Preparation of cellulose/polyvinyl alcohol biocomposite films using 1-n-butyl-3-methylimidazolium chloride

Ali Abdulkhani a, Ebrahim Hojati Marvast a, Ali Reza Ashori b,∗, Yahya Hamzeh a, Ali Naghi Karimi a,c

a Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Karaj, Iran
b Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), P.O. Box 15815-3538, Tehran, Iran
c Institute of Tropical Forestry and Forest Products (INTROP), University of Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia

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A B S T R A C T

This study has been focused on developing cellulose/polyvinyl alcohol (PVA), a biocomposite film, pre-treated with 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]). The dissolved polymers were blended and their biocomposite films including cellulose and cellulose/PVA were prepared. The effect of PVA composition with cellulose was evaluated by comparing the physical, mechanical, chemical and thermal characteristics of produced films with neat cellulose film. The results showed that the ionic liquid had a great capability in dissolving the polymers. Furthermore, in composition of the raw cellulose some chemical bonds were incorporated between the two components. Water uptake, thickness swelling and water vapor permeability of blend films were increased compared to cellulose film. Mechanical strength and Young’s modulus of the films made of cellulose/PVA were decreased while the strain at break was increased. The optical transparency and thermal properties of the blend films were almost the same as neat cellulose film. This work demonstrated a promising route for the preparation of biodegradable green composites. In addition, this biocomposite film is composed of sustainable biodegradable resources, which is suitable for release to the environment. The biocomposite films showed good optical transparency, thermal stabilities properties.

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1. Introduction

Polyvinyl alcohol (PVA) is a water-soluble, semi-crystalline, biodegradable, non-toxic, and environmentally friendly polymer, with excellent chemical stability. PVA based composites have been successfully used in multiple studies including tissue scaffolding, filtration materials, membranes technology, protective coveralls, biotechnology and pharmaceutical applications. Additionally, PVA as a safe and compatible material has been used in drugs coating formulation, surgical suture and controlled drug delivery system [1,2]. Recent studies indicated that PVA would be a promising polymer in environmentally friendly packaging industry provided that its mechanical properties can be improved. Several studies have been conducted to improve the mechanical properties of PVA and its functional properties in conjunction with other polymers or fillers [3]. However, the cellulose film is difficult to be manufactured because its raw material cannot be melted to be fabricated into a desired form or is difficult to be dissolved in a common solvent because of the strong inter and intermolecular hydrogen bonding, high degree of polymerization (DP), and high degrees of crystallinity [4]. The fundamental problem in this context is to increase the mechanical properties of PVA without changing the basic properties of the polymer. Composition of carbon nanotubes [5,6], mineral hydroxypapatite nanoparticles [7], gold [8], silver [9], clay [10,11], silica [12], and chitin whisker with PVA have been reported. Meanwhile, a numerous efforts have been done on the use of renewable resources as reinforcing agents in nano-composite materials [2]. Development of eco-friendly packaging materials is still a challenging area and many studies have been focused on the improvement of PVA mechanical and barrier properties by combination with other polymers or fillers in order to use it in the packaging industry [3]. For many applications, mechanical properties of PVA should be substantially improved without damaging its valuable properties. Low cellulose fibers addition could be an appropriate solution. Many studies emphasized the effectiveness of large amount of cellulose fibers in improving mechanical properties of PVA.

It has been reported that mechanical properties of PVA composites are improved significantly by introducing of cellulose fibers.
Nowadays, biodegradable and renewable cellulose whiskers have gained great interest primarily due to the characteristics of high mechanical strength, aspect ratio and reactive surface [13]. To fabricate a composite, different component are generally blended together in solid state. In this concept, the characteristic of resulting composite is not optimal due to heterogeneity, poor physical mixing, thermal and chemical incompatibility of blended materials. Moreover, such processes are often lead to the thermal decomposition of material, energy dissipation and releasing of chemical contaminants. Cellulose is a rigid macromolecule that is insoluble in a variety of solvents. Cellulose/PVA composite films have been prepared by suspending cellulose fibers in water dissolved PVA and removing the solvent [14–16]. Ionic liquids (ILs) have been used versatile as green solvents in various chemical processes [17]. The melted salts have the ability to dissolve a wide range of natural and synthetic polymers including cellulose. Dissolving cellulose materials and polymers will provide a better composition of the polymers and may lead to a composite with optimized properties.

The main aim of present study is to explore the possibility of cellulose and PVA composition in liquid phase using 1-n-butyl-3-methylimidazolium chloride ([bmim][Cl]) as the polymer solvent.

2. Materials and methods

2.1. Raw materials and chemicals

Cotton linter (CL) was used as the cellulosic (99% α-cellulose) material. Imidazole-based ionic liquid, namely ([bmim][Cl]), was synthesized. The preparation procedure of ([bmim][Cl]) was reported elsewhere [18]. PVA and all other chemical reagents were purchased from Merck Company (Germany) and used without further purification.

2.2. Dissolution process

Since water competes with the IL to establish hydrogen bonds, the presence of water in the solution water may decrease CL solubility in the ILs. The CL sample was oven-dried for 24 h at 102 ± 3 °C and then kept in sealable polyethylene bags. The PVA, CL and IL were placed in a flask under a N₂ atmosphere and heated on a hot plate with magnetic stirring. The dissolution conditions used for the respective prepared mixes are given in Table 1.

2.3. Preparation of blend films

The resulting suspensions were periodically mixed and heated at 70 °C for 30 min. Subsequently, the mixture was spread in a Petri dish with the diameter of 7.5 cm to give a ca. 2 mm thick layer. The air bubbles were removed in a vacuum oven (at 100 °C and for 30 min). The composite gel was slowly formed, and further kept in the ambient temperature for 2 days. Then, the blend film was washed with running deionized water and methanol to remove the IL, and finally oven-dried.

2.4. Testing

2.4.1. Chemical characterization

2.4.1.1. Analysis of 13C NMR. The NMR spectra of PVA and cellulose dissolved in [bmim][Cl] were recorded on a JOEL JNM-ECS500 500MHz spectrometer. Sample solutions were placed in a 5-mm diameter NMR tube: a 75 pulse width, 1.4s acquisition time, and 4s relaxation delay were used. A total of 2000 scans were collected.

2.4.1.2. X-ray diffraction (XRD). Crystallinity of the samples was determined by X-ray diffraction using a D5000 SIEMENS diffractometer (Germany). The diffraction spectrum was taken by the 0–20 method. Samples were scanned at 1°/min from 2\(\theta\) = 2–40° with a step size of 0.01°. The films crystallinity was determined as the percentage of crystalline material in the sample expressed as the crystallinity index (CrI) as following:

\[
CrI = \frac{l_{002} - l_{am}}{l_{002}} \times 100
\]  

(1)

where \(l_{002}\) is the maximum intensity of the (0 0 2) lattice diffraction (2\(\theta\) = 22.5°) and \(l_{am}\) is the intensity at 2\(\theta\) = 18.7°. The average size of crystallites was calculated from Scherrer equation, which was based on the width of the diffraction patterns obtained in the X-ray reflected crystalline region.

The crystalline sizes were determined using the diffraction pattern obtained from 0 0 2 (h k l) lattice planes of cellulose samples,

\[
D_{hkl} = \frac{K\lambda}{B_{hkl}\cos\theta}
\]  

(2)

where \(D_{hkl}\) is the size of crystallite, (h k l) is the lattice plane, K is the Scherrer constant (0.84), \(\lambda\) is the X-ray wavelength (0.154 nm), \(B_{hkl}\) is the full width half maximum (FWHM) of the measured h k l reflection, and 2\(\theta\) is the corresponding Bragg angle (reflection angle).

2.4.1.3. Fourier transform infrared spectroscopy (FTIR). IR spectra of the films were recorded using a Perkin Elmer Spectrum RXI FTIR spectrometer (Perkin Elmer, UK). The spectra were recorded in the absorption band mode in the range of 4000–400 cm⁻¹. The ratio of crystallinity was determined by two methods:

- The absorbance ratio from 1372 cm⁻¹ \((A_{1372})\) and 2900 cm⁻¹ \((A_{2900})\) bands:

\[
Cr.R_1 = \frac{A_{1372}}{A_{2900}}
\]

- The absorbance ratio from 1430 cm⁻¹ \((A_{1430})\) and 893 cm⁻¹ \((A_{893})\) bands:

\[
Cr.R_2 = \frac{A_{1430}}{A_{893}}
\]

Table 1

Dissolving conditions for the used materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ratio(^*) (w/w)</th>
<th>First stage</th>
<th>Second stage</th>
<th>Third stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>1/25</td>
<td>Mixing (rpm) 500</td>
<td>Time (min) 10</td>
<td>Temp. (°C) 70</td>
</tr>
<tr>
<td>PVA</td>
<td>1/10</td>
<td>Mixing (rpm) 500</td>
<td>Time (min) 120</td>
<td>Temp. (°C) 90</td>
</tr>
</tbody>
</table>

\(^*\) Ratio of CL or PAV to IL.
The energy of hydrogen bonds \( (E_H, \text{kJ}) \) was calculated with the following equation:

\[
E_H = \frac{V}{K} \left( \frac{v_0 - v}{v_0} \right)
\]

where \( v_0 \) is standard frequency corresponding to the free OH groups (cm\(^{-1}\)), \( v \) is frequency of the bonded OH groups (cm\(^{-1}\)), and \( K = 1.6 \times 10^{-2} \text{ kcal}^{-1} \).

2.4.2. Physical properties

2.4.2.1. Optical transparency (OT). The percentage of OT or optical transmittance of the composite films was measured with a visible lux meter (Testo 540, UK). The thickness of the composites was about 0.5 mm. The results are the average of at least 5 specimens from each composite.

2.4.2.2. Water absorption (WA) and thickness swelling (TS). The WA and TS tests were conducted in accordance with ASTM D570. Before testing, the weight and thickness of each specimen were measured. Conditioned samples of each type of composite were fully immersed in distilled water at room temperature for 1, 6, 24, 48, and 72 h. Samples were removed from the water at certain time, patted dry and then measured again. The sample dimensions were 1.5 cm \( \times \) 1.0 cm \( \times \) 0.2 mm. A minimum of three samples were tested for each composite.

2.4.2.3. Water vapor permeability (WVP). WVP tests were carried out according to ASTM E 96 with some modifications [19]. The films were cut into circles, sealed over with melted paraffin, and stored in a desiccator at 20 \( ^\circ \)C. Relative humidity (RH) was maintained 0% using anhydrous calcium chloride (CaCl\(_2\)) in the cell. Each cell was placed in a desiccator, containing saturated sodium chloride, to provide a constant RH of 75%. Water vapor transport was determined by the weight gain of the permeation cell. Changes in the weight of the cell were recorded as a function of time. Slopes were calculated by linear regression (weight change vs. time) and correlation coefficients for all reported data were \( >0.99 \). The water vapor transpiration rate (WVTR) is defined as the slope (g/s) divided by the transfer area (m\(^2\)). After the permeation tests, film thickness was measured and WVP (g/smPa) was calculated according to the following Equation:

\[
WVP = \frac{WVTR}{P(R_1 - R_2)}x
\]

where \( P \) is the saturation vapor pressure of water (Pa) at the test temperature (20 \( ^\circ \)C), \( R_1 \) is the RH in the desiccator, \( R_2 \) is the RH in the permeation cell and \( x \) is the film thickness (m). Under these conditions, the driving force \( [P(R_1 - R_2)] \) was 1753.5 Pa.

2.4.2.4. Thermal gravimetric analysis (TGA). Degradation behaviors of composite films were characterized by a thermo-gravimetric analyzer TGA (Q50, TA Instruments, New Castle, DE) in a nitrogen atmosphere. Specimens of 5–10 mg each were tested in a temperature range from 25 to 600 \( ^\circ \)C. The heating rate was 20 \( ^\circ \)C/min and the nitrogen flow rate was 65 mL/min. The weight-loss rate was obtained from derivative thermogravimetric (DTG) data.

2.4.2.5. Differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) was performed on a Mettler DSC-1 (Mettler Toledo, Switzerland). Specimens of 6 to 8 mg were heated from 20 to 300 \( ^\circ \)C at a 10 \( ^\circ \)C/min heating rate.

2.4.3. Mechanical properties

After conditioning (20 \( \pm 1 \) \( ^\circ \)C, 65 \( \pm 5 \) RH) for at least 2 weeks, all the specimens were tested following ASTM D 882. The tensile strength \( (\sigma_b) \) and strain at break \( (\varepsilon_b) \) of the films were measured on a universal testing machine (Testometric M350-10CT) at a crosshead speed of 5 mm/min. The distance between the jaws was set at 1 mm. Composite films were cut in strips about 0.2 mm thick, 5 mm wide and 20 mm long. The \( \sigma_b \) and \( \varepsilon_b \) values are the averages of 5 measurements.

2.4.4. Morphological study

Studies on the morphology of the composite films were carried out using a scanning electron microscopy (SEM). SEM micrographs of the surfaces of specimens were taken using SEM model Philips XL 30 at 17 kV accelerating voltage. The oven-dried specimens were mounted on SEM holder using double sided electrically conducting carbon adhesive tabs to prevent surface charge on the specimens when exposed to the electron beam.

3. Results and discussion

3.1. Chemical characterization

3.1.1. NMR spectra

Fig. 1 shows \(^{13}\)C NMR spectra of the dissolved PVA in [bmim]Cl ionic liquid. The assignments of the peaks are completely consistent with data presented by other studies [20]. Also, IL could dissolve the PVA polymer as it could be seen in \(^{13}\)C NMR spectrum of PVA solution (Fig. 1).

Fig. 1. \(^{13}\)C NMR spectrum of PVA dissolved in [bmim]Cl and its chemical structure.
It has been reported that [bmim]Cl has a great capability in dissolving the cellulose [21].

3.1.2. XRD measurements

The X-ray obtained for the raw cellulose, regenerated cellulose and cellulose/PVA composite are presented in Fig. 2. The cotton linter diffractograms represents the normal pattern of cellulose I with the corresponding peaks in 2θ = 14.6°, 15.2°, 16.8° and 22.7° [22,23]. The regenerated cellulosic sample gave diffractogram, which clearly indicates an amorphous structure. This character is demonstrated by the absence or strong reduction of all peaks corresponding to planes {1 0 1}, {1 0 0} and {0 0 2}, to values of the Bragg angle characteristic to cellulose I. In addition, the regenerated cellulose diffractogram shows peaks in 2θ = 12.1°, 20° and 21.9°, which is the corresponding characteristic of cellulose II [20,22,24]. The peak of 2θ = 19.8° is relating to PVA crystals [22]. Moreover, by comparing the X-ray diffraction patterns of the initial cellulose with those of the obtained amorphous samples, it may be remarked that the Segal method for calculating the crystallinity index. In this respect, the obtained samples can be successfully used as an internal amorphous standard. Crystallinity of cellulose was calculated using the Segal formula. Crystallinity index of raw cellulose regenerated cellulose and cellulose/PVA were calculated as 93.1%, 82.5% and 59.6%, respectively. Table 2 presents the crystallinity degrees and average size of crystallites of the studied samples before and after dissolution and composite structure. A strong decrease of the crystallinity degree, to values of around 30%, is observed for all amorphous cellulosic samples. Thus, for regenerated cellulose, crystallinity decreases by 11%, while for cellulose/PVA film, the value is 33.5% lower. This fact can be explained by a reduction in the intra and intermolecular hydrogen bonds, occurring during the continuous transformation of cellulose I into amorphous cellulose. Moreover, this suggested that the interaction between the hydroxyl groups of PVA and cellulose had destroyed the crystallization of the cellulose [4]. The increase of the amorphous region of films could be good for the improving toughness of the blend films. The increasing in broadening pattern of regenerated cellulose diffractograms indicated the reduction crystallites size occurred as a result of dissolution in ionic liquid. The average size of crystallites in original cellulose (45.7 nm) has been reduced to 14.9 nm after dissolution process.

3.1.3. FTIR spectroscopy

FTIR spectroscopic elucidations represent the capacity of different absorption bands to characterize the interaction of polymers in composite structure (Fig. 3). An alteration of the crystalline organization leads to a significant simplification of the spectral contour through reduction in intensity or even disappearance of the bands characteristic of the crystalline domains. The broad band in the 3600–3100 cm⁻¹ region, which is due to the OH-stretching vibration in cellulose and PVA, gives considerable information concerning the hydrogen bonds [2]. The overall characteristics of both polymers could be found in the spectra. The peaks characteristic of hydrogen bonds from the spectra of amorphous celluloses became sharper and with lower intensity, compared to the initial cellulosic samples in regenerated cellulose. The presence of amorphous cellulosic samples can be further confirmed by the shift of the band from 2900 cm⁻¹, corresponding to the C–H stretching vibration, to higher wavenumber values and by the strong decrease in the intensity of this band. The adsorption bands from the 1500–899 cm⁻¹ region are strongly reduced in intensity, or even absent. Besides, the FTIR absorption band at 1430 cm⁻¹, assigned to a symmetric CH₂ bending vibration, decreases. This band is also known as the “crystallinity band”, indicating that a decrease in its intensity reflects reduction in the degree of crystallinity of the samples. The FTIR absorption band at 898 cm⁻¹, assigned to C–O–C stretching at β-(1–4)-glycosidic linkages, is designed as an “amorphous” absorption band, an increase in its intensity occurring in the amorphous samples, compared to the initial ones—as actually plotted in Fig. 3, the absorption band at 1733 cm⁻¹, assigned to C=O bending vibration in cellulose/PVA film. Also, the corresponding vibration bond of C–O could be seen in 1259 cm⁻¹ (Table 3).

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystallinity (%)</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw cellulose</td>
<td>93.1</td>
<td>45.7</td>
</tr>
<tr>
<td>Cellulose film</td>
<td>82.5</td>
<td>14.9</td>
</tr>
<tr>
<td>Cellulose/PVA film</td>
<td>59.6</td>
<td>8.32</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignments</th>
<th>Raw cellulose</th>
<th>Regenerated cellulose</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΨOH</td>
<td>3346</td>
<td>3418</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΨCH</td>
<td>2900</td>
<td>2924</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΨO=O</td>
<td>−</td>
<td>−</td>
<td>1733</td>
<td></td>
</tr>
<tr>
<td>δCH</td>
<td>1430</td>
<td>−</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δCH, ΨCH</td>
<td>1373</td>
<td>−</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΨC=O, ΨCH, ΨCH</td>
<td>1165</td>
<td>1160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΨC=O</td>
<td>1060</td>
<td>1055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δCH2</td>
<td>899</td>
<td>899</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_h$ (kJ)</th>
<th>Cr.R1 (%)</th>
<th>Cr.R2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose film</td>
<td>3.87</td>
<td>1.17</td>
<td>2.4</td>
</tr>
<tr>
<td>Regenerated cellulose</td>
<td>2.84</td>
<td>0.96</td>
<td>2.04</td>
</tr>
<tr>
<td>Dissolved cellulose</td>
<td>2.87</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4 shows that the initial cellulosic samples have the highest energy of the hydrogen bonds (EH), decreasing values being recorded for the corresponding amorphous samples, which indicate a decrease in the number of hydrogen bonds and, consequently, changes in the crystalline structure of cellulose–namely, a reduction in the degree of crystallinity. The ratios of crystallinity obtained from FTIR spectra (Cr.R1 and Cr.R2) agreed with the crystallinity indices presented in Table 2, as established by X-ray diffraction.

3.2. Physical properties

3.2.1. OT

Usually, transparency is a useful criterion for the miscibility and compatibility of the composite elements [25]. The composite films prepared with the cellulose/PVA exhibited excellent optical transmittance, indicating perfect miscibility. As expected, the cellulose/PVA film had slightly lower transparency value than neat cellulose film (95.08 and 95.31, respectively). This trace amount of discrepancy in transparency could originate from the PVA polymer. These results could also explain the phenomenon shown in the dissolution process.

3.2.2. WA and TS

Fig. 4a illustrates the percentages of the WA for the composites at different periods of immersion. Based on the test results, WA values ranged from 33% to 42% for cellulose film and from 73% to 78% for cellulose/PVA film. Weight gain upon exposure to water increased as the immersion time increased for all the tested composites. It is to be noted that the maximum WA occurred during the first immersion time. This was possible due to the hydrogen bonding of the water molecules to the free hydroxyl groups present in the cellulose cell wall of fibrous materials and the diffusion of water molecules into the microfibrils interfaces. From chemical view, this result could be explained by the differing chemical compositions of PVA compared to cellulose. Cellulose is a macromolecule with a compact chemical structure, hence its hydroxyl groups are less accessible comparing to PVA, therefore it would be expected to show lower water uptake compared to PVA containing composites.

The poor absorption resistance of the cellulosic materials is mainly due to the presence of polar groups, which attract water molecules through hydrogen bonding. This phenomenon leads to a moisture build-up in the fiber cell wall (fiber swelling) and also in the microfibrils interfaces. This is responsible for the changes in the dimension of composites, particularly the thickness and the linear expansion due to reversible and irreversible swelling of the composites. As it can be seen from Fig. 4b, the TS increased sharply during the first hour of immersion. A further increase in immersion time showed a little change (increase) in the dimensional stability of films. Like WA, the cellulose/PVA composites exhibited inferior dimensional stability compared to the cellulose films. For example, the maximum value of TS was 70% for cellulose/PVA film, while the value for cellulose film was only 30%. As mentioned earlier, this is probably due to several reasons in terms of chemical compositions.

3.2.3. WVP

As a food packaging, film is often required to avoid or at least decrease moisture transfer between the food and the surrounding atmosphere, with water vapor permeability as low as possible. Water vapor easily went through cellulose/PVA film with the WVP value of $0.18 \times 10^{-9}$ (g/smPa), while neat cellulose film reached $0.17 \times 10^{-9}$ (g/smPa).

3.2.4. Thermal properties

Starting from the idea that thermal degradation is influenced by the supramolecular structure of cellulosic materials, the effect of the structural organization form of cellulose on thermal behavior of PVA composite was analyzed. The thermal stability of cellulose and cellulose/PVA composite was compared by using TGA (Table 5). Both TGA and DTG data are illustrated in Fig. 5. As it is expected, the samples weights have been gradually decreased as the temperature was increased from 25 to 600°C. Both samples show an initial weight loss in the region 75–150°C caused by the evaporation of water. It can be observed in Fig. 5a that the differences in TGA curves are negligible for neat cellulose and cellulose/PVA composites. TGA’s first order derivative shows a broadening of the main decomposition peak and a shift of the onset temperature for the PVA containing composite to higher temperatures. From Fig. 5a, it can be seen that the weight loss of cellulose and cellulose/PVA occurred in a one-step degradation process from 300 to less than 400°C. This result may be confirmed by the presence of only one peak in DTG curve, at temperature of 451°C (Fig. 5b). The mass loss of cellulose film starts at 275°C and continues very slowly at temperature below 300°C. Above 300°C, this process takes place very rapidly and the quantity of film residue is very low due to further breakdown of it into gaseous products at higher temperature.

![Fig. 4. Water absorption and thickness swelling of cellulosic (C) and cellulose/PVA (C/P) films.](image-url)
Table 5
Thermogravimetric analysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Residual ash (%)</th>
<th>Initial degradation point (°C)</th>
<th>Maximum degradation point (°C)</th>
<th>Degradation rate (%/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulosic film</td>
<td>15.2</td>
<td>265</td>
<td>293</td>
<td>1.9</td>
</tr>
<tr>
<td>Cellulose/PVA film</td>
<td>45.2</td>
<td>265</td>
<td>299</td>
<td>1.7</td>
</tr>
</tbody>
</table>

![Fig. 5. TGA (a) and DTG (b) of cellulosic and cellulose/PVA films.](image)

![Fig. 6. DSC of the cellulosic and cellulose/PVA films.](image)

![Fig. 7. Tensile strength of the used biocomposite films.](image)

3.3. Mechanical properties

The mechanical properties of the composite materials, which can provide important information about the internal structure of materials, are strongly influenced by the microstructure. Stress–strain curves of all the composite films are shown in Fig. 7. Table 6 shows the average values of tensile properties of provided films. As it can be seen, the cellulose film underwent the most significant changes with a large increase in tensile strength, Young’s modulus and elongation at break, indicating the cellulose matrix taken on the sufficient stress transfer as a result of stiffness of the self-reinforced material. Obviously, the presence of the PVA (as impurities) in the cellulose matrix has led to the weakening of the materials. In summary, each polymer not only contributes to the properties of composite films, but also engages in polymer–polymer interactions, which affect the mechanical properties of overall systems. In general, the mechanical properties of composites prepared in this study have been dramatically increased compared to other studies that were conducted using aqueous suspension. Froze et al. [15] reported the ultimate tensile strength 29 MPa in their study of cellulose/PVA films prepared from aqueous suspension. Similarly, Laxmeshwar et al. [16] also have been reported a 20 MPa tensile strength for a 50:50 PVA:cellulose (w:w) film [14,27]. Zimmermann et al. [28] reported an

The degradation process illustrates that the thermal degradation temperature of the cellulose/PVA is lower than neat cellulose film.

The extended thermal properties of cellulose fibers reinforced PVA were determined from DSC thermogram. The main thermal transitions, glass transition temperature ($T_g$) and melting point ($T_m$), were evaluated and compared with those of the neat cellulose films. DSC results of PVA composite containing of cellulose is shown in Fig. 6. PVA exhibits an endotherm close by 55 °C corresponding to the glass transition temperature of PVA. The appearance of one $T_g$ in the composite samples highlights the good interaction of cellulose and PVA in the amorphous phase. The glass transition temperature of PVA depends on its characteristics (hydrolysis degree, polymerization degree) and particularly, on moisture content, a broad interval of temperature of 61 to 110 °C being reported for these characteristics [26]. From the thermogram of Fig. 6 the rubbery properties and the increase of the mobility of the macromolecules will appear from lower temperatures. Cellulose/PVA composite exhibits a sharp endothermic curve with a peak at 267 °C, corresponding to the melting of the crystalline phase of PVA.
improvement of the elastic modulus and tensile strength of up to five times and three times, respectively, in the case of dispersing 20 wt% cellulose fibers in PVA. An increase of about five times of the tensile strength relative to the reference polymer was reported by Bruce et al. [29] at 50 wt% cellulose fibers in PVA and an increase by a factor of 3.5 at the same concentration of fibers in the work of Leitner et al. [30]. Nevertheless, no increase in tensile strength and modulus was observed by Lu et al. [23] above 10 wt% cellulose fibers in PVA.

3.4. Morphology observation

SEM images of the surfaces for composite films are shown in Fig. 8. From these micrographs, it is clear that the both cellulose based films have a smooth surface (Fig. 8a and b). It suggested that the cellulose nano-particles were embedded in the regenerated cellulose matrix because of the strong interaction between cellulose fibrils. Furthermore, Fig. 8b showed clearly that the nano-cellulose particles were spherical in shape with a diameter range of 20–40 nm. The SEM observation revealed that the cellulose nanoparticle with a uniform diameter ranging from 20 to 40 nm and a nanoball structure were obtained. For the fiber-reinforced composite materials, a general concept is that fibers with a relatively high aspect ratio are beneficial for the composites’ physical properties [31]. On the other hand, the dispersion of fibers in matrix and the adhesion between matrix and fiber reinforcement are also crucial factors for the efficient stress transfer [32].

4. Conclusions

The chemical, physical, mechanical and thermal properties of cellulose/PVA as a biodegradable composite prepared by dissolution in liquid phase were evaluated in this research. The obtained composites showed improved strain at break, preserving the transparency and flexibility of the original films. Favorable interfacial properties and the lack of agglomerations in cellulose/PVA films were supposed to explain the high values of the mechanical properties. Cellulose/PVA films showed lower crystallinity than raw and regenerated cellulose, as resulted from XRD analysis. Slightly higher onset degradation temperatures were obtained for PVA composites as regard to reported PVA data, showing an increase of the thermal stability caused by the addition of cellulose fibers. The biocomposite presented in this study is advanced biomaterial with large possibilities of application in packaging and other fields.

References