Preparation and Characterization of Polyvinyl Alcohol-Based Composite Reinforced with Nanocellulose and Nanosilica

Yern Chee Ching,[a,*] Ashiqur Rahman,[a] Kuan Yong Ching,[a,b] Nazatul Liana Sukiman,[a] and Cheng Hock Chuah [c]

This work reported the thermomechanical and morphological properties of polyvinyl alcohol (PVA) nanocomposites reinforced with nanosilica and oil palm empty fruit bunches derived nanocellulose. The nanocomposites were characterized by mechanical, thermal, XRD, optical, and morphological studies. Uniformity dispersion of the nanofillers at a 3 wt% concentration has been shown by scanning electron microscopy, whereas the changes in crystallinity were demonstrated by X-ray diffraction analysis. Addition of nanosilica resulted in increased thermal stability of PVA/nanocellulose composites due to the reduction in mobility of the matrix molecules. Visible light transmission showed that the addition of 0.5 wt% nanosilica only slightly reduced the light transmission of PVA/nanocellulose composites with 3 wt% nanocellulose. The addition of a small concentration of nanosilica successfully improved the tensile and modulus properties of PVA/nanocellulose composite films. The increases in tensile strength and thermal stability were evidence of a nanosilica contribution in PVA/nanocellulose composites, inducing reinforcement, as detected by the thermomechanical properties.

*Contact information: a: Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; b: Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, United Kingdom; c: Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia; *Corresponding author: chingyc@um.edu.my*

INTRODUCTION

The use of natural fibers as reinforcing agents in composites has increased in recent years as global concerns over environmental issues rise. One of the common types of natural fibers is cellulose, an abundant natural resource. Cellulose contains nanosize fibrils that can be classified into a crystalline part (nanocellulose) and an amorphous part (Cho and Park 2011; Ching and Ng 2014). The cellulose chains are linked by hydrogen bonds between the hydroxyl groups that yield high stiffness and structural strength to the material. It has been reported that native cellulose crystal regions and tunicin whiskers have elastic modulii of 167.5 GPa (Tashiro and Kobayashi 1991) and 143 GPa (Eichhorn *et al.* 2010), respectively, compared to e-glass fiber with an elastic modulus of 73 GPa (Saheb and Jog 1999). The cellulosic materials are generally cheaper to produce, require less energy consumption, and are low-density, biodegradable, and biocompatible. The specific strength is also higher, hence it is less susceptible to fracture during processing (Kalaitzidou *et al.* 2007; Mandal and Chakrabarty 2011, 2014). Furthermore, the disposal of the composites can be done by combustion, which converts them into H_2O and CO_2

(Azizi Samir *et al.* 2005). This utility increases the potential of nanocellulose as a source of nanosize reinforcing materials in composites. Polymer nanocomposites consist of nanometric particles, known as nanofillers, in a polymeric matrix. The addition of nanofillers could yield composites with enhanced properties to suit the current technological development trends (Whitesides 2005). The typical inorganic filler-reinforced nanocomposites possess good mechanical properties, such as high temperature creep resistance, stiffness, hardness, and strength (Richardson and Sauer 1976; Menendez and White 1984; Cogswell 1987; Nguyen and Ishida 1987; Malik *et al.* 1988).

The extracted cellulose fibers are processed into nanosize fibers that increase the reinforcement of polymer matrices compared to conventional cellulose fibers. This strength is contributed by the crystallinity, surface area, and active interfaces of the nanometer size fibers (Panaitescu *et al.* 2008). Crystalline cellulose nanofibers are typically known as nanowhiskers, with an elastic modulus range of 120 to 150 GPa (Šturcová *et al*. 2005). The cellulose nanowhiskers tend to self-associate in response to the strongly-interacting surface hydroxyl groups (van den Berg *et al.* 2007). This feature is useful in the formation of load-bearing percolating architectures within the polymer matrix (Chun *et al.* 2011). The outstanding reinforcing ability is due to the formation of a rigid network of nanowhiskers, resulting from hydrogen bonding between the nanowhiskers (Capadona *et al.* 2009) and van der Waals interactions (van den Berg *et al.* 2007). However, interactions between the nanowhiskers can lead to aggregation during fabrication (Schroers *et al.* 2004). Such aggregation generally decreases the mechanical properties of the composites from the expected values (Capadona *et al.* 2008).

Nanocellulose- or nanofiber-reinforced PVA is a biodegradable polymer composite with good tensile strength and flexibility, as well as outstanding film forming and emulsifying properties (Roohani *et al.* 2008). The biodegradability of PVA enables the production of green nanocomposites when cellulosic materials are used as fillers. In recent years, nanomaterials such as nanosilica have been widely used in various applications, particularly in the medical sector (Nabeshi *et al.* 2011). For instance, nanosilica is used as a fluorophore carrier (Ow *et al.* 2005; Ali *et al.* 2014), for the controlled release of drug molecules, as an antiseptic agent (Verraedt *et al.* 2010; Depla *et al.* 2011), and as a biosensor (Monton *et al.* 2011). There are various silanol groups in the nanosilica that can change the crystalline behaviors of the polymeric matrix, increase hydrogen bonding effects, and affect the fluorescent properties of composite end products. Furthermore, thermal resistance is the most significant property of polymeric materials, as it controls their spectral stability, mechanical properties, shelf lives, and durability (Cho *et al.* 2003; Jin *et al.* 2003; Peng *et al.* 2006; Peng and Kong 2007; Saat and Johan 2014). In this paper, the modification of the properties of PVA by the incorporation of highly reactive nanocellulose, isolated from oil palm empty fruit bunches (OPEFB), and nanosilica were studied. The effects of nanocellulose and nanosilica addition on the thermomechanical, optical, and morphological properties of PVA were investigated.

MATERIALS AND METHODS

Materials

Poly(vinyl alcohol) (Kuraray PVA-220S) was obtained from Kuraray Co., Ltd. (Singapore). Oil palm empty fruit bunch (OPEFB) fibers were purchased from Sabutek

Sdn. Bhd., Malaysia. OPEFB underwent a sieving process to obtain fiber particles in the range of 4 to 6 mm. The fiber particles were then sent for grinding and sieving to obtain powder with a diameter size between 100 and 150 µm. Hydrophobic fumed silica, with a specific surface area of 130 m^2g^{-1} and a mean particle size of 16 nm (Aerosil R972), from Degussa Chemicals was used for the preparation of nanocomposites. Hydrogen peroxide and formic acid were obtained from Fisher Scientific (USA). All the other solvents and chemicals (analytical grade) were used as received.

Pretreatment of OPEFB Fibers

OPEFB fibers were first washed several times with 1.0 wt% washing detergent to remove all the contamination and dirt. Next, the OPEFB raw fiber was dried in an oven (SOV 70B, Thermoline) at 100 ±2 °C until constant weight was achieved. The fiber was then dewaxed with ethanol (70% v/v) using a Soxhlet apparatus (Favorit) for 6 h. This step was followed by washing the dewaxed fibers with distilled water to remove the traces of alcohol. Later, the dewaxed fibers were suspended in a mixture of 100 mL of 10% NaOH and 100 mL of 10% H_2O_2. The mixture was autoclaved at 1.5 bar and 120 °C for 1 h. Finally, the fibers were separated from the dark brown supernatant and washed thoroughly with clean water.

Extraction of OPEFB Cellulose

During the extraction process, the fibers were soaked in a mixture of 20% formic acid and 10% hydrogen peroxide, which was prepared in a 1:1 ratio (v/v). The mixture was placed in a water bath at 85 °C for 2 h (Jahan *et al*. 2011, 2012). The delignified fibers were sent through a filtration process, and the samples were washed thoroughly with 10% formic acid prior to cleaning with distilled water. The extracted cellulose was light yellow in color. The cellulose was prepared as a suspension by re-suspending it in 10% hydrogen peroxide (pH 11) at 60 °C for a duration of 90 min.

Preparation of PVA/Nanocellulose Film Reinforced with Nanosilica

PVA-based composite films were prepared by the solution casting method. A 10 wt% aqueous solution of PVA was prepared by stirring at 1,000 rpm at room temperature to avoid clumps. Subsequently, the PVA solution was continuously stirred at 90 °C for 2 h, then sonicated for 5 min. Various compositions of PVA/nanocellulose composites were prepared with a nanocellulose content ranging from 1 to 7 wt%. 0.5 wt% of nanosilica was introduced into the suspension and stirred for 1 h. The solutions were then poured into a mold and dried at room temperature for 7 days before being demolded. The thickness of the films was controlled to approximately 150 µm. The resulting thin composite films were then dried in an oven at 50 °C for 1 day before characterization.

Characterization Methods

The mechanical properties of the composite sheets were tested at a crosshead speed of 10 mm/min using a universal testing machine (model AG-IS, Shimadzu, Japan). For each test and each type of composite, five samples were tested. Thermal decomposition analysis was observed using Mettler Toledo 851^e TGA/SDTA (Mettler Toledo, Switzerland). The samples were heated from 30 to 600 °C, with a scan rate of 20 °C/min. A sample of 5 to 10 mg was used for each run, and changes in weight were recorded. X-ray diffraction analysis of the nanocomposite samples was performed using

an X-ray diffractometer (Siemens D5000). Experiments were conducted using a voltage of 40 kV, and an anode current of 40 mA was applied. Cu Kα radiation ($\lambda = 0.15405$ nm) was used in a continuous scanning mode with a 0.02 step size and a 0.5 second set time for collecting the data in a 2θ scan range of 4° to 80°. Optical transmission properties of the cellulose and OPEFB suspensions were measured by a Varian-Cary-50 UV-Vis spectrometer in the wavelength range of 200 to 800 nm.

The cross-section of the fracture surface morphology of the samples was examined by using a scanning electron microscope (Hitachi S-3400N, Thermo Scientific) with an accelerating voltage of 10 kV. The composite film was soaked in nitrogen liquid for 10 seconds. Then, the sample was fractured immediately to get a freeze-fractured surface. Before the SEM observation was done on the sample film, the cross-section surface of the fractured film was sputter-coated with a gold layer for 1 h to avoid electrostatic charging and poor image resolution.

RESULTS AND DISCUSSION

Mechanical Properties

Tensile strength

The tensile strength of PVA and the nanomaterials-reinforced PVA composites is presented in Fig. 1(a). Significant improvement in the tensile modulus of PVA was achieved *via* the inclusion of small amounts (1 wt%) of nanocellulose in the PVA/nanocellulose composite. The tensile strength increased with increasing nanocellulose loading from 0 to 7 wt%. The addition of 0.5 wt% of nanosilica to these PVA/nanocellulose composites further increased the tensile strength of the nanocomposites. The increase in tensile strength was due to the crystalline nature of nanosilica particles. However, the tensile strength exhibited very little tendency to increase when the incorporation of nanocellulose exceeded 5 wt%. The same observation has been reported by previous researchers (Bhatnagar and Sain 2005; Sturcova *et al*. 2005; Qua *et al*. 2009; Ibrahim *et al.* 2010). This behavior could be explained by the fact that small amounts of nanofillers allowed the creation of strong hydrogen bonds between nanocellulose and PVA, which contributed to good dispersion of nanofillers in the PVA matrix and resulted in superior load transfer from the matrix to the nanocellulose and nanosilica reinforcements.
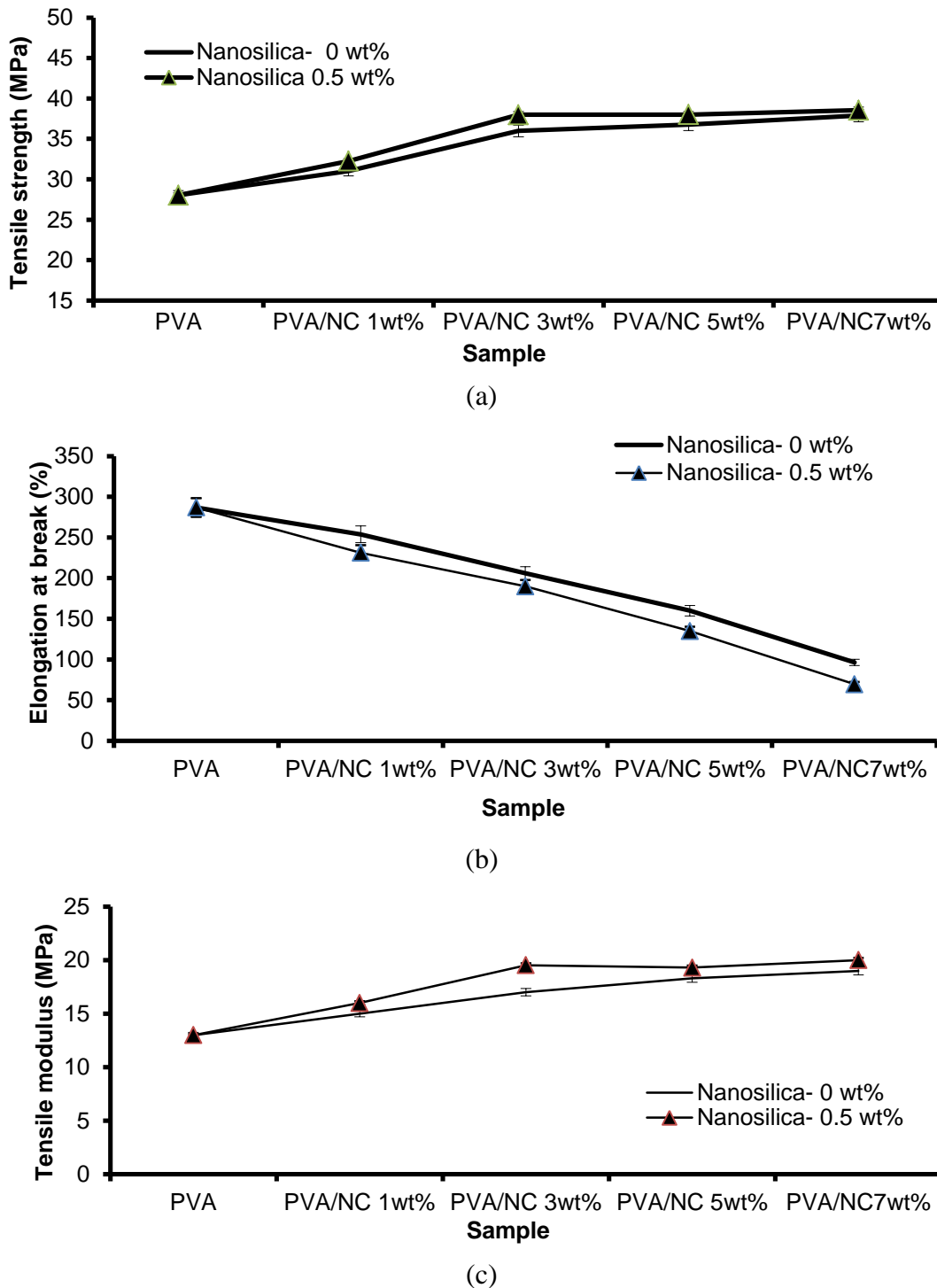
(a)

(b)

(c)

Fig. 1. Effect of nanosilica on PVA/nanocellulose composite (a) tensile strength, (b) % elongation at break, and (c) tensile modulus

Elongation at break

Figure 1(b) shows that incorporation of the nanocellulose resulted in a severe reduction in the elongation at break of polyvinyl alcohol. The further increase of nanocellulose content led to an even more significant decrease in elongation, to as low as a 96% reduction for a composite with 7 wt% nanocellulose content. The elongation at

break was decreased further with the addition of 0.5 wt% of nanosilica. The increase in nanofillers content, which led to the decrease in elongation percentage, is similar to other filled polymer composites (Alemda and Sain 2008; Jonoobi *et al*. 2010). With the addition of nanomaterials, PVA might form either intramolecular or intermolecular hydrogen bonds with the nanofillers. The hydrogen bonding between the nanocellulose and PVA matrix resulted in a decrement in the elongation at break but gains in crystallinity. According to Cheng *et al*. (2014), low deformability of composites under tensile loads is due to the high interfacial adhesion between the matrix and nanofillers. Since the nanocellulose and nanosilica were not as deformable as the matrix, the strong interactions between the nanoparticles and matrix molecules did not allow PVA to elongate.

Tensile modulus

Figure 1(c) shows the effect of the introduction of nanosilica on the tensile modulus of PVA reinforced with various nanocellulose contents. Significant improvement in the tensile modulus of PVA was achieved via the inclusion of even small amounts (1 wt%) of nanocellulose in the PVA/nanocellulose composite. A further increase in the tensile modulus was observed with the introduction of nanosilica; the inherent chain stiffness and rigidity of nanosilica resulted in the restriction of movement by the nanosilica in PVA/nanocellulose macromolecules. The homogeneous distribution of the nanofillers and high interfacial surface area between the nanofillers and the PVA matrix might have also led to a significant increase in the tensile modulus. The PVA composite with 3 wt% of nanocellulose and 0.5 wt% of nanosilica exhibited the highest increase in tensile modulus compared to the other composites. With a further increase in nanocellulose content up to 7 wt%, it was found that the increase in tensile modulus was not significant in both the PVA/nanocellulose and the PVA/nanocellulose/nanosilica composite systems. This result indicated that nanosilica, with high surface area, can provide improved tensile modulus properties for nanocomposite films which have a good distribution of nanocellulose filler contents up to 5 wt%.

Morphological Analysis

The fractured surfaces of pure PVA and nanomaterials-reinforced PVA composite films were examined using SEM, as shown in Fig. 2. This examination was important in determining the failure mechanisms and the interactions, thus, mechanical properties, between the matrix and filler (Haafiz *et al*. 2013). Compared to the pure PVA film, the morphology of the PVA/nanocellulose and PVA/nanocellulose/nanosilica composites could be easily identified.

After nanocellulose (Fig. 2(b)) and nanocellulose/nanosilica (Fig. 2(c)) were added into the PVA matrix, the fractured surface cross-section of the composites showed disoriented protrusions. This result is a typical fractographic feature of a rigid fracture, and such observation was due to the agglomerated cellulose protruding out from the fractured surface (Haafiz *et al*. 2013). This protrusion explains the deterioration of the elongation at break of PVA composites compared to pure PVA.
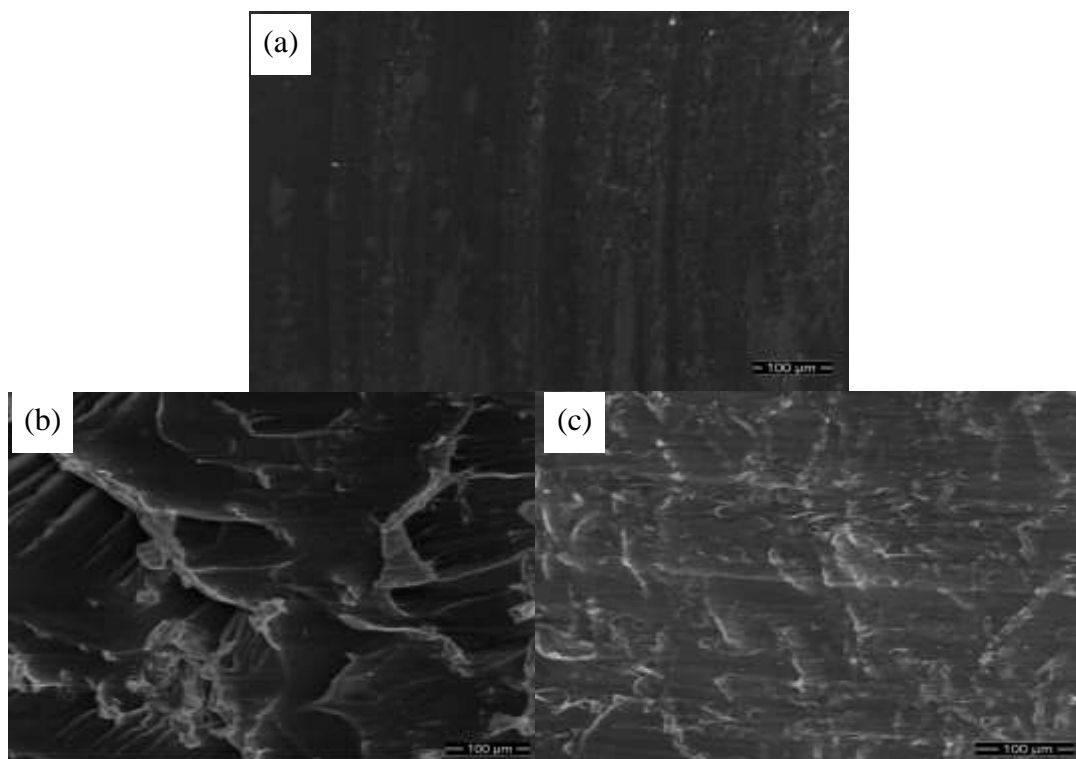
Fig. 2. SEM images of a fractured surface of (a) PVA, (b) PVA composites reinforced with nanocellulose (3.0 wt%), and (c) PVA composites reinforced with both nanocellulose (3.0 wt%) and nanosilica (0.5 wt%).

In this study, larger aggregates were formed on the fractured surface of the PVA reinforced with nanocellulose. These aggregates may have affected the mechanical performance of the composite (Chen *et al.* 2012). A few granules and a more homogeneous distribution of the nanofillers in the PVA composite were observed with the introduction of 0.5 wt% of nanosilica, as shown in Fig. 2(c). This result implied that better interfacial adhesion was achieved with the introduction of nanosilica to the PVA/cellulose composite. In this study, the tensile modulus of PVA composites improved significantly due to the stiffening phenomena of nanofiller materials (especially nanosilica materials), which is a typical filled polymer behaviour (Haafiz *et al*. 2013).

X-Ray Diffraction

The XRD patterns of PVA, nanocellulose, nanosilica, PVA/nanocellulose, and PVA/nanocellulose/nanosilica composite systems are compared in Fig. 3. A major peak was observed at 19.5°, representing the (110) plane of the semicrystalline region of partially hydrolysed PVA (Sriupayo *et al*. 2005). The intensity of the (110) plane in PVA was comparatively higher due to the hydroxyl groups in its side-chains (Shao *et al*. 2003). The incorporation of nanocellulose into PVA did not deteriorate the intensity of the (110) plane due to the presence of crystalline cellulose from nanocellulose in the (200) plane. However, it was found that the crystallinity of the PVA/nanocellulose composite with the presence of 3.0 wt% nanocellulose was lower than the neat PVA matrix; the original crystallinity of the PVA matrix was never achieved in the nanocellulose-reinforced PVA composite due to heterogeneous phase nucleation in the synthesizing solution (Mandal and Chakrabarty 2014). The peak for the PVA/nanocellulose/nanosilica composite

systems was more prominent than that of the PVA/nanocellulose composite systems, as the presence of nanosilica increased the overall crystallinity of the composite. With the introduction of 0.5 wt% of nanosilica, the high crystallinity of nanosilica further increased the number of nucleating agents and bundled together a number of small crystallites in the composite.
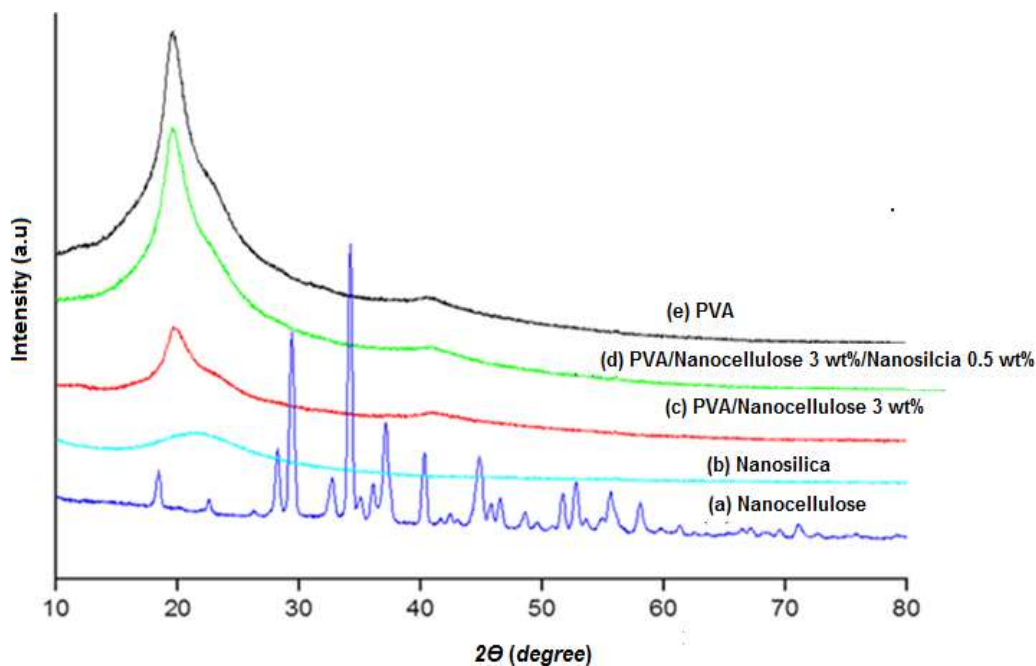

Fig. 3. Comparison of XRD patterns between pure PVA, nanofillers, and PVA composites reinforced with nanomaterials

Optical Transparency Analysis

Fig. 4 shows the UV-Vis spectra of PVA and nanocellulose- and nanosilica-reinforced PVA composites. The addition of nanocellulose reduced the visible transmission of the PVA matrix. The transmittance of the pure PVA composite was higher than the PVA/nanocellulose composite, possibly because the agglomerations of nanocellulose became a barrier to the penetration of light. The visible light transmission was further reduced with the addition of 0.5 wt% of nanosilica into the PVA/ nanocellulose composite. The higher loading of nanomaterials increased the probability of these nanomaterials to interact and aggregate within the PVA matrix, leading to this reduction in light transmission.
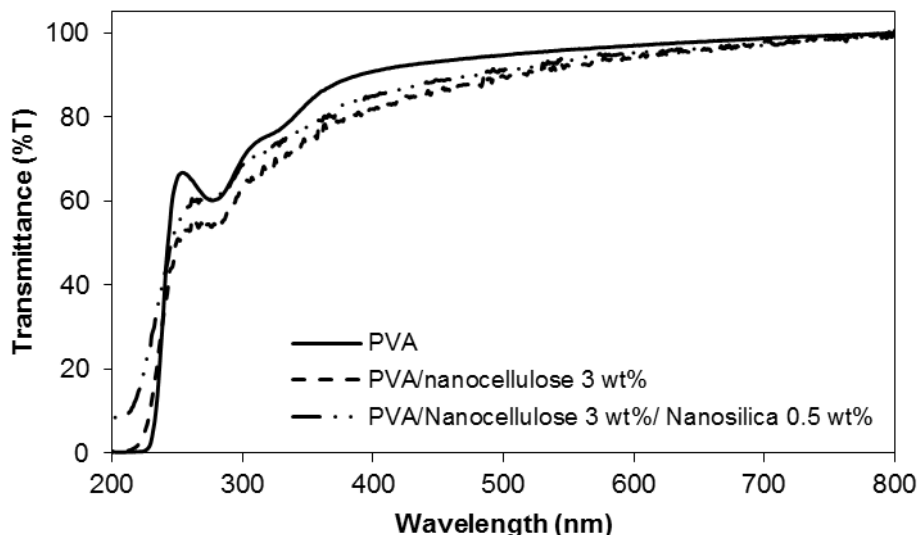
Fig. 4. Comparison of UV-Vis transmittance spectra of PVA, PVA composites reinforced with nanocellulose, and PVA composites reinforced with both nanocellulose and nanosilica

Thermogravimetric Analysis

The thermal properties of PVA reinforced with nanocellulose and nanosilica are shown in Fig. 5. In the first stage of the degradation (70 to 150 °C), PVA/nanocellulose composites experienced a higher weight loss than neat PVA. The reduction of thermal stability at this point was due to the incorporation of nanocellulose, which has a lower thermal stability compared to the PVA matrix (Ng *et al*, 2014). PVA composites became more thermally stable during the second (300 to 450 °C) and third (above 500 °C) stages of the TGA thermograms curve. The thermal stability of the PVA/nanocellulose composites increased with the introduction of small amounts of nanosilica. This result proved that the thermal properties of cellulose-reinforced PVA can be improved with a low nanosilica content, possibly due to the high thermal stability behavior of nanosilica. The high specific surface area of nanosilica also contributed to the greater interactions between the nanofillers and the PVA matrix, which led to the enhancement of both interfacial bonding and thermal stability. Thus, thermal stability of PVA/nanocellulose was induced by the reinforcement of small amounts of nanosilica. This result also indicated that the well-dispersed nanosilica particles successfully acted as effective nucleation agents in the PVA/nanocellulose composites.
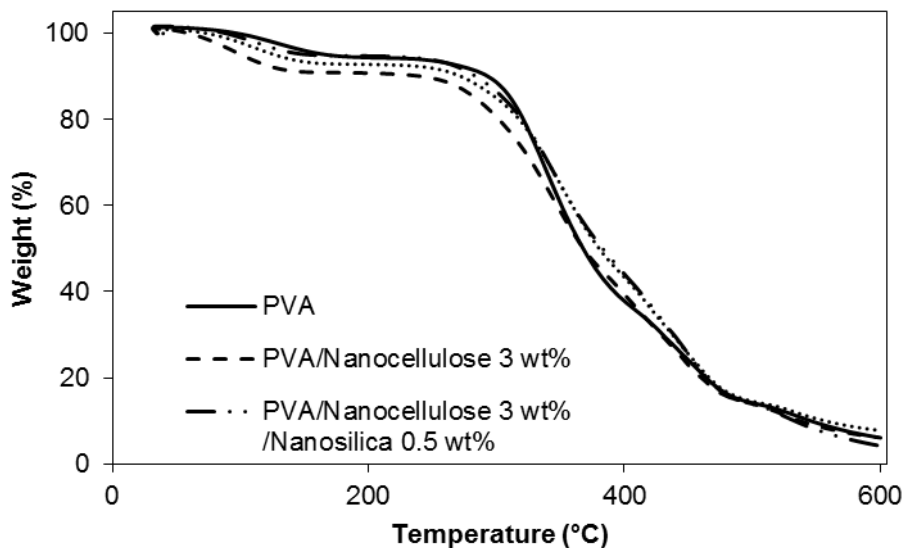
Fig. 5. TGA thermograms of PVA, a composite of PVA/3 wt% nanocellulose, and a composite of PVA/3 wt% nanocellulose/0.5 wt% nanosilica

CONCLUSIONS

1. Nanocomposites of PVA reinforced with nanocellulose and nanosilica were prepared using the film casting technique. The effect of nanosilica on the mechanical, thermal, and optical properties of PVA/nanocellulose composites was investigated. The composites exhibited increased tensile strength primarily due to the increase in nanocellulose content, the introduction of secondary reinforcement, and the restriction of mobility of the PVA/nanocellulose composites due to the addition of nanosilica particles.

2. The tensile strength and tensile modulus were found to be optimized at 3 wt% of nanocellulose. With the introduction of small amounts of nanosilica, remarkable improvements in the tensile and modulus properties were achieved for PVA composites at a nanocellulose content of up to 5 wt%.

3. The addition of 0.5 wt% of nanosilica successfully improved the thermal stability and crystallinity of the PVA/nanocellulose composites.

4. In this study, the nanomaterials-reinforced PVA composites containing 3 wt% of nanocellulose and 0.5 wt% of nanosilica presented significant improvements in thermomechanical properties and retained good optical properties due to effective dispersion and polymer-filler interaction.

ACKNOWLEDGMENTS

bioresources.com

REFERENCES CITED

Alemda, A., and Sain, M. (2008). "Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties," *Composites Science and Technology* 68(2), 557-565. DOI:10.1016/j.compscitech.2007.05.044

Ali, M. E., Yong, C. K., Ching, Y. C., Chuah, C. H., and Liou, N. S. (2014). "Effect of single and double stage chemically treated kenaf fibers on mechanical properties of polyvinyl alcohol film," *BioResources* 10(1), 822-838. DOI: 10.15376/biores.10.1.822-838

Azizi Samir, M. A. S., Alloin, F., and Dufresne, A. (2005). "Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field," *Biomacromolecules* 6(2), 612-626. DOI: 10.1021/bm0493685..

Bhatnagar, A., and Sain, M. (2005). "Processing of cellulose nanofiber-reinforced composites," *Journal of Reinforced Plastics and Composites* 24(12), 1259-1268. DOI: 10.1177/0731684405049864.

Capadona, J. R., Shanmuganathan, K., Trittschuh, S., Seidel, S., Rowan, S. J., and Weder, C. (2009). "Polymer nanocomposites with nanowhiskers isolated from microcrystalline cellulose," *Biomacromolecules* 10(4), 712-716. DOI: 10.1021/bm8010903.

Capadona, J. R., Shanmuganathan, K., Tyler, D. J., Rowan, S. J., and Weder, C. (2008). "Stimuli-responsive polymer nanocomposites inspired by the sea cucumber dermis," *Science* 319(5868), 1370-1374. DOI: 10.1126/science.1153307.

Ching, Y. C., and Ng, T. S. (2014). "Effect of preparation conditions on cellulose from oil palm empty fruit bunch fiber," *BioResources* 9(4), 6373-6385. DOI: 10.15376/biores.9.4.6373-6385

Cheng, S., Panthapulakkal, S., Sain, M., and Asiri, A. (2014). "*Aloe vera* rind cellulose nanofibers-reinforced films," *Journal of Applied Polymer Science* 131(15), Article ID40592. DOI: 10.1155/2014/903498

Cho, H. J., Jung, B. -J., Cho, N. S., Lee, J., and Shim, H. -K. (2003). "Synthesis and characterization of thermally stable blue light-emitting polyfluorenes containing siloxane bridges," *Macromolecules* 36(18), 6704-6710. DOI: 10.1021/ma034622r

Cho, M. J., and Park, B. D. (2011). "Tensile and thermal properties of nanocellulose-reinforced poly (vinyl alcohol) nanocomposites," *Journal of Industrial and Engineering Chemistry* 17(1), 36-40. DOI:10.1016/j.jiec.2010.10.006.

Chun, S. -J., Lee, S. -Y., Doh, G. -H., Lee, S., and Kim, J. H. (2011). "Preparation of ultrastrength nanopapers using cellulose nanofibrils," *Journal of Industrial and Engineering Chemistry* 17(3), 521-526. DOI: 10.1016/j.jiec.2010.10.022

Cogswell, F. (1987). "The processing science of thermoplastic structural composites," *International Polymer Processing* 1(4), 157-165. DOI: 10.3139/217.870157.

Depla, A., Lesthaeghe, D., van Erp, T. S., Aerts, A., Houthoofd, K., Fan, F., Li, C., Van Speybroeck, V., Waroquier, M., and Kirschhock, C. E. (2011). "29Si NMR and UV−Raman investigation of initial oligomerization reaction pathways in acid-catalyzed silica sol-gel chemistry," *The Journal of Physical Chemistry C* 115(9), 3562-3571. DOI: 10.1021/jp109901v.

Eichhorn, S., Dufresne, A., Aranguren, M., Marcovich, N., Capadona, J., Rowan, S., Weder, C., Thielemans, W., Roman, M., and Renneckar, S. (2010). "Review: Current international research into cellulose nanofibres and nanocomposites," *Journal of Materials Science* 45(1), 1-33. DOI: 10.1155/2011/837875.

Ibrahim, M. M., El-Zawawy, W. K., and Nassar, M. A. (2010). "Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films," *Carbohydrate Polymers* 79(3), 694-699. DOI:10.1016/j.carbpol.2009.09.030

Jahan, M. S., Saeed, A., He, Z, and Ni, Y. (2011). "Jute as raw materials for the preparation of microcrystalline cellulose," *Cellulose* 18 (2), 451-459. DOI:10.1007/s.10570-010-9481-z.

Jahan, M. S., Saeed, A., and Ni, Y. (2012). "Extraction of cellulose microfibrils," *Lignocellulose* 1(3), 185-195.

Jin, J., Smith, D. W., Topping, C. M., Suresh, S., Chen, S., Foulger, S. H., Rice, N., Nebo, J., and Mojazza, B. H. (2003). "Synthesis and characterization of phenylphosphine oxide containing perfluorocyclobutyl aromatic ether polymers for potential space applications," *Macromolecules* 36(24), 9000-9004. DOI: 10.1021/ma035241g.

Jonoobi, M., Harun, J., Mathew, A. P., and Oksman, K. (2010). "Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion," *Composites Science and Technology* 70(12), 1742-1747. DOI: 10.1016/j.compscitech.2010.07.005.

Kalaitzidou, K., Fukushima, H., and Drzal, L. T. (2007). "Mechanical properties and morphological characterization of exfoliated graphite–polypropylene nanocomposites," *Composites Part A: Applied Science and Manufacturing* 38(7), 1675-1682. DOI:10.1016/j.compositesa.2007.02.003.

Malik, T. M., Carreau, P. J., Grmela, M., and Dufresne, A. (1988). "Mechanical and rheological properties of carbon black filled polyethylene," *Polymer Composites* 9(6), 412-418. DOI: 10.1002/pc.750090607.

Mandal, A., and Chakrabarty, D. (2011). "Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization," *Carbohydrate Polymers* 86(3), 1291-1299. DOI:10.1016/j.carbpol.2011.06.030.

Mandal, A., and Chakrabarty, D. (2014). "Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly (vinyl alcohol) and nanocellulose from sugarcane bagasse," *Journal of Industrial and Engineering Chemistry* 20(2), 462-473. DOI:10.1016/j.carbpol.2011.06.030.

Menendez, H., and White, J. L. (1984). "A wide-angle X-ray diffraction method of determining chopped fiber orientation in composites with application to extrusion through dies," *Polymer Engineering & Science* 24(13), 1051-1055. DOI: 10.1002/pen.760241310.

Monton, M. R. N., Forsberg, E. M., and Brennan, J. D. (2011). "Tailoring sol–gel-derived silica materials for optical biosensing," *Chemistry of Materials* 24(5), 796-811. DOI: 10.1021/cm202798e.

Nabeshi, H., Yoshikawa, T., Arimori, A., Yoshida, T., Tochigi, S., Hirai, T., Akase, T., Nagano, K., Abe, Y., and Kamada, H. (2011). "Effect of surface properties of silica nanoparticles on their cytotoxicity and cellular distribution in murine macrophages," *Nanoscale Res. Lett.* 6(1), 93. DOI:10.1186/1556-276X-6-93.

Ng, T. S., Ching, Y. C., Awanis, N., Ishenny, N., Rahman, M. R. (2014). "Effect of bleaching condition on thermal properties and UV-transmittance of PVA/cellulose biocomposites," *Mater. Res. Innov*. 18, 400-404.

Nguyen, H. X., and Ishida, H. (1987). "Poly(aryl-ether-ether-ketone) and its advanced composites: A review," *Polymer Composites* 8(2), 57-73. DOI:10.1002/pc.750080202

Ow, H., Larson, D. R., Srivastava, M., Baird, B. A., Webb, W. W., and Wiesner, U. (2005). "Bright and stable core-shell fluorescent silica nanoparticles," *Nano Res. Lett.* 5(1), 113-117. DOI: 10.1021/nl0482478.

Panaitescu, D. M., Vuluga, D. M., Paven, H., Iorga, M. D., Ghiurea, M., Matasaru, I., and Nechita, P. (2008). "Properties of polymer composites with cellulose microfibrils," *Molecular Crystals and Liquid Crystals* 484(1), 86/[452]-98/[464]. DOI: 10.5772/14682.

Peng, Z., and Kong, L. X. (2007). "A thermal degradation mechanism of polyvinyl alcohol/silica nanocomposites," *Polymer Degradation and Stability* 92(6), 1061-1071. DOI:10.1016/j.polymdegradstab.2007.02.012.

Peng, Z., Kong, L. X., Li, S. -D., and Spiridonov, P. (2006). "Poly (vinyl alcohol)/silica nanocomposites: morphology and thermal degradation kinetics," *Journal of Nanoscience and Nanotechnology* 6(12), 3934-3938. DOI:10.1016/j.polymdegradstab.2007.02.012.

Qua, E., Hornsby, P., Sharma, H., Lyons, G., and McCall, R. (2009). "Preparation and characterization of poly (vinyl alcohol) nanocomposites made from cellulose nanofibers," *Journal of Applied Polymer Science* 113(4), 2238-2247. DOI: 10.1002/app.30116.

Richardson, G. C., and Sauer, J. A. (1976). "Effect of reinforcement type on the mechanical properties of polypropylene composites," *Polymer Engineering & Science* 16(4), 252-256. DOI: 10.1002/pen.760160406.

Roohani, M., Habibi, Y., Belgacem, N. M., Ebrahim, G., Karimi, A. N., and Dufresne, A. (2008). "Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites," *European Polymer Journal* 44(8), 2489-2498. DOI:10.1016/j.eurpolymj.2008.05.024.

Saat, A. M., and Johan, M. R. (2014). "The surface structure and thermal properties of novel polymer composite films based on partially phosphorylated poly(vinyl alcohol) with aluminium phosphate," *Scientific World Journal,* Article ID 439839, http://dx.doi.org/10.1155/2014/439839

Shao, C., Kim, H. -Y., Gong, J., Ding, B., Lee, D.-R., and Park, S. -J. (2003). "Fiber mats of poly(vinyl alcohol)/silica composite via electrospinning," *Materials Letters* 57(9-10), 1579-1584. DOI:10.1016/S0167-577X(02)01036-4

Saheb, D. N., and Jog, J. (1999). "Natural fiber polymer composites: A review," *Advances in Polymer Technology* 18(4), 351-363. DOI: 10.1002/(SICI)1098-2329(199924).

Schroers, M., Kokil, A., and Weder, C. (2004). "Solid polymer electrolytes based on nanocomposites of ethylene oxide–epichlorohydrin copolymers and cellulose whiskers," *Journal of Applied Polymer Science* 93(6), 2883-2888. DOI: 10.1002/app.20870.

Sriupayo, J., Supaphol, P., Blackwell, J., and Rujiravanit, R. (2005). "Preparation and characterization of α-chitin whisker-reinforced poly (vinyl alcohol) nanocomposite films with or without heat treatment," *Polymer* 46(15), 5637-5644. DOI:10.1016/j.polymer.2005.04.069.

Sturcova, A., Davies, G. R., and Eichhorn, S. J. (2005). "Elastic modulus and stress-transfer properties of tunicate cellulose whiskers," *Biomacromolecules* 6(2), 1055-1061. DOI: 10.1021/bm049291k.

Tashiro, K., and Kobayashi, M. (1991). "Theoretical evaluation of three-dimensional elastic constants of native and regenerated celluloses: Role of hydrogen bonds," *Polymer* 32(8), 1516-1526. DOI: 10.1016/0032-3861(91)90435-L.

van den Berg, O., Schroeter, M., Capadona, J. R., and Weder, C. (2007). "Nanocomposites based on cellulose whiskers and (semi) conducting conjugated polymers," *Journal of Materials Chemistry* 17(26), 2746-2753. DOI: 10.1039/B700878C.

Verraedt, E., Pendela, M., Adams, E., Hoogmartens, J., and Martens, J. (2010). "Controlled release of chlorhexidine from amorphous microporous silica," *Journal of Controlled Release* 142(1), 47-52. DOI: 10.1016/j.ijpharm.2011.06.053.

Whitesides, G. M. (2005). "Nanoscience, nanotechnology, and chemistry," *Small* 1(2), 172-179. DOI: 10.1002/smll.200400130.