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Preparation and properties of composite films from modified cellulose fibre-reinforced with PLA

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ABSTRACT

Now a day there is an emerging interest in replacing non-renewable additives with biodegradable compounds. Cellulose plays very important role in this modification. Their low cost and low density associated with high specific mechanical properties represent a good renewable and biodegradable alternative to the most commonly used synthetic reinforcement. The cellulose was modified by using 2-(Trifluromethyl) benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by solubility and IR studies. The biodegradable composite films were developed by film casting method using modified cellulose with Poly (lactic acid) in different compositions. The film composite were characterized by mechanical, moisture absorption, water vapor permeability, oxygen permeability and biodegradable properties.

Keywords: Poly (lactic acid); Mechanical properties; Oxygen permeability; Biodegradable films.

INTRODUCTION

Cellulose, the most abundant natural homopolymer, is considered to be one of the most promising renewable resources and an environmentally friendly alternative to products derived from the petrochemical industry. Recently, modified cellulose has been used as reinforcements for various composites due to its excellent mechanical performance and fully biodegradable [1-3] in a wide variety of environmental conditions. As a result, various cellulose-based composites have been prepared. Currently, more and more researchers are developing fully biodegradable composites, the so-called green composites [4, 5], ecocomposites or biocomposites which are composed of natural fibers and natural matrices or synthetic biodegradable matrix [6-8]. Composites are usually fabricated with biodegradable polymers as matrix phase and natural fibers as enhancement phase. Poly (e-caprolactone) (PCL), poly (vinyl alcohol) (PVA), poly

(lactic acid) (PLA), poly (butylene succinate) (PBS) and poly (3-hydroxybutyrate-co-3-hydroxybutyrate) (PHBV) are most commonly used as matrix phase of composites.

Cellulose is a poly- β -1,4-D-glucopyranose and it is biodegradable, nontoxic, biocompatible, hydrophilic, safe, has high moisture-retentivity and chiral. However, cellulose has not reached its potential application in many areas because of its infusibility and insolubility. But at the same time, cellulosic fibers are hygroscopic in nature; moisture absorption can result in swelling of the fibers which may lead to micro-cracking of the composite and degradation of mechanical properties. This problem can be overcome by treating these fibers with suitable chemicals to decrease the hydroxyl groups which may be involved in the hydrogen bonding within the cellulose molecules. Chemical treatments may activate these groups or can introduce new moieties that can effectively interlock with the matrix. A number of fiber surface treatments like silane treatment, benzoylation and peroxide treatment were carried out which may result in improved mechanical performance of the fiber and composite [9, 10]. By limiting the substitution reaction on the surface of the fibers, good mechanical properties were obtained and a degree of biodegradability was maintained [11]. As a result, various cellulose based composites have been prepared [12-14]. However, there is no literature regarding the combination of modified cellulose and poly (lactic acid) which is excellent mechanical properties and processing capabilities. So far no information on mechanical properties, moisture absorption and environmental biodegradability of the modified cellulose/poly (lactic acid) composite has been reported. To this end, biocomposites based on modified cellulose/poly (lactic acid) were developed by a solution casting method in this work. The main objective of the present study is to characterize the mechanical, moisture absorption, biodegradation properties of the modified cellulose/poly lactic acid composites.

MATERIALS AND MATERIALS

2. Experimental

2.1 Materials

The fibre used in this work was commercial microcrystalline cellulose supplied by Loba Chemie. 2-(Trifluromethyl) benzoylchloride and Pyridine was purchased from Aldrich and used as received. The biopolymer of Poly (lactic acid) (Mw is between 195,000 and 205,000 g/mol) used in this work was obtained from Cargill Dow LLC and used as such. The composite films were developed using Magic mould releasing agent and with Teflon mould of one Square feet with 3 mm depth. The solvent acetonitrile was purchased from Rankem and used with purification. Finally the composite films were air dried in hot air oven.

2.2 Modification of cellulose

Cellulose was treated with sodium hydroxide solution at room temperature and stirred for 2hrs. Then solid obtained was filtered off. Salt formation was confirmed by solubility test, since it is freely soluble in water. This salt was treated with 2-(Trifluromethyl) benzoylchloride in presence of pyridine as a base cum solvent and stirred overnight at 100°C. Then dumped in to water; solid was filtered off. This product was confirmed by I.R analysis, which shows the absence of peak at 3332 cm⁻¹. Figure 1 and Figure 2 represents the I.R spectra of cellulose and modified cellulose.

2.3 Preparation of films

Modified cellulose was taken in a water with Poly (lactic acid) in different composition like 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, 95:05 ratio [15-22]. The reaction mixture was heated to 100°C for 24 hrs. After 24 hrs the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed

before by mould releasing spray and dried under vacuum oven at 100°C to remove water contents completely. After complete drying, the films are stored in moisture free environment.

2.4 Moisture absorption experiments

From the composite sheets, all the specimens for moisture absorption experiments were cut with dimensions of 30 mm by 10 mm. Moisture absorption measurements [23, 24] were performed under 75% RH (relative humidity) at 25°C. Specimens were thoroughly washed and then vacuum dried until a constant weight was attained prior to the absorption experiments. At predetermined intervals, specimens were taken out from the chambers and weighed using a PGB200 model analytical balance.

The moisture uptake at any time points as a result of moisture absorption was determined by

Moisture uptake =
$$\frac{Wh - Wo}{Wo} \times 100$$

Where Wh and Wo denote weight of humid specimens and the original dry value respectively. All data from three repeated tests were averaged.

2.5 Soil burial degradation experiments

Under moisture controlled conditions soil burial degradation experiments [25, 26] were carried out at ambient temperature. Specimens of each composite were placed in a series of boxes containing moisturized soil. The specimens (30 X 10 mm) were buried 100 mm beneath the surface of soil which was regularly moistened with distilled water. At predetermined time points the samples were removed, carefully washed with distilled water in order to ensure the stop of the degradation, dried at room temperature to a constant weight and then were stored in darkness. The specimens were weighed on the PGB200 model analytical balance in order to determine the average weight loss:

Weight loss =
$$\frac{Wo - Wt}{Wo} X 100$$

Where Wo is the initial mass and Wt is the remaining mass at any given time, t. All results are the average of three replicates.

2.6 Mechanical testing

Tensile strength, Young's Modulus and Elongation at break were measured according to the ASTM standard method D882-Test method A (ASTM 1997) with application of an Lloyd universal tensile machine with a 5 KN capacity at $23\pm2^{\circ}$ C and $48\pm5\%$ RH. Test specimens with a length of 30 mm and a width of 10 mm were cut from composite sheets. All specimens were equilibrated in a chamber kept at 18° C and 35% relative humidity for 24 hr before testing. All these tests were conducted at ambient temperature and an average value of four repeated tests was taken for each material.

2.7 Oxygen permeability test

In accordance with ASTM D3985 (ASTM 1995), the oxygen transmission rate (OTR) was determined. The film samples were equilibrated at $22 \pm 2^{\circ}$ C and $48 \pm 5\%$ RH for at least 48 hr in a controlled environment cabinet containing a saturated magnesium nitrate solution prior to the analysis. Oxygen permeability (OP) was calculated by the multiplication of the OTR at steady

state by the average film thickness divided by the partial pressure difference between the two sides of the film.

2.8 Water vapor permeability test

Based on the ASTM E96-9223 the gravimetric modified cup water method was used to determine water vapor permeability (WVP). Film samples were tested in circular test cups made of polymethylmethacrylate (PMMA). The fan speeds in the cabinets were set at an air velocity of 185 m min⁻¹. The weight loss was monitored until it was certain that water vapor transmission through the film samples had attained a steady state.

2.9 Scanning electron microscopy

For the evaluation of the film microstructure scanning electron microscopy (SEM) was used. Before the analysis the samples were sputter-coated with a thin layer of gold to avoid electrical charging.

RESULTS AND DISCUSSION

3.1 Moisture absorption behavior

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance. Though the poly (lactic acid) has been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. Moisture absorption test was carried for all the ten composite films in which the modified cellulose and matrix poly lactic acid are in the ratio of 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05. We observed that as the percentage of modified cellulose increases, moisture absorption decreases. This behavior clearly reflects the presence of hydrophobic moieties onto the fiber surface increase in their resistance towards moisture. Table 1 shows the moisture absorption behavior for all the ten films.

3.2 Biodegradation in soil

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms.

The studies on biodegradation behavior are important for the application of biocomposites in environment. In this work, soil burial experiment were performed for all the ten ratio films. Table 2 presents weight loss of various films as a function of biodegradation time. Note that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 16%. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results

obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

3.3 Mechanical properties

Tensile properties [27-31] of all the ten ratio films are presented in Table 3. We observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. An increasing trend in tensile strength and Young's modulus with modified cellulose fiber content is found from Table 3. This enhancement indicates the effectiveness of the modified cellulose as reinforcement. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases. With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

3.4 Oxygen Permeability Test

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance.

Figure 1 represents OTR (Oxygen Transmission Rate) values for all the ten ratio films. Generally, hydrophilic polymeric films have shown good oxygen barrier property. As can be observed in Figure 1, there was an improvement in oxygen barrier properties of the films as the percentage of modified cellulose increases. We observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fibre and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of modified cellulose. This result indicates the potential of these films to be used as a natural packaging to protect food from oxidation reactions.

3.5 Water vapor permeability test

Figure 2 represents WVTR (Water Vapor Transmission Rate) values for all the ten ratio films. The water vapor permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. We observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that modified cellulose is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapor permeation. This results shows that these films may impede moisture transfer between the surrounding

atmosphere and food, or between two components of a heterogeneous food product. This property is very much use full in packaging application.

No	%wt.	% wt.	% wt.	%wt.						
of	increase									
hrs	10:90	20:80	30:70	40:60	50:50	60:40	70:30	80:20	90:10	95:05
2	2.9	2.7	2.7	2.4	1.9	1.7	1.7	1.5	1.4	1.4
4	5.1	4.9	4.8	4.4	3.9	3.6	3.6	3.1	2.9	2.8
6	7.2	6.9	6.7	6.2	5.6	5.1	5.0	4.5	4.3	4.2
8	9.0	8.7	8.4	7.8	7.1	6.5	6.4	5.9	5.6	5.5
10	10.6	10.3	9.7	9.0	8.2	7.5	7.3	6.8	6.4	6.2
12	12.3	12.0	11.0	10.1	9.3	8.6	8.2	7.7	7.2	6.9
14	13.9	13.5	12.2	11.3	10.4	9.6	9.1	8.6	8.0	7.6
16	15.7	15.3	14.5	12.5	11.4	10.7	10.1	9.4	8.7	8.2
18	17.2	16.7	15.8	13.6	12.5	11.8	11.0	10.2	9.5	8.9
20	18.6	18.1	17.1	14.8	13.6	12.9	11.9	11.1	10.2	9.5
22	20.1	19.5	18.3	16.0	14.7	13.9	12.8	12.0	11.0	10.1
24	21.0	20.3	19.5	17.2	15.7	14.9	13.8	12.8	11.7	10.6

Table 1 Moisture absorption studies of ten film composites

Table 2 Biodegradable studies of ten film composites

No.of	% wt.									
days	decrease									
	10:90	20:80	30:70	40:60	50:50	60:40	70:30	80:20	90:10	95:05
2	2.7	2.8	3.0	2.9	2.8	3.1	2.9	3.0	3.3	3.2
4	3.9	3.8	4.1	3.9	3.9	4.2	3.7	4.2	4.2	4.4
6	5.8	5.6	5.9	5.7	5.5	5.6	5.3	5.5	5.7	5.6
8	7.7	7.5	7.6	7.4	7.5	7.4	7.7	7.6	7.8	7.6
10	9.3	9.5	9.4	9.2	9.3	9.6	9.6	9.8	9.7	9.8
12	11.7	11.6	11.7	11.5	11.4	11.6	11.4	11.6	11.7	11.9
14	13.2	13.4	13.6	13.7	13.5	13.8	13.7	13.8	13.9	14.0
16	15.4	15.7	15.6	15.9	15.4	15.6	15.6	15.7	15.5	15.7
18	15.6	15.8	15.7	15.9	15.5	15.6	15.8	15.8	15.6	15.9

3.6 Morphological observation

SEM micrographs [32] of the film composites are shown in Figure 3. SEM micrographs were taken for four film composites in different magnification. Figure 3(a) corresponds to 10:90 (modified cellulose +PLA) ratio film composite and clearly shows that the interfacial adhesion between the cellulose fiber and matrix was slightly poor. Moreover, the presence of cellulose fiber aggregates, some of them visible with the naked eyes, provided strong evidence of the poor dispersion of the reinforcement within the polymeric matrix and consequently of the nonhomogeneity of the material. Figure 3(b) corresponds to 50:50 (modified cellulose +PLA) ratio film composite and provided strong interfacial adhesion between two components and good dispersion within the matrix. Figure 3(c) and 3(d) corresponds to 70:30 (modified cellulose +PLA) ratio film composite which shows a better compatibility of the fibers with the matrix. Figure 3(e) and 3(f) corresponds to 90:10 (modified cellulose +PLA) ratio film composite, showed a more uniform morphology, i.e. the fibers were less visible because they were buried more effectively in the matrix. However, the fibre pull-out length is not large, indicating a good fibre-matrix bonding. In this connection, it can be argued that there is an improvement of interfacial strength in the film composite as the percentage composition of modified cellulose increases. In other words bulk fibre reinforcing film composites have the most uniform distribution of fibre and the most compatible interface in film composite.



Figure 1 Oxygen permeation curves for different film composites





S.No	Modified cellulose+ PLA	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at break (mm)	
1	10+90	22.4113919	827.7663445	302.0270283	
2	20+80	22.77639517	870.4413104	272.0983709	
3	30+70	22.79334137	880.8504405	262.4007171	
4	40+60	25.66678791	970.3255093	211.9548209	
5	50+50	38.44624355	1342.92477	166.7931105	
6	60+40	38.50031124	1510.097827	151.4551531	
7	70+30	39.53851798	1800.787343	107.2811558	
8	80+20	39.73762708	3184.806139	96.60724882	
9	90+10	40.15141639	4361.228034	39.44458505	
10	95+05	41.30330563	4947.642641	33.76678709	

Table.3 Typical tensile properties of ten film composites





 (b)

 200 nm
 Mag = 100.00 K X
 EHT = 20.00 kV
 Date :25 Jun :2011
 ZEXXX

 WD = 0 mm
 Signal A = VPSE
 Time :16:08:49
 ZEXXX

 CC

 200 mm
 Mag = 200.00 K X WD = 6 mm
 EHT = 20.00 K/ Signal A = VPSE
 Date :25 Jun 2011 Time :16.09:48
 ZEXXX

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CONCLUSION

Composites were developed by film casting method. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less. Film composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. The produced film composites possess higher tensile strength as the proportion of modified cellulose increases and higher elongation at break as the proportion of PLA increases. So modified cellulose plays vital role in increasing the tensile strength of film composites.OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Hence these films can be used as a packaging to protect food from oxidation reaction and moisture.

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