA. The scanning scope of 2θ was 5°–80° at room temperature. The morphologies of the samples were studied by using a transmission electron microscope (HITACHI H-700, Japan) with acceleration voltage of 120 kV at room temperature. The sample powder was prepared by dropping a sample of the suspension onto a copper grid coated with carbon film. The specimens were then negatively stained with 1% uranyl acetate and allowed to dry at room temperature. The ultrathin sections of bionanocomposite sample were prepared at –120 °C using a microtome equipped with a diamond knife, and then placed on a copper grid. The surface morphology of the sample films was examined using a scanning electron microscope (SEM), Philips XL30, with an acceleration voltage of 15 kv. Before examination the specimens were mounted on a metal stub using carbon tape and then gold-coated under nitrogen atmosphere using a Bal- Tec SCD 005 sputter coater. The tensile properties of the sample films were measured as per ASTM D 638 test methods, using an Instron 4032 Universal Testing Machine. The samples, cut into dumb-bell shapes, employed a steel template and router machine. Seven specimens were tested and the average result of the values of five specimens was taken. The thermogravimetric analysis data were recorded using a thermogravimetric Analyzer TGA7, Perkin-Elmer. The samples were heated at the rate of 10 K/min from 50 °C to 600 °C under nitrogen atmosphere. The weight of the samples was about 10 mg. The weight loss of samples during heating was recorded and plotted as a function of temperature. Oxygen transmission rate of the sample films were evaluated by using of an oxygen transmission rate test (Labthink BTY-B1, China) instrument. The sample film with a diameter around 30 mm was placed in a cell and oxygen flowed on one side of the films, and the oxygen transmission rate was measured. This is the capacity of molecule gas that transfers through a surface per unit of time. Five specimens were tested and the reported results were average of the values of at least four OTR measurements.

RESULTS AND DISCUSSION

Transmission Electron Microscopy of the Cellulose Nanocrystals

A fraction of the cellulose aqueous suspension was more diluted; then TEM was carried out on the evaporated extraction (Fig. 1). The individual CNCs observable in the micrograph have diameters in the range of 8 nm and lengths up to about 250 nm, which are in consistent with values typically reported for cellulose nanocrystals^[28]. Some agglomerations could be observed, which may have made during the evaporation or been existing in the original suspension.

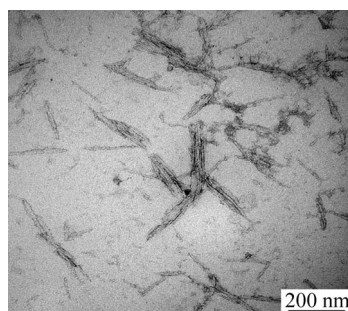


Fig. 1 TEM image of CNCs

X-ray Diffraction (XRD)

X-ray diffraction patterns of the CNCs, pure PVA/Cs blend and PVA/Cs/CNCs bio-nanocomposites with various amounts of the CNCs content are shown in Fig. 2. The PVA/Cs film exhibits the characteristic pattern of an

amorphous phase with the main halo of the typical peak at $2\theta = 19.05^\circ$ and another of low intensity at $2\theta = 22.15^\circ$ ^[30]. There is observed a steady increase in the intensity of the peaks at $2\theta = 14.7^\circ$, 16.4° and 22.8° corresponding to the (110), ($1\bar{1}0$) and (200) planes of cellulose nanocrystals, respectively, with increase of CNCs contents. In particular, when high levels of CNCs were introduced, for example in PVA/Cs/CNCs 3.0 wt% and in PVA/Cs/CNCs 5.0 wt%, the presence of CNCs, and even self-agglomerated CNCs, caused the crystalline character attributed to the cellulose nanocrystals in the bio-nanocomposite more clear. There is neither a new peak nor a peak shift compared to pure PVA/Cs, which specifies that the PVA/Cs/CNCs bio-nanocomposite films all consist of two phase structures, *i.e.*, polymer and cellulose nanocrystals. As the CNCs content were increased from 0 wt% to 5.0 wt%, the 2θ value of the peak slightly increased from 19.05° to 19.44° . The Bragg equation was used to calculate the mean intermolecular distance; the distance decreased from 0.487 nm to 0.471 nm as the CNCs content was increased. These results display that the incorporation of CNCs does not change the structural uniformity of the matrix polymer blend, but rather improves molecular ordering in the amorphous polymer blend matrix.

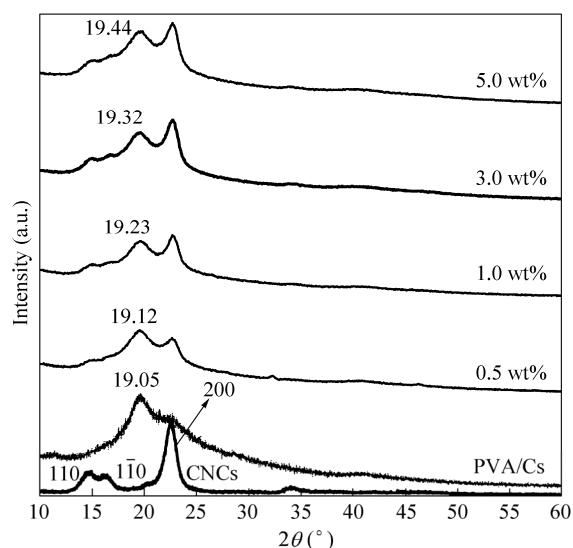


Fig. 2 XRD patterns of CNCs, PVA/Cs blend and its CNCs bio-nanocomposites

Transmission Electron Microscopy of PVA/Cs-Based Films

The distribution of CNCs in polymer blend matrices has been observed by TEM analysis. As shown in Figs. 3(a) and 3(b), the rod-like cellulose nanocrystals were dispersed well into polymer matrix, when the low contents of CNCs were used. The nanocrystals at 1.0 wt% filler loading have an average width of (5.7 ± 1.2) nm and length of (238 ± 16) nm, giving rise to an aspect ratio of about 41.75. This value is generally in the aspect ratio range of cellulose nanocrystals^[31]. A study showed that an effective reinforcement effect can be obtained in composites, when nano-sized cellulose with an aspect ratio about 50 are introduced into a polymer matrix in comparison with micro-sized fibers^[32]. On the other hand, it is seen that, with the increase of CNCs contents into polymer matrices, most of the cellulose nanocrystals were agglomerated by hydrogen-bonded free hydroxyl groups (Figs. 3c and 3d).

Tensile Properties

The effects of CNCs contents on the tensile properties of the PVA/Cs bio-nanocomposite films are given in Table 1. Tensile values show that the addition of CNCs helped to increase the tensile strength (T_s) and modulus (T_m) of the films. The highest values were obtained when 1.0 wt% of cellulose nanocrystals were incorporated in the PVA/Cs blend matrix. The bio-nanocomposite showed ~78% and 75% tensile strength and modulus improvements, respectively compared to that of the original polymer blend. The improvement is due to

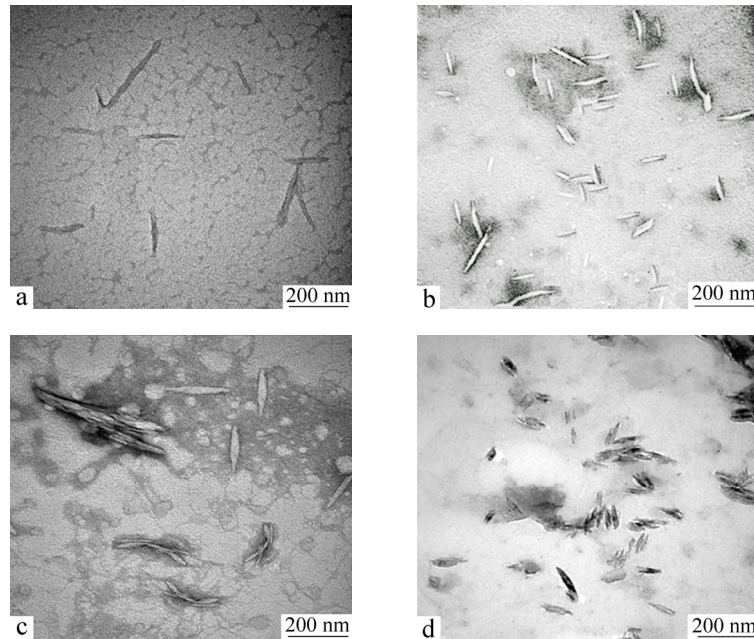


Fig. 3 TEM images of PVA/Cs/CNCs bio-nanocomposites with 0.5 wt% (a), 1.0 wt% (b), 3.0 wt% (c) and 5.0 wt% (d) CNCs contents

Table 1. Tensile data of PVA/Cs and its CNCs bio-nanocomposites

Sample	CNCs (wt%)	T_s (MPa)	T_m (MPa)	E_b (mm)
PVA/Cs	0	55.1 ± 1.6	395 ± 23	10.2 ± 0.2
PVA/Cs/CNCs	0.5	78.5 ± 2.3	598 ± 31	7.4 ± 0.1
PVA/Cs/CNCs	1	98.2 ± 1.2	690 ± 29	5.9 ± 0.7
PVA/Cs/CNCs	3	66.4 ± 1.0	632 ± 32	8.5 ± 0.4
PVA/Cs/CNCs	5	54.9 ± 1.4	501 ± 28	8.9 ± 0.9

formation of a network structure resulted from filler-matrix interactions in composites, which increases hard portion crystallinity, decreases molecular mobility and promotes rigidity^[33]. On the other hand, a mean field mechanical model may be adopted to interpret the reinforcing effect of CNCs in the polymer matrix. The model is based on the notion that the CNCs are homogeneously distributed in the polymer matrix, but there is no interaction among the nanocrystals^[34]. The high strength and modulus properties of the bio-nanocomposite films may result from effective load transfer to the nanocrystal network, which leads to further uniform stress distribution and minimization of the stress concentration region^[35]. Beyond the 1.0 wt% of CNCs content, the tensile strength and modulus values decrease. This showed that because of the heterogeneous size distribution and aggregation of nanocrystals within the polymer blend matrix, CNCs did not act as reinforcing filler in PVA/Cs. In fact, excess of CNCs content was a likely reason of phase separation, poor nanocrystals distribution and more aggregates formation, which led to insignificant tensile properties^[36]. On the other hand, the addition of cellulose nanocrystals reinforcement from 0 wt% to 5.0 wt% decreased the elongation at break (E_b) of PVA/Cs bio-nanocomposites films with maximum reduction at 1.0 wt% loading level. This phenomenon can be explained by the fact that the stiff filler network structure, responsible for the enforcing effect, was created perfectly as the CNCs content was 1.0 wt% which strongly restricted the chain mobility of the matrix and therefore significantly decreased elongation at break^[37]. Such changes in the elongation at break of composite films were reported by other researchers^[36, 38].

Thermal Properties

TGA and DTG curves of pure PVA/Cs and PVA/Cs/CNCs films are shown in Figs. 4(a) and 4(b) respectively. Thermal parameters including T_{onset} and $T_{0.5}$ are summarized in Table 2. T_{onset} of pure blend was 247 °C, while PVA/Cs/CNCs bio-nanocomposite, with the 0.5 wt% and 1.0 wt% CNCs, had T_{onset} of higher than 270 °C. $T_{0.5}$ of bio-composites also showed a similar trend. The PVA/Cs/1.0 wt% CNCs bio-nanocomposite had the highest T_{onset} and $T_{0.5}$ values, representing that it had an enhanced thermal resistance. The influence of CNCs on the thermal resistance of PVA/Cs could be explained by interactions between the abundant hydroxyl groups of CNCs and the free hydroxyl groups of PVA/Cs through hydrogen bonding. The presence of hydrogen bonds should raise the value of thermal degradation because of the formation of a confined structure in the nanocomposites^[39].

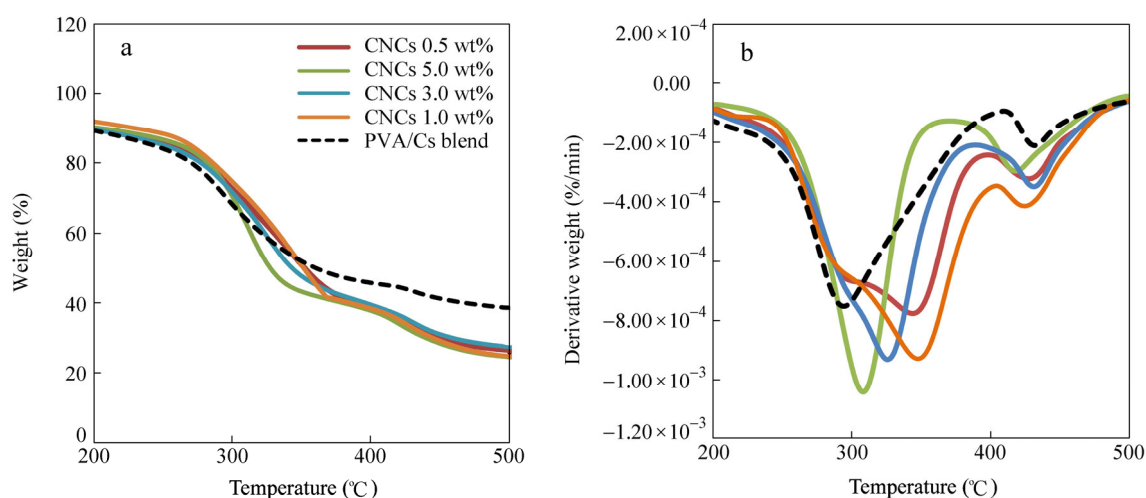


Fig. 4 TGA and DTG thermograms of PVA/Cs and its CNCs bio-nanocomposites

Table 2. Thermal data of PVA/Cs and its CNCs bio-nanocomposites

Sample	CNCs (wt%)	First step	
		T_{onset} (°C)	$T_{0.5}$ (°C)
PVA/Cs	0	247	288
PVA/Cs/CNCs	0.5	273	337
PVA/Cs/CNCs	1	275	340
PVA/Cs/CNCs	3	265	322
PVA/Cs/CNCs	5	260	311

Oxygen Transmission Rate

Figure 5 showed the OTR versus percentage of cellulose nanocrystals. From Fig. 5, it is seen that the oxygen permeability is most largely reduced, *i.e.* by 69%, in the 1.0 wt% PVA/Cs/CNCs compared to the control PVA/Cs sample. The permeability of the bio-nanocomposite films is always lower than that of pure PVA/Cs. These results suggest that the incorporated CNCs create tortuous path for the penetration of oxygen molecules. When the low levels of CNCs were used, the CNCs were dispersed to a higher extent as shown in the TEM micrograph, therefore yielding a further effective barrier effect^[1]. Therefore an suitable affinity between the polymer blend and the surface of the CNCs can be suggested. A poor affinity would lead to the existence of cavities that permit the oxygen molecules to diffuse faster through the film. The permeability is not reduced more with a higher content of CNCs. This can be because of agglomeration of the CNCs. The agglomeration observed beyond 1.0 wt% level may provide channels, or pores, in the film that permit more quick permeation^[40].

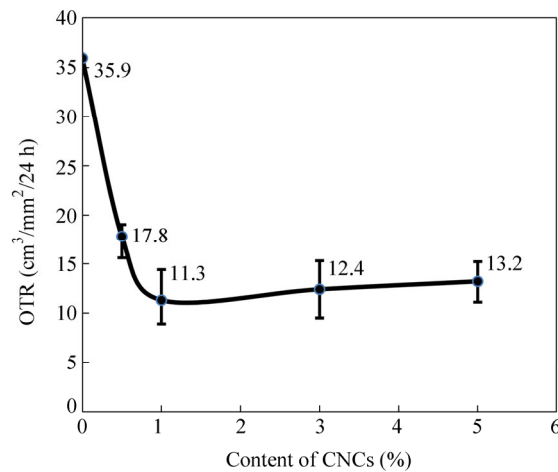


Fig. 5 OTR of PVA/Cs and its CNCs bio-nanocomposites

Surface Morphology of PVA/Cs-Based Films

The morphological inspection of the fractured surfaces of the films was performed using scanning electron microscopy (SEM) as is shown in Fig. 6. It is observed that addition of CNCs caused changes in the film microstructure. The SEM micrograph of polymer blend film (Fig. 6a) exhibits PVA and Cs are homogeneously dispersed and flexible with some cracks. Addition of 1.0 wt% CNCs affects the microstructure of the PVA/Cs films positively (Fig. 6b). The homogenous dispersion of CNCs at 1.0 wt% content caused a proper adhesion between the polymer phase and the surface of the CNCs. Also, the flexibility of biocomposites considerably decreased. On the contrary, addition of 5.0 wt% CNCs (Fig. 6c) due to agglomeration of CNCs and poor affinity between filler-matrix led to increasing density of crack deflection sites and formation of some pores. Furthermore, the flexibility of biocomposites slightly increased with further addition of CNCs. Finally, the SEM clarifications have allowed supporting the measured mechanical, thermal and barrier results.

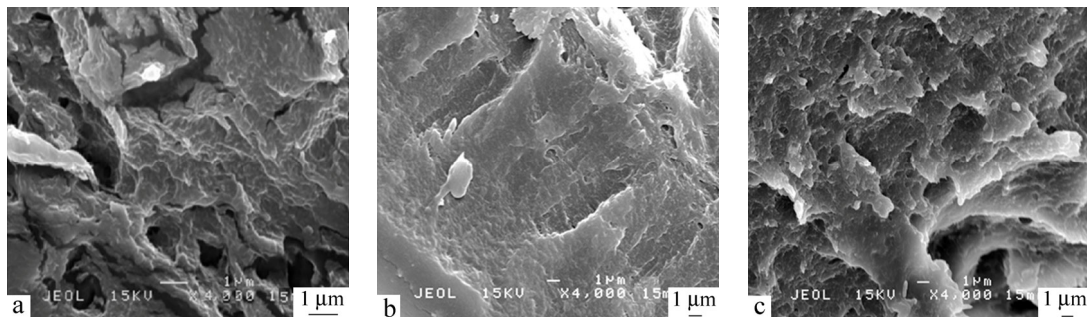


Fig. 6 SEM image of the cross-section of (a) PVA/Cs, (b) PVA/Cs/CNCs 1.0 wt% and (c) PVA/Cs/CNCs 5.0 wt% films

CONCLUSIONS

The reinforced bio-composites of biopolymer blend matrix with cellulose nanocrystals were prepared and potentiality of cellulose nano-sized filler was evaluated on the structure and properties of resulted hybrids. The observation of TEM-based structures illustrated that the CNCs were homogeneously dispersed at lower filler loading. While compared the control PVA/Cs film and the PVA/Cs/CNCs film, the bio-nanocomposite films exhibited higher tensile strength; decreased elongation at break; increased thermal resistance and reduced oxygen transmission rate. This is owing to the parameters such as the nano-scale size effects of the CNC (high L/D), the high content of cellulose crystalline districts, the well dispersion of CNCs within PVA/Cs matrix, and the strong interaction between CNC and PVA/Cs matrix.

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