

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Effect of Nanocellulose on the Biodegradation, Morphology and Mechanical Properties of Polyvinylchloride/ Nanocellulose Nanocomposites.

Ghada kadry^a and Abou El Fettouh Abd El-Hakim^{b*}.

^a Chemical Engineering Department, high Institute of Engineering, Alshrouk Academy, Egypt.

^b Professor of Polymer Chemistry, Packaging Materials Department National Research center, Cairo, Egypt

ABSTRACT

Cellulose nanocrystals were prepared by sulfuric acid hydrolysis of cellulose isolated from rice straw by an alkaline pulping process. TEM studies confirm the formation of nanocomposites from nanocellulose with polyvinyl chloride, where the range of size of nanocrystals was found from 44nm to 66 nm and show a good dispersion of nanocellulose particles in polyvinylchloride (PVC) .Significant improvements of elongation % at break and tensile strength was observed as a result of addition of nanoparticles to the PVC matrix especially at low nanoparticles loading. It was added as reinforcing materials in (PVC) matrix. The interaction between nanocellulose and PVC was confirmed by FT-IR. The effect of nanoparticles loading on tensile properties, thermal properties, and soil biodegradation were studied. Thermogravimetric analysis (TGA) of PVC/cellulose nanocomposites showed slightly lower onset degradation temperature (~250 °C) than neat PVC. It was found that, the presence of nanocellulose in the nanocomposites increases the rate of biodegradation of PVC in soil.

Keywords: Nanocellulose, polyvinyl chloride, nanocomposites, biodegradation.

**Corresponding author*

INTRODUCTION

The mechanical properties of composites are enhanced by microcomposites and nanocomposites preparations. The filler particles can be considered as a nanoparticle when at least one of its dimensions is lower than 100 nm., it simultaneous and growing interest in developing and using of bio-based products that can reduce the dependence on fossil fuel and move to a sustainable materials basis[1-2]. This particular situation provides unique bionanocomposites possessing outstanding properties, which have been never found in conventional composites [3]. So biodegradable bio-based nanocomposites are the next generation of materials for the future [4].

It is possible to obtain nanoelements from different renewable resources depending on their biological origin, e.g., cellulose, starch, chitin [5], but main research are dedicated to cellulose whiskers as it is the polymer is the most abundant on earth. Most studies found in the literature about biocomposites use cellulosic materials as a filler which in some cases contributes to enhance the rigidity but mostly embrittles the polymer. Actually the study of cellulosic nanoparticles as a reinforcing phase in nanocomposite materials started 20 years ago. Since that time an important literature and recent review [4] have been devoted to nanocellulose that becomes a topical subject. Different terms of these nanoparticles are used, including whiskers and nanocrystals. The designation "whiskers" is used to designate elongated crystalline rod-like nanoparticles. It is obtained by the digestion of amorphous cellulosic domains, generally via acid hydrolysis. Valorization of crops and residues is also an important topic. Rice straw is one of the most important residues and it will become more and more important with the development of biofuels. The use of rice straw for paper and composite panels production is a common practice in several countries without large supplies of wood resources [6]

Although PVC produced worldwide counts for almost 30% of the total production of thermoplastics, second to a combined product of all polyolefin. PVC plastic pollution has become a serious concern to the environmentalists for the last few years. [7] Since plastics are non-biodegradable and emit carcinogenic gases when incinerated [8-9]. The blend PVC with biodegradable cellulose derivative to thermally support the polymer during the molding process as well as to enhance the biodegradability of PVC waste products [10-11]. The biodegradation of plastic waste become a viable solution to combat such a problem[12-13]

In this work, effort has been made to develop PVC blends containing natural polymer with improve its mechanical properties. Also PVC has been selected to blend with nanocellulose which is a natural polymer and gives advantage where it acts as a biodegradable additive, where PVC is needs to long time to degrade.

EXPERIMENTAL

Materials

PVC prepared by Suspension polymerization (PVC WS-800, DP 800) was product by Shanghai Chlor-Alkali Chemical Co. Ltd, China. Nanocellulose prepared in according to method given latter. Various processing additives for PVC, such as organic tin thermal stabilizer, plasticizer (DOP), lubricant (paraffin) were industrial grade products.

Isolation of cellulose from rice straw

Unbleached cellulose (consists of: α cellulose, 79.33%; lignin, 15.60%) was prepared from rice straw by an alkaline pulping process, in which the rice straw was cut into small pieces, then 10 times its weight of 1.0% w/w sodium hydroxide solution was added. Pulping was allowed for 2 hours at 160 °C in a rotary autoclave, after that the pulp was thoroughly washed with water till neutrality. Bleached rice straw pulp (α -cellulose, 66.66%; lignin 8.98 %) consists of chemical fibers obtained from rice straw pulp by dissolving and extracting the lignin and most of the hemicelluloses using the two stage bleaching method hypochlorite. The unbleached cellulose fibers were treated with sodium hypochlorite solution equivalent to 60% of the chlorine requirement for 2 hr at 40 °C. The liquor to fiber ratio was 10:1 and the pH was maintained at 9 during the hypochlorite process. At the end of the second stage, the bleached cellulosic fibers were washed till neutrality, and left to dry in air. Thus, bleached rice straw is made up mainly of exposed cellulose molecules, which comprise a number of reactive hydroxyl groups.

Preparation of Nanocellulose

Nanocellulose, was obtained by sulfuric acid hydrolysis of the eucalyptus rice straw pulp performed as described in the literature [14] with minor modifications. Briefly, eucalyptus rice pulp was ground until fine particulate was obtained using a Willey mill, then 10 g of cellulose was added to 160 ml of (64wt. %) sulfuric acid under strong mechanical stirring. Hydrolysis was performed at 50 °C for about 50 min. After hydrolysis, the dispersion was diluted with 2-foldin water, and then washed using three repeated centrifuge cycles. The last washing was conducted using dialysis against deionized water until the dispersion reached pH6. Afterward, that the dispersions were dried at 40°C. The residue is investigated using transmission electron microscopy (TEM). It was found that, the range of size of particles was found from 44 nm to 66 nm.

Preparation of PVC/Cellulose nanocomposites

PVC/Cellulose nanocomposites were prepared by melt mixing 150 gm of PVC, with 0.1% , 0.5%, 1%, 3%, 5%, 8% nanocellulose respectively and various required processing additives in the mixing chamber of brebender. The mixing temperature was set at 164°C, the rotor speed was 80 rpm, and the mixing time was 8 min. The nanocomposite samples prepared were then molded into sheets of 1 and 3 mm in thickness and dimensions of 10X10 cm by hot press at 170 °C and 20 MPa for 10 min, followed by cooling to room temperature at 10 MPa. The sheets were used for structure characterization and mechanical properties measurements.

FTIR spectroscopy

FTIR spectra were studied by a FTS-40, USA FTIR spectrophotometer using KBr discs containing 2.5% finely ground sample. It was recorded in the absorption mode in the range 4000– 400 cm^{-1} with an accumulation of 32 scans and a resolution of 2 cm^{-1} .

Transmission electron microscopy

The nanocomposite samples for transmission electron microscopy (TEM) observation were ultrathin-sectioned using a microtome equipped with a diamond knife. The sections (100–200 nm) were cut from a piece of about $1 \times 1 \text{mm}^2$, and collected in a trough filled with water and placed on a 200 mesh copper grid. The transmission electron micrographs measurements were carried out with a JEM- 1200EX apparatus running at an acceleration voltage of 80 kV.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on a TGA7 thermal analysis system of Perkin Elmer Co. at a heating rate of 10 °C/min with flowing nitrogen atmosphere. The temperature scan ranged from room temperature up to 250 °C.

Mechanical measurement

Tensile strength and Elongation properties measurements were performed using an Instron 4465 Universal Tensile Tester according to ASTM D638M-93/89 and ASTM D 790-92 standards, respectively. The tensile tests were conducted at a crosshead speed of 10 mm/min. The flexural tests were conducted using the three-point bending experiment, in which the support span and the rate of crosshead motion were kept at 50 mm/min, respectively. Notched Izod impact tests were performed with a RAY-RAN Universal Pendulum Impact Tester according to ASTM D256-97 standard, with a hammer speed of 3.5 m/s and pendulum weight of 0.818 kg at room temperature was used.

Biodegradation of nanocomposites in soil

Biodegradation of PVC/nanocellulose whiskers nanocomposites in soil was carried out as reported in [15]. The soil was taken from the surface layer and the inert materials were removed to obtain a homogeneous mass. 100 g soil was poured into a plastic pot up to a thickness of about 3 cm. Nanocomposite samples with the above mentioned compositions were accurately weighed. The samples were previously dried at 50 °C for

24 h. They were buried in the pots to a depth of 1 cm. Water was sprayed once a day to sustain the moisture. The samples were weighed every week for 4 weeks. After each period the samples were carefully taken out, washed with distilled water, dried at 50 °C for 24 h then weighed.

Moisture sorption test

Moisture sorption of PVC nanocomposites sheet was carried out by keeping the sheets in a desiccators having relative humidity of about 75% at 25 °C. This was achieved using saturated solution of sodium chloride in the container and putting the samples on racks over the solution.[16]

RESULTS AND DISCUSSION

FTIR spectroscopy

FT-IR spectroscopy has been extensively used in cellulose research, since it presents a relatively easy method of obtaining direct information on chemical structure of cellulose and the interaction with PVC. In Fig.1 it can be illustrated that the FT-IR spectra of nanocellulose isolated from rice straw. The absorption bands are shown the presence of band at 3432cm⁻¹ for OH stretching, 2902 cm⁻¹ for C-H stretching, 1641cm⁻¹ for C=O stretching, 1430 cm⁻¹ for OH bending, 1163 and 1113cm⁻¹ for C-O stretching, 610 cm⁻¹ for C-H bending vibration [17-18]. The absence of the band at 1726cm⁻¹ and the band relating to lignin aromatic ring vibrations at 1513cm⁻¹ revealed that the treatments of rice straw by delignification with 1 %NaOH under the used conditions completely removed lignin from the cell wall of rice straw, resulting in the cellulosic preparation, which are free of lignin. Absorption bands of PVC/ with 8% nanocellulose exhibited the peak at 3304cm⁻¹ (OH stretching), 2963cm⁻¹ (CH stretching) 1742 cm⁻¹ (OH) bending. Generally from the FTIR spectra of PVC/nanocellulose nanocomposites. It was found that the intensity of hydroxyl peak decreased as well as shifted to lower wave number in the nanocellulose polymer composites. The decrease in peak intensity in nanocomposite might be attributed to participation of hydroxyl group of nanocellulose in the cross linking reaction with PVC. The shifting of absorption peak corresponding to hydroxyl group to 3289 cm⁻¹ for PVC/0.5 nanocellulose, to 3290cm⁻¹ for PVC/ 3% nanocellulose and 3304 for PVC/8% nanocellulose

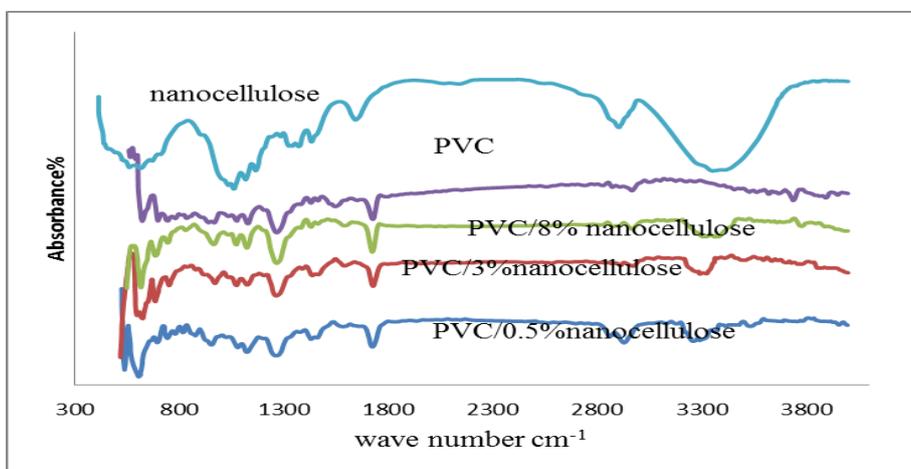


Figure 1: FT-IR spectra of nanocellulose, PVC, PVC/0.5% nanocellulose, PVC3% nanocellulose and PVC/8% nanocellulose

Morphology observations

The TEM micrographs of Nanocellulose results are represents in Fig. 2. As shown in Fig. 2(a), most of the nanocellulose particles have a diameter 30–45 nm, and these particles tend to aggregate together as it is observed. Figure 1(b) reveals example for that the nanoscale dispersion of nanocellulose in PVC matrix at the content of nanocellulose 0.5%, 3%, 5%, 8% nanocellulose. Some aggregates are found when the content of nanocomposite is increased up to 8%. Also it was observed that the dispersion of nanocellulose is good in PVC/nanocellulose composites, where it is distributed in polymer matrix and the particles was in the nanoscale.

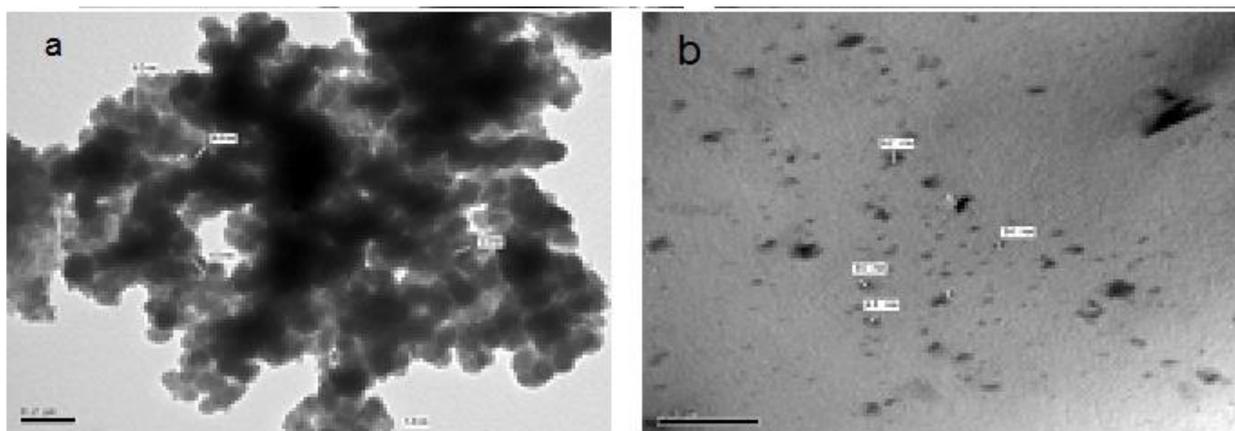


Figure : TEM of (a) of nanocellulose (b) PVC/nanocellulose containing 8%nanocellulose

TG of PVC and nanocellulose composites

According to the literature [19-20], the TG curve of PVC revealed two main degradation steps , where residue of 65.2% at about 200–370 °C was observed in the first stage. The second degradation step of PVC took place around 370-700 °C, corresponding to the mass loss of 29.7%. This are attributed to HCl and C₆H₆ evolved in first degradation, but in the second degradation step , which could be attributed to toluene or to a fragment of other alkyl-benzenes. The above observations are in agreement with the known mechanism of PVC degradation; where the first step is dehydrochlorination and formation of macromolecules with conjugated double bonds C=C, on the second step degradation continues with cracking and pyrolysis to low hydrocarbons of linear or cyclic structure[21-23]. HCl is the main volatile degradation product of the first step. Small quantities of benzene and other hydrocarbons are also emitted. In the second step, up to 527 °C, more aromatic products are evolved than aliphatic. Our interest will be the first degradation step. Fig.3 shows the TG curves for the PVC and nanocomposites up to 200 °C . From these curves, it can be observed that up to 300 ° C the PVC loss weight was 5 % , that may be due to dehydrochlorination , but in the case of 0.5 PVC/ nanocellulose nanocomposite the weight loss was 10% . At the 3% w/w nanocellulose in the nanocomposites the weight loss was 45 % while at 8 % w/w nanocomposite the weight loss was 55 % . PVC/cellulose nanocomposites containing 8 wt% nanocellulose showed slightly lower onset degradation temperature than the neat PVC(≈250 °C). The lower onset degradation in the case of PVC/cellulose nanocomposites could be due to the lower onset degradation temperature of nanocellulose than PVC. The onset degradation temperature of nanocellulose was at about 170 ° C [24] or may be the presence of nanocellulose accelerates the degradation of composites. The relatively low onset degradation temperature of PVC/nanocellulose may be due to the presence of sulfate groups on the surface of the whiskers as a result of the use of sulfuric acid in their preparation [5]. Starting from about 350 °C, both PVC and PVC/nanocellulose composite followed almost the same thermal degradation behavior.

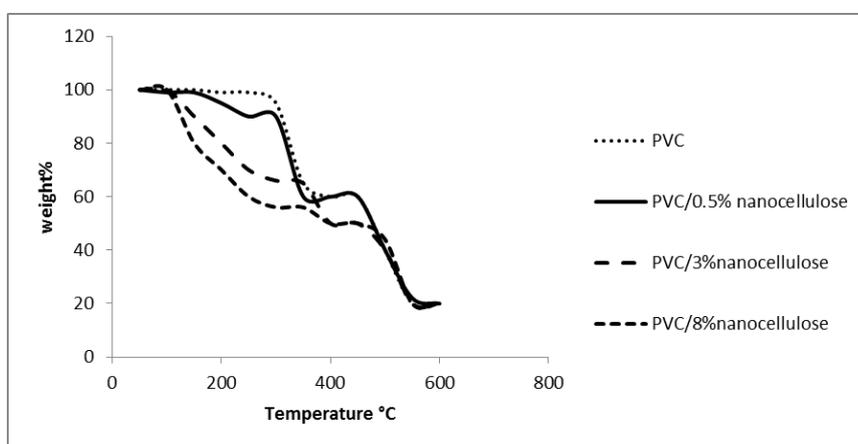


Figure 3: TGA curve of PVC and PVC/nanocellulose composites

Mechanical properties PVC/nanocellulose composites

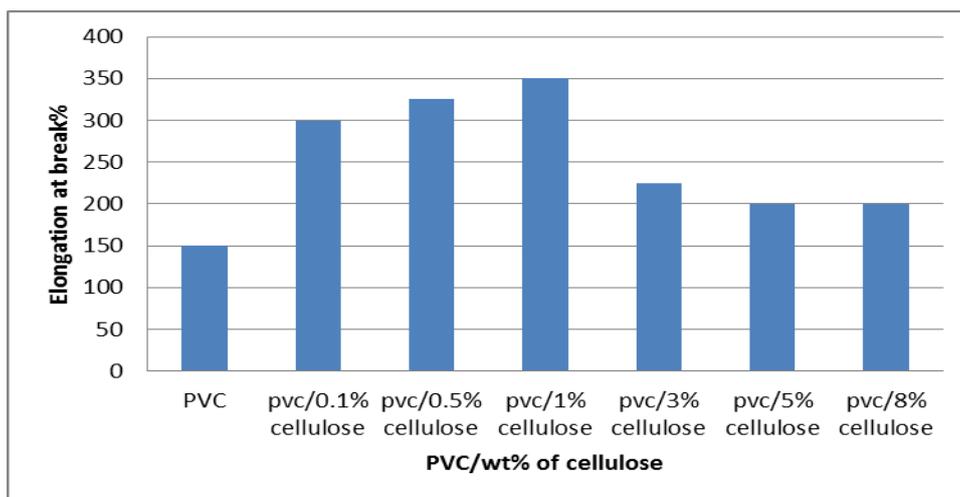


Figure 4: The change in elongation of nanocomposites at break with nanoparticle loading

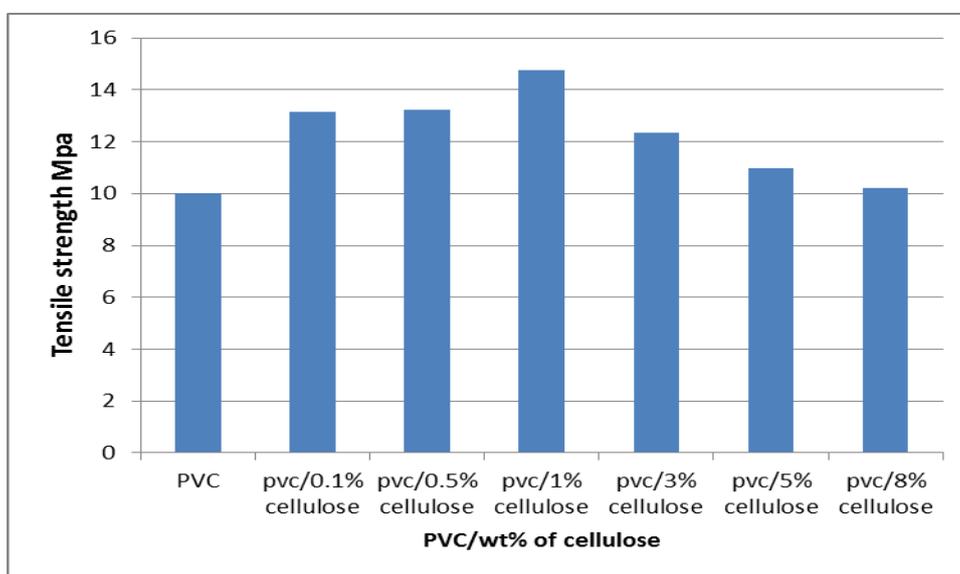


Figure 5: The change in tensile yield strength of nanocomposites with nanoparticle loading

The value of mechanical properties (tensile strength and elongation % at break of nanocomposites) are summarized in Figs 4,5. Addition of nanocellulose fiber to PVC, yield a composite material with a higher tensile strength and elongation % this improvement corresponds to an increase of 133.33% and 44.197 % for elongation % and tensile strength respectively. From Fig5 the elongation % at break clearly increase at 1% of nanocellulose this due to strong interaction between nanocellulose fiber and matrix caused by large interfacial areas led to much higher elongation % to break, then it start to decrease with further increase the amount of nanocellulose in the nanocomposite due to the aggregation effect of nanoparticles in PVC matrix [25] Fig 5 shows that PVC matrix had interact with nanocellulose surface effectually, then improved dispersion of nanocellulose in PVC matrix. The improvement of interfacial adhesion made the fiber act as an agent of reinforcement in PVC matrix. So the addition of nanocellulose increases the tensile strength of PVC, however the tensile strength slightly decrease after 1% due to agglomeration of nanocellulose.

Biodeintegration in soil of PVC/nanocellulose composites

The degradation half-life $t_{1/2}$ of regenerated cellulose in soil at 10–20 °C was given to be 30–42 days, and after 2 months the cellulose were decomposed into CO₂ and water. The fast degradation of cellulose

compared to PVC nanocomposites is attributed to random breakdown of bonds of cellulose macromolecules resulting from the microorganism cleavage. In this work, the effect of nanocellulose on biodegradability of PVC in soil was studied and the results are presented in Fig. 6. It is clear from the figure that the presence of nanocellulose whiskers significantly enhanced biodegradation of PVC in soil. Neat PVC lost about 10% of its weight after being buried in soil for 4 weeks while PVC containing 3,5 and 8 wt% of nanocellulose whiskers lost about 55, 60 and 69%, respectively after the same period buried in soil. The increases in biodegradation of PVC in soil as a result of presence of nanocellulose whiskers could be interpreted by the mechanism suggested by Kiatkamjornwong et al. who found faster disintegration of polyethylene in presence of starch [26]. Because cellulose as natural polymer biodegradation is faster than PVC, nanocellulose component in the nanocomposites sheet is consumed by the microorganisms faster than PVC leading to increased porosity, void formation, and the loss of the integrity of the PVC matrix. The PVC matrix will be broken down into smaller fragments. Therefore overall faster disintegration of nanocomposites containing nanocellulose than that of neat PVC is observed.

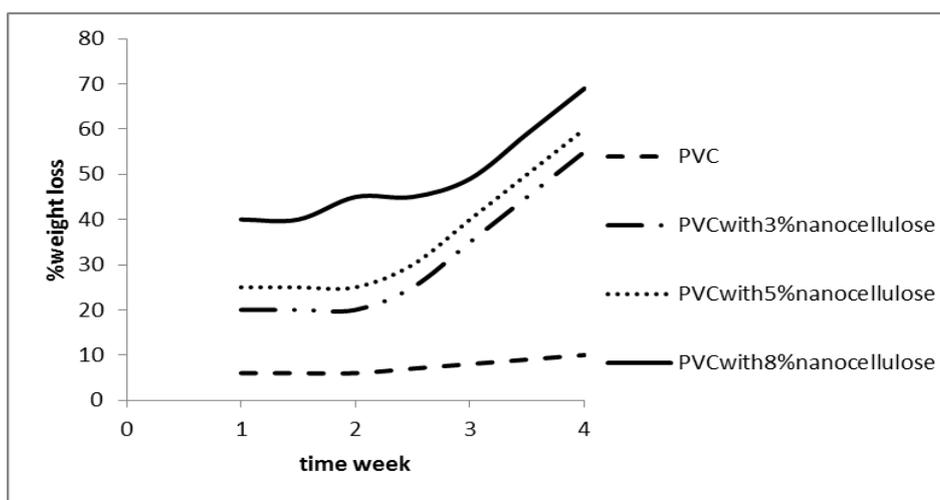


Figure 6: Biodegradable of PVC, PVC/nanocellulosecomposites.

Moisture sorption of PVC/cellulose whiskers nanocomposites

Moisture sorption of the prepared nanocomposites was measured at 75% relative humidity at 25 °C and the results are presented in Fig. 7. Adding rice straw whiskers to PVC resulted in increasing moisture sorption of the nanocomposites due to the hydrophilic nature of cellulose whiskers; the increase in moisture sorption was significant at whisker loading of 3%. However, increasing the whisker loading from 0.5 to 1.5% resulted in no increase in moisture sorption of the nanocomposites and a slight decreases in moisture sorption was noticed at 8% loading.[16]

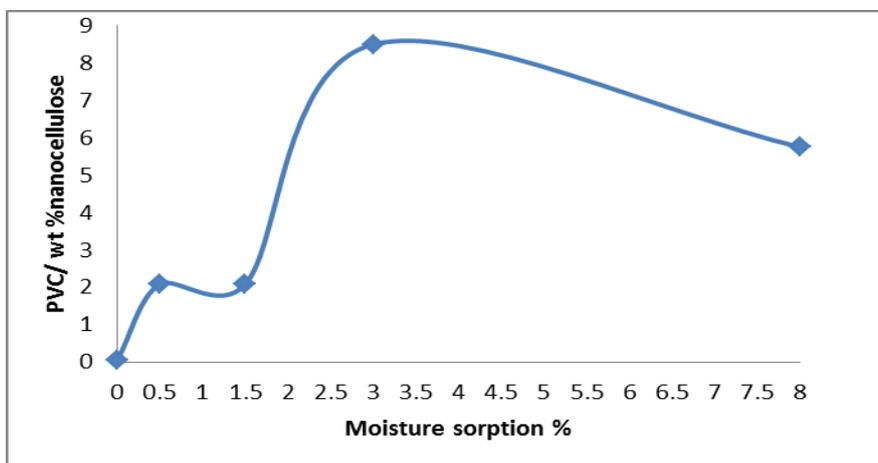


Figure 7: The change in moisture sorption % of nanocomposites with nanoparticle loading

CONCLUSION

Biodegradable nanocomposites were prepared by melt mixing mixture of PVC and nanocellulose whiskers isolated from rice straw; it was found that the dispersion of the nanocellulose in the PVS to form nanocomposites is good. Incorporation of cellulose whiskers into PVC result nanocomposites with enhanced mechanical properties as well as biodegradability of polyvinyl chloride. Aspect ratio of cellulose whiskers is an important property in enhancing the tensile strength and elongation to break %.It was found the biodegradation of the prepared nanocomposites increases with increasing the nanocellulose percentage in the nanocomposites

REFERENCES

- [1] Dufresne A. Cellulose-based composites and nanocomposites. In: Gandini, A, Belgacem, M.N. (Eds.), Monomers, polymers and composites from renewable resources. Great Britain, 2008a;pp 401–418.
- [2] Dufresne A. *Canada J Chem* 2008b;86:484–494.
- [3] Samir AMA, Alloin F, Dufresne A. *Biomacromol* 2005;6:612–626.
- [4] Habibi Y, Lucia LA, Rojas OJ. *Chem Rev* 2010;110 (6):3479–3500.
- [5] Wang N, Ding E, Cheng R. *Polymer* 2007;48 (12):3486–3493.
- [6] Marcovich NE, Auad ML, Bellesi NE, Nutt SR, Aranguren MI. *J Mater Res* 2006;21 (4):870–881.
- [7] Chakrabarti S, et al. *J Hazard Mater* 2008;154(1–3):230-236.
- [8] Sil D, Chakrabarti S. *Solar Energy* 2010;84(3):476-485.
- [9] Behl A, Sharma G, Kumar G. *Constr Build Mater* 2014;54:113-117.
- [10] Abdel-Naby, AS, Al-Ghamdi, AA. *Int J Biol Macromol* 2014;70:124-130.
- [11] Matuana LM Balatinecz, JJ and Park CB. 1997 In fluence of plasticizer on the melt flow and michenical properties of PVC/new sprint fiber composites special areas annual technical conf. Antec ,conf. proceedings 3580-3585.
- [12] Sen SK, Raut S. *Journal of Environmental Chemical Engineering* 2015;3(1):462-473.
- [13] Das G, *J Hazard Mater* 2012;209–210, 434-442.
- [14] Villanova JCO, et al. *European Journal of Pharmaceutical Sciences* 2011.
- [15] Dalev PG, et al. *J Appl Poly Sci* 2000;78(7):1341–1347.
- [16] Julien Brasa, Mohammad L. Hassan, Cecile Bruzessea, Enas A. Hassan, Nahla A. El-Wakil, Alain Dufresnea. *Industrial Crops and Products* 2010;32(3):627–633.
- [17] Ibrahim, M.H, Agblevor, FA, Elzawawy. WK. *Bioresource* 2010;5:397-76.
- [18] Liu CF, Ren JL, Xu F, Liu JJ, Sun JX, Sun, RC. *Agric food Chem*, 2006;54:5742-5748.
- [19] He Y, Ma X. *Bioresource Technol* 2015;189:71-80.
- [20] Zhu HM, Jiang XG, Yan JH, Chi Y, Cen KF. *J Anal Appl Pyrol* 2008 ;82:1–9.
- [21] Xu J, Liu C, Qu H, Ma H, Jiao Y, Xie J. *Polymer Degradation and Stability* 2013;98(8):1506-1514.
- [22] Jiménez A, Berenguer V, López J, Sánchez A. *J Appl Polym Sci* 1993:50, 1565–1573.
- [23] Statheropoulos M. *J Anal Appl Pyrol* 1986 ;10: 89–98.
- [24] Williams PT, Besler S. *Fuel* 1995;14 (9):1277–1283.
- [25] Xie X, liu Q, et al. *Polymer* 2004 ;45: 6665-6673.
- [26] Kiatkamjornwong S, Thakeow P, Sonsuk M. *Polymer Degradation and Stability* 2001;73 (2): 363–375.