PVA Based Composite Films with Cellulose Fibers Prepared by Acid Hydrolysis

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Two types of cellulose fibers were obtained from microcrystalline cellulose (MCC) by acid hydrolysis and ultrasound treatment using different concentrations of sulphuric acid. The effect of acid concentration on cellulose fibers characteristics was studied by scanning electronic microscopy (SEM), dynamic light scattering (DLS), and X-ray diffraction analysis (XRD), pointing out interesting features from the standpoint of different end-use properties. An important increase of MCC crystallinity, from 51.4% to 74.3%, was observed by XRD analysis after the treatment with 60% sulphuric acid. The cellulose fibers were used as reinforcements in a polyvinyl alcohol (PVA) matrix and the crystallinity, transparency and mechanical properties of the resulted composites being investigated. The incorporation of the two types of cellulose fibers into PVA led to transparent composites films with improved mechanical properties. A steady improvement of the tensile modulus of PVA composites was observed with the increasing amount of fibers, an increase of 83.3 % being obtained with cellulose fibers resulted from MCC treatment with higher acid concentration (60%).

Key words: PVA composites, cellulose nanofibers, acid hydrolysis of cellulose, mechanical properties

The most abundant organic polymer in nature, cellulose is a widely used material for the preparation of environmental friendly products [1-4]. Starting from cellulose, at least two different types of nano-reinforcements can be prepared, nanofibers and whiskers: nanofibers contain both amorphous and crystalline regions while cellulose whiskers have only mono-crystalline regions [5]. Cellulose nanofibers have interesting physical characteristics, especially a large specific surface area and a high elastic modulus, which recommend them as reinforcing nanofillers for polymers. These promising features have determined an increased researcher's interest in finding new methods and new sources for cellulose nanofibers isolation [5-17]. Usually, cellulose fibers can be obtained by chemical [8, 11, 18-20], mechanical [10, 21-22], physical [23-25], and enzymatic treatments [9, 26], the first two being the most frequently applied. Acid hydrolysis is one of the most convenient methods applied in order to isolate cellulose nanofibers. The amorphous regions of cellulose fibers are attacked by concentrated acids giving rise to a much more crystalline material. The crystalline bridges between the partial hydrolyzed microfibers can also be broken in the presence of concentrated acids [22]. The isolation of cellulose whiskers from microcrystalline cellulose by applying sulphuric acid hydrolysis was reported [27]. The cellulose whiskers, obtained with 30% yield, were suitable for polymer composites preparation. Cellulose nano-crystals with an aspect ratio of 6 to 8 were isolated from filter paper by an acid hydrolysis based method [27]. Lee et al. prepared cellulose nanofibers with higher crystallinity and higher thermal stability as compared with the MCC source by using hydrobromic acid, in two concentrations [28]. The characteristics of cellulose nanofibers obtained by acid hydrolysis depend on several factors including the degree of polymerization of fibrous material before chemical treatment, mineral acid concentration, process duration and temperature as well as the drying conditions applied to cellulose fibers [22].

Cellulose fibers bring a lot of benefits when they are used as reinforcements in natural or synthetic polymers, including biodegradability, low cost, low density, high stiffness, low energy consumption per unit of product, low abrasivity for processing equipment, and reduced emissions of carbon dioxide [29]. Moreover, Young' modulus of native cellulose is very high (137 GPa - calculated value), higher than glass fibers modulus (75 GPa) and similar to that of Kevlar fibers [22]. Due to these advantages, many attempts for the preparation of polymer composites with micro or nanocellulose fibers have been carried out [14, 19, 22, 28-39]. Among the first attempts of cellulose nanofibers and polymer composites preparation belong to CERMAV research group (Grenoble), who were able to isolate cellulose nanostructures from wheat straw and tunicin and to produce nanocomposites using starch and other polymers [27]. Other researchers obtained nano-composites with improved thermal and mechanical properties, as disclosed by the dynamic mechanical analysis, by modifying potato starch with cellulose nanowhiskers [40].

Poly(vinyl alcohol) (PVA) is a water-soluble polymer with excellent physical, mechanical and optical properties [41] which make it suitable for polymer composites preparation. It is used in a wide range of applications including biomedicine [42], paper industry [43] and, particularly, in the packaging industry [44], being a convenient matrix for cellulose fillers. Some experimental results concerning the isolation of cellulose nanofibers from microcrystalline cellulose by combining acid hydrolysis with ultrasounds treatment are presented in this paper. Two concentrations of sulphuric acid were used in these tests. The obtained cellulose fibers were characterized by scanning electron microscopy (SEM), dynamic light scattering (DLS), and X-ray diffraction (XRD) and the influence of acid concentration on the morphology of cellulose fibers was studied. These cellulose fibers were tested as reinforcements in a polyvinyl alcohol (PVA) matrix and the

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crystallinity, transparency and mechanical properties of the resulted composites were investigated. A correlation between the mechanical results and the morphological features of cellulose fibers was attempted.

Experimental part

Materials and methods

Microcrystalline cellulose (MCC) with 20 - 40 μm particle size was purchased from Sigma-Aldrich Chemicals and sulphuric acid (H_2SO_4) 96% from Chimopar Romania. Poly(vinyl alcohol) (PVA) with a degree of hydrolysis of 99% and a polymerization degree of 1200, from Chemical Enterprise Râsnov (Romania), was used for the nanocomposites preparation.

Preparation of cellulose fibers

Acid hydrolysis of MCC was performed in the following conditions: H_2SO_4 was slowly added under continuous stirring to a MCC/water suspension (20 wt% MCC) placed in an ice bath, the final concentration of H_2SO_4 being 45% (sample P1) and, respectively, 60% (sample P2). The suspensions were then heated at 44°C with continuous stirring for 150 min. The obtained mixtures were washed and centrifuged using a Universal 320R Ultracentrifuge at a temperature of 20°C for 20 min with 7000 min^{-1} (3 - 4 times) in order to remove the excess acid, and ultrasonicated for two hours using an Elmasonic S40H ultrasonic bath.

Preparation of PVA/cellulose fibers composite films

PVA/cellulose fibers composites films were prepared in two steps. An aqueous solution of PVA (10%) was obtained by slowly adding the PVA powder in distilled water under vigorous stirring, at room temperature for almost 30 minutes and then at 80°C for 30 min. A complete dissolution of PVA occurred in these conditions. The PVA solutions were mixed with cellulose fibers at a ratio of 99/1 to 95/5 (table 1) at 80°C for another 60 min. The final mixtures were degassed for 10 min in an Elmasonic S40H ultrasonic bath and cast on a PET sheet. The films were kept for 2 days under laboratory conditions at 20°C and 40% RH until complete drying. Composite films with a thickness of 0.03 mm were obtained. A neat PVA film was prepared applying the same conditions (vigorous stirring, at room temperature for 30 min and at 80°C for 90 min) and considered as a reference. The names and composition of PVA films are given in table 1.

Experimental Methods

To investigate the morphology of cellulose fibers a Quanta 200 scanning electron microscope with an acceleration voltage between 10 and 15 kV was used. Droplets of dilute suspensions containing cellulose fibers (sample P1 and, respectively, P2) were deposited on microgrids for scanning electron microscopy (SEM) investigation.

Size distribution of cellulose aggregates was estimated by dynamic light scattering (DLS) using a Zetasizer Nano ZS instrument (Malvern, UK). The DLS measurements were performed with an angle of 170° by using a He–Ne laser (4 mW) operated at 633 nm. The samples of cellulose fibers were diluted with distilled water at a concentration of 0.01% and ultrasonicated before performing DLS analysis.

The morphology of both cellulose fibers and composite films was investigated by X-ray diffraction (XRD) using a DRON-UM diffractometer with Bragg-Brentano geometry and Co Kα radiation (wavelength = 1.79021Å). The samples were scanned at a rate of 0.05 step/5 s in reflection mode.

The transparent nature of composite films and the dispersion of cellulose fibers in the matrix were examined with an UV-VIS spectrophotometer M42 type at room temperature, the value of transmittance at a wavelength of 540 nm being reported.

The mechanical properties of the composite films were evaluated using tensile test measurements according to SR EN ISO 527-3. The specimens were prepared from the 0.03 mm thick films by cutting rectangular strips with a width of 10 mm and a length of 110 mm. They were tensile tested at room temperature using an Instron 3382 Universal Testing Machine with video extensometer and Bluehill 2 Software which is able to automatically display the following data: video axial strain at break, tensile stress at break, Young's modulus, tensile stress at yield and other optional features. Four specimens were used to characterize each composite sample. The tensile modulus was determined at a crosshead speed of 2 mm/min, while the tensile strength and elongation at break was performed at 10 mm/min.

Results and discussion

Cellulose fibers characterization

SEM images of microcrystalline cellulose (MCC) and acid treated samples, P1 and P2, are shown in figure 1. SEM micrographs reveal a distribution of fiber diameters ranging from 20 to 40 μm for MCC (fig. 1a), from 3 to 8 μm for P1 sample (fig. 1b) and from 0.8 to 2.5 μm for P2 sample (fig. 1c). The aspect ratio of acid treated MCC samples, from 3 to 10, is significantly greater than the aspect ratio of MCC (between 2 and 4). The increase of

Table 1

CODIFICATION AND COMPOSITION OF PVA/CELLULOSE FIBERS COMPOSITE FILMS

Nanofibers	Sample	PVA/Nanofibers ratio
None	PVA	100/0
Cellulose fibers type P1	PVA/P1-1%	99/1
	PVA/P1-2%	98/2
	PVA/P1-3%	97/3
	PVA/P1-4%	96/4
	PVA/P1-5%	95/5
Cellulose fibers type P2	PVA/P2-1%	99/1
	PVA/P2-2%	98/2
	PVA/P2-3%	97/3
	PVA/P2-4%	96/4
	PVA/P2-5%	95/5

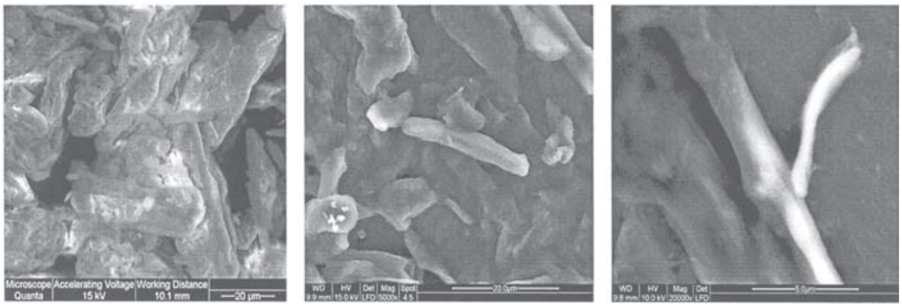

Fig. 1. SEM images of cellulose samples (a) MCC, (b) P1 - MCC treated with lower acid concentration and (c) P2 - MCC treated with higher acid concentration

Table 2
DLS DATA CONCERNING THE NANO-SIZE DISTRIBUTION OF ACID TREATED CELLULOSE SAMPLES

Sample	Diameter [nm]		Intensity [%]	
	Peak 1	Peak 2	Peak 1	Peak 2
P1	109.9	13.03	82.2	17.8
P2	79.28	0.98	74.5	25.5

acid concentration led to an advanced reduction of cellulose fibers size and to a much higher aspect ratio, as revealed by P1 and P2 samples images (fig. 1).

It is difficult to detect nano-sized cellulose fibers and aggregates in SEM images, at this magnitude. With this purpose, the DLS analysis on cellulose samples was used. DLS analysis has been developed for measuring the dimensions of spherical particles, so that the measurement of rod-shaped materials like our fibers will result only in approximate values. The DLS data concerning the nano-scale distribution of cellulose aggregates in water suspensions of P1 and P2 samples are presented in table 2. Cellulose aggregates larger than 5 μm are not detected by this method. The analysis was performed with the assumption that the samples were ideal monodisperse systems containing spherical aggregates of cellulose [45]. These results highlight the influence of the acid concentration on the intensity of MCC disintegration: higher acid concentration leads to smaller cellulose dimensions at nano-scale. Smaller cellulose dimensions at micro-scale were observed in SEM analysis for the same acid concentration.

The diffraction patterns of MCC and acid treated samples, P1 and P2, are shown in figure 2. Similar patterns were obtained for all three samples. The three diffraction peaks, which appeared in XRD patterns at 2θ = 17.17, 19.13 and 26.26° correspond to the crystalline structure of cellulose I, and are very close to previously reported values, considering the different wavelength [27, 28].

The degree of crystallinity (*C*) was significantly improved in both treated cellulose fibers by comparison with the cellulose source: *C* is 59.4% for P1 and 74.3% for P2, much higher than the degree of crystallinity of MCC (51.4%). The large increase of *C* values in P1 and P2 samples indicates the efficiency of acid treatment leading to the removal of a great part of the amorphous phase and hemicelluloses, and resulting in a higher percentage of cellulose I. An increase of crystallinity was also signaled when an optimized acid sulphuric hydrolysis treatment was applied

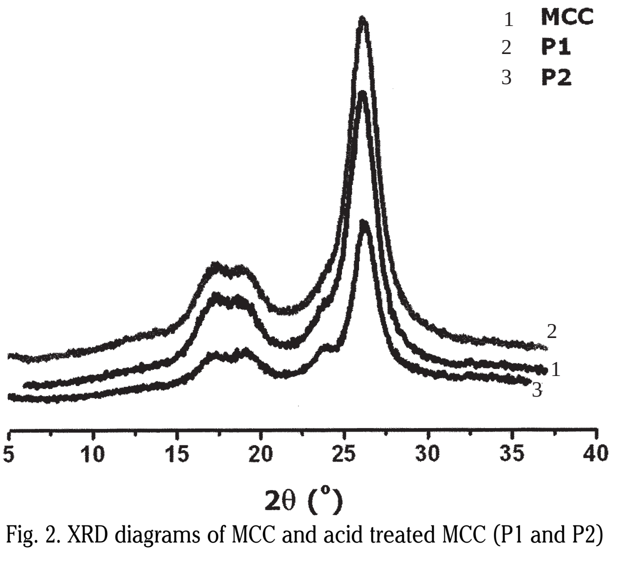

Fig. 2. XRD diagrams of MCC and acid treated MCC (P1 and P2)

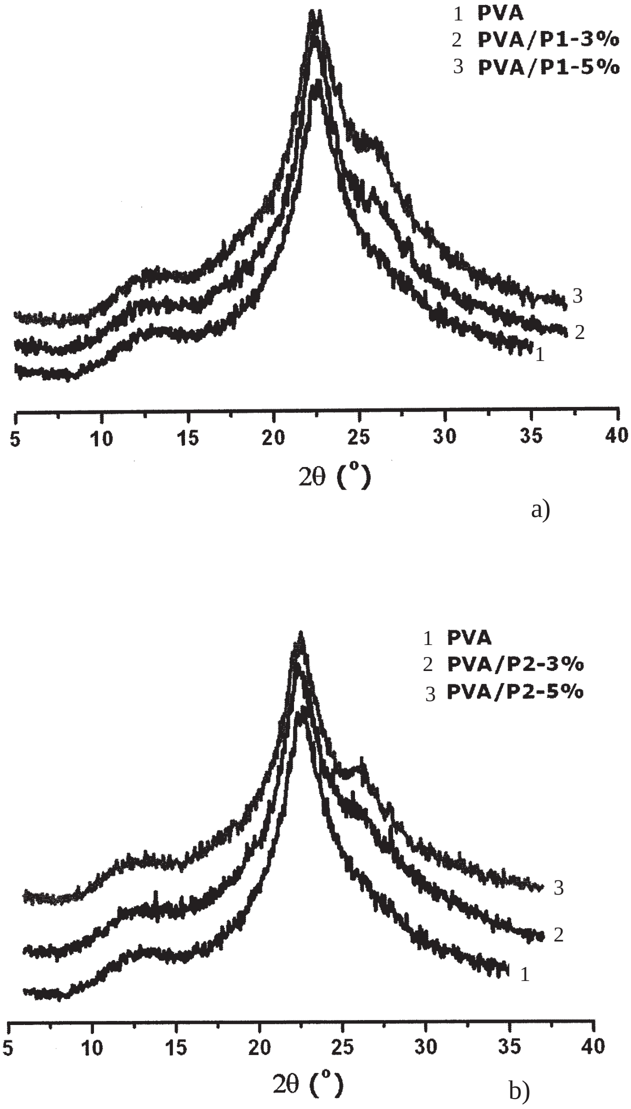

Fig. 3. XRD diagrams of PVA composite films with different concentrations of P1 cellulose fibers (a) and P2 cellulose fibers (b)

to MCC [27]. Moreover, in the case of HBr hydrolysis of cellulose, the degree of crystallinity was significantly increased demonstrating the efficiency of concentrated acids in removing accessible amorphous regions [28].

Morphological Characterization of Nanocomposite Films

XRD diagrams of PVA/cellulose fibers films are shown in figure 3a and 3b.

The PVA films showed two diffraction peaks at 2θ = 12.53° and 22.78°, respectively, which correspond to the PVA crystalline phase. Similar results were reported for a pure PVA film cast from its aqueous solution [46]. The diffraction peak at 2θ = 26.2°, which appears in both composites, represents the maximum intensity peak of cellulose. Comparison of the integrated intensities (peak areas) revealed a decrease of PVA crystallinity when 3 and 5% of P1 and P2 cellulose fibers were added.

The transparent nature of PVA composite films with different concentrations of treated cellulose fibers is shown in figure 4, by placing the films on a quadrille paper and with a dark pad above for better visualization. The dependence of the transmittance (*T*) of PVA composites films, determined from UV-VIS spectra, on the amount of cellulose fibers is shown in figure 5.

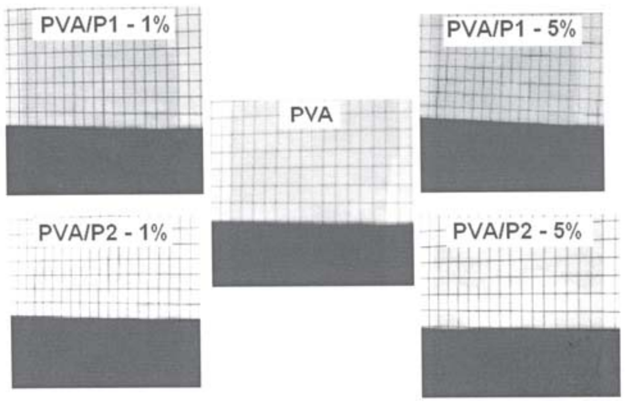

Fig. 4. PVA composite films with different concentrations of MCC treated fibers. The transparent nature of the films was highlighted by placing them on a quadrille paper with a dark pad above for better visualization

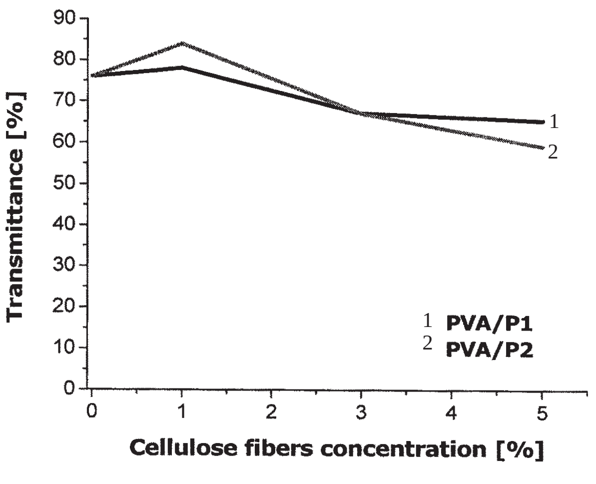

Fig. 5. Transmittance of the PVA composite films with different cellulose fibers concentrations

The transmittance of PVA/P2 composites was higher than that of neat PVA for fiber concentration bellow 3% indicating that the addition of the cellulose fibers increased the transparency of PVA films: *T* has increased from 76% for neat PVA to 85% for PVA/P2-1% composite (fig. 6). This behavior resulted from both a good dispersion of the nanocellulose fibers in the matrix and the sizes of nanocellulose fibers well bellow the wavelength of incident light. It was reported the obtaining of PVA composites with high transparency using MCC and flax nanofibers as fillers [47]. In this case, the higher degree of transparency was explained by the high level of compatibility and interaction between cellulose nanofibers and PVA matrix. The high level of interaction between P1 and P2 cellulose nanofibers and PVA will be proved by mechanical tests results. At higher concentration of fibers the absorption at 540 nm wavelength increases, suggesting a higher percentage of agglomerated fibers in composites. Chen et al. studied the transmittance of nanocomposites based on pea starch and cellulose whiskers in the wavelength range from 200 to 800 nm [8]. In the ultraviolet range an increased absorption was observed for nanocomposites as comparing with neat pea starch, and for higher wavelength (> 600nm) the transmittance values of composite films were very close to, and even higher than those of the neat pea starch.

Mechanical Properties of Nanocomposite Films

The mechanical properties of PVA films reinforced with cellulose fibers in comparison with those of neat PVA are shown in figures 6 - 8.

In terms of tensile strength, one can notice the different behaviour of PVA composites containing P2-type fibers as compared to those containing P1-type fibers: an increase of the tensile strength with the increase of fibers concentration up to 3wt% is observed in the first case and a decrease in the second one (fig. 6). At 5wt% fibers, both types of composites show similar values for the tensile strength, and close to that of neat PVA.

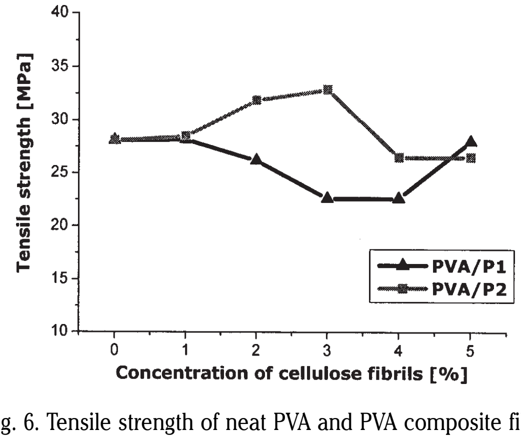

Fig. 6. Tensile strength of neat PVA and PVA composite films

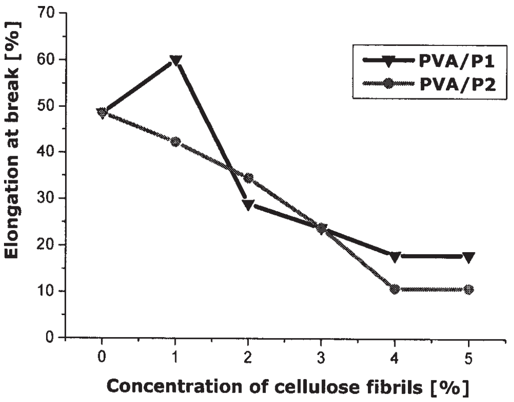

Fig. 7. Elongation at break of neat PVA and PVA composite films

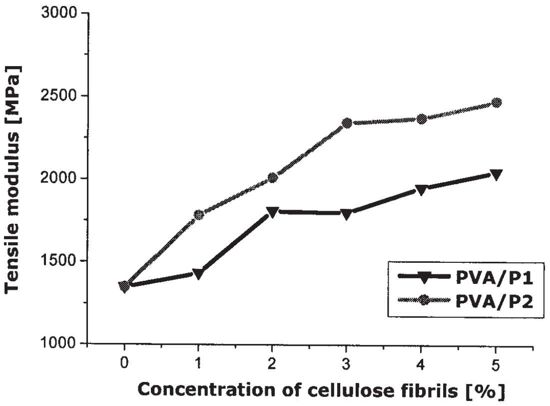

Fig. 8 Tensile modulus of neat PVA and PVA composite films

A strong decrease of the elongation at break with the increase of the amount of cellulose fibers is observed in figure 7 for both types of composites (by 2.5 - 4.5 times at 5wt% fibers) and an important increase of the tensile modulus (by 1.5 – 1.8 times at 5wt% fibers) in figure 8. A similar improvement of the tensile modulus was signaled by [28], which studied the tensile properties of PVA composite reinforced with nanocellulose, obtained by hydrobromic acid hydrolysis of MCC. They obtained a tensile modulus increase of 79.1% at 5wt% nanocellulose in PVA, very close to the increase of 83.3 % for PVA composites with 5wt% P2-type fibers. The high level of compatibility between the cellulose fibers and PVA and the strong hydrogen bonding between the hydroxyl groups of cellulose and matrix could explain the improved mechanical characteristics of PVA composites, in comparison with neat PVA and, therefore, the strong reinforcing action of cellulose fibers [28].

The differences in the mechanical behaviour of the 2 types of composites (with P1 and P2-type fibers) could be caused by the different size of these fibers as shown by SEM and DLS and by the higher tendency of agglomeration of high aspect ratio fibers. The smaller size and the higher aspect ratio of P2-type fibers, leading to increased interfaces in composites and increased adhesion at cellulose/matrix interface explain the better mechanical characteristics of PVA composites containing these fibers.

Conclusions

Two types of cellulose fibers were obtained from microcrystalline cellulose (MCC) by acid hydrolysis and ultrasound combined treatment using two different concentrations of H_2SO_4, the same temperature and reaction time.

The effect of acid concentration on cellulose fibers characteristics was studied by scanning electronic microscopy (SEM), dynamic light scattering (DLS), and X-ray diffraction analysis (XRD). SEM images showed an important decrease of cellulose fibers size that was obtained by applying acid hydrolysis combined with ultrasound treatment.

The higher acid concentration led to a more advanced reduction of cellulose fibers size and to a much higher aspect ratio. DLS analysis confirmed SEM results, the important influence of the acid concentration on the intensity of MCC disintegration being revealed by this analysis. An important increase of MCC crystallinity, from 51.4 to 74.3%, was observed by XRD analysis after the treatment with 60% sulphuric acid, demonstrating the efficiency of concentrated acids in removing accessible amorphous regions from cellulose.

Two types of cellulose fibers were tested as reinforcements in a PVA matrix from the view point of the crystallinity, transparency and mechanical properties of the composite systems. Transparent composites films were obtained when less then 5wt% cellulose fibers were added in PVA. On the other hand, a steady increase of the tensile modulus with the increasing amount of fibers was observed in PVA composites films, better results being obtained with cellulose fibers resulted from MCC treatment with higher acid concentration (60%). An increase of tensile modulus with 83.3 % was also obtained.

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