CELLULOSE CHEMISTRY AND TECHNOLOGY

IMPROVING THE DISPERSIBILITY OF CELLULOSE MICROFIBRILLATED STRUCTURES IN POLYMER MATRIX BY CONTROLLING DRYING CONDITIONS AND CHEMICAL SURFACE MODIFICATIONS

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The aim of this paper was to investigate some possibilities to improve the compatibility of cellulose microfibrillated structures at the fibre-polymer matrix interface level, when they are used as reinforcement in polymer composite materials. The cellulose microfibrillated structures isolated from bleached softwood pulp by chemical-mechanical methods were subjected to surface modification by acetylation, aiming to reduce their hydrophilic character. Fourier transform infrared spectroscopy (FTIR) analyses indicated the acetylation of the hydroxyl groups of cellulose; the increase of the elastic modulus of the polymer composite materials was due to the good dispersion of the surface modified cellulose microfibrillar elements in the polymer matrix.

Another method that was tested to reduce the hydrophilic character of cellulose microfibrillated structures in contact with a polymer matrix was the spray drying, using the atomization of cellulose microfibrils. This method produces particulate materials with unchanged size and very good potential as reinforcement in composite manufacturing, utilizing conventional thermoplastic compounding techniques. The improvement in the mechanical properties of the composites reinforced with spray dried cellulose microfibrillar elements shows that this drying method is the most suitable for cellulose fibres that are used as reinforcement in hydrophobic polymer matrix, because this procedure reduces the advanced irreversible hornification phenomenon, which occurs during the oven drying process.

Keywords: cellulose microfibrillar structures, surface modification, drying, acetylation, polymer matrix, composites

INTRODUCTION

It is widely recognized that new technologies that can economically convert biomass resources into commercially advanced and viable materials are needed. Identifying and exploring these new fields will allow converting plant tissues into new-generation materials with high scientific and innovative value.[1] The last two decades or more have seen a resurgence of interest in natural vegetable fibres, of both wood and non-wood origin, as reinforcement in polymer matrix composites for example, in automotive, building materials, or for specific properties in packaging, paper industry, food industry, pharmaceutical, cosmetic and biomedicine applications. For example, vegetal fibres have been extensively explored since 1990 by research institutions and automotive companies as an environmentally friendly alternative to traditional glass fibre reinforcement. A major reason for using vegetal fibres is their perceived lower environmental impact (renewability, recyclability and biodegradability), along with their low density and the exceptional mechanical properties (modulus and stiffness), non-abrasive nature, high level of filler loadings or ease of separation. On the other hand, plant fibres are an annually renewable raw material and their availability is more or less unlimited. Their abrasive nature is much lower compared to that of glass fibres, which leads to advantages with regard to technical, material recycling or processing of composite materials in general. In this context, cellulose is the most widely used candidate among biomass resources, and therefore, during the last decade, major efforts have been made to develop adequate and commercially viable processes for disintegrating cellulose fibres into their structural components. Thus, microfibrillated cellulose (MFC), also referred to as nanocellulose, is one of the most promising innovations in the forest sector.[2]

The results of studies and research[3] emphasize that the potential of using cellulose fibres as composite reinforcement or in high tech applications increases as cellulose fibre structure is advanced to the isolation and separation of micro- or nanofibrillated elements. Therefore, the elastic modulus of cellulose microfibrils has different values (70-150 GPa), depending on the structural element (Figure 1).

These structural elements may be extracted from mass-produced sulphite or sulphate pulp by mechanical and chemical methods. The ratio aspect of the fibrils varies according to the isolation procedure: purely mechanical processing produces microfibrillated structures of several micrometers long and between 20 and 100 nanometres in diameter; combining chemical and mechanical processes permits to achieve even finer fibril structures, only a few nanometres in diameter.[4]

Due to the economic and environmental advantages emphasized, these structural elements facilitate the obtaining of high strength and durable composite materials with applications in different fields.

According to evidence given in the literature[4,5] regarding the characterisation of a variety of microfibrillated cellulose structures and qualities, it appears that these materials may be composed of nanofibrils, fibrillar fines, fibre fragments and fibres. This implies that MFC is not necessarily synonymous with microfibrils, nanofibrils or any other cellulose nanostructures. In this respect, Table 1 presents the components and size of microfibrillated cellulose structures.[5]

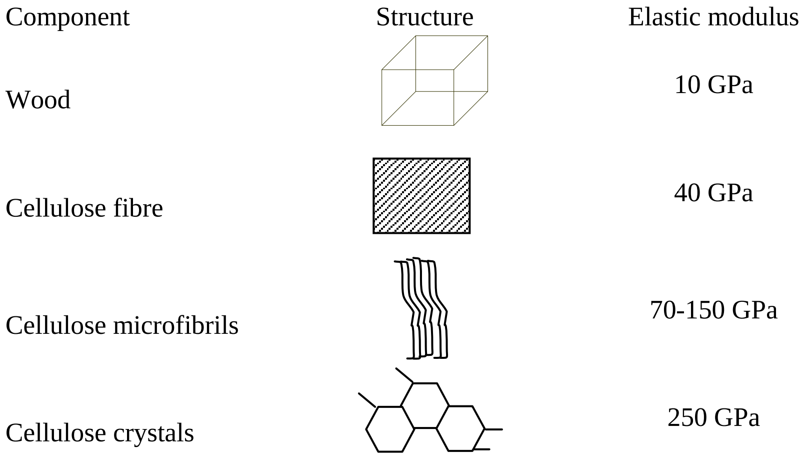


Figure 1: Relation between structure and properties of cellulose fibres[3]

Table 1
Components of microfibrillated cellulose structures[5]

Diameter, µm	Biological structure	Technological terms
10÷50	Tracheid	Cellulose fibre
<1	Macrofibrils	Fibrillar fines, fibrils
<0.1		Nanofibrils, nanofibres
<0.035	Microfibrils	
0.0035	Elementary fibril	

Despite their attractive characteristics, cellulose fibers also have a few disadvantages due to their polar and hydrophilic character, which hinders their dispersion in non-aqueous media or in polymer matrices. If the isolation method of these micro- or nanofibrillated structures is somewhat elucidated, the difficulty of dispersing the highly polar fibrillated cellulose in a polymer matrix is one of the main challenges to meet.[6]

The uniform dispersion of micro- or nanosized materials in liquids, as well as in polymers, is difficult due to their high surface energy. In order to improve compatibility in the fiber-matrix interface and their dispersibility, the surface characteristics of cellulose microfibrillated structures must be changed from hydrophilic to more hydrophobic by the chemical modification of cellulose hydroxyl groups, which are located on the surface of the cellulose fibers.

The hydrophilic nature of cellulose causes two major issues, namely, irreversible agglomeration during drying and agglomeration of microfillated cellulose in non-polar matrices during compounding.

In this respect, cellulose microfibrillated structures can be submitted to specific surface modification, such as reactions to form ionic groups on cellulose surfaces (sulfonation, carboxylation, grafting) or reactions to create hydrophobic surfaces (acetylation, silanization treatments), adsorption (surfactants, polyelectrolytes).[4,6]

Another problem of poor dispersibility of microfibrillated structures into polymer matrices consists in cellulose fibre hornification as a result of irreversible agglomeration of cellulose fibres during the drying process by the formation of additional hydrogen bonds among the amorphous parts of the cellulose fibrils during drying.[7,8] During the drying process of cellulose fibres, water removal results in the contraction of fibres and cell walls, and consequently in high intensity bond forces. In this case, the hydrogen bonds formed by water turn into real bonds created when between neighbouring OH groups there is a distance of about 0.25-0.275 nm. In these crystalline parts of cellulose, water cannot break the formed hydrogen bonds during the rewetting of hornificated cellulose.[9,10] To prevent this phenomenon, the isolation of cellulose micro- or nanofibrillated structures is preferentially done by spray drying of never-dried pulp in an aqueous suspension.

Consequently, the preparation of a nanofibrillated cellulose powder, which can be easily dispersed in water avoiding hornification, would be of great industrial interest from both economic and ecological points of view. Furthermore, the water-redispersible microfibrillated cellulose powder is an attractive alternative to the conventional micro- or nanofibrillated cellulose aqueous suspensions used as reinforcement for polymer matrix composites. This would not only allow reducing storage volume and shipping costs, but also would increase the storage life of the product against bacterial degradation.[11]

Preparation of microfibrillated cellulose structures by spray drying has the advantage of low cost and scalable continuous drying process and controllable particle size by maintaining microscale dimensions of the fibrils.[12]

In this context, in the present paper, some possibilities to improve the compatibility and dispersibility of cellulose microfibrillated elements at the fiber–polymer matrix interface are analysed, aiming to increase their reinforcement potential in polymer matrix composites. Thus, the chemical surface modification of microfibrillated cellulose structures by homogenous acetylation and spray drying through atomization in contact with hot air is tested and analysed.

EXPERIMENTAL

Obtaining of microfibrillated cellulose structures

Cellulose microfibrillated elements with diameters from below one micron to a couple of microns were obtained using a low-cost mechano-chemical disintegration method applied to wood cellulose fibres. A high purity softwood pulp (content of α-cellulose of about 97%) was processed in the following way: after hollander fiberizing and individualization, the pulp slurry was dewatered until 25-27% consistency and then subjected to alkali swelling treatment (NaOH 17.5%, t = 24 hours, T = 20 °C), aiming to remove the hemicelluloses and degradation products and to increase the cellulose fibres reactivity in acid hydrolysis reactions. After washing and neutralizing, the pulp slurry was refined in the laboratory hollander (40 °SR) in the presence of high viscosity carboxymethyl cellulose grade. The advanced fibrillated pulp slurry was washed and dewatered until 25-27% consistency, and subjected to the further refining treatment at high shearing forces in a laboratory colloidal mill (2000-3000 rpm). After these mechanical treatments, the cellulose fibres were chemically treated with dilute hydrochloric acid (2 hours at 80 °C).

Chemical surface modifications of microfibrillated cellulose structures

Acetylation is a chemical modification method, when the reaction agent reacts with the hydroxyl groups of cellulose, thereby modifying the hydrophilic surface of cellulose, making it more hydrophobic.[13,14,16] The acetylation of cellulose depends on the accessibility and susceptibility of the OH groups in the amorphous and crystalline regions within the cellulose polymer chain.[15]

Compared with other chemical methods for cellulose fibre surface modification, the acetylation present some advantages: good dispersibility of cellulose fibres in the polymer matrix during compounding, low costs and ease of use, shorter process duration (about 3 hours), and environmental friendliness.

Three successive steps of the acetylation reaction were performed. The dewatered microfibrillated cellulose suspension was treated with glacial acetic acid (1 h at 50÷80 °C temperature). The activated cellulose microfibrils were then treated with the acetylation mixture (acetic anhydride, glacial acetic acid, sulphuric acid) with gentle stirring of the reaction vessel. The reaction vessel was heated at constant temperature (30 °C) until the cellulose suspension has no longer a fibrous appearance. This gelatinous suspension was stirred in a 10% acetic acid solution for precipitation of the cellulose acetate, which was intensively washed to remove the excess of reaction products and stabilised by water boiling during 30 min. The acetylated microfibrillated cellulose was washed until a neutral pH was reached, and then was oven dried (100-105 °C).

The surface modifications of cellulose microfibrillated elements were observed by Fourier transform infrared spectroscopy (FTIR), using a Spectrum FT-IR Excalibur Digilab FTS 2000, in order to determine the changes in functional groups, which may have been caused by the treatments. Prior to the analysis, 100 mg fibres were ground and mixed with KBr. The resultant powder was pressed into transparent pellets and analysed in the absorbance mode within the range of 4000-400 cm^{-1}, and resolution of 4 cm^{-1}.

Drying of microfibrillated cellulose structures

Drying of microfibrillated cellulose is essential for ensuring its usability in processes where dry or waterfree material is needed, e.g. in composites. Therefore, the drying route of cellulose microfibrillated structures has a high influence on their dispersibility in the polymer matrix during compounding.

Two methods of drying the cellulose microfibrillated structures were used: oven and spray drying. Oven drying was performed at 105 °C for 24 h in glass beakers, after dewatering of microfibrillated cellulose suspensions. Spray drying was performed through atomization in contact with hot air (Figure 2) at 180-200 °C as diluted suspension. It is a well-known thermal drying method, typically used for producing powdered products from solutions, and an effective way of preparing a feed of wood pulp, and/or other hydrophilic materials, after they are chemically or mechanically modified for subsequent flash drying.[17] Spray drying of cellulose microfibrillated suspensions is a well-established technique that has been used in many areas, including the food, pharmaceutical, ceramic, polymer, and chemical industries.[12] The relatively low labour and maintenance costs demonstrate that spray drying can be used for those applications where specific product characteristics are required. Spray drying is generally carried out by placing the slurry or pulp into a large chamber through which a hot gas is blown, thereby removing most or all of the volatiles and enabling the recovery of the dried fibers. The suspension of cellulose microfibrillated elements of about 2% consistency was dried in the spray dryer through atomization in contact with hot air (Figure 2) at 180-200 °C.

In this drying method, the suspension of cellulose microfibrils is dispersed as small droplets that come into contact with hot air. The suspension spraying is realised by the atomization system, which consists of a rotating nozzle disc. This means that no thermal destruction occurs and the dimensions and structure of the cellulose microfibrillated elements are maintained.

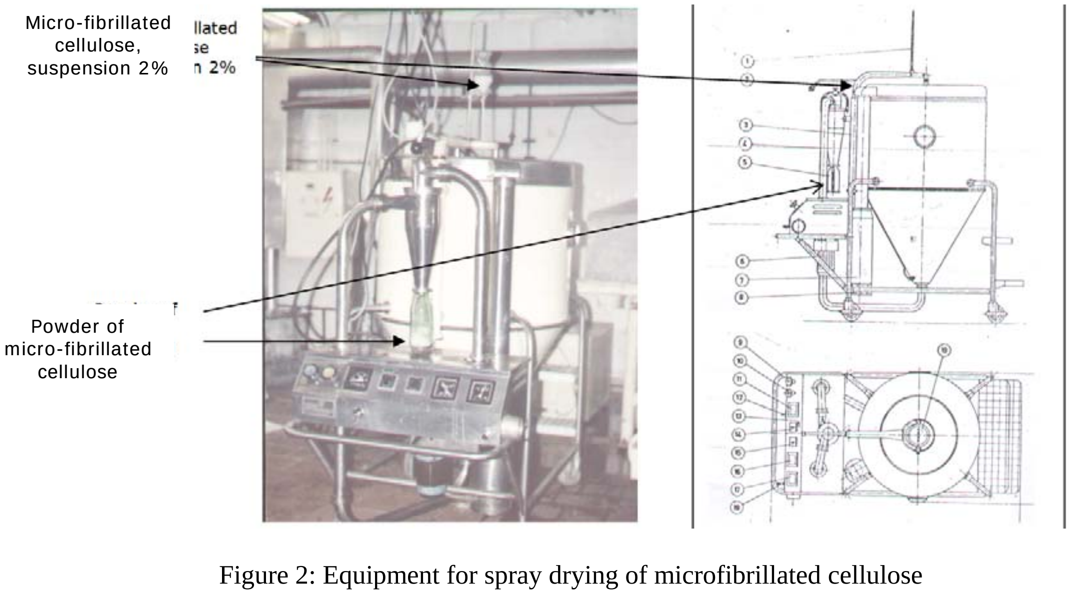


Figure 2: Equipment for spray drying of microfibrillated cellulose

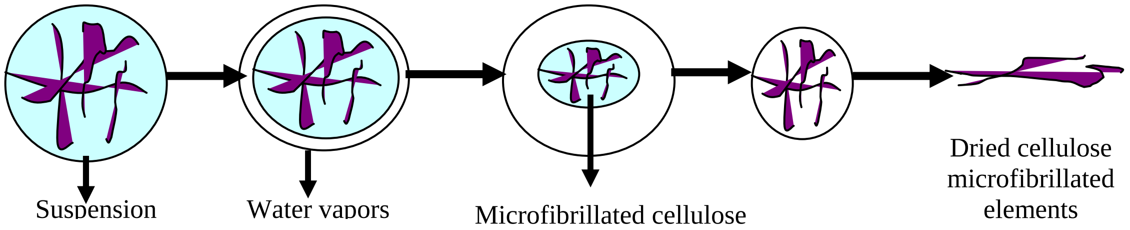
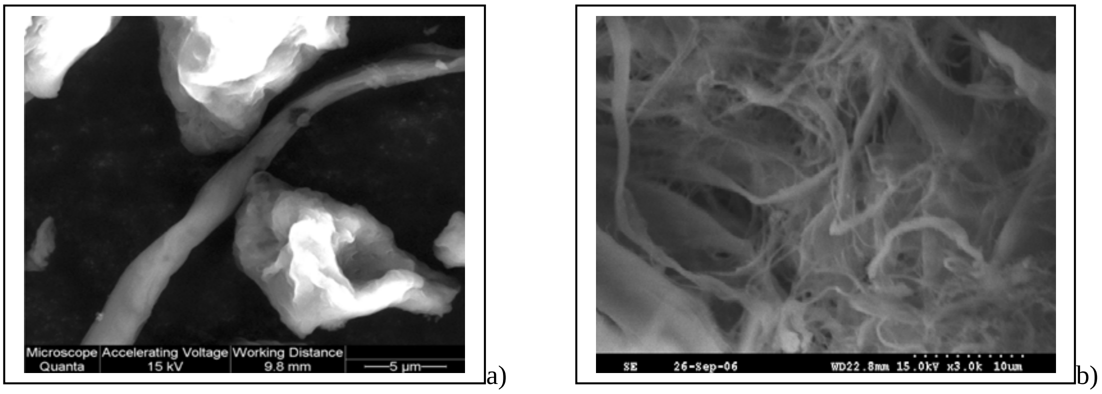


Figure 3: Mechanism of water removal from cellulose microfibrillated suspensions during spray drying



a) b)

Figure 4: SEM images of cellulose microfibrillated structures: a) oven dried; b) spray dried (magnification x 4000)

The feed of the microfibrillated cellulose suspension is performed tangentially and the fibres get on the top of the dryer, where they come into contact with hot air. The drying process is instantaneous by the evaporation of a large water quantity from each suspension droplet (Figure 3). The detent produced as a result of heat consumption for evaporation assures the protection of microfibrils against thermal destruction. The dried microfibrils as powder are gathered on the bottom of the dryer and then collected into the cyclone, which incorporates fine-particle exhaust air and returns it in the drying tower.

Preparation of polymer–microfibrillated cellulose composites

Aiming to confirm the improvement in the dispersibility and compatibility of microfibrillated cellulose structures with the polymer matrix, both acetylated and nonacetylated microfibrils, oven and spray dried, were used to obtain the polypropylene composites under the following conditions: the mixture of HP 500N polypropylene homopolymer and microfibrillated cellulose was blended for 10 min at 175-180 °C and 60 rpm rotor speed. The samples used for measurements were prepared by press moulding in an electrically heated press at 190 °C for 10 min with a force of 50 kN. After moulding, the samples were cooled at room temperature under pressure and the mechanical properties were tested.[18,19]

RESULTS AND DISCUSSION

Influence of drying conditions

Cellulose microfibrillated structures obtained by combined chemical and mechanical isolation methods were analyzed using a Quanta Scanning Electron Microscope 200 (accelerating voltage 15 kV, no coating) (Figure 4).

Microfibrillated elements with a diameter of 1-2 µm or less than 1 µm could be observed, the isolation process being more intensive in the case of the spray dried structures. The length of the microfibrillated elements was of about 100-800 µm, which means a good ratio aspect for reinforcement in a polymer matrix. Analysing the diagram and micrographs presented in Figures 5 and 6, it can be emphasized that the drying method of cellulose microfibrillated structures has a great influence on the mechanical properties of the polymer composite materials. It can be observed an increase in the elastic modulus of the composite material with the increase of the charge of microfibrillated elements, higher in the case of spray dried structures, resulting from the good dispersibility of the powder of microfibrillated elements during compounding.

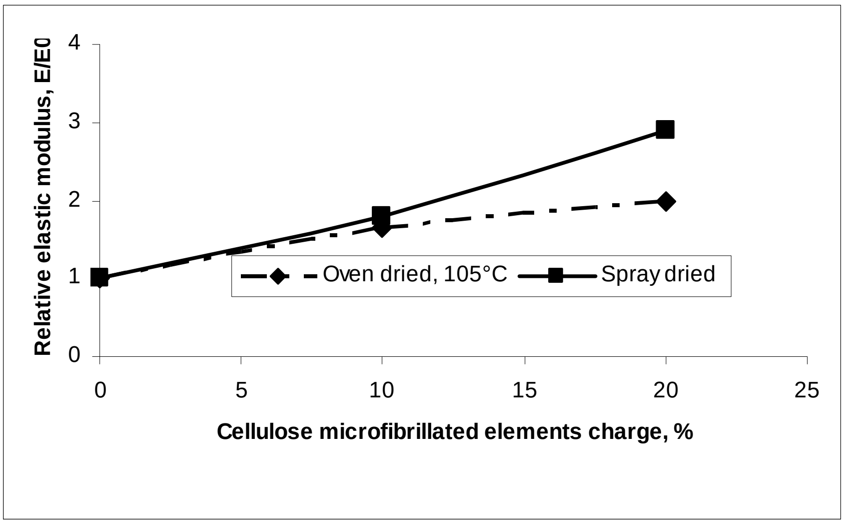
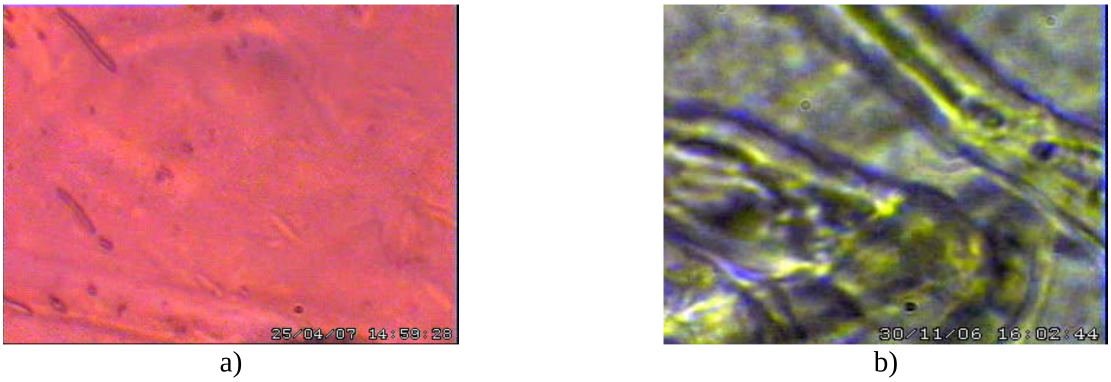


Figure 5: Influence of drying method on the mechanical characteristics of polymer composites reinforced with cellulose microfibrillated elements



a) b)

Figure 6: Optical micrographs of polymer composites reinforced with cellulose microfibrillated elements (10% microfibrils charge): a) spray dried; b) oven dried

Influence of surface modifications

The FTIR spectra of the microfibrillated cellulose were used to investigate the chemical characteristics of the acetylation reaction by determining the presence of specific bonds in the cellulose substrate, comparing the intensity of the different absorption peaks. The FTIR spectra are presented in Figure 7 (a) and (b).

The analysis of these spectra leads to the following conclusions:

- the absorption peaks between 2000-4000 cm^{-1} are due to the stretching vibrations of OH groups (3338-3431 cm^{-1}), CH and CH_2 groups (2852-2916 cm^{-1}) specific to native cellulose fibres;
- the absorption peaks at 1000-2000 cm^{-1} are assigned to the presence of new valence vibrations specific to acetyl groups (1598-1629 cm^{-1}) and to the stretching vibrations of OH bonds from CO_2H groups (1155-1413 cm^{-1}) CO_2H;
- after three consecutive steps of acetylation, the spectra clearly show carbonyl peaks of acetyl groups (1708-1739 cm^{-1}) and a decrease in the intensity of stretching vibrations of OH, CH and CH_2 groups;
- it can be observed that the absorbance increases with an increase in the number of acetylation steps;
- in the range 997-1053 cm^{-1}, the stretching vibrations of C-O, C-C bonds, piranose cycles (1050 cm^{-1}) and the stretching vibrations of CH_2OH groups are present.

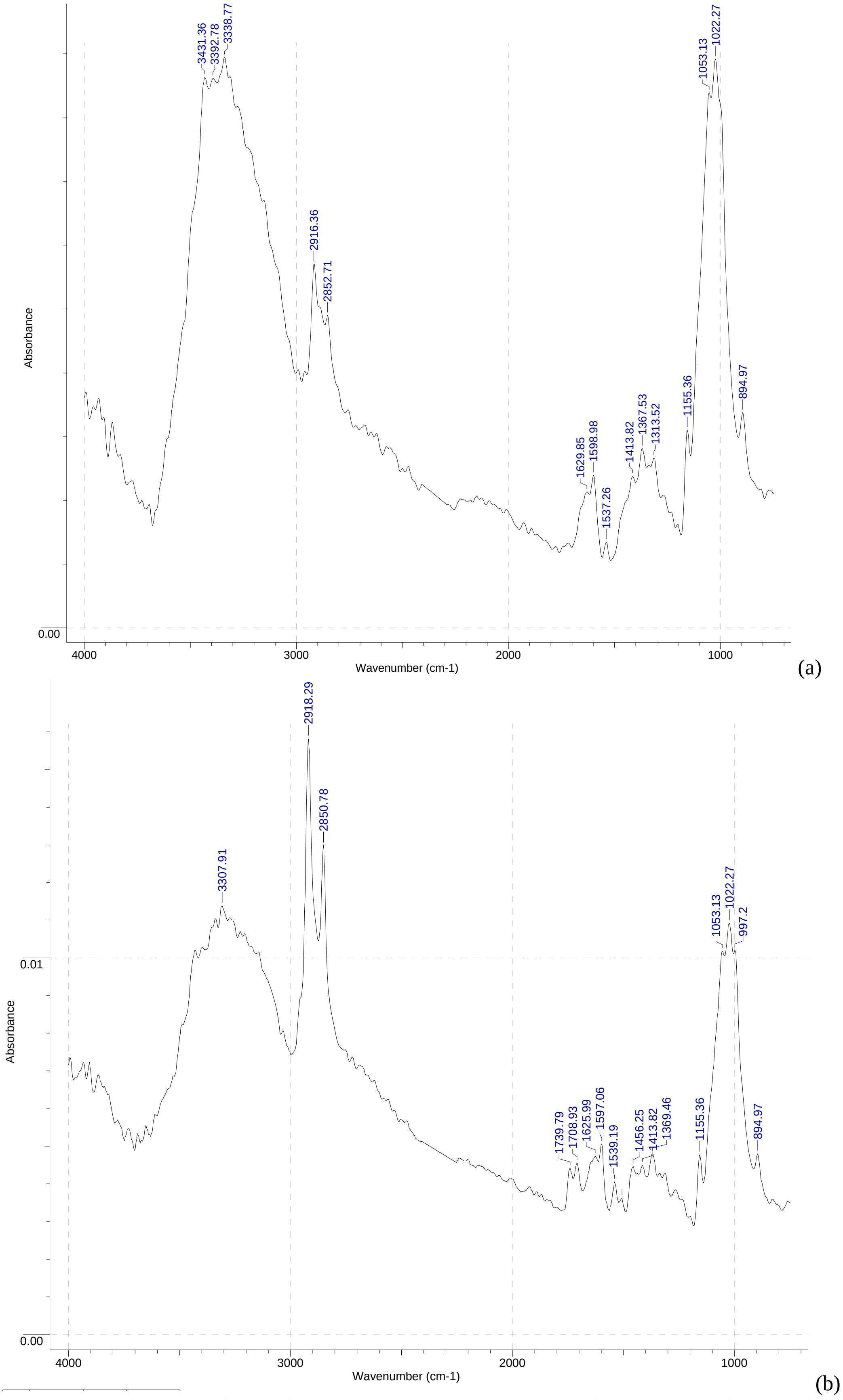


Figure 7: FTIR spectra of microfibrillated cellulose structures: (a) after two steps of acetylation; (b) after three steps of acetylation

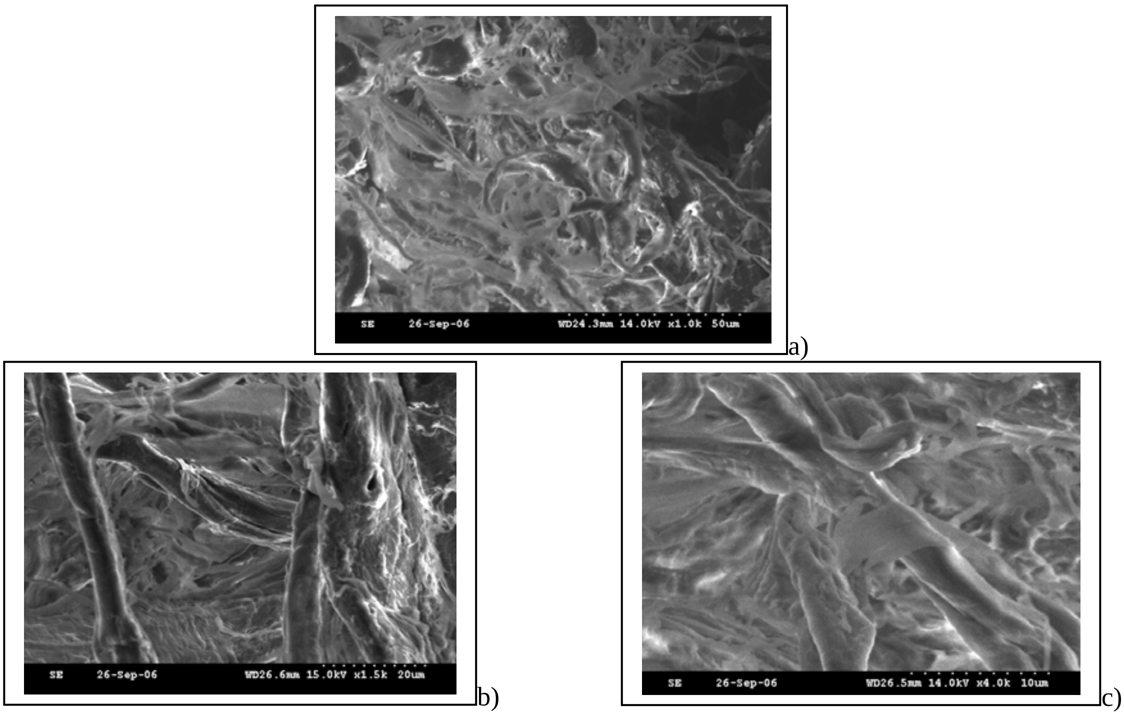


Figure 8: SEM images of cellulose microfibrillated elements: a) non-acetylated; b) two steps of acetylation; c) three steps of acetylation

Table 2
Elastic modulus of polymer composite materials reinforced with surface modified cellulose microfibrillar elements

PP composites	Elastic modulus [MPa]
Polypropylene PP	0.85
PP/5% non-acetylated cellulose microfibrils	1.0
PP/5% acetylated cellulose microfibrils	1.4

The morphology of microfibrillated cellulose structures before and after acetylation was studied using scanning electron microscopy (SEM) – Figure 8. It can be seen that the acetylated microfibrils are finer, compared to the non-acetylated ones.

The mechanical characterization of the PP composites reinforced with microfibrillated structures (Table 2) emphasized an increase in the elastic modulus when acetylated cellulose microfibrils were used as reinforcement, which resulted from the good compatibility of the chemically modified fibres (more hydrophobic) with the polymer matrix.

CONCLUSION

The cellulose microfibrillated structures produced from bleached softwood pulp, using chemical-mechanical isolation methods, were subjected to chemical surface modification by homogenous acetylation reactions and spray drying by the atomization process.

The microfibrillated structures thus obtained were used as reinforcement in the polymer matrix composites.

According to SEM images, FTIR analyses and mechanical properties of the polymer composite materials, acetylation seems to be an efficient method to increase the dispersibility of cellulose fibres in a hydrophobic polymer matrix.

The spray drying of cellulose microfibrillated structures is a suitable method to produce a particulate material with unchanged size and a very good potential as reinforcement in composite manufacturing, utilizing conventional thermoplastic compounding techniques.

The improvement in the mechanical properties of the composite materials is the result of the high dispersibility of spray dried cellulose microfibrillar structures in the polymer matrix, due to reducing the cellulose fibre hornification phenomenon, which occurs during the oven drying process.

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