Effects of Silane Surface Treatment of Cellulose Nanocrystals on the Tensile Properties of Cellulose-Polyvinyl Chloride Nanocomposite
(Kesan Rawatan Permukaan Nanohablur Selulosa dengan Silana ke atas Sifat Regangan Nanokomposit Selulosa-Polivinilklorida)

Rasha M. Sheltami, Hanieh Kargarzadeh & Ibrahim Abdullah*

ABSTRACT

Cellulose nanocrystals (CNC) from mengkuang *leaves* (Pandanus tectorius) *were investigated as potential reinforcement in poly(vinyl chloride) (PVC) matrix. The surface of CNC was modified with silane coupling agent to improve filler-matrix adhesion. Solution casting method was used to prepare PVC nanocomposites with various amounts of modified (SCNC) and unmodified (CNC) nanocrystals. Both SCNC and CNC were examined by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) which showed that surface chemical modification has occurred. An increase in tensile strength was observed with the addition of SCNC compared to the CNC. However, the elongation at break of the nanocomposites was found to decrease with the increase of both fillers loading. An increasing trend was observed in the tensile modulus with the addition of CNC to the PVC matrix, but decreasing with the addition of SCNC. The morphology of a fractured surface of nanocomposites showed silane modification reduced the number of voids in the structure of PVC. The observation indicated the adhesion between the fiber and the matrix had improved upon surface modification of the nanocrystals with silane.*

Keywords: Cellulose nanocrystals; nanocomposite; poly(vinyl chloride); silane modification

ABSTRAK

Potensi nanohablur selulosa (CNC) daripada daun mengkuang (Pandanus tectorius) *sebagai pengisi penguat bagi matriks polivinil klorida (PVC) telah dikaji. Permukaan CNC telah di rawat dengan agen pengkupel silana bagi meningkatkan lekatan pengisi-matriks. Nanokomposit PVC dengan pelbagai amaun selulosa terawat (SCNC) dan CNC telah disediakan secara larutan tuangan. Penelitian ke atas CNC dan SCNC yang dilakukan secara spektroskopi transformasi Fourier inframerah dan pembiasan X-ray (XRD) menunjukkan modifikasi kimia berlaku ke atas permukaan selulosa. Kekuatan regangan ketara meningkat dengan pertambahan SCNC berbanding CNC tetapi pemanjangan takat putus komposit menurun dengan pertambahan kedua-dua pengisi. Walau bagaimanapun berlaku tren peningkatan bagi modulus regangan dengan pertambahan CNC tetapi menurun dengan SCNC. Morfologi permukaan patah komposit menunjukkan rawatan silana mengurangkan bilangan rongga terjadi dalam matriks. Pemerhatian ini menunjukkan penambahbaikan dalam lekatan pengisi-matriks selepas rawatan permukaan dengan silana.*

Kata kunci: Nanohablur selulosa; nanokomposit; polivinil klorida; rawatan silana

INTRODUCTION

Composites consisting of natural fibers and thermoplastics have received extensive attention in the scientific literature as well as in industry (Bledzki & Gassan 1999). The use of fibers in plastic composites is a particular interest because of their availability and properties (Bledzki & Gassan 1999; Wambua et al. 2003). Compared to traditional composites, nanocomposites are unique in their ability to develop one or more properties with incorporation of very small quantities of filling material. Nanocomposites are known to improve stiffness, toughness, barrier properties and resistance to fire and ignition. The research on nanocomposites reinforced by cellulose nanocrystals has grown very fast since 1995 (Azizi Samir et al. 2005; Favier et al. 1995b).

Cellulose is a linear natural polymer, it has repeating units of D-anhydroglucose ($C_6H_{11}O_5$) joined by 1,4-β-D-glycosidic linkages. Naturally the cellulose chains are aggregated in microfibrils via the strong inter and intra-molecular interactions. Cellulose microfibrils can be considered as a flexible strand with cellulose crystals, linked along the microfibril by amorphous domains (Azizi Samir et al. 2005). For the demand of nanoparticles from renewable resources for different applications, the structure of cellulose microfibrils can be deconstructed in order to generate cellulose nanofibres. In literature, there are different descriptors for the nanofibres. These include rod-like colloidal particles, 'nanowhiskers' (or just simply whiskers), 'nanocrystals' or 'monocrystals'. The term 'whiskers' is used to indicate elongated crystalline rod-like nanoparticles, whereas the designation 'nanofibrils' is used to indicate long flexible nanoparticles consisting of both crystalline and amorphous strings as alternated

domains (Eichhorn et al. 2010; Habibi et al. 2010; Lavoine et al. 2012). Generally, the terms 'nanowhiskers' and 'cellulose nanocrystals' are used to describe material that acid hydrolysed from plants and 'nanofibrils' for material extracted by mechanical methods or from native sources such as bacterial cellulose. The term 'nanofibres' is used as a general term of both these sub-forms of cellulose (Eichhorn et al. 2010). In the present work, the term 'cellulose nanocrystals' (CNC) is used.

CNC can be produced from microcrystalline cellulose (MCC) (Bondeson et al. 2006). Microcrystalline cellulose is a purified and partially depolymerized cellulose, which can be prepared from all forms of natural celluloses (Battista & Smith 1962). Many different sources have been used to prepare cellulose nanocrystals, such as tunicate (Favier et al. 1995a, 1995b), wheat straw (Helbert et al. 1996), cotton (Ebeling et al. 1999), wood fibres (Beck-Candanedo et al. 2005), sisal (Garcia de Rodriguez et al. 2006; Moran et al. 2008), flax fiber (Cao et al. 2007), ramie (Habibi et al. 2008), mulberry (Li et al. 2009), coconut husk fibres (Rosa et al. 2010), pineapple leaves (Cherian et al. 2010), bananas (Deepa et al. 2011), kenaf bast fibers (Kargarzadeh et al. 2012), rice husk (Johar et al. 2012), rice straw (Lu & Hsieh 2012), *mengkuang* leaves (pandanus tectorius) (Sheltami et al. 2012) and pandanus utilis (Chenampulli et al. 2013).

The worldwide development and growth in the applications of natural fibers led to the necessity for finding and establishing new sources of them. The rationale to choose a new source for natural fibres are high fibre content, easy availability, high growth potential, neutrality to other crops (means the crops do not pose a threat to acreage under the other crops) and traditional knowledge and existing human resource are good for chosen fibres at local levels. *Mengkuang* is a popular name in Malaysia for *Pandanus tectorius*, which is a plant belonging to the Pandanaceae family. This family has about 600 known species. These species vary in size and grow along mangroves and in local jungles. The leaves yield strong fibres that are used for making rope, weaving hats and mats (Giesen et al. 2007). *Mengkuang* leaves contain about 37.3% of cellulose fibers with crystallinity of 69.5% and its cellulose nanocrystals has an aspect ratio in the range 10-20 (Sheltami et al. 2012). A group of researchers in Malaysia used woven leaf fibre mats of a pandanus plant for reinforcing unsaturated polyester (USP) matrix (Jannah 2008; Mariatti et al. 2008). The mechanical properties, as well as the water absorption of the composite, is higher than the matrix; however, they have not been examined for cellulose isolation. A thorough literature survey indicated that a group of researchers in India has explored the cellulose isolation from pandanus plant (*Pandanus utilis*) and converted it to nanometer size (Chenampulli et al. 2013). Although the fibres were found to contain higher cellulose than the one of *mengkuang* leaves (*Pandanus tectorius*), the percentage of crystallinity was lower than the latter (Chenampulli et al. 2013; Sheltami et al. 2012). The leaves are widely used in Asia.

Poly(vinyl chloride) (PVC) based natural fiber composites are currently experiencing a dramatic increase in usage (Jiang & Kamdem 2004). They are widely used in building construction applications because they offer acceptable mechanical properties, chemical and water resistance, stain and paint-ability, as well as long lifetime (UV resistance, free from maintenance). Mechanical properties of PVC based natural fiber composites are influenced by the fiber treatment, content, size, and distribution (Jiang & Kamdem 2004; Wirawan et al. 2009). The global demand of poly(vinyl chloride) has been a steady increase due to its industrial interest (Esckilsen 2008; Matuana et al. 1998a). Nevertheless, just a few studies on PVC/cellulose nanocomposites and no studies on the use of modified nanocrystals in PVC have been conducted to date.

Despite the advantages of natural fibers, the nature of adhesion between hydrophilic cellulosic fibers and hydrophobic thermoplastics is critical for both the manufacturing and performance of such materials. In general, the interfacial adhesion between cellulosic fibers and plastic matrix is poor and as a consequence, the strength properties deteriorate (Matuana et al. 1998a). The surface treatments could enhance the compatibility of these materials and improve the strength. The treatments and modifications have been intensely investigated and reviewed by researchers over the recent years (Belgacem & Gandini 2008; Bledzki & Gassan 1999; Dufresne 2012; Habibi 2014). Coupling agents are the chemical substances that function at the interface to create a chemical bridge between the reinforcement and matrix. It improves the interfacial adhesion with just small quantities used. Different type of coupling agents are used for natural fibre reinforced polymer composites, such as silanes, copolymers containing maleic anhydride and isocyanates (Belgacem & Gandini 2008; Xie et al. 2010).

According to literature, silanes are known as efficient coupling agents extensively used in composites and adhesive formulations (Xie et al. 2010). The main advantages are the commercial availability in large scale with several chemical functional groups and they can couple with virtually any polymer or mineral in composites. The organofunctional group is responsible for bonding with the polymer via covalent reaction or physical interaction with other phases. Matuana et al. (1998a; 1998b) found that the adhesion between PVC and cellulosic fibers was significantly improved with aminosilane. Figure 1 shows a schematic illustration of the possible interface between silane modified cellulose nanocrystals (SCNC) and poly (vinyl chloride) matrix (PVC).

Several researchers used other silane coupling agents to improve the compatibility and dispersion of nanocelluose into the polymer matrix. CNC resulting from acid hydrolysis of bacterial cellulose microfibrils have been chemically modified with hexamethyldisilazane in formamide in an attempt to reduce the nanocrystals hydrophilicity by obtaining trimethylsilylation surface for further use as reinforcements in cellulose acetatebutyrate matrixes (Grunert & Winter 2002, 2000). Gousse´ et al.
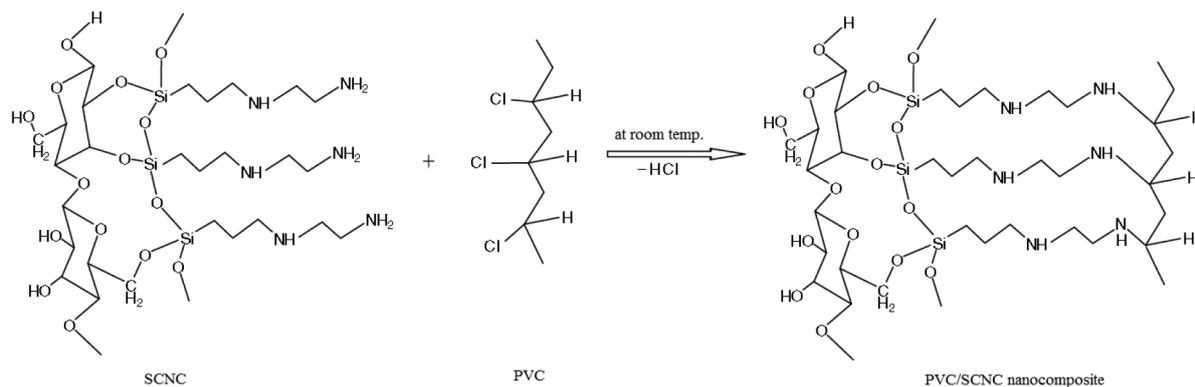
FIGURE 1. Schematic illustration of possible interface between silane modified cellulose
nanocrystals (SCNC) and poly (vinyl chloride) matrix (PVC)

(2002) partially silylated CNC (from tunicate) using a series of alkyldimethylchlorosilanes. The researchers found that the modified nanocrystals could be homogeneously dispersed in organic solvents of medium polarity (such as acetone or THF). Ben Mabrouk et al. (2011) prepared aqueous nanocomposite dispersions of poly(styrene-co- 2-ethyl hexyl acrylate) copolymer and cellulose nanocrystals via mini-emulsion polymerization, using methacryloxypropyltriethoxysilane as a coupling agent to stabilize the dispersion of the whiskers on polymer particles. Recently, de Oliveira Taipina et al. (2013) used a silane with isocyanate groups (isocyanatepropyltriethoxysilane, IPTS) to modify nanocrystals from cotton fibers.

In this work, cellulose nanocrystals from *mengkuang* leaves were used as reinforcements in polyvinyl chloride matrix. Silane coupling agent was used to modify the CNC. The nanocomposites were prepared by solution casting method. The effects of the silane modification on the microstructure of CNC was studied using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The mechanical properties and morphology of the nanocomposites were analyzed by tensile test and Field emission scanning electron microscope (FESEM), respectively.

MATERIALS AND METHODS

MATERIALS

Cellulose nanocrystals (CNC) from *mengkuang* leaves were used. Polyvinyl chloride (PVC) was purchased from Malayan Electro-Chemical Industry Co., Sdn. Bhd., tetrahydrofuran (THF) was provided by SYSTERM and Z-6020 silane [N-(β-aminoethyl)-γ-aminopropyl-trimethoxysilane (AEAPTMS)] from Dow Corning.

EXTRACTION OF CELLULOSE NANOCRYSTALS FROM *MENGKUANG* LEAVES

The extraction was in two stages, preparation of cellulose fibers from the leaves and preparation of the nanocrystals.

Firstly, *mengkuang* leaves were purified to obtain cellulose fibers in two steps, alkali and bleaching treatments. The ground leaves were treated with 4% NaOH at 125°C for 2 h followed by bleaching treatment. Bleaching was carried out using 1.7 w/v% $NaClO_2$ at pH 4.5 and 125 °C for 4 h. Each step was repeated several times in order to eliminate other substances such as hemicelluloses and lignin, the leaves were washed with distilled water after each treatment. Secondly, cellulose nanocrystals were prepared by acid hydrolysis of the cellulose fibers obtained. Acid hydrolysis was carried out using 60 wt. % H_2SO_4 solution at 45°C for at 45 min. The hydrolyzed cellulose sample was washed several times by centrifugation (10000 rpm, 10 min and 10°C). The suspension was then dialyzed against distilled water until a constant pH was reached. The resulting suspension was sonicated for 30 min.

MODIFICATION OF CELLULOSE NANOCRYSTALS

The modification of CNC was done in two steps neutralization followed by silanization. The neutralization was carried out with NaOH. The suspension of CNC was washed with 1M of NaOH solution and washed with distilled water by using a centrifuge at pH=7.

The silanization of CNC with 3 wt. % of silane was carried out in aqueous solution at pH=4 for 2 h. Centrifuge was used to wash and separate SCNC. The resulting suspensions were subsequently stored in a refrigerator after adding several drops of acetone in order to avoid bacterial growth. The percentage (wt/v%) of cellulose nanocrystals in the suspensions was measured after freeze drying of a known volume of the suspension.

PREPARATION OF PVC NANOCOMPOSITES

THF suspension of CNC was obtained by solvent exchange procedure (water to tetrahydrofuran) and centrifugation. Then, it was dispersed by ultrasonic treatment for about 30 min. PVC solution and suspension of nanoparticles were mixed and stirred for 24 h. The solution was cast in a Petri dish and allowed to evaporate at room temperature for a day. Further drying of the sample was allowed in

an oven at 60°C for 24 h. The nanocomposite was then peeled off from the Petri dish. The nanocomposites at different loading of CNC and SCNC loading (0, 2, 4, 6 & 8 wt. %) were prepared and characterized. The thickness of the nanocomposites was fixed at 0.25±0.05 mm. In order to fix the thickness of the obtained nanocomposites, the total amount of the components were fixed as well as the size of petri dishes. For each sample, the total weight of polymers (matrix and the nanocrystals) was 6 g and the volume of solvent was 100 mL. The samples were then kept in a desiccator.

CHARACTERISATIONS

Fourier Transform Infrared Spectroscopy (FTIR) The FTIR spectra were recorded on an ATR-FTIR Perkin-Elmer Spectrum 2000 in the range 4000-500 cm^{-1} with a scanning resolution of 4cm^{-1}. The samples were simply placed onto the ATR crystal and then the samples spectra were collected.

X-Ray Diffraction (XRD) The crystallinity of the nanocrystals was studied using an X-ray diffractometer (D8 Advance, Bruker AXS) equipped with CuKα radiation (λ = 0.1541 nm) in the 2θ range 10°-50°. The operating voltage was 40 kV and the current was 40 mA. The empirical method (Segal et al. 1959) was used to obtain the crystallinity index of the samples Xc, as shown in (1):

$$Xc = \frac{I_{002} - I_{am}}{I_{002}} \times 100, \qquad (1)$$

where I_{002} & I_{am} is the peak intensities of crystalline and amorphous materials, respectively. Which are located at 2θ value around 22.6° and 18°, respectively.

Field Emission Scanning Electron Microscopy (FESEM) The morphology of the fractured surface of nanocomposites was examined by using field emission scanning electron microscope (FESEM) Zeiss Supra 55VP model. The accelerating voltage was 3 kV. All micrographs were taken in an uniform magnification of 10000.

Tensile Test Tensile parameters of the nanocomposites were measured by a tensile tester, Instron 4301 at room temperature according to ASTM D882. With a crosshead speed of 50 mm/min and a load of 50 N. The tensile test data were reported based on the average of 5 measurements for each set of samples.

RESULTS AND DISCUSSION

MODIFICATION OF CELLULOSE NANOCRYSTALS

Figure 2 represents the FTIR spectrum of SCNC, the spectrum of CNC was added to the figure as a comparison. The appearance of a new broad peak at around 1560 cm^{-1}, which is attributed to the N–H bending vibration of primary amine (Pavia et al. 2009), indicates the presence of the functional group on the CNC surface. The absorption band at around 1638 cm^{-1} in the spectra is attributed to water adsorption (Hon & Shiraishi 2001). The absorption bands of O–H and N–H stretches appear in the same region at around 3330 cm^{-1}. On the other hand, the area of this absorption band was slightly reduced after modification. It could be assigned to a reduction in O–H bonds. The two weak peaks which are found at around 1249 and 802 cm^{-1} are attributed to Si–C stretching bond (Hassan & Khan 2008; Pacheco et al. 2011).

Figure 3 shows XRD patterns of cellulose nanocrystals after neutralization and silanization. The X-ray diffractograms show the crystalline structure of cellulose I. The intensity of the peak around 22.6° was dramatically reduced after the silanization. The crystallinity index of cellulose nanocrystals was calculated by Segal method (1959), the values were 66.7 and 51.3% for CNC and SCNC, respectively. The crystallinity index decreased after silane
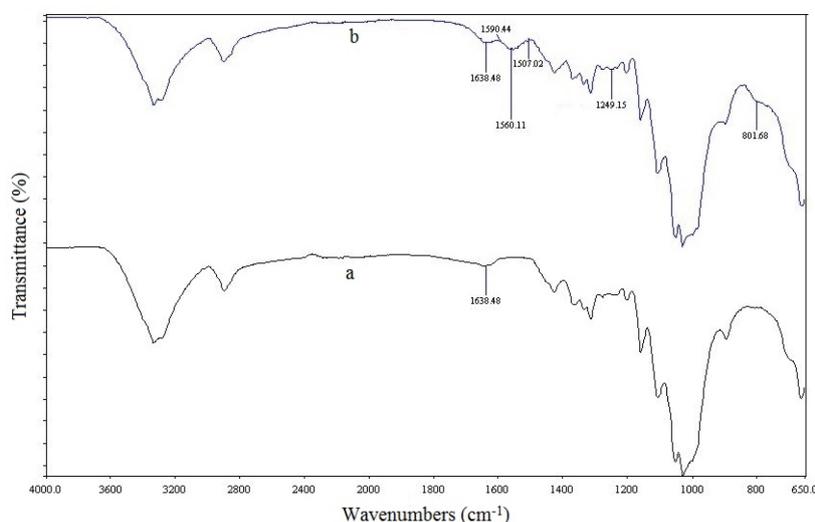

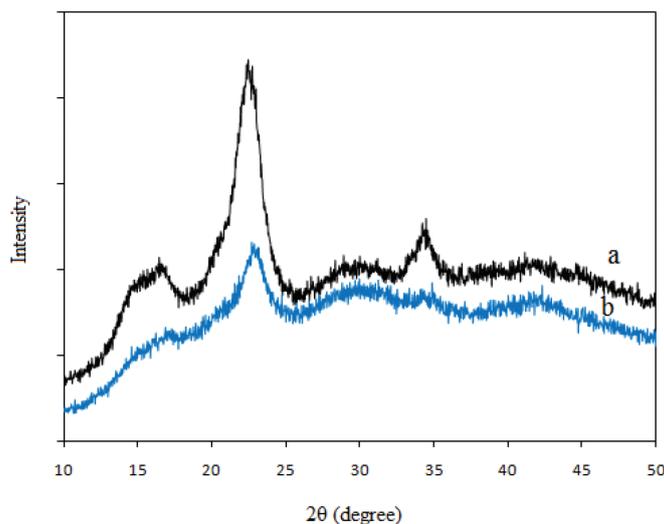FIGURE 2. FTIR spectra of (a) CNC and (b) SCNC

FIGURE 3. X-ray diffraction patterns of (a) CNC and (b) SCNC

modification. The dramatic reduction of crystallinity index value after silanization could be due to the introduction of the silane coupling agent into the polycrystalline domains. The size of aminosilane molecules is bigger than that of -OH groups, which means the distance between the polymer chains increased after modification. It is well known that the energy of intermolecular attraction decreases with increasing the distance between the polymer chains. The other reason, is (South 2008), aminosilane molecules have NH groups that have less electronegativity than OH; hence, the hydrogen bonds tend to be weaker in SCNC. This will imply different reinforcing effect if the fillers incorporate into nanocomposites.

PVC/CNC NANOCOMPOSITE

The tensile properties of PVC matrix and its nanocomposites reinforced with CNC and SCNC are shown in Figures 4, 5 and 6. The tensile strength (Figure 4) shows slight improvement at 2% CNC loading; it increased from around 29 to 32 MPa for PVC matrix and nanocomposite of 2% CNC, respectively. However a further increased in CNC loading reduces the tensile strength of the nanocomposites. Silane modification enhanced the compatibility between the filler and PVC matrix. It is shown in Figure 4 that the tensile strength of the nanocomposites improved after modification with silane. The highest value is about 39 MPa at 4% of SCNC. The change in tensile strength is not significant for the nanocomposites with 4% SCNC compared to 6% SCNC after which it decreased. It is well known that aggregation and phase separation increase with increasing filler content (Ratnam et al. 2010). So, it is the reason for the reduction of tensile strength at high filler loading. These findings suggest the compatibility of CNC filler with PVC matrix and increased the adhesion between the filler and matrix after the silane modification. The optimum fillers loading are taken based on the highest tensile strength which is at 2 and 4 wt. % of CNC and SCNC loadings, respectively.

Figure 5 shows the tensile modulus of PVC matrix and PVC nanocomposites. The modulus was increased on adding CNC. This observation indicates that incorporation of CNC into the PVC matrix improves the stiffness of the PVC. It increases from about 2.4 to 2.6 GPa at 4% of CNC loading, further loading of CNC causes to reduction of modulus. It is attributed to the phase separation and voids as can be seen from the FESEM micrographs of the nanocomposites (Figure 6). Lower values of tensile modulus are observed for SCNC reinforced PVC nanocomposites. It is proven that modification of the CNC with silane reduces the stiffness of the nanocomposite. The lower modulus of the SCNC reinforced nanocomposites compared to PVC/CNC nanocomposites could be associated to the crystallinity nature of the nanofillers. According to the XRD results (Figure 3), SCNC has the lower degree of crystallinity than CNC. Thus, the stiffness of SCNC is lower and leads to reducing the stiffness of the PVC/SCNC nanocomposites. Additionally, the nature of interfacial bonding in the nanocomposites could be the other reason. Both fillers (CNC and SCNC) have different interaction with PVC matrix, as confirmed by XRD, FTIR, FESEM and tensile strength. Different interaction leads to a different orientation and distribution for the fillers in the matrix. The changes in the orientation of the filler may also result in the reduction of modulus (Mallick 2008; Weon & Sue 2005).

Figure 6 shows the elongation at break of PVC matrix and PVC nanocomposites. The addition of both modified and unmodified nanocrystals to PVC matrix was found to reduce the elongation at break drastically. Such a decline is associated with the decreased deformability of a rigid interphase between the filler and polymer matrix (Raju et al. 2008). The nanocomposites show a tendency of less elongation at break with the addition of SCNC as compared to CNC. This observation is attributed to the strong interfacial bonding between the filler and matrix after silane modification (Katz & Mileski 1987).
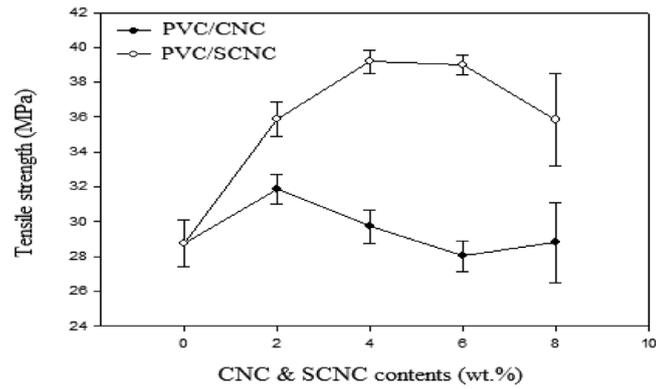
FIGURE 4. Tensile strength of PVC nanocomposites
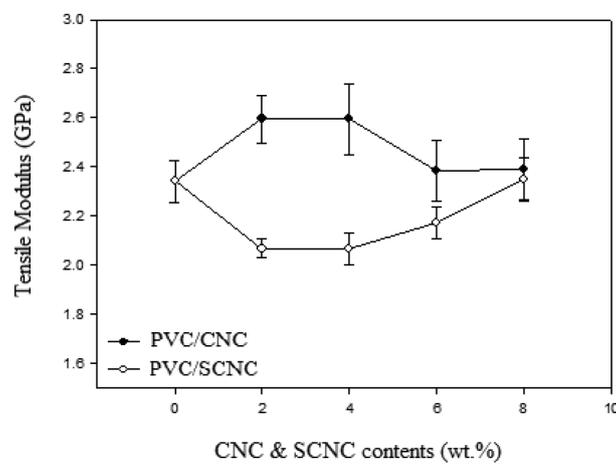

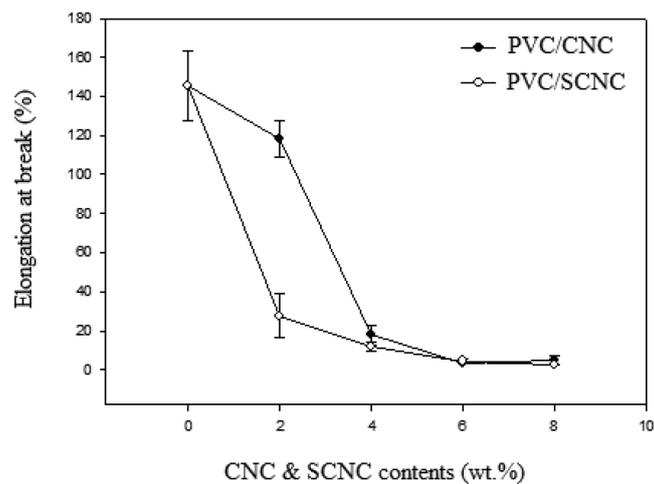FIGURE 5. Tensile modulus of PVC nanocomposites

FIGURE 6. Elongation at break of PVC nanocomposites

As a comparison with other PVC composites, tensile strength of PVC were reduced after addition of rice husk powder, although it was treated with maleic anhydride (Chand & Jhod 2008), as well as it decreased with untreated and benzoylated oil palm empty fruit bunch short fiber (Abu Bakar & Baharulrazi 2008). Matuana et al. (1998a) reported an improvement in both tensile strength and modulus of PVC/wood composite after treatment with aminosilane. Moreover, Shu et al. (2013) reported an increase in the tensile strength of PVC after doping,

nanosilica with functionalized by vinyl silane and trimethyl silane.

Figure 7 shows FESEM micrographs of fractured surfaces of the matrix and PVC/CNC nanocomposites at various wt. % of CNC. The distribution of the fillers in PVC cannot be distinguished in these micrographs of FESEM. The micrographs show the effect of fillers on the surface of PVC nanocomposites. The fractured surface of a pure matrix (Figure 7(a)) has uniform surface with fine fibrils compared to those of nanocomposites. Rippled surface morphology appeared after adding 2% of CNC (Figure 7(b)). Ripples and lines as well as voids on nanocomposites surfaces increased by increasing the contents of CNC to 4% (Figure 7(c)). Phase separated and voids can be seen in Figure 7(d) and 7(e)) of PVC/CNC nanocomposites at 6 and 8% of CNC loading.

Figure 8 shows the FESEM micrographs of fractured surfaces of PVC matrix and nanocomposites at the optimum loading of CNC and SCNC at different magnifications (Mag. 10000 and 50000). The fractured surface of the PVC matrix (Figure 8(a) & 8(d)) represents a smooth surface accompanied by voids. The size of voids increased after addition of CNC (Figure 8(b) & 8(e)). The morphology of the fractured surface of PVC/SCNC nanocomposite (Figure 8(c) & (f)) is smoother than PVC/CNC nanocomposite. The voids are smaller and less on the surface of PVC/SCNC, which in turn indicates better interfacial strength. This demonstrates that the aminosilane modification should be adopted to incorporate cellulose nanocrystals into the PVC matrix to improve the properties of the polymeric nanocomposites more efficiently.

CONCLUSION

FTIR results confirmed that the surface chemical modification was successfully achieved. The crystallinity of the nanocrystals was decreased after chemical modification. The tensile modulus was decreased with the use of the SCNC in PVC nanocomposites. However, the tensile strength was enhanced and increased compared to the use of CNC as well as the neat PVC. The optimum tensile strength, which recorded, was about 32 and 39 MPa for nanocomposites filled with CNC and SCNC, respectively. This result showed that the modification with silane could contribute to the improvement in interfacial bonding between the filler and matrix. The increase in the interfacial adhesion between PVC matrix and the filler upon the silane modification was further confirmed by the morphological observation of the PVC nanocomposites.
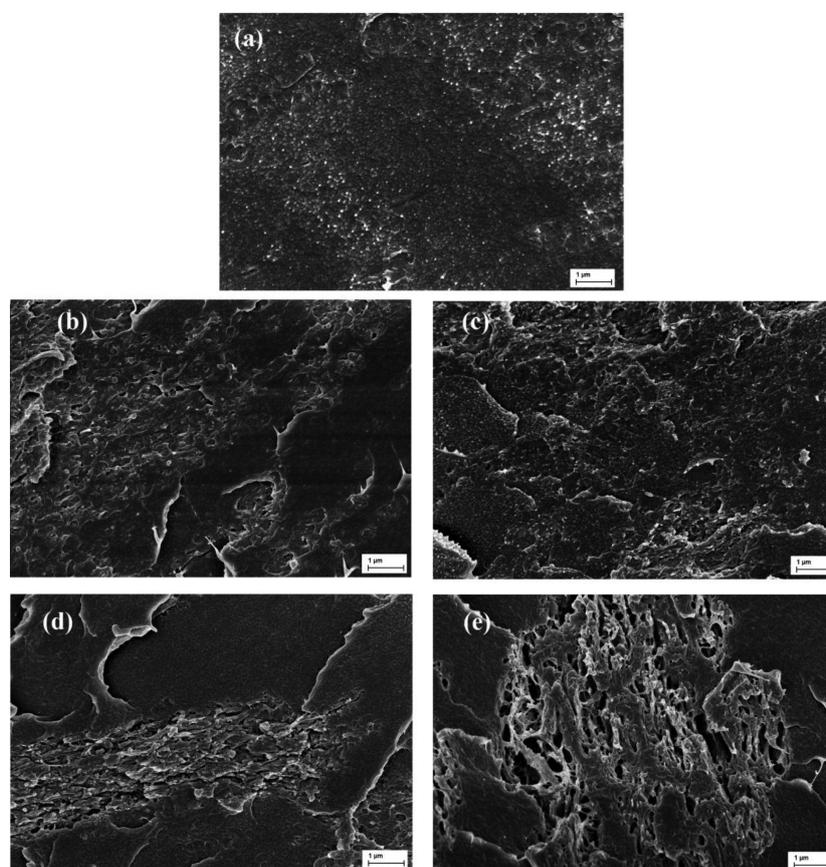

FIGURE 7. FESEM micrographs (Mag. 10000) of PVC matrix and nanocomposites with different loading of CNC: (a) 0%, (b) 2%, (c) 4%, (d) 6% & (e) 8%
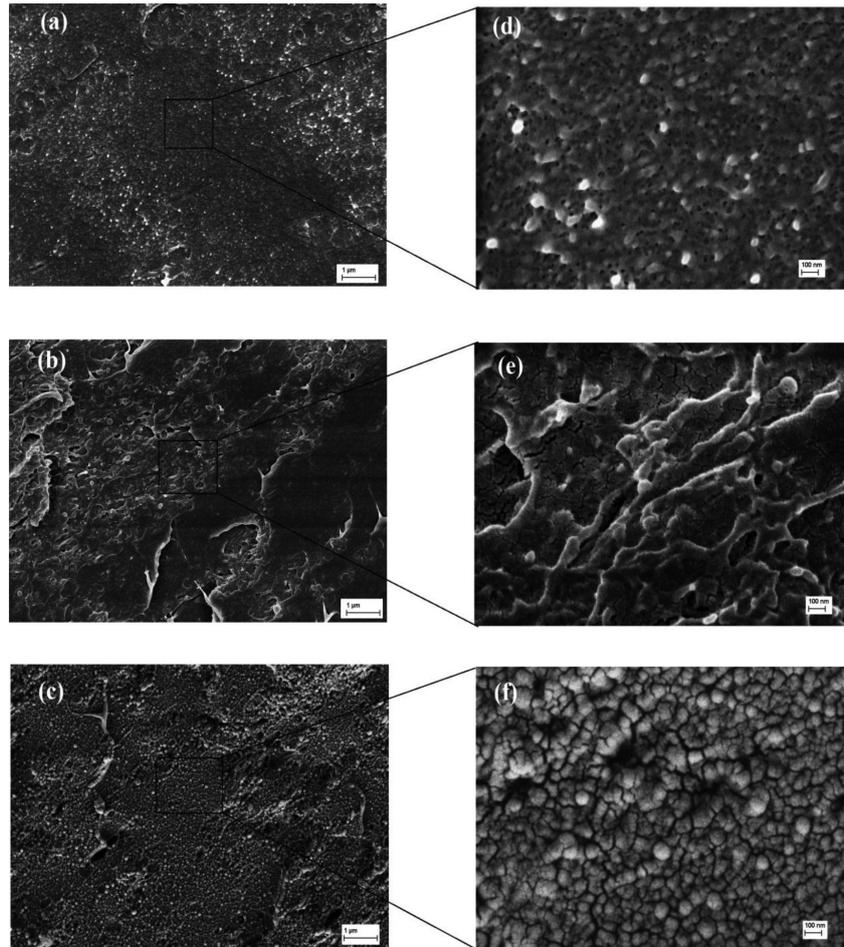
FIGURE 8. FESEM micrographs of PVC matrix and nanocomposites with optimum loading of CNC and SCNC: (a) PVC,
(b) 2% CNC & (c) 4% SCNC (Mag. 10000); and (d) PVC, (e) 2% CNC & (f) 4% SCNC (Mag. 50000)

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Rasha M. Sheltami, Hanieh Kargarzadeh & Ibrahim Abdullah*
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

Rasha M. Sheltami
Chemistry Department, Faculty of Science
University of Benghazi, Benghazi
Libya

*Corresponding author; email: dia@ukm.edu.my