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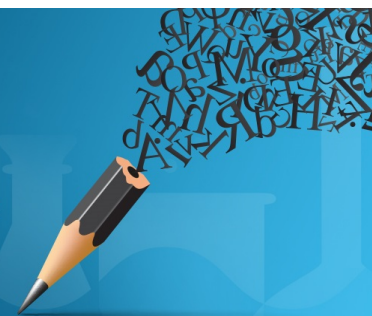# Effect of Cellulose Nanocrystals (CNC) on Thermal Properties of Polyvinyl Alcohol (PVA)/CNC Biocomposites

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Abstract. In this research, the effect of cellulose nanocrystals (CNC) on the thermal properties of polyvinyl alcohol (PVA) / cellulose nanocrystal (CNC) biocomposite was investigated. The PVA/CNC biocomposite films were prepared by solvent casting method with different CNC content (3; 6; and 9 wt. %,). The prepared biocomposites were characterized using scanning electron microscopy (SEM) while the thermal properties were studied using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). SEM showed the morphology of all samples where the difference among samples where the surface roughness of the samples was more at higher concentration of CNC. TGA results showed that the highest onset thermal degradation temperature was recorded at 254 °C for PVA/CNC 6 wt% compared to other samples. The value of char residue also increased up to 3.2% for PVA/CNC 9 wt% indicating the good thermal effect of CNC on PVA for the biocomposites heating-resistant properties. DSC results revealed that with the addition of CNC, all of the biocomposites peaks move to higher temperatures showing that CNC improves the thermal stability of the composites.

INTRODUCTION

For decades, petrochemical-based polymers such as polyamide (PA), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET) are widely used as packaging materials, especially in food packaging (Siracusa et al., 2008). Despite that, there is a severe environmental problem globally due to their poor biodegradability in nature. The properties of polymer material that are low production cost, sound

gas barrier, and high mechanical properties are not sufficient for the progressively environmentally aware community, which requests more eco-friendly materials and processes (Espinosa et al., 2019; Nur Aiman et al., 2020).

Polyvinyl Alcohol (PVA) is one of the synthetic polymers that soluble in water obtained by polyvinyl acetate hydrolysis. The properties of PVA comply with the demand of industry with excellent chemical resistance, optical and physical properties (Popescu, 2017). Furthermore, PVA is also effective in film building, blend well in a compound, and adhering to quality as a suitable polymer. In a previously conducted preliminary study, PVA is synthesized with other synthetic materials to improve its barrier properties and production. Nevertheless, the materials combined are inorganic; thus, it still lacks biodegradability, biocompatibility, and processability (Espinosa et al., 2019).

Cellulose nanocrystal (CNC) main benefits are best eco-friendly effect, low density, less effort needed for recycling, low-energy use in production, and comparatively easy processability due to their nonabrasive nature (Popescu, 2017). Depending on the cellulosic source and isolation method, sizes and phases of CNC are small crystalline particles with diameters of 3-40 nm and lengths around 100-500 nm (Trache et al., 2017). CNC shows a higher degree of crystallinity than cellulose nanofibers, resulting in higher specific mechanical properties, biocompatible, and incomparable to other nanomaterials such as carbon nanotubes (Moon et al., 2011; Abdullah et al., 2015).

In this study, bio-composite from polyvinyl alcohol as a polymer matrix and cellulose nanocrystal was prepared to reinforce the composite. The CNC and PVA were characterized by scanning electron microscopy (SEM) while the thermal properties were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Polyvinyl alcohol (PVA), 89 % hydrolysed was purchased from R&M Chemicals in powder form. Cellulose nanocrystal (CNC) 6 wt. % was obtained CelluForce (CelluForce NCC®, Montreal, Canada) and distilled water. All chemicals and reagents were used as received without further purification.

Preparation of Polyvinyl Alcohol (PVA) solution

Preparation of 5 wt. % of PVA water solution by adding 5 g PVA in 100 mL of distilled water at 75°C for 1 hour under constant stirring. Then, the CNC solution with three different weight percentages was prepared by dissolving a 3 g, 6 g, and 9 g of CNC in 100 ml of deionized water, respectively, at 75 °C for 1 h under agitation. The CNC solution with 3 wt. %, 6 wt. %, 9 wt. % were prepared. The PVA/CNC solutions were then cast in glass petri dishes and dried at ambient conditions for 24 - 48 hr. The biocomposite thin films with different CNC content (3; 6; and 9 wt. %) were produced and denoted 3% PVA/CNC, 6% PVA/CNC, and 9% PVA/CNC. The biocomposite thin film was then stored in a zipper bag for further characterization.

Characterization of PVA/CNC Biocomposites

The morphology of PVA/CNC biocomposites was realized by using scanning electron microscopy (SEM). The thermal decomposition of the samples was measured by thermogravimetric analysis (TGA) & differential scanning calorimetry (DSC) using Mettler Toledo TGA/DSC 2- thermogravimetric analyzer. The samples were analyzed under a nitrogen atmosphere with a gas flow of 50 mL min^{-1} from 25 °C to 600 °C at a heating rate of 30 °C/min. The volume of the sample that was used is 1 mg of ca. measurement. The resulting data were evaluated by STARe Software to determine the composite's thermal degradation, phase transition, and thermal stability.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

SEM was used to observe the surface morphologies of the CNC, PVA, and the biocomposite thin films of the PVA/CNC. Figure 4.5 showed the morphological photographs of CNC, PVA, and 3% PVA/CNC, 6% PVA/CNC, and

9% PVA/CNC biocomposite thin films. Compared to the other sample of PVA/CNC thin films, the PVA had a smooth surface, indicating a distribution pattern of CNC with some aggregation, which increased with the increase in CNC percentages (Singh et al., 2018).
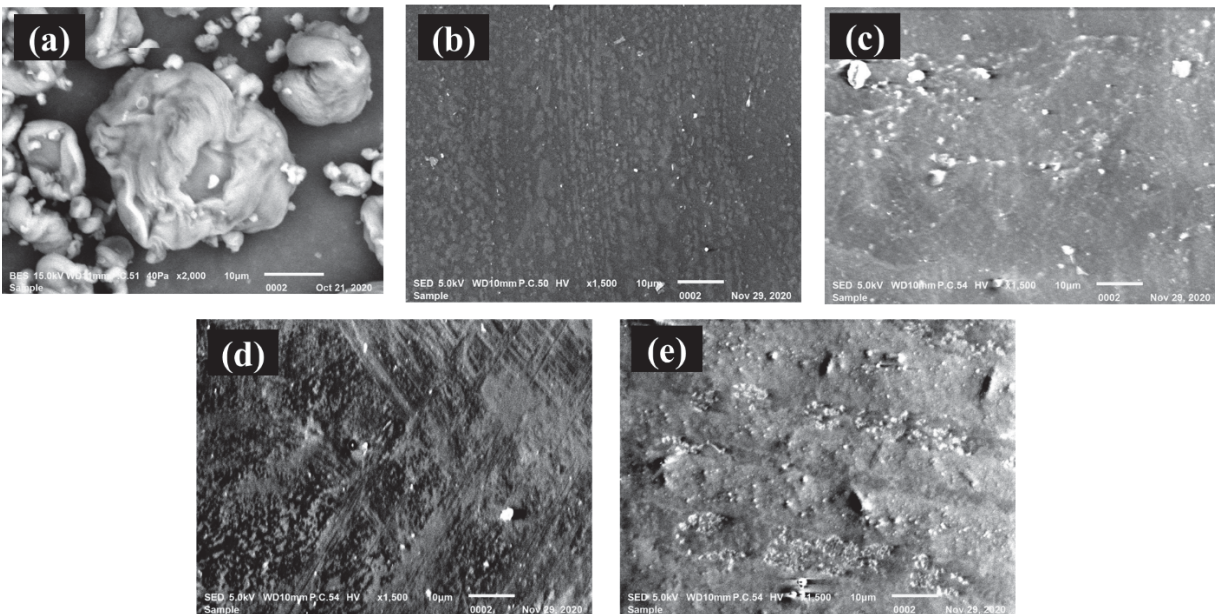

FIGURE 1. SEM images for (a) CNC (b) PVA (c) 3% PVA/CNC (d) 6% PVA/CNC, and (e) 9% PVA/CNC

Thermogravimetric Analysis (TGA)

TGA was used to study the thermal performance of the CNC, PVA, 3% PVA/CNC, 6% PVA/CNC, and 9% PVA/CNC biocomposite thin films as illustrated in Figure 2. Thermal degradation can be split into three main degradation stages. In the early stage, all of the samples show an initial mass loss starting in the region of 60°C to 150°C due to water evaporation (Voronova et al., 2015). The significant weight loss happened in the second stage (in between the region of 240°C) due to molecules and gaseous compounds (Wang et al., 2020). Lastly, in the degradation stage above 400°C, the product of the residues was decomposed into char residue and gas (Yang et al., 2010). Table 1 showed the onset thermal degradation (T_0), the maximum thermal decomposition temperature (T_{max}), and the amounts of the char residues of the CNC, PVA, PVA/CNC biocomposites derived from Figure 2.
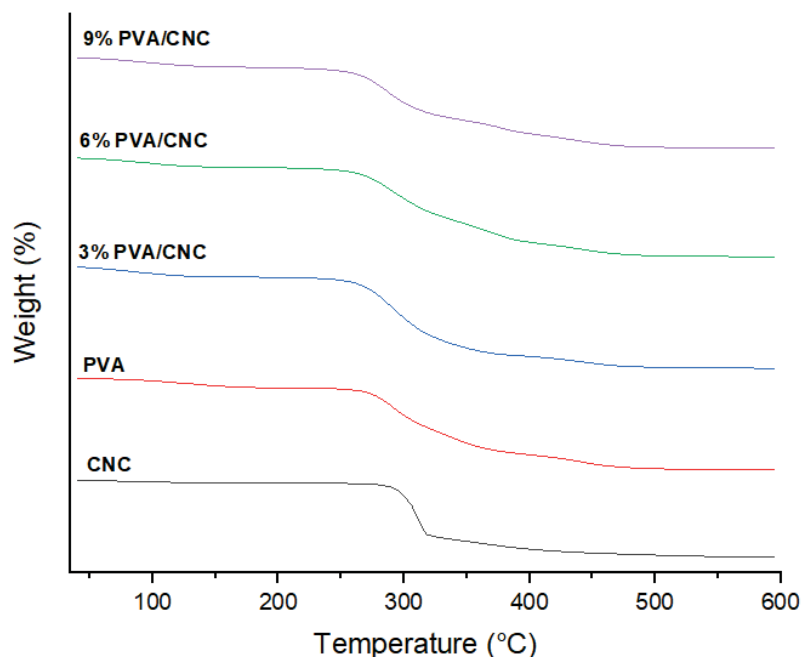
FIGURE 2. TGA curves for CNC, PVA, PVA/CNC biocomposites with different CNC content

As shown in Table 1, the highest onset thermal degradation temperature as high as 285°C compared to 225, 248, 254, and 250 °C for PVA, 3% PVA/CNC, 6% PVA/CNC, and 9% PVA/CNC, respectively. After CNC is added to PVA, the thermal stability was improved significantly (Song et al., 2018). Moreover, the effect addition of CNC to PVA increases the value of char residue. These results have proven the good thermal effect of CNC to PVA for the heating-resistant properties of the biocomposites.

TABLE 1. The thermal parameters of CNC, PVA, PVA/CNC biocomposites

Sample	T_0 (°C)	T_{max} (°C)	Char residue (%)
CNC	285	308	6.56
PVA	225	263	2.32
3% PVA/CNC	248	280	2.74
6% PVA/CNC	254	285	3.08
9% PVA/CNC	250	290	3.20

Differential scanning calorimetry (DSC)

DSC was carried out to study the effect of CNC on the thermal properties of the PVA/CNC biocomposite thin films; this has been presented graphically in Figure 3. Based on Figure 3, with the addition of CNC, all of the biocomposites peaks move to higher temperatures showing that CNC improves the thermal stability of the composites (Zhang et al., 2014). However, for the 6% PVA/CNC, the heat of fusion is lowered than the 3% PVA/CNC, and the 9% PVA/CNC, although very small, this is due to nanocomposites gets slightly absorbed over a range of temperature (Mandal & Chakrabarty, 2014).
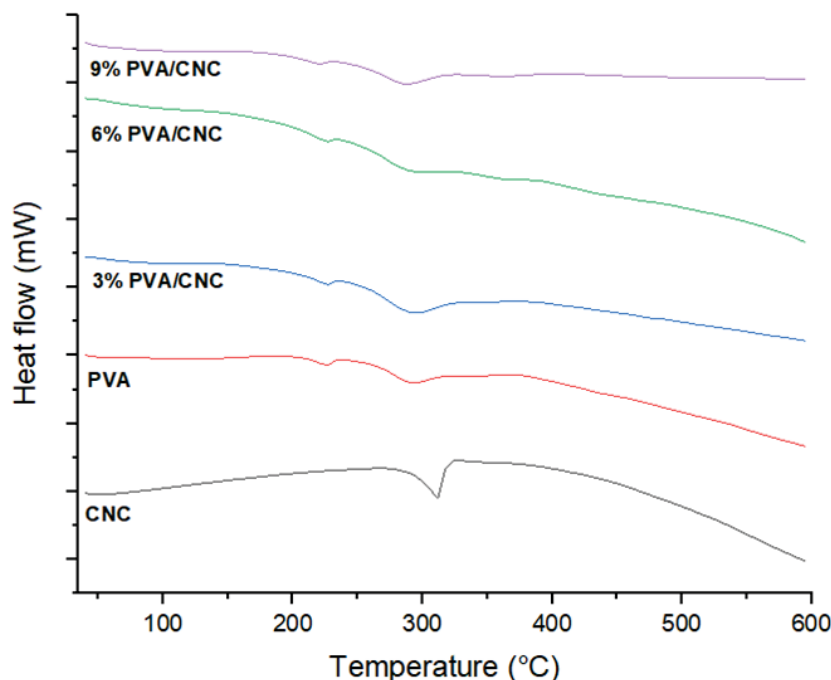
FIGURE 3. DSC curves for CNC, PVA, PVA/CNC biocomposites with different CNC content

Water has been observed to decrease the interactions of PVA chains and enhance chain mobility, and when CNC is added to PVA, the effect is amplified. As a result, higher filler loading and interfacial adhesion are thought to impede the regular arrangement of polymer chains to some extent, inhibiting PVA crystallisation.(Voronova et al., 2015). Table 2 exhibited the onset thermal degradation temperature (T_o), the melting temperature (T_m), and the heat of fusion (ΔH_m) of the CNC, PVA, PVA/CNC biocomposites.

TABLE 2. Results of DSC of CNC, PVA, PVA/CNC biocomposites

Sample	T_0 (°C)	T_m (°C)	ΔH_m (J/g)
CNC	281.99	307.78	-
PVA	205.05	221.53	-
3% PVA/CNC	205.86	220.95	37.75
6% PVA/CNC	200.46	219.57	31.11
9% PVA/CNC	199.65	216.30	45.35

CONCLUSION

In this research, PVA/CNC biocomposite thin films with different CNC concentrations (3 wt. %, 6 wt. %, and 9 wt. %) were successfully synthesized by using the solution casting technique. The morphology of the samples was different as depicted by SEM where the increased CNC content would display the higher surface roughness. Thermal degradation temperature was recorded at 254 °C for PVA/CNC 6 wt% and char residue also increased up to 3.2% for PVA/CNC 9 wt% compared to other samples as shown by TGA. DSC results exposed that with the addition of CNC, all of the biocomposites peaks move to higher temperatures indicating that CNC improves the thermal stability of the composites.

ACKNOWLEDGMENTS

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