Biocomposites based on castor oil polyurethane and organosilane modified cellulose fibers

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Abstract

Chemical modification of cellulose fibers with a trialkoxysilane has been performed and modified cellulose-castor oil polyurethane composites have been successfully studied. The modified cellulose and all composites was characterized by Fourier transform infrared spectroscopy (**FTIR**), differential scanning calorimetry (**DSC**), thermogravimetry (**TGA**) and water uptake test (**WU**). Compared with the crude cellulose fibers, the organosilane treatment reduces the hydrophilicity of the natural fibers and increases the fiber/matrix compatibility. In addition, the better dispersion of treated cellulose fibers was characterized by scanning electron microscopy (**SEM**). Cellulose fiber modification effect on mechanical properties was investigated by uniaxial traction test. Results show an improvement of Young modulus and tensile strength. Composites thermal properties of are also improved after the organosilane treatment of fibers. These results are due to the interfacial adhesion improvement by the formation of chemical bonding between prepolymer isocyanate extremities and the glycidol grafted on cellulose surface.

Keywords: Polyurethane; cellulose; surfaces and interfaces; grafting; mechanical properties.

1. Introduction

Since petroleum-based plastic products do not degrade in landfill or composting environments, they pose a serious environmental problem [1]. Nowadays, cellulose fiber-reinforced composites are considered as a suitable alternative to overcome these problems of waste disposal. Natural cellulosic fibers have numerous specific properties, such as low cost, lightweight, renewable character, high specific strength and modulus, availability in a variety of forms everywhere, reactive surface and, possibility to generate energy, without residue, after burning at the end of their life-cycle [2-4]. These interesting characteristics motivate their association with organic polymers to elaborate composite materials. However, the polar surface associated to the hydroxylated nature of the constituting anhydroglucose units of cellulose is responsible for their high hydrophilicity [5, 6]. Moreover, the polar character of these fibers causes their low compatibility with partially or totally hydrophobic polymer matrices. Owing to the poor wettability and adsorbability towards polymers, the surface modification of the fibers surface is essential, in order to improve the fiber/polymer compatibility and their interfacial adhesion. Without such treatment, natural fibers embedded in a polymeric matrix generate unstable interfaces and the stress applied to the fiber/polymer composite is not efficiently transferred from the matrix to the fiber. Consequently, the beneficial reinforcement effect of the fiber remains underexploited [7]. Thus, considerable efforts have been focused to develop either physical or chemical methods for surface modification of natural fibers [8]. The physical treatment methods change structural and surface properties of

the fiber and thereby influence the mechanical properties of composite materials. While chemical methods consist in changing the chemical composition of the fibers by introducing a coupling agent. The latter forms a bridge of chemical nature between fiber and matrix.

Alkyltrialkoxysilanes R'Si(OR)$_3$ are currently used in many industrial applications as coupling agent to improve adhesion between a polymeric matrix and inorganic materials, such as glass fibers. They have also been used in vegetable fiber–polymer composites to modify fiber surface [9]. Actually, to couple efficiently natural fibers and polymer matrices, the silane molecule should have at least two functional groups which may react with both phases, thereby forming a covalent bridge between the two phases [10]. Furthermore, the alkoxysilanes were found to react directly with -Si-OH groups of silica forming -Si-O-Si- bonds. However, they do not undergo the same reaction with the hydroxyl groups of cellulose fibers even at high temperature. This has been attributed to the lower acidity of cellulose hydroxyl groups compared with silanols. In addition, cellulose is generally unreactive toward many chemicals since the OH groups of the microfibrils have very low accessibility. Based on this fact, an optional strategy is to activate the alkoxysilane by hydrolyzing the alkoxy groups off, thereby forming the more reactive silanol groups (Fig 1).
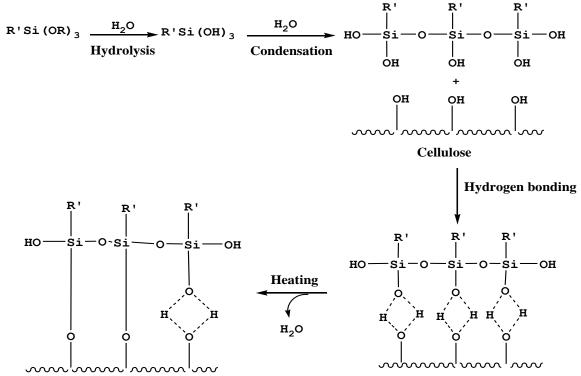

Figure 1: Mechanism of chemical treatment of cellulose fibers with a trialkoxysilane.

Thus, the trialkoxysilanes (R'-Si(OR)$_3$) dissolved in a water–ethanol solution hydrolyze giving the corresponding silanol derivative R'–Si(OH)$_3$ (totally or partially hydrolyzed); the resulting hydroxyl groups can establish either chemical bonding and/ or hydrogen bonds with cellulose [5]. Heating treatment promotes the condensation of free resultant silanol groups forming the solid polysiloxane layers on the fiber surface. Hydrogen bonding is another possible crosslinking process between the -Si-O-Si- backbone and the hydroxyl groups of cellulose fibers [10].

Recently, we investigated the effect cellulose fibers loading on structure, thermal, mechanical and physic-chemical performances of thermoset polyurethane matrix synthesized by polycondensation of castor oil and isophorone diisocyanate[11]. The obtained results showed slight increase of glass transition temperature and young modulus and a decrease of tensile strain up to 20% of fibers. At higher filler loading, the contact fiber-fiber increases and mechanical properties dropped quickly. To overcome this problem, we studied in the present paper the surface silane treatment effect on interfacial adhesion and on thermal, mechanical and physico-chemical properties of cellulose-polyurethane based on castor oil and isophorone diisocyanate composites.

2. Materials and methods

2.1. Apparatus

- Infrared spectra of **CF** and **mCF** fibers and all composites were recorded by attenuated transmittance reflection–Fourier transform infrared mode with FTIR 8400 S SHIMADZU in a range of 4000 to 700 cm^{-1}. Samples were scanned 128 times.

- Thermal properties were studied by differential scanning calorimetry (**DSC**) and thermogravimetric analysis (**TGA**). The **DSC** analyses were determined using DSC 204 F1 Pheonix NETZSCH (Germany). 15 mg of sample was placed in a closed aluminum capsule. Each sample was subjected to two heating/cooling cycles between -50 and 200°C with a scanning rate of 10°C/min, only the second heating thermograms are shown. The **TGA** thermograms were obtained using TG 209 F3 TARSUS NETZSCH 51 apparatus. The heating program starts from 25 to 700°C with a heating rate of 10°C/min. The obtained thermograms show the weight loss in response to the increase in temperature.

2.2. Reagents

(3-Glycidyloxypropyl)trimethoxysilane ≥ 98%(**GPTMS**), castor oil (**CO**), isophorone diisocyanate 98% (**IPDI**), and dibutyl tin dilaurate (**DBTDL**) were purchased from Aldrich. Ethanol 99.9° (absolute alcohol) and acetone were supplied from CHARBONNEAUX BRABANT and toluene 99.5% for analysis was bought from CHIMIEPLUS Laboratoire. All reagents were used as received without any further purification.
Cellulose fibers (**CF**) were extracted from alfa stems according to Kraft method on alkali medium [12].

2.3. Reactions and water uptake measurements
2.3.1. Modification of cellulose surface with organosilane:
The reaction was carried out for 24h under mechanical stirring (rpm=100) and reflux in heterogeneous system, containing **GPTMS** in a solution of 50% toluene/ethanol (40/10, v/v) and 50% distilled water. The **CF** was soaked in the mixture with molar ratio **CF**/**GPTMS** was 3/1 [13]. The modified cellulose fibers obtained are referenced **mCF.**

2.2.2. Castor oil polyurethane and cellulose composites elaboration:
   a) Polyurethane synthesis:
The polyurethane matrix was synthesized by one shot method according to the procedure detailed in our previous work [11]. The obtained polyurethane (PU) is referenced as IPU.

   b) Preparation of cast films:
All films were prepared by solution casting by the same procedure described in our previous study [**Erreur ! Signet non défini.**]. The mCF composites dispersion solution was cast on alumina dishes. The prepared composites with mCF fibers are referenced as mIPUi. The abbreviation used for all prepared films are summarized in Table 1.

Table 1: Abbreviation of the composite films **IPUi** and **mIPUi**.

Percentage of cellulose fibers	Film based on CF (IPUi)	Film based on mCF (mIPUi)
0%	**IPU100**	**mIPU100**
5%	**IPU95**	**mIPU95**
10%	**IPU90**	**mIPU90**
15%	**IPU85**	**mIPU85**
20%	**IPU80**	**mIPU80**
30%	**IPU70**	**mIPU70**
40%	**IPU60**	**mIPU60**

The results obtained for the composites renforced with raw cellulose fibers (CF) are used as reference in the study of surface treatment efficiency.

*c) Moisture uptake (**MU**) measurements*

2g of **CF** and **mCF** are placed in a desiccator under vacuum with P_2O_5 for at least 24h until obtaining a constant dry mass. Then the weighted samples were conditioned in a chamber of 44% relative humidity (saturated aqueous solution of K_2CO_3) at 22°C. The two containers were weighed at desired time intervals (10 to 20min) until the equilibrium state (M_∞) was reached. The moisture uptake (**MU**) of the samples was calculated as follows [14]:

Equation 1:   Moisture uptake: **MU** (%) = [($M_t - M_0$)/ M_0]x100

Where M_0 and M_t are respectively the initial sample weight and the sample weight at time t, under 44% RH.

*d) Water uptake (**WU**) measurements*

Water uptake of the composites was determined by immersing pre-dried samples in distilled water at 30°C during 30 days. After a time interval, the samples were removed from water, carefully blotted to remove the excess water on the surface, and immediately weighed. The **WU** were calculated by using equation 1. The plotted values are the average of three samples for each material type.

3. Results and discussion

3.1. Modification of cellulose surface efficiency

The normally hydrophilic fibers are converted into a hydrophobic reinforcement for non-polar polymer matrices after surface and/or bulk treatment of the cellulose with silanes. The crude **CF** fibers extracted from alfa stems were treated during 24h with **GPTMS** in biphasic medium in presence of a mixture of distilled water and toluene/ethanol (Fig.1).

The **ATR-FTIR** spectrum of **CF** fibers given in figure2 is characterized by the small signal around 896 cm^{-1} attributed to the β-glucosidic bonds between glucose units. The signals at 1035, 2904 and 3340 cm^{-1} are attributed to the stretching vibration of C—O, C—H and O-H groups of glycosidic units, respectively. However, in **mCF FTIR** spectra (Fig.2), the peak at 3340cm^{-1} is shifted to higher wave number near 3381 cm^{-1} due to the decrease in intermolecular hydrogen bonding between OH groups[15].

Moreover, asymmetric stretching of Si-O-Si and/or Si-O-C bonds are depicted in the region between 856 and 1264 cm^{-1} and overlay the peaks of C-O bonds of epoxide functions. A slight increment in the broadness around 1000–1200 cm^{-1} is observed for the silane-treated fibers [16]. The Si-O-Si bond indicates the existence of silica deposited on the fiber surface, whereas the Si-O-C confirms the occurrence of a condensation reaction between the silane coupling agent and the fibers.

The change in the hydrophilic character of cellulose fibers after the silane treatment was investigated by moisture uptake measurements. First, weighted samples of **CF** and **mCF** were conditioned in a chamber of 44% relative humidity at 22°C, then, the two containers were weighed at desired time intervals until the equilibrium state (M_∞) was reached. The moisture uptake versus time curves (Fig.3) show clearly that **CF** and **mCF** adopt a similar profile of moisture absorption kinetics characterized by a two steps sorption behavior. The initial uptake is due to the capillary action resulting from the porous structure of **CF** and of **mCF** leading to the formation of a monolayer, where one molecule of water is bonded to each accessible hydroxyl group at the cellulose fiber surface [17]. After 100 min, the rate of moisture sorption of **mCF** slows down while that of **CF** continues to increase. At the end of the test, silane treatment of **CF** fibers reduces the overall moisture uptake up to 28.61% with respect to that of crude **CF** in the same conditions. In fact, the bulk treatment could mask the cellulose hydroxyl groups and hence, water sorption reduces due to decreased capillary action [6]. Therefore, the decrease in moisture uptake values for **mCF** fibers can be attributed to the physical and the chemical changes occurred on and in the fibers. In fact, silane treatment induces a coating on fiber surface. The shrinkage of micropores and collapse of capillaries upon treatments block the capillary absorption, and the interstices between microfibrils of the fiber would be blocked by the coupling agent which reduces the water accessibility [6].
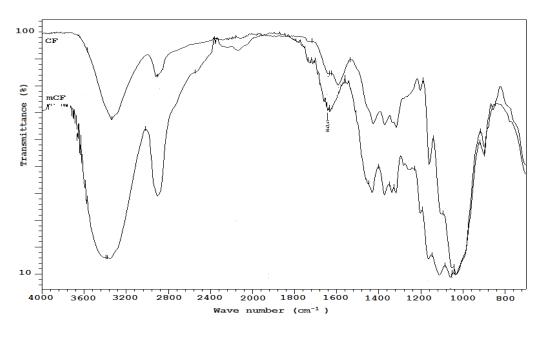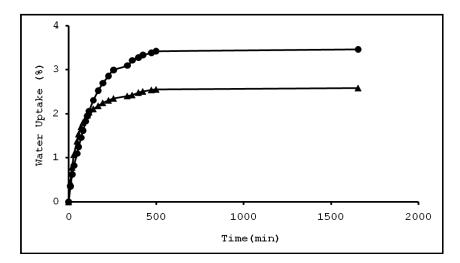
Figure 2: ATR-FTIR of **CF** and **mCF.**

Figure 3: Moisture uptake percentage versus time of **CF** (●) and **mCF** (▲) .

These results corroborate with DSC results where endothermic peaks appear within the range 50–200°C in the first scan **DSC** curves (Fig.4). Due to the vaporization of the moisture absorbed from the environment [18], this peak is shifted to lower temperature after organosilane grafting treatment. The total vaporization of absorbed water takes place at 110.8°C for **CF** and at 88°C for **mCF**. These results suggest that the moisture absorption of **CF** is reduced after the silane treatment. Indeed, the reactive silanol groups have a high affinity with the fiber hydroxyl groups, while unreacted silanol groups can undergo further condensation forming -Si-O-Si- network linkages on the fiber surface. Consequently, the surface coated by the hydrophobic polysiloxane network inhibits the moisture uptake [**Erreur ! Signet non défini.**].

The change of cellulose hydrophilic character after modification with **GPTMS** is ascertained by thermal analysis of **CF** and **mCF**. The **TGA** profiles and the corresponding differential **TG** (**DTG**) displayed in Figure5 show two weight loss steps for both samples. The first one occurs in the range of 60 –100°C and is attributed to the thermodesorption of physisorbed water [19].
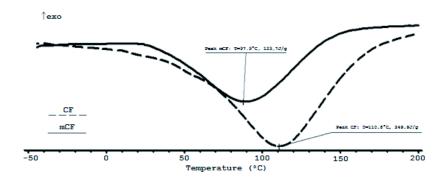
Figure 4: First scan **DSC** curves of **CF** and **mCF**.

The change of cellulose hydrophilic character after modification with **GPTMS** is ascertained by thermal analysis of **CF** and **mCF**. The **TGA** profiles and the corresponding differential **TG** (**DTG**) displayed in Figure5 show two weight loss steps for both samples. The first one occurs in the range of 60 –100°C and is attributed to the thermodesorption of physisorbed water [20]. At this range, the weight loss of **mCF** is lower than that of **CF** confirming that the grafting of **GPTMS** on **CF** surface reduces their hydrophilic character. The unique degradation step of **CF** and **mCF** starts around 248°C**,** through the formation of levo-glucosan (1,6-anhydro-β-D-glucopyranose) and its subsequent decomposition [21]. This peak is shifted to higher temperature, around 296°C, after the surface treatment. At 700°C, the residual masses are 33% and 18% for **CF** and **mCF**, respectively. The reduction of the residual mass of **mCF** may be due to the organosilane coating degradation in the range of 300 – 500°C [22] and further degradation of cellulose fibers induced by the presence of the siloxane moieties or their degradation byproducts.
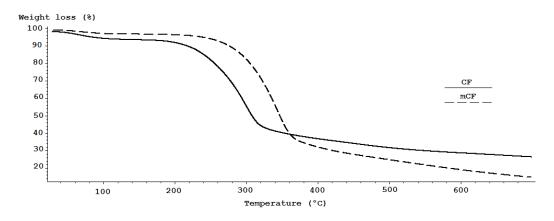

Figure 5: **TGA** and **DTG** thermograms of **CF** and **mCF.**

3.2. Characterization of the composites:
3.2.1. Structural characterization
To show the effect of silane treatment on the properties of castor oil polyurethane and cellulose fibers based composite, the results obtained for the composites **IPUi** [14] are used as a reference to compare the studied parameters. In **IPUi** or **mIPUi** equivalent amounts of **CF** and **mCF**, respectively, were added to reinforce the polyurethane matrix **IPU**. The structural characterization of **IPUi** and **mIPUi** via FTIR (Figs.6) shows that all composites have identical spectra. In **IPU100**, the peaks around 3360 cm^{-1} are assigned to stretching vibration —N—H functions and the broad band in the range 1703 – 1695 cm^{-1} is attributed to the carbonyl groups of the urethane functions present in the matrix. Furthermore, the band at 1520 cm^{-1} is characteristic of the C—N deformation in urethane group. The introduction of **CF** or **mCF** in the matrix shifts the N—H group peaks (3360 cm^{-1} in **IPU100**) to lower wave numbers in composites (3341 cm^{-1} in **IPU60** and 3338 cm^{-1} in **mIPU60**) (Table 2).
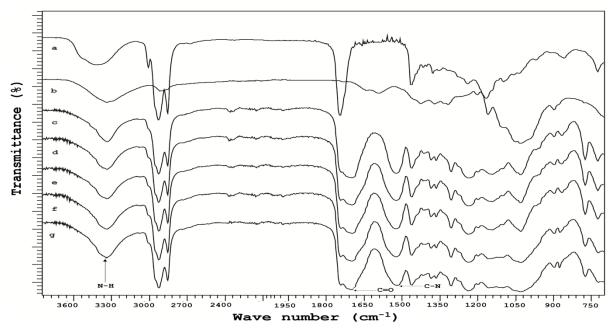
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Figure 6: ATR-FTIR spectra of (a) **CO,** (b) **mIPU100,** (c) **mIPU80**, (d) **mIPU60** and (e) **mCF.**

Table 2: Wave numbers of N-H elongation obtained by FTIR analyses of **IPUi** and **mIPUi** composites.

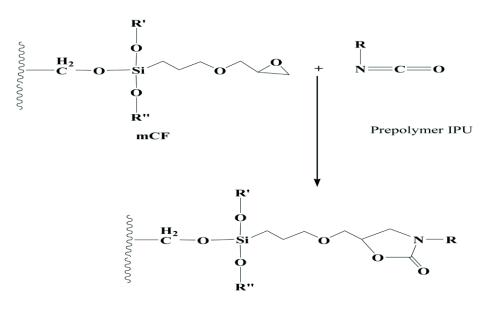| Fiber content (%)	wave number of NH elongation in IPUi (cm^{-1})	wave number of NH elongation in mIPUi (cm^{-1})
0	3360	3360
5	3357	3350
10	3356	3350
15	3353	3350
20	3350	3348
30	3346	3340
40	3341	3338

The greater is the percentage of cellulose in the composite; the lower is the wave number of N-H vibration. Moreover, this peak is larger in composites than in **IPU100**, indicating the presence of hydrogen bonding between N—H groups of urethane functions and the hydroxyl groups O—H on the cellulose surface [23,24]. At equivalent fiber percentage, matrix/fiber interactions are stronger in the **mIPUi** since the N-H elongation peaks are wider than those of **IPUi**. In fact, the prepolymer isocyanate chain ends could establish chemical interaction established between the silane coupling agent and [1,25]. According to previous results [26] it has been showed that the glycidol extremities of the grafting siloxane can undergo chemical linking with the isocyanate function of IPDI forming an oxazolidone function (Fig.7). Unfortunately, it is not possible to confirm such reaction in the studied composites due to possible overlaping between oxazolidone and urethane functions.
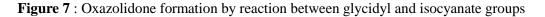
3.2.2. Thermal properties:

Generally, the incorporation of cellulose fibers into polymeric matrix increases the thermal stability of the system [27]. **DSC** analysis shows that all samples are characterized by a unique glass transition temperature. The **Tg** of composites increases linearly with increasing amount of the filler embedded in the matrix (Fig.8). This is due to the existence of interactions between fibers and the PU matrix. Such interactions are mostly of hydrogen bonding type which can be established between N-H of the urethane functions of **IPU** and hydroxyl groups of **CF** cellulose fibers. According to figure 8, it is also observed that the **Tg** values of **mIPUi** are

sensitively higher than those of **IPUi**. The shift of **Tg** to higher temperatures can be associated with the decreased mobility of the matrix chains, which indicates enhanced interfacial adhesion between **mCF** and polymer matrix via oxazolidone bonding.

Figure 7 : Oxazolidone formation by reaction between glycidyl and isocyanate groups
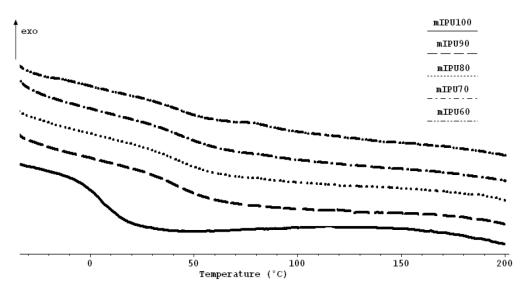

Figure 8: DSC thermograms **IPUi** and **mIPUi** versus fiber percentage.

The **TGA** analysis conduced nitrogen atmosphere thermograms are shown in Fig.9. The polyurethane is characterized by three decompositions stages. The first one is related to the degradation of urethane linkage and the ester bond. The second stage corresponds to the decomposition of the soft segments of **PU** and the last stage is associated to the degradation of the remaining **CO** structures and the C—C bond cleavage [28,29]. In **mIPUi** composites, the mass loss in the range of $300 – 500°C$ is due to the decomposition of grafted silane overlapping with the degradation step of **CF** and the polyurethane matrix. It is found that char yields (Table 3) of composites at 700°C increase with increasing filler content. Obviously, the char yield is directly correlated to fibers amount.

These results reveal that the fibers addition to **PU** matrix would effectively raise the char yield of the sample [15]. The decrease of **mIPUi** char yield suggest that the mixing of **mCF** fibers with the PU matrix inhibit fibers thermal degradation by slowing down silane coupling agent degradation, since the silanol groups are evolved in strong chemical bonding with the polymer matrix.
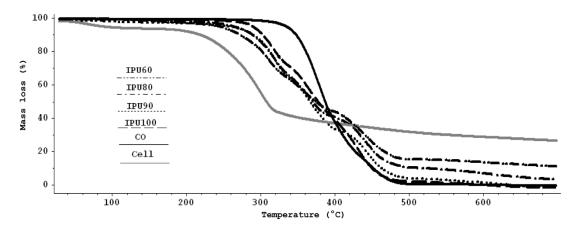

Figure 9: **TGA** thermograms of **CO**, mCF and **mIPUi**.

Table 3: Char yield values of **IPUi** and **mIPUi** at 700°C determined by **TGA**.

Cellulose percentage (%)	Char yield of IPUi (%)	Char yield of mIPUi (%)
0	0	0
5	3.70	2.55
20	5.29	8.65
30	8.81	9.69
40	12.74	13.36

3.2.3. Water uptake:

One of the major drawbacks of cellulose fibers use is their high hydrophilicity which usually reduces dramatically the mechanical performances of polymer composites [2]. The water uptake test is an efficient technique to measure the effect of fiber treatment on composite hydrophilic character. The results obtained after immersion of **IPUi** and **mIPUi** in deionized water at 30°C during 30 days are plotted in Figs.14 & 15, respectively. This results proves that **IPU** matrix is extremely hydrophobic with a total WU_∞ =1.35%. In **IPUi** and **mIPUi** composites, water uptake tendency increases with fiber amount in the matrix. This **WU** behavior with increasing fiber content is common to cellulosic fiber-filled composites [30]. The increase in fiber loading induces the increase in hydroxyl group number in composites, which consequently increases the water absorption [31]. It is worth noting that the two series of composites adopt similar water absorption profiles. Nevertheless, a sensitive reduction of water uptake ratio is observed for **mIPUi** composites. Indeed, after the organosilane treatment, at equivalent filler content, **WU** is lowered from WU_∞(IPU70)=47.55% to WU_∞(mIPU70)=11.52% at 30% of fiber content, and from WU_∞(IPU60)=63.85% to WU_∞(mIPU60)=31.47% for 40% of fiber content. This observation agree with the moisture uptake test results obtained for **CF** and **mCF**, which suggest the decrease of hydrophilic character of **CF** after **GPTMS** grafting. In fact, glycidoxy propyl coating is good candidate for improving the fiber–matrix interface stability and enhances matrix adhesion onto the fibers probably via oxazolidone chemical linkage [26]. Consequently, the contact fiber/fiber reduces, and hence the number of microvoids decreases. Indeed, the water diffusion inside composite material reinforced with silane treated fibers **mCF** is limited [2,6,9,32].

Conclusion

Chemical modification of cellulose fibers with a trialkoxysilane was achieved in mild conditions and composites of modified cellulose/castor oil polyurethane have been successfully prepared. Spectroscopic

analysis of the composites revealed the presence of strong interactions between cellulose fibers and polymer matrix through siloxane and oxazolidone bonding. The latter are the result of the reaction between glycidyl groups and isocyanate chain ends of polyurethane. **DSC** analysis showed an increase in the **Tg** values of composites suggesting the efficiency of the interaction of the polymer matrix with cellulose fibers while thermal and physico-chemical showed enhanced properties of the prepared composites up to 30% of **mCF** in the matrix. Beyond this percentage, the contact fiber/fiber increases leading to discontinuity apparition.

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