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Nanocellulose / Polystyrene nanocomposites: Biodegradation, Morphology and Mechanical Properties.

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ABSTRACT

Nanocellulose/polystyrene (NC/PS) nanocomposites were prepared by a conventional solvent casting technique with different concentrations of NC (0.1, 0.4, 0.8, 2, 4 and 7 wt%). The biodegradation behavior of the nanocomposites was performed by the soil burial method, where the weight loss and average molecular weight results of the NC/PS as a function of biodegradation time obtained from the soil before and after burial test are determined. Scanning electron microscopy images of the NC/PS nanocomposite surfaces (0.1 and 2 wt.%) before and after biodegradation in soil is investigated. The change in the structure of was confirmed by Fourier transform infrared spectroscopy before and after buried for 4 months. The effect of NC on the nanocomposites mechanical properties; tensile strength and elongation at break were examined. Derivative differential scanning calorimetry curves were used to determine the thermal degradation, thermal stability and glass transition of the prepared nanocomposites. Finally, the pathogenic strains of nanocomposites were studied, where the microbial degradation of PS and NC/PS nanocomposites sheets was verified using ASTM G22-76 standard method that conformed nanocellulose helps in degradation of nanocomposites through the formation of porous in the structure of NC/PS nanocomposites.

Keywords: Nanocellulose, Nanocomposites, Polystyrene, Biodegradation, Mechanical Properties.

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INTRODUCTION

Thermoplastics polystyrene (PS) is considered as the most commonly used polymer, as it is used in different industrial applications such as food industry (packaging and storage), appliances, automotive and foam industry [1, 2]. Its high stiffness, strength and transparency, non-toxicity, good solvent resistance, excellent surface gloss, good processability and good machinability are some of the favorable properties of polystyrene [1, 3], but one-third of the world's landfills has filled up with its waste. The plastics get off by burning is locally forbidden because it causes great environmental problems [4, 5]. Many researchers are interested in studying the degradation of PS [6, 7]. Incorporation of natural, renewable fillers like cellulose into the polymer matrix is expected to enhance its degradation properties and render improved biodegradability to the composite material as cellulose or starch where it is susceptible to degradation by microorganisms. These composites under certain regulated conditions like in aerobic compost or in the soil are likely to show a significant biodegradability depending on their chemical constituents, structural characteristics, and availability of desired microorganisms in that environment [8]. This work aims to extract cellulose from rice straw using sulphuric acid hydrolysis then blended with PS to form NC/PS composites. The effect of NC was studied by investigations its biodegradability, thermal stability and mechanical properties.

MATERIALS AND METHOD

Materials

Polystyrene (PS) was obtained from Shanghai Chlor-Alkali Chemical Co. Ltd, China. Nanocellulose (NC) was prepared according to the method is given in [9]. Toluene was purchased in industrial grade.

Preparation of nanocellulose/polystyrene nanocomposites

NC/PS nanocomposites were prepared by a conventional solvent casting technique. Where about 50 g of PS was dissolved in 300 mL toluene at different loadings of NC. The solutions were sonicated for 3 h to obtained ratios of 0.1, 0.4, 0.8, 2.0, 4.0 and 7.0 wt.% (wt./wt. of NC/PS). The samples were given codes as NC/PS-0.1, NC/PS-0.2,.....and NC/PS-7.0, respective to NC content. Then transferred to a glass petri dish that to prepare the polymer nanocomposites film by casting and allowing to evaporate the solvent to get a thin film.

Determination of the average molecular weight of nanocellulose/polystyrene nanocomposites

The weight-average (M_w) and number average (M_n) of NC/PS samples were determined, before and after burying using GPC apparatus. Every sample (0.01 g) was dissolved in 2 mL of THF solvent, then filtrated by siring filter 0.45 micro using GPC device (PI gel particle size (5 μm), 2 columns of pore type (10^3 and 10^5 \AA) on series, length 7.5x300 mm (M_w 1000, 3000000) (Agilent Germany). Where the decrease in $M_w\%$ can calculate from the decreases in molecular weight by the following equation.

$$M_w = \frac{\text{average molecular befor buried} - \text{average molecular after buried}}{\text{average molecular befor buried}}$$

FTIR spectroscopy

FTIR spectra were determined with an FTS-40, USA FTIR spectrophotometer using KBr discs containing 2.5% finely ground sample. Absorption mode was recorded in the range 4000–400 cm^{-1} .

Mechanical testing

Tensile strength and elongation tests 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 50 mm/min.

Scanning electron microscopy

The nanocomposite samples for transmission electron microscopy (SEM) observation were ultrathin-sectioned using a microtome equipped with a diamond knife. The sections (100–200 nm) were cut from a piece of about 1×1 mm², were collected and placed on a 200 mesh copper grid. The transmission electron micrographs used were the type of JEM-1200EX apparatus running at an acceleration voltage of 80 kV.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on a TGA thermal analysis system of Perkin Elmer Co. at a heating rate of 10 °C/min. under a flowing nitrogen atmosphere. The temperature scan ranged from room temperature up to 700 °C.

Differential scanning calorimetry

The preparation of the samples that used for the differential calorimetric was similar to the TGA. Meanwhile, the analysis in the DSC was performed using the Mettler Toledo DSC822 analyzer. The temperature was programmed in the range of 25 to 400 °C, under a nitrogen atmosphere.

Biodegradation of nanocomposites

The biodegradation of NC/PS nanocomposites in soil was carried out as reported elsewhere [10], where the soil was taken from the surface layer. All inert materials were removed to obtain a homogeneous mass. Around 100 g of 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 after 4 months where the samples were carefully taken out, washed with distilled water, dried at 50 °C for 24 h and then weighed.

Pathogenic strains

Staph. aureus (ATCC 6538), *Pseudomonas aeruginosa* (ATCC9027), *Bacillus cereus* B-3711 and *Bacillus subtilis* (ATCC 6633) were provided by the Northern Regional Research Laboratory in Illinois, USA. *Listeria monocytogenes* was provided by the Department of Food Science, University of Massachusetts, Amherst MA, USA. *Escherichia coli* O175: H7 were isolated and serologically identified by dairy microbiological Lab., National Research Center. *Aspergillus niger* (An) and *candidia albicans* (Can) (ATCC 36232) were provided by the Institute of Applied Microbiology, University of Tokyo, Japan.

RESULTS AND DISCUSSION

The effect of burial on weight loss

The results of the nanocomposite NC/PS as a function of biodegradation time obtained from the soil before and after burial test is shown in Table 1. The nanocomposites samples with functionalized cellulose fillers exhibited a weight loss after 4 months of 0.70, 4.73, 4.79, 5.25, 6.80 and 8.60% for NC/PS-0.1, NC/PS-0.4, NC/PS-0.8, NC/PS-2.0, NC/PS-4.0 and NC/PS-7.0 respectively compared to that of PS alone that showed no degradation in soil [11]. NC/PS-7.0 showed highest weight loss compare to the other samples, which might be due to the lower

nanocellulose content. This might be due to the homogeneous dispersion of cellulose fillers into the polymer matrix and chemical bonding between them. The soil microorganisms could consume the cellulose component of nanocomposites, but the cellulose degradation in the nanocomposites lead to chemical bond breakage between the PS molecules and functionalized cellulose fillers. This might have caused weak points in the PS molecules and facilitated fragmentation of the long PS chains into smaller ones that could become easily available to the microorganisms for further breakdown [12]. This clearly shows that the chemical structure of the nanocellulose fillers and their interaction with the PS molecules had a significant influence on the nature of the degradation of the composite and its weight loss.

Table 1. The composition and degradation ratio of NC/PS nanocomposites.

Sample	Amounts of NC (%)	Weight before buried (g)	Weight after 4 months of buried (g)	Degradation ratio (%)
NC/PS-0.1	0.1	14.2	14.1	0.70
NC/PS-0.4	0.4	6.12	5.83	4.73
NC/PS-0.8	0.8	5.42	5.16	4.79
NC/PS-2.0	2.0	5.90	5.59	5.25
NC/PS-4.0	4.0	5.44	5.07	6.80
NC/PS-7.0	7.0	5.00	4.57	8.60

Effect of nanocellulose on the molecular weight

The number average molecular weight (M_n) and the weight average molecular weight (M_w) of NC/PS nanocomposites before and after biodegradation in soil were studied and the obtained results are shown in Table 2. M_n of NC/PS-0.1, NC/PS-2.0 and NC/PS-7.0 was found to be 1.4198×10^5 , 1.6931×10^5 and 2.0669×10^5 g/mol, respectively. The decrease in M_n was found to be 9.70, 23.04 and 43.05%, for the nanocomposites, respectively. On the other hand, M_w of NC/PS-0.1, NC/PS-2.0 and NC/PS-7.0 was found to be 4.9209×10^5 , 5.0361×10^5 and 5.0436×10^5 g/mol, respectively. The decrease in M_w was found to be 7.50, 13.40 and 20.32%, for the nanocomposites, respectively.

Table 2. The number average molecular weight (M_n) and the weight average molecular weight (M_w) before and after buried.

Sample	M_n before buried ($\times 10^5$)	M_n after buried ($\times 10^5$)	Decreases in M_n (%)	M_w before buried ($\times 10^5$)	M_w after buried ($\times 10^5$)	Decreases in M_w (%)
NC/PS-0.1	1.4198	1.2814	9.70	4.9209	4.5511	7.50
NC/PS-2.0	1.6931	1.3020	23.04	5.0361	4.3570	13.40
NC/PS-7.0	2.0669	1.1777	43.05	5.0436	4.0180	20.32

Morphological analysis of nanocellulose/polystyrene nanocomposite

Fig. 1. shows the SEM images of NC/PS nanocomposite surfaces (NC/PS-0.1 and NC/PS-2.0) before and after biodegradation in soil. NC/PS-0.1 and NC/PS-2.0 films showed a smooth surface before biodegradation as seen in Fig. 1(a and c). While, after biodegradation, the composite films exhibited rougher surfaces due to the presence of the fillers (Fig. 1(b and d)). The nanocomposite films exhibited a smoother surface than the degradable nanocomposite due to the presence of cellulose nanofibers which enhanced the biodegradability of the NC/PS composites and rapid degradation of the cellulose fibers left behind a rougher surface.

For the nanocomposite films (NC/PS-0.1 and NC/PS-2.0) after keeping under the soil for 4 months, distinct holes appeared of biodegradation due to microbial attack. The homogeneous dispersion of the nanocellulose fibers into the polymer matrix and good filler/matrix interfacial bonding [13] helps to increase the rate of

biodegradation in a uniform and rapid way providing sufficient surface area for microbial activity and easier microbial migration into the NC/PS nanocomposite matrix [14].

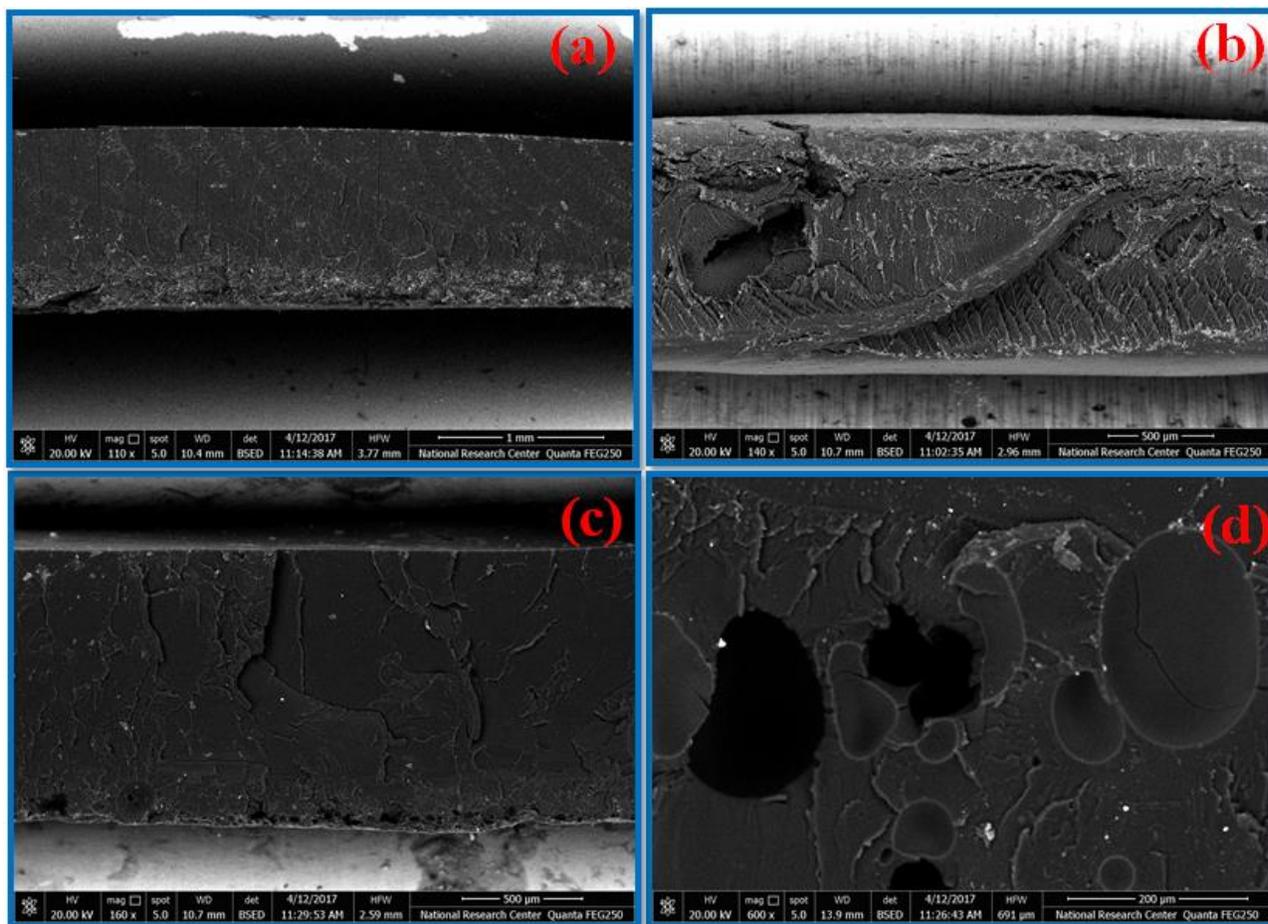


Fig. 1. SEM images for NC/PS-0.1 and NC/PS-2.0 nanocomposites before (a and c) and after (b and d) biodegradation.

The mechanical properties

For the tensile strength (TS) measurements, it was found that with increasing the NC content from 0 to 0.8 wt.%, TS increased from 42.4 to 52.0 MPa as shown in Fig. 2. It is known that the addition of fillers to the rigid matrix causes higher stiffness but simultaneously has an embrittling effect on the composite in compare to a native polymer matrix [15]. NC interacted successfully with PS and its effect in the improvements in strength and stiffness below 1 wt.% loadings indicates that there is potential for utilizing NC as a reinforcing filler in gluten-based composites. On the other hand, the increasing of NC loading above 0.8% resulted in decreasing in TS as a result of the aggregation effect of nanoparticles in the PS matrix [15]. NC surface interacted successfully with the PS matrix, where NC dispersion is improved in the PS matrix. That nanocellulose reinforced the nanocomposites due to the interfacial adhesion enhancement of NC in the PS matrix. It was found that NC addition increases the TS and flexibility. However, the TS slightly decreases after 0.8% due to agglomeration of nanocellulose.

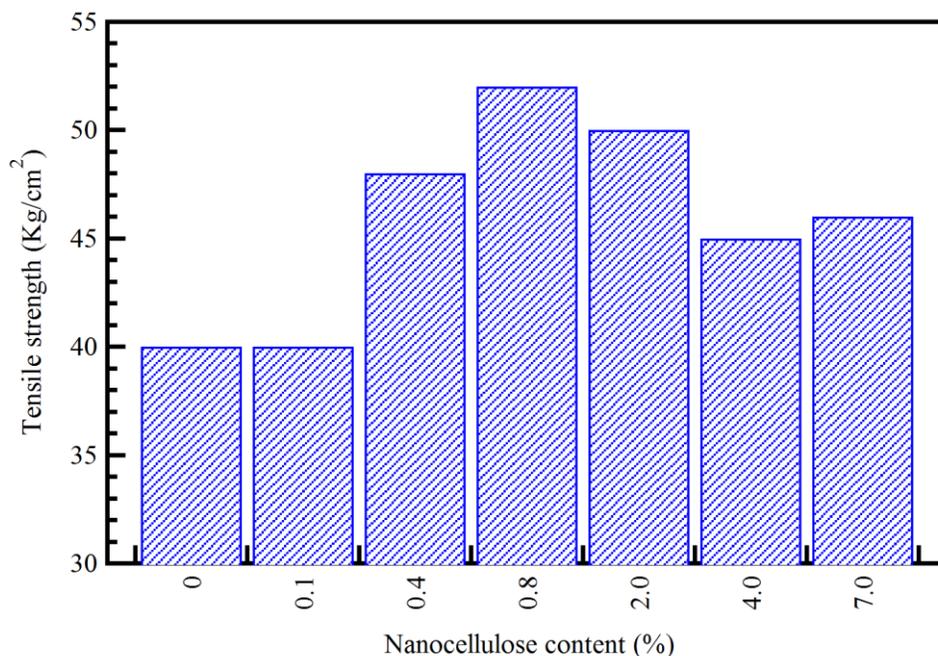


Fig. 2. The tensile strength of nanocomposites as a function of nanocellulose content.

The increase in the NC content from 0 to 0.4 wt.% led to an increase in the elongation at break from 3 to 8% as displayed in Fig. 3. That may be due to the strong interaction between NC fiber and matrix caused by large interfacial areas which led to much higher elongation at break or the cellulosic fiber work as a lubricant for the PS chains, then it starts to decreases with further increase the amount of NC in the nanocomposite. That due to the aggregation effect of nanoparticles in the PS matrix [16].

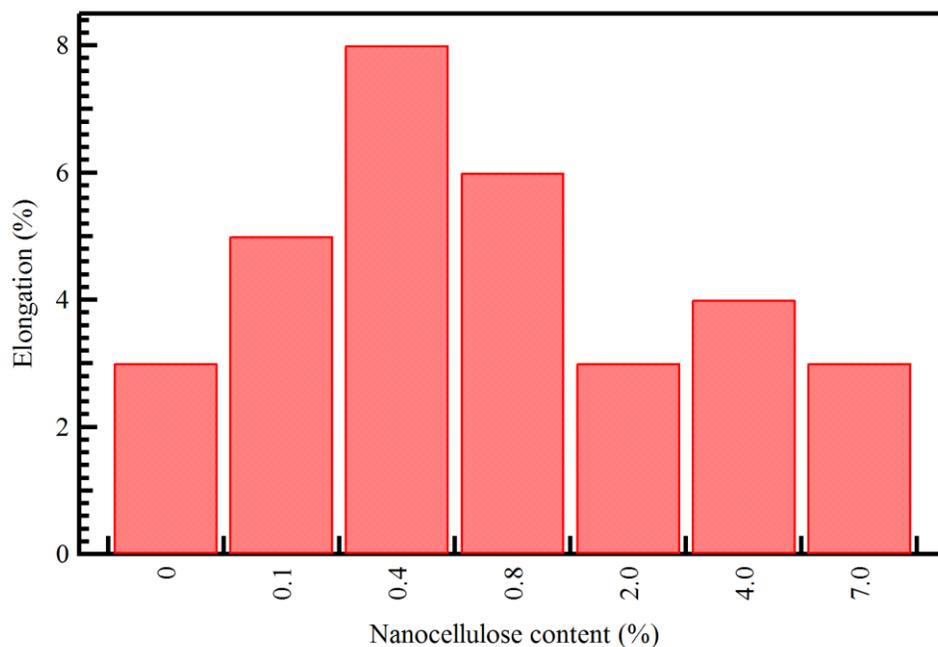


Fig. 3. Elongation at break of nanocomposites as a function of nanocellulose content.

The change in the nanocomposites chemical structure

The FTIR spectra of NC/PS-7.0 nanocomposites are shown in Fig. 4. The spectral peaks of nanocellulose rice straw and its functional groups are observed [9]. PS demonstrated sharp bands at 3080, 2940, 2866, 1666, 1472, 1379, 754, and 687 cm^{-1} . The asymmetric and symmetric stretching vibrations CH_2 bands were correlated at 2940 and 2866 cm^{-1} . The band at 1666 cm^{-1} was due to the $\text{C}=\text{C}$ of the vinyl group while the band at 1472 and 1379 cm^{-1} resulted from the deformational vibrations of both $-\text{CH}_2$ and the benzene ring of the styrene molecule [17]. However, the CH bending band (1379–1290 cm^{-1} region) in nanocomposites was double-peaked as compared to a large single peak for nanocellulose. The bands that are related to NC are decreased as the peaks related to PS becomes moderately major, during the composting. The band at 3324 cm^{-1} is due to the presence of $\text{O}-\text{H}$ band as evidence for the presence of nanocellulose. The presence of two bands at 992 and 1049 cm^{-1} are linked to $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{H}$ stretching vibrations, respectively, that confirm the presence of NC in PS composites.

After 4 months of buried of the composites, the bands due to $\text{C}-\text{O}-\text{H}$ at 1049 cm^{-1} due to intermolecular interactions between NC and PS has been disappeared. While the band at 992 cm^{-1} corresponding to $\text{C}-\text{O}$ stretching vibration remain with non-significant change. These results attributed to the degradation of NC and hence the breakdown of intermolecular interactions with polystyrene. The band at 1666 cm^{-1} of $\text{C}=\text{C}$ was shifted to 1680 cm^{-1} (an increase of 14 cm^{-1}) indicating that weakening of $\text{C}=\text{C}$ stretching. Other bands at 2866 and 2940 cm^{-1} which corresponds to CH_2 symmetric and asymmetric stretching vibrations, respectively, has been shifted upfield to 2868 and 2943 cm^{-1} with decreasing indicating more degradations of NC/PS composite. The bands at 1472 and 1379 cm^{-1} which are related to CH_2 and phenyl ring of the styrene molecule deformational vibrations were shifted to 1501 cm^{-1} and 1458 cm^{-1} , respectively, indicating more degradation of the composites. The $\text{O}-\text{H}$ band at 3450 cm^{-1} region is due to the existence of some nanocellulose in nanocomposites. The band at 754 cm^{-1} indicates the $\text{C}-\text{H}$ in the aromatic ring was shifted to 775 cm^{-1} indicate the degradation of nanocomposites. From the above, the polystyrene related bands at 1666, 1472, 1379, 754 and 687 cm^{-1} were shifted to higher values proposing that some of the bands in polystyrene had been weakened.

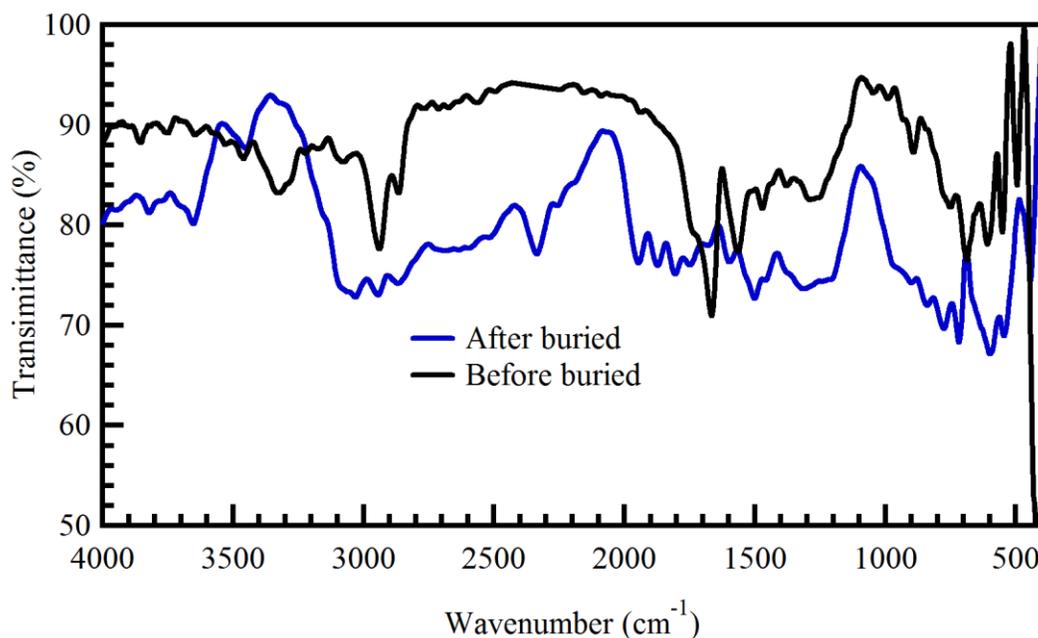


Fig. 4. The FTIR NC/PS composites NC/PS-7.0 before and after buried for 4 months.

Thermal analysis

Fig. 5a, 5b and 5c shows TGA, DTG and DSC curves of PS, NC/PS-0.1 and NC/PS-7.0, respectively to determine the thermal degradation and thermal stability of PS, NC/PS nanocomposites. PS degraded very slowly to remove the moisture content as there was only one stage of weight loss process, which had a transition temperature (T_i) that began from 320 °C and the final transition (T_f) at 460 °C. It is clear that the peak transition temperature of PS is located at 414 °C (Fig. 5b). The final weight loss of PS is found to be 99.8%. According to the literature [17-20] nanocellulose shows one main step of weight loss apart from a small weight loss at 50-70 °C as a result of moisture, the onset of weight loss of the main step of degradation lies at about 275 °C. The NC/PS composites degradation temperatures lie between the degradation temperatures for the NC and PS. For NC/PS-0.1 nanocomposite the T_i is at 120 °C and the T_f at 451.9 °C, however, NC/PS-7.0 the T_i is at 90 °C and T_f is at 461 °C. That means the NC has no effect on the degradation process of composites. The degradation process of the nanocomposites takes place in two stages. The first stage is the evaporation of the moisture, then NC degradation takes place. The first step for NC/PS-7.0 degradation starts from 90 °C and ends at 298 °C, with the peak temperature at 205 °C, but for NC/PS-0.1 it starts at 120 °C and ends at 294 °C with the peak temperature at 178 °C. The tiny peak of the DTG curve confirms that the moisture and NC content in the first step were less. For NC/PS-7.0 of thermal degradation occurred in the range from 298 to 461 °C, with the peak of this transition at 413 °C but for NC/PS-0.1, the major weight loss occurred in the range from 294 to 451 °C. This step of degradation indicates the degradation of the PS polymer is partially and the rest is for NC. The slightly lower transition peak value of the PS matrix indicates that the thermal degradation of NC/PS composites is enhanced more than that of PS.

The glass transition temperature (T_g) of PS was at 165 °C, while the melting point (T_m) was at 313 °C. It has been reported that, that T_g and T_m of PS were at 90 °C and 120 °C or 160 °C, respectively [20, 21]. T_g of NC/PS-0.1 is at 176 °C which means the addition of NC to reinforce PS increased the T_g value. It could be seen that T_g of NC/PS-7.0 is at 190 °C, indicating that T_g of the nanocomposite increased as compared to PS. The T_g values of NC/PS composites are within the same range of PS homopolymer, that means the NC completely miscible with PS in the composites. According to FTIR results (Fig. 4), the broad peaks of O-H content declined. Since the hydroxyl groups of nanocellulose are covalently bonded with PS, they cause the increase of the T_g . Not only the hydroxyl group improve the T_g values but also the other functional groups in NC and PS and the maximum value of T_g is 7 % NC/PS composites (NC/PS-7.0).

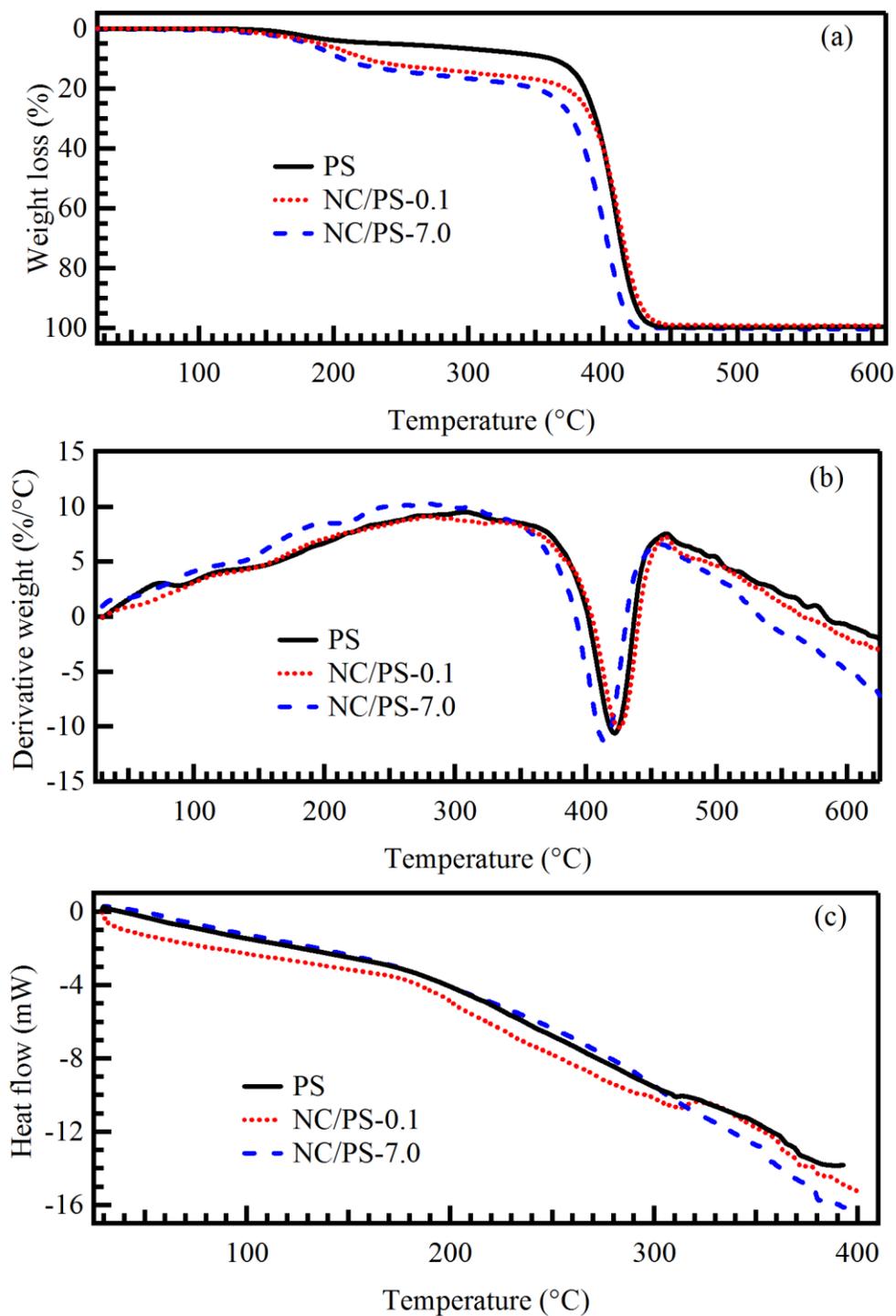


Fig. 5. TGA (a), DTG (b) and DSC (c) curves of PS, NC/PS-0.1 and NC/PS-7.0

Table 3. The thermal degradation of nanocellulose polystyrene nanocomposites.

Sample	Transition temperature (°C)			Weight loss (%)	Residual weight (%)
	T _i	T _m	T _f		
PS	320	414	460	99.85	0.15
NC/PS-0.1	120	178	294	6.37	93.39
	294	411	451	93.24	0.43
NC/PS-7.0	90	208	298	14.40	85.40
	298	413	461	84.39	1.10

3.7. Microorganism degradation of nanocomposite

The resistance degradation of PS and NC/PS nanocomposites sheets was verified using ASTM G22-76 standard method. Where *Pseudomonas aeruginosa* (ATCC9027) was used without carbon source nutrient salt. The utilization of NC as nutrient sources for microorganisms causes the microbial degradation of plastic sheets [22]. The changes in surface morphology of nanocomposites were measured as shown in Fig. 6a. The accessible structure of nanocellulose causes the microbial easily degradation. PS degraded much faster due to its extrusion expansion, in addition to PS is a rigid structure. NC enhanced the surface area compared to mass and availability of oxygen for microorganisms in PS structure due to the formation of porous in PS structure. Microorganisms fed on NC that surround the NC/PS composites increasing biodegradation since the synthetic PS lost its reliability structure through increasing porous in its structure [17]. Their final weights were decrees as in Table 1, The biodegradable surface of PS became yellowish while that unaffected by microorganism keep on unchanged. That means it is important to contact the NC/PS composites surface area by microorganisms to biodegrade [22-25]. In Fig. 6a, the NC/PS sheets become yellowish due to the consumed areas of NC that are the beginning of biodegradation. It highly appears for NC/PS-2.0 and NC/PS-7.0.

Also the *Aspergillus niger* (An) and *Candida albicans* (Can) fungus fed on NC present in since there are no carbon nutrient sources. *Aspergillus niger* (An) formed black spots as an evidence of biodegradation of NC/PS sheets during fungus growth as shown in Fig. 6b. It appears for NC/PS-0.4 and NC/PS-4.0 for *Aspergillus niger* (An) while white as colonies was observed to grow for *Candida albicans* (can) growth Fig. 6c. For NC/PS-2.0 and NC/PS-7.0 in case of *Candida albicans* (Can), signifies the result of microbial degradation through the growth of fungal/proceeding the surface of NC/PS nanocomposites sheets for the duration of the incubation period (90 days). We use blank petri dish (with no polymer) there are no colonies It proposed that fungus fed on NC/PS sheets as a source of carbon. The fungus was easy feeding on short chains as a source of energy that appeared as high colonization through incubation period in a culture which achieves that the polymer was bio blend during microbial degradation.

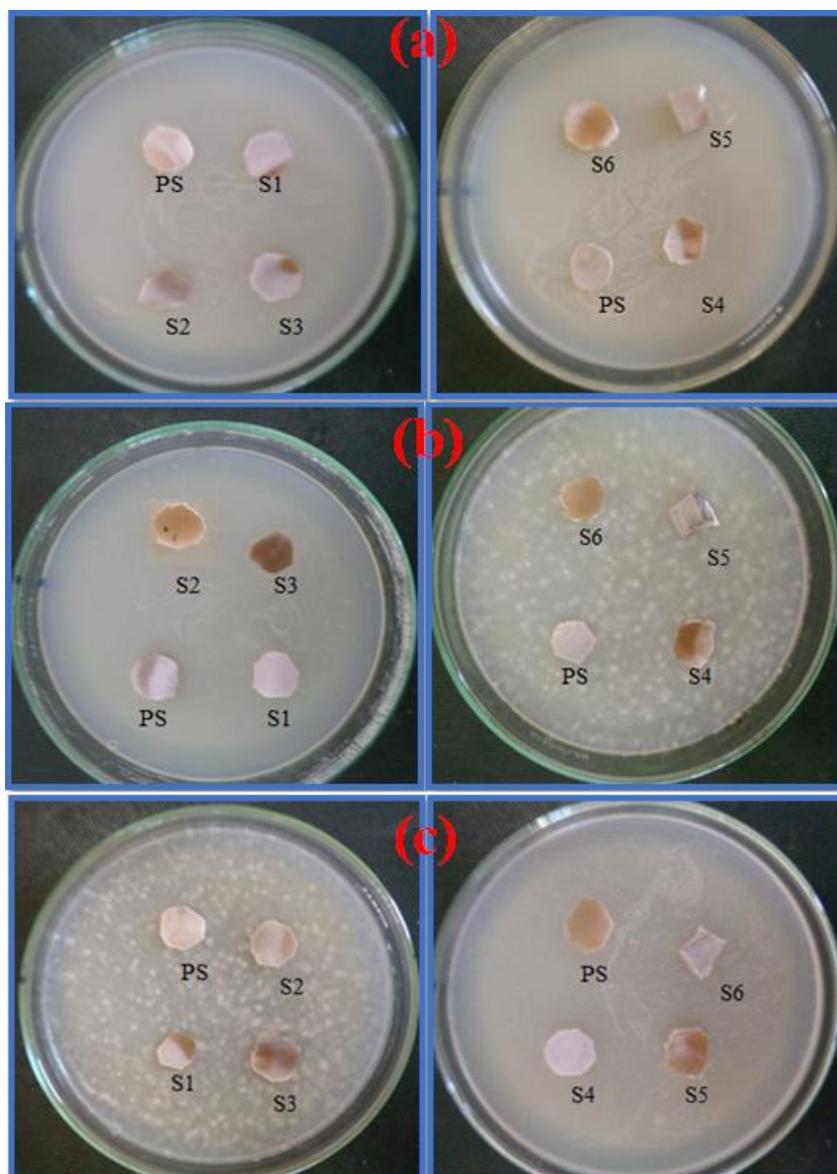


Fig. 6. Microorganisms effect on nanocomposites *Pseudomonas aeruginosa* (a), *Aspergillus niger* (b) and *Candidia albicans* (c).

CONCLUSIONS

Nanocellulose/polystyrene nanocomposites were prepared by a conventional solvent casting technique. TGA analysis shows that the nanocellulose fibers enhances the thermal stability of the prepared nanocomposites than polystyrene. The mechanical and morphological characterizations of polystyrene nanocomposites are studied. It was found that the mechanical properties are improved with the incorporation of nanocellulose fiber. The weight loss and average molecular weights were studied as an indication of biodegradation of nanocomposite polystyrene. It proved that a higher weight loss and a higher drop in weight average molecular weight (43%) and number average molecular weight (20%) with respect to 7% nanocellulose. The microbial biodegradation behavior of nanocomposites was evaluated by soil burial method and pathological treatment using *Pseudomonas aeruginosa*, *Aspergillus niger* and *Candida albicans*. The results indicated that nanocellulose indicated that nanocellulose improved the porous structure of polystyrene, due to the enhancement of the ratio between the

surface and mass. Also, the nanocellulose accelerated the accessibility of polystyrene to oxygen and microorganisms degradation.

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