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Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films

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ABSTRACT

A procedure for synthesizing cellulose nanospheres with size of 5.9 and 10.9 nm for cotton linter and linen, respectively, was developed. A series of polyvinyl alcohol (PVA)/nano-cellulose films were cast. Mechanical, biodegradation and scanning electron micrograph (SEM) of nano-cellulose-filled PVA films were studied. With the addition of 20% nano-cellulose from linen there was an increase in the tensile strength and percentage elongation at break. The SEM indicates the change in the morphological structure of the PVA films in the presence of different percent of nano-cellulose.

1. Introduction

Naturally renewable biopolymers, such as polysaccharides, proteins and lipids, can form into either coatings or stand-alone films (Kester & Fennema, 1986). Biopolymer films have been the focus of worldwide attention for the past few decades because they offer favorable environmental advantages in terms of recyclability and reutilization compared to conventional synthetic polymeric films. Many research studies on biopolymer coatings and films for food packaging applications have been reported (Gennadios, 2002; Gennadios & Weller, 1990; Kester & Fennema, 1986; Miller & Krochta, 1997). However, biopolymer films are limited in their ability to obtain wide commercial application due to disadvantages in mechanical properties and brittleness. Although plasticizers are generally added into film-forming solutions to prevent film brittleness or cracking caused by intermolecular forces (Lieberman & Gilbert, 1973; Sothornvit & Krochta, 2001), the weakness of biopolymer films in mechanical properties may not be easily overcome.

Polyvinyl alcohol (PVA) is a material with technological potential as a water-processable polymer. It has wide commercial application due to its unique chemical and physical properties (Masuhiro, Giuliano, & John, 1994). PVA is a nontoxic, highly crystalline, and water-soluble polymer and has good film-forming and high hydrophilic properties. However, PVA as a soluble polymer cannot be used in the treatment of waste waters. Thus, it has to be converted to a completely insoluble material with high mechanical properties.

Development of ecofriendly packaging materials is a continuing area of challenge for packaging technologists. The excellent chemical resistance, optical and physical properties of PVA resins, has resulted in its broad industrial uses. PVA is often modified by combination with other polymers or fillers to enhance its performance and barrier properties. Incorporation of naturally occurring polymers or fillers like cellulose and/or starch into other polymeric materials enhances the ecofriendliness.

Over the past decades, interest in sustainability and green chemistry has lead to a renewed interest in novel cellulosic materials (Ragauskas et al., 2006) and composites (degree Well et al., 2004) derived from a variety of cellulosics (Samir, Alloin, & Dufresne, 2005). Cellulose, which is a natural polysaccharide, is one of the most abundant materials in the natural world, and its biosynthesis, chemistry, and ultra structure remains as active field of study (Klem, Heublein, Fink, & Bohn, 2005; Klemm, Schmauder, & Heinze, 2002). It is a linear (1–4)-β-glucopyranan having three hydroxyl groups at the C2, C3, and C6 positions per anhydro glucose unit. In addition, the cellulose molecule has only one hemiacetal at the reducing end and one secondary hydroxyl group at the C-4 position of the non-reducing end. The hemiacetal hydroxyl group, different from the others, can be substituted with some nucleophiles by nucleophilic substitution, i.e., glycosidation. A functional group can be, therefore, introduced only into the

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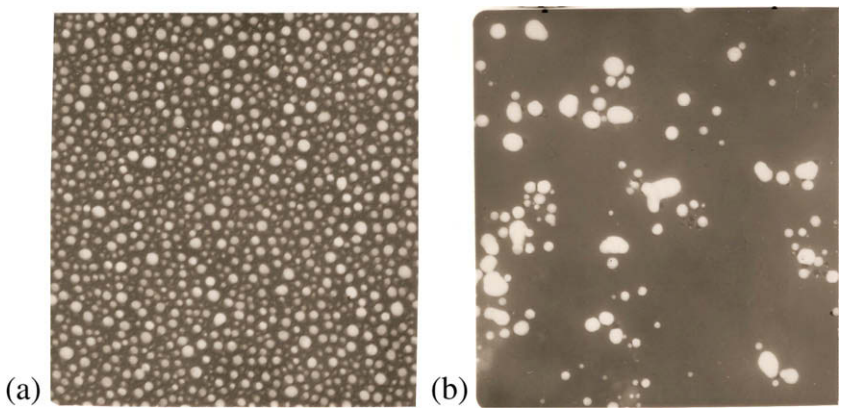

Fig. 1. TEM images of cellulose nano-particles with an average size of (a) 5.9 nm for cotton linter, and (b) 10.9 nm for linen (×40,000).

hemiacetal carbon at the reducing end with high regioselectivity (Kamitakahara & Nakatsubo, 2005).

PVA, cellulose and starch are polar polymers; thus a composite of PVA and cellulose or starch is likely to produce a material having excellent mechanical properties. Incorporation of starch and cellulose into the PVA matrix changes the physicochemical properties of the material and thus modifies the polymer structure at both the molecular and the morphological levels (Siddaramaiah, Nagarahalli, Ravi, Kumar, & Jagadeesh, 1999). This study reports on the effect of nano-cellulose content, resulted from cotton linter and linen, on the properties of PVA films, such as mechanical, and microstructural parameters. These studies were carried out to assess their potential uses as packaging films.

2. Experimental

2.1. Materials

Cellulose fibers from cotton linter and bleached linen were used for the production of nano-cellulose. PVA [degree of polymerization: 17,000–18,000; and hydrolyzed between 99.0% and 99.8% from poly(vinyl acetate) used in this study] was obtained from M/s. Loba Chem (India) and corn starch was obtained from M/s. Riddhi Siddhi Chemicals Ltd. (India).

2.2. Pretreatment

Cellulose fibers, from cotton linter and bleached linen, were treated in a method described by Zhang, Elder, Pu, and Ragauskas (2007), where 30.0 g of the cellulose fibers was transferred into 5.0 M sodium hydroxide (NaOH) solution (250.0 mL) warmed to 80 °C for 3 h. The slurry was then filtered and thoroughly washed with distilled water until the wash water was neutral. The resulting cellulosic fibers were air-dried, and then added to 250.0 mL dimethylsulfoxide (DMSO) in a 80 °C water bath for 3 h. The fibers were then filtered and washed with distilled water (3 × 250 mL).

2.3. Synthesis and purification of nano-cellulose

The pretreated fibers were transferred into an acidic aqueous solution consisting of 1000 mL mixed acid (made of 600 mL distilled water, 100 mL of 10.0 N HCl and 300 mL of 36.0 N H_2SO_4) and this suspension was heated in a water bath at 80 °C with a continuous stirring until the fiber slurry turned into milky colloid suspension. The mixture was then transferred into centrifuge bottles and centrifuged. The fractions were continuously washed by addition of distilled water and centrifuged. After washing, the products

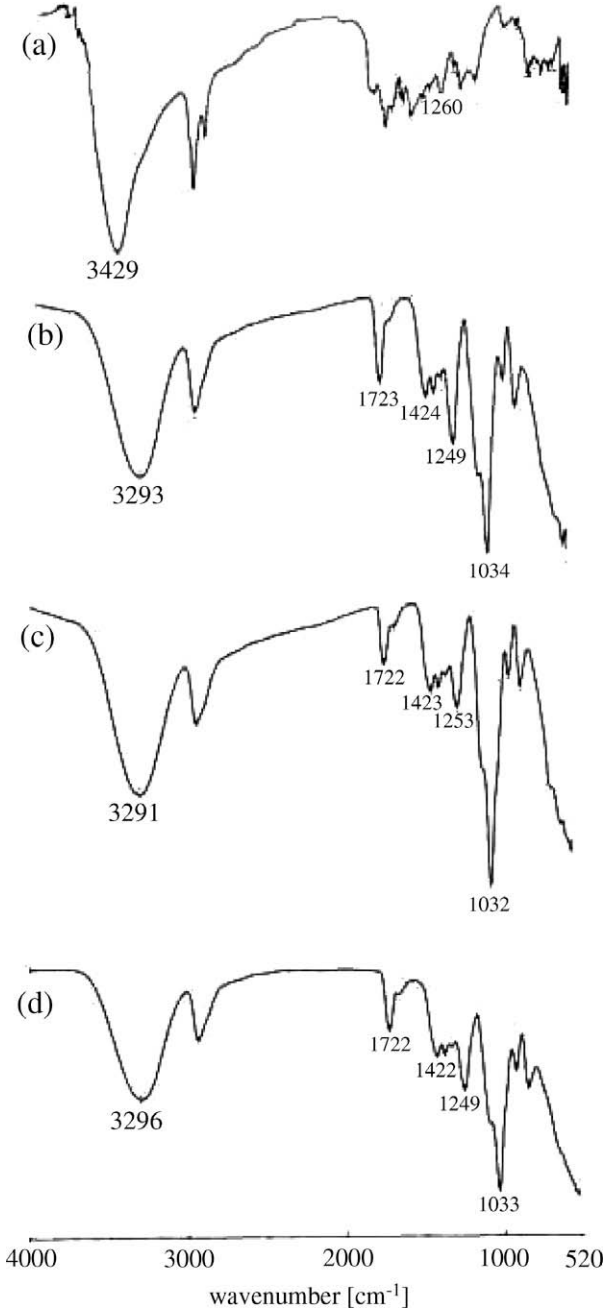

Fig. 2. FT-IR and ATR for (a) PVA, (b) PVA/20% CL, (c) PVA/40% CL and (d) PVA/60% CL.

were neutralized with 2.0 N NaOH to pH 7.0. The neutralized products were further washed another three times (3 × 150 mL). The thoroughly washed products were dried and stored for further testing.

2.4. PVA/nano-cellulose films

An aqueous solution containing 5% starch (wt.%), 75%, 55% and 35% PVA (wt.%), and 20%, 40% and 60% nano-cellulose fiber (wt.%), 2.5% glycerol and 40 mL of distilled water was used to cast films. In the presence of water, PVA was dissolved first, then starch was gelatinized in a beaker by heating it in a hot plate for 15–20 min with continuous mixing. Gelatinized starch, nano-cellulose fibers and glycerol were added to the soluble PVA while stirring until the powder nano-cellulose fiber completely dispersed in the solution.

Cast films were prepared by pouring the warm solution onto the Petri-dish plate. Plates were left to dry at room temperature overnight.

2.5. Tensile tests

The mechanical behavior of the PVA film prepared with different nano-fibers was analyzed with a LLOYD Instrument, Model LR 10K with a load cell of 100 N. Experiments were performed with a crosshead speed and distance between jaws of 5 mm/min and 50 mm, respectively at room temperature, 25 °C. The dimensions of the test samples were: length 100 mm, width 16.5 mm and thickness below 1.0 mm. Extension percent and tensile strength were calculated on the basis of initial sample dimensions, and the results were averaged over five measurements.

2.6. Biodegradation

The biodegradability of different PVA/nano-cellulose films was determined by exposing the samples to compost mud. In this study, the degradation of the film was evaluated by measuring its weight loss, which refers to the erosion of molecules from the solid phase into the aqueous phase. The dissolved components are not recalcitrant and would be easily degraded by microorganisms in a natural environment.

2.7. Image morphometry

The word morphometry means measurement of Form. Electrophoretic mobilities of the particles in pure water were measured. The nanocrystalline cellulose suspension was prepared, and analyzed with a Zesiss EM-10 (W. Germany) at 60 kV with a magnification of 40,000.

The morphometric analysis was performed at the Pathology Department, National Research Center using the Leica Qwin 500 Image Analyzer (LEICA Imaging Systems Ltd, Cambridge, England) which consists of Leica DM-LB microscope with JVC color video camera attached to a computer system Leica Q 500IW.

The morphometric analysis is carried out on nanocrystalline celluloses from cotton linter and linen. We start measuring the length of the nucleus (*x*-axis) by drawing a line starting from one edge to the other. Then we measure the width of the nucleus (*y*-axis) by drawing a line from one edge till the opposite by using the interactive measurement software of the system on a total magnification of (200×). We can also measure the nuclear area or diameter by choosing the suitable software. The results appear automatically on the monitor in the form of the distant measured in (μm) or area in (μm^2) with the mean, standard deviation, the minimum length and the maximum length measured.

2.8. FT-IR spectra

FT-IR spectroscopy was used to confirm a reaction occurred between PVA and nanocrystalline celluloses. The IR spectra of PVA were compared with the ATR spectra of PVA/nano-cellulose films and were performed using a Thermo-Nicolet Model 670 Instrument (Thermo Electron, Inc, Madison, WI).

2.9. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the morphology of the different types of films, i.e. PVA/20% nano-cellulose, PVA/40% nano-cellulose and PVA/60% nano-cellulose by using a JEOL JXA-840 A electron microprobe analyzer (JEOL USA Inc, Peabody, MA). The specimens for the PVA/nano-cellulose films were frozen under liquid nitrogen, fractured, mounted, coated with gold/palladium and observed using an applied tension of 30 kV.

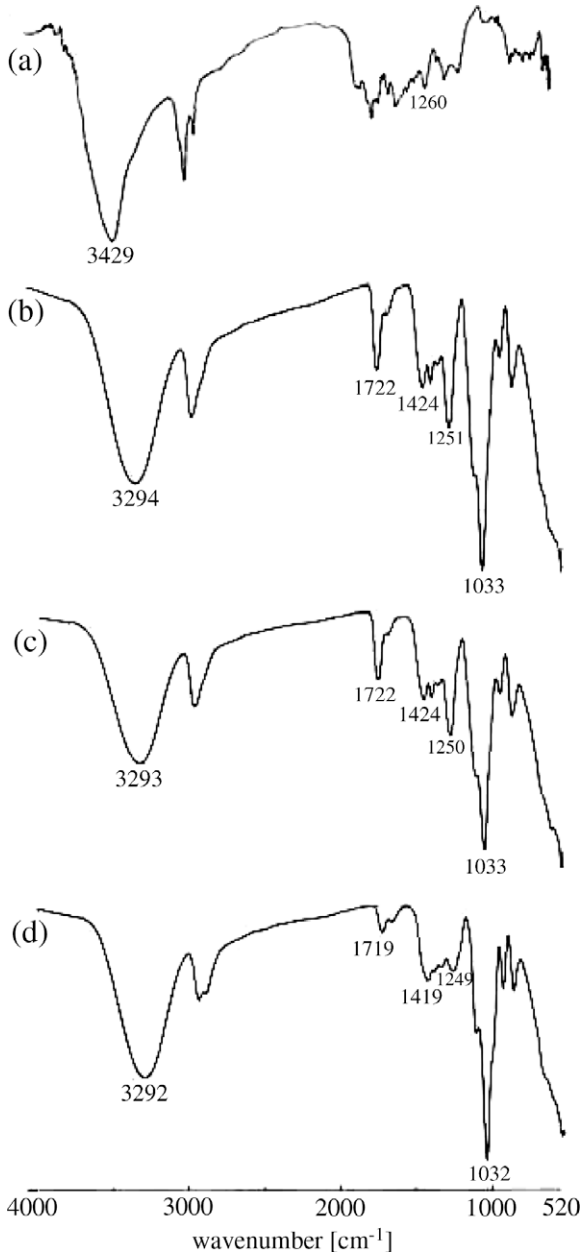

Fig. 3. FT-IR and ATR for (a) PVA, (b) PVA/20% L, (c) PVA/40% L and (d) PVA/60% L.

3. Results and discussion

3.1. TEM image

Synthesis of cellulose nanosphere structures involved an initial swelling of cellulose cotton linter and cellulose linen with 5.0 M NaOH solution at 80 °C for 3 h, followed by treatment with DMSO. The pretreated cellulose was then acid hydrolyzed with a mixed $HCl–H_2SO_4$ solution at 80 °C till milky solution. The resulting hydrolyzed products were purified by centrifugation. Particle size analysis of the hydrolyzed cellulose suspension indicated that the product consisted of two different particle size depending on the starting cellulose type. The average size was approximately 5.9 and 10.9 nm for nano-cellulose resulted from cotton linter and linen, respectively.

Additional studies on the Image Morphometry demonstrated that particle area for the nano-cellulose resulted from cotton linter is 16.35 μm^2 with a distance of 15.76 μm, while the area was 29.41 μm^2 for that resulted from linen with a distance of 19.76 μm.

The TEM image shown in Fig. 1a is that of cellulose nano-particles obtained from acid hydrolysis of cellulose cotton linter, while that shown in Fig. 1b is obtained from acid hydrolysis of cellulose linen. The particle shapes were irregular for those resulted from cellulose linen but overall spherical in shape.

3.2. IR spectrum

The reaction between the PVA and nano-celluloses was confirmed by FT-IR (see Figs. 2 and 3). FT-IR spectra of PVA (Spectrum a) and ATR spectra of PVA–nano-cellulose from cotton linter and linen at different percents (Spectrum b–d) are presented in Figs. 2 and 3. A band at 3429 cm^{-1} in Figs. 2a and 3a is attributed to the O–H stretching vibration of hydroxyl group of PVA. For PVA/nano-cellulose films, a board band around 3290 cm^{-1} can be seen, Figs. 2b–c and 3b–c, which represents the O–H stretchings for the films formed, indicating that all the hydroxyl groups of PVA and nano-celluloses are involved in the reaction. A sharp band around 1250 cm^{-1} corresponds to an acetyl C=O group present on the PVA backbone can be seen for the produced PVA/nano-celluloses, Figs. 2b–c and 3b–c. The peak due to the aliphatic C–H stretching vibrations appeared around 2931 cm^{-1}. The absorption peak observed around 1722 cm^{-1} may be due to the carbonyl (C=O) stretching vibration of the α-keto carbonyl present in the nano-celluloses thus confirming the reaction between the nano-celluloses and the PVA. The band around 1423 cm^{-1} (CH stretch) belongs to the spectrum of PVA, Figs. 2b–c and 3b–c. Furthermore, the bands around 1429 cm^{-1}, Figs. 2b–c and 3b–c, are associated with CH in-plane deformation of CH groups of the nano-celluloses. While the bands around 1033 cm^{-1} involve the C–O stretching vibrations of aliphatic primary and secondary alcohols in nano-celluloses (Khan, Idriss Ali, & Basu 1993; Kolboe & Ellefsen 1962), Figs. 2b–c and 3b–c.

3.3. Mechanical properties and SEM

The calculated mechanical properties such as tensile strength and percentage elongation at break of the PVA and PVA/nano-cellulose films are illustrated in Figs. 4 and 5. The tensile strength,

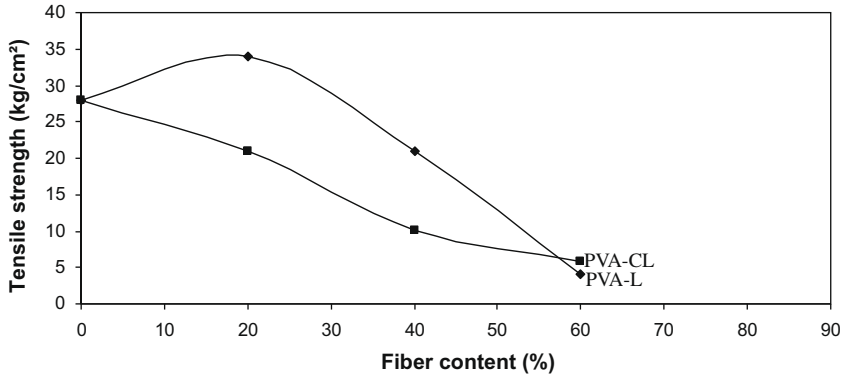

Fig. 4. Tensile strength for PVA–nano-cellulose from cotton linter and linen.

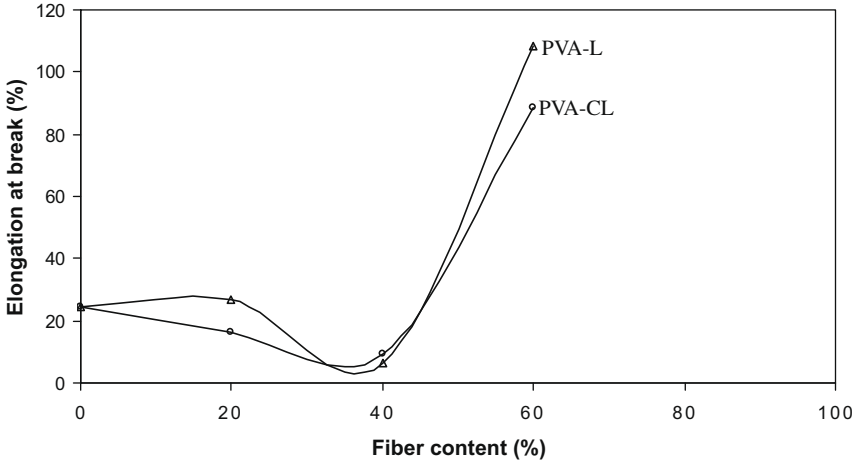

Fig. 5. Elongation at break for PVA–nano-cellulose from cotton linter and linen.

which is a measure of the resistance to direct pull, is important in application. It was observed that there was a slight variation in the tensile strength for all the compositions of PVA/nano-cellulose compared with the tensile strength of plain PVA film. From Fig. 4, one can noticed an increase in the tensile strength when a 20% of nano-cellulose from linen was added, while increasing the percentage to 40% and 60% results in a decrease in the tensile strength of the PVA/nano-cellulose film. On the other hand, the presence of the nano-cellulose from cotton linter results in a decrease in the tensile strength. Moreover, the percentage elongation

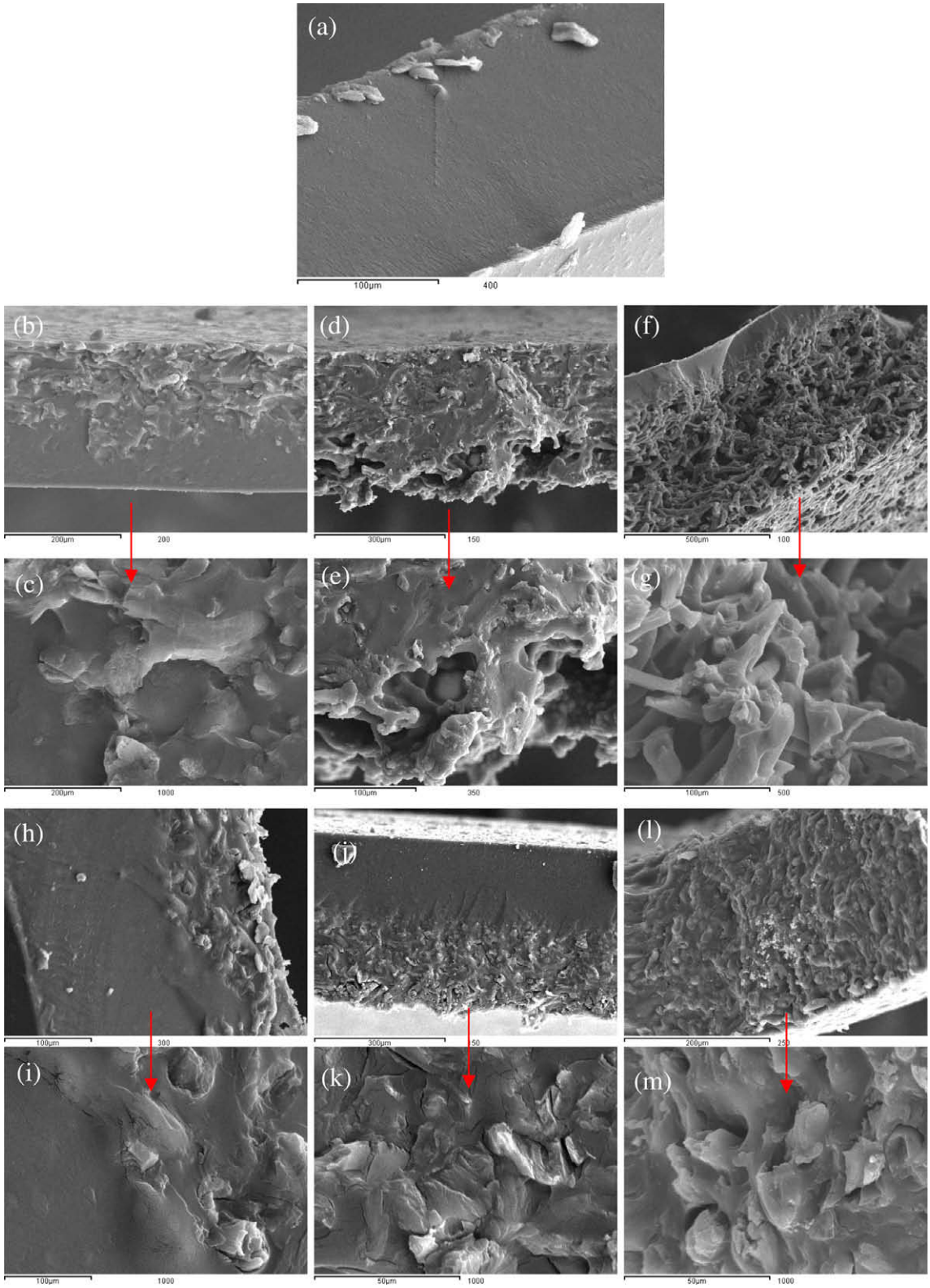

Fig. 6. Scanning electron micrographs showing a cross-section of (a) PVA, (b) and (c) PVA/20% L, (d) and (e) PVA/40% L and (f), (g) PVA/60% L, (h) and (i) PVA/20% CL, (j) and (k) PVA/40% CL and (l) and (m) PVA/60% CL.

at break of PVA/nano-cellulose from linen and cotton linter is in the range 26.8–108.53 and 16.58–88.74, respectively, whereas for plain PVA film it is 24.44, Fig. 5. The improvement or reduction in the tensile behavior of PVA/nano-cellulose may be attributed to the change in the morphological structure of the resulted film. This can be seen from the SEM of the PVA and PVA/nano-cellulose films shown in Fig. 6.

The morphology of the PVA/nano-cellulose films was examined using scanning electron microscopy (SEM). A scanning electron micrograph of typical PVA film is shown in Fig. 6a. The cross-section shows a smooth dense surface. PVA films with added nano-cellulose from linen and cotton linter are shown in Fig. 6b–g and h–m, respectively. Fig. 6b, d and f represents a cross-section for PVA/nano-cellulose from linen where the higher magnification, Fig. 6c, e and g shows a porous structure to the produced film by increasing the percent of the nano-particles to 60%. This can give an indication to the reduction of the tensile strength by increasing the percent of the nano-particles from the linen to 40% and 60%, Fig. 4. Furthermore, cross-section for PVA/nano-cellulose from cotton linter, Fig. 6h, j and l, indicating disperse of the nano-particles with the PVA forming a holes which can be seen at higher magnification, Fig. 6i, k and m. That change of the morphological structure compared to the PVA film, Fig. 6a, gives an explanation of the reduction of the tensile strength as can be seen from Fig. 4.

3.4. Biodegradation

The weight loss of biodegradation of PVA and PVA/nano-cellulose films is presented in Table 1. From the Table, it may be observed that the degradation occurred in a faster rate in the presence of the nano-cellulose particles in the PVA matrix. The released from PVA/nano-cellulose films might be theoretically nano-cellulose and PVA-metabolites such as low-molecular organic acids and ketonic compounds (Bastioli, Bellotti, Del Giudice, & Gilli 1993). This film can be easily degraded in natural condition.

4. Conclusions

The present work demonstrates that nanoscale spherical cellulose particles could be synthesized from cellulosic fibers. These cellulose spherical structures were studied by TEM and Image Morphometry. The nano-cellulose particles from cotton linter and linen can be used in a PVA films. The presence of 20% of nano-cellulose particles from linen in the PVA matrix increases the mechanical properties, such as tensile strength and percentage elongation at break. Higher percent of the nano-cellulose particles decreases the tensile strength due to the change in the morphological structure of the PVA film. The resulted PVA/nano-cellulose films can be easily degraded in natural condition.

Table 1
Biodegradation for the PVA and PVA/nano-cellulose films.

Films	Weight loss (g)			
	1st Day	2nd Day	4th Day	5th Day
PVA	0.8774	0.5681	0.4411	0.1386
PVA/20% L	1.3064	0.9281	0.1886	0.0975
PVA/40% L	0.4523	0.4145	0.2160	0.1097
PVA/60% L	1.0238	0.7183	0.5467	0.2117
PVA/20% CL	1.2847	1.0172	0.3245	0.0696
PVA/40% CL	0.8550	0.6996	0.2655	0.1254
PVA/60% CL	0.5689	0.3625	0.1527	0.0829

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