EFFECTS OF ACETYLATION PROCESS AND CELLULOSE CONTENT ON THE MECHANICAL, THERMAL, MORPHOLOGICAL AND RHEOLOGICAL PROPERTIES OF POLY (VINYL CHLORIDE)/CELLULOSE COMPOSITES

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The aim of the present work is the chemical modification of microcrystalline cellulose (MCC) by acetic anhydride and using it as reinforcement in poly (vinyl chloride) (PVC). The treatment efficiency was assessed by Fourier Transform Infrared Spectroscopy (FTIR) analysis and contact angle measurements. Likewise, the morphological, mechanical, thermal and viscoelastic properties of the composites were studied. The different changes in the FTIR spectra and contact angle measurements corroborate the occurrence of chemical modification. The acetylation has improved the compatibility between the PVC and MCC by diminishing the surface energy of the fiber. This contributes to the amelioration of the interfacial adhesion, which appears in the SEM images. The treated and untreated cellulose has decreased the mechanical properties of PVC. The modulus and the thermal stability of PVC were improved by the introduction of both untreated and treated cellulose.

Keywords: cellulose, poly (vinyl chloride), acetylation, composites, interfacial adhesion

INTRODUCTION

Polymeric composite materials are frequently prepared using mineral fillers or glass fibers as reinforcement to achieve desired properties. Some disadvantages of these composites have been observed, such as significant increase in the weight of the final article and increased abrasion of processing equipment during the composite preparation process. Recently, significant efforts have been directed to investigating the use of natural fibers as a reinforcement of the polymeric matrix as an alternative to mineral fillers and glass fiber.[1,2] Incorporating tough and light-weight natural fibers into a polymer (thermoplastic and thermoset) matrix produces composites with a high specific stiffness and strength. In general, polymer waste is disposed of in large landfills causing serious problems to the environment, while the renewable and biodegradable characte-ristics of natural fibers facilitate their ultimate disposal by composting or incineration, options not possible with most industrial fibers.[3]

Compared with polypropylene (PP) and polyethylene (PE) based composites, PVC/cellulosic fiber composites provide superior properties in terms of weatherability and flame retardancy, and the cost of PVC is lower than that of the other polymers.[4] Consequently, the demand for PVC/wood composites increases by about 200% a year, against 130% for PP-based composites, and 40% for PE-based composites.[5] Although natural fibers can offer the resulting composites many advantages, the poor interfacial bonding between the highly polar natural fibers and the non-polar polymer matrices can lead to a loss in final properties of the composites and ultimately hinders their industrial usage. Different

strategies have been applied to complement this deficiency in compatibility, including the use of coupling agents and/or surface modification techniques.[6-10] Surface modification of natural fibers can be achieved by chemical or physical means. Esterification by means of acetylation is one of the most used techniques with the aim to improve the fiber/matrix interfacial bonding.

The objective of the present work is to elaborate PVC based composites from raw and chemically treated cellulose and subsequently investigate the effect of chemical treatment and filler content on the properties of the composites. To gain insights into the effect of fiber treatment on the filler/matrix interfacial adhesion, the morphological features of the fractured surfaces of both raw and treated PVC/cellulose composites were recorded using scanning electron microscopy (SEM). The mechanical, thermal and viscoelastic properties of the composites were also reported.

EXPERIMENTAL
Materials
The polymer used as matrix was polyvinyl chloride (PVC) type SE-1200 produced by the company CABEL in Algiers (Algeria). It has the following physical characteristics: K-value of 71 and powder density of 0.52 g/mL. The additive used as plasticizer, in the preparation of various formulations, was the dioctylphthalate (DOP). The heat stabilizer system was based on Ca/Zn stearates, and stearic acid was used as lubricant.

Avicel type microcrystalline cellulose (Art 2330 Merck Darmstadt) was used as filler; its diameter is lower than 100 μm. Acetic anhydride (AA) (purity, 98%) purchased from PR NORMAPUR AR was employed for the chemical treatment of cellulose.

Fiber surface treatment
The chemical treatment was carried out according to the experimental protocol reported by Luz *et al.*[11]

Initially, 15 g of sample (cellulose) was placed in a round bottom flask with 76 g of glacial acetic acid. The reaction was performed in a thermostatic bath at 35 °C for 45 min under magnetic agitation. After that, more 25 g of glacial acetic acid was added with 0.1 mL concentrated H_2SO_4 and the bath was maintained for more 1 h. After this step, the mixture was cooled at 18 °C for slow addition of 41 mL acetic anhydride with 0.6 mL concentrated H_2SO_4 during 3 h under constant stirring. The temperature of 18 °C was maintained for over 15 min and then was slowly increased to 50-55 °C to finalize the esterification process. The mixture was filtered, washed with distilled water, dried in an oven at 50 °C for 24 h to obtain cellulose acetate.

Preparation of composites
The blend based on PVC powder and various additives was placed in a mixer and processed at a speed of 2000 rpm at a temperature below 80 °C to obtain a compound. This was used to prepare films by calendering at 140 °C. Untreated or treated microcrystalline cellulose was added once the mixture softened. The films thus obtained were placed in a mould, which was placed between two steel plates. The film was subjected to compression molding under a pressure of 250 kN at a temperature of 170 °C for 5 min. The 2 mm thick plates obtained were then removed and characterized. The compositions of the various formulations are summarized in Table 1.

Techniques
Fourier Transform Infrared Spectroscopy (FTIR)
Fourier transform infrared spectroscopy (FTIR) was used to characterize the functional group composition of pure and treated cellulose. A SHIMADZU FTIR-8400S spectrometer operating in diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) mode was used, with a total of 20 scans and a resolution of 4 cm^{-1}. Anhydrous potassium bromide (KBr) was used as a dispersing material and all spectra were scanned within the range 400-4000 cm^{-1}.

Table 1
Formulations of PVC/cellulose composites

Components			F0	F10U	F20U	F30U	F10T	F20T	F30T
PVC compound % (w/w)	PVC (phr)	100							
	DOP (phr)	30							
	Ca/Zn (phr)	4	100	90	80	70	90	80	70
	Stearic acid (phr)	0.5							
Cellulose % (w/w)	Untreated cellulose (UC)		0	10	20	30	0	0	0
	Treated cellulose (TC)		0	0	0	0	10	20	30

Contact angle measurements

Contact angle measurements were carried with two liquids of different polarity (water and diiodomethane (DIM)). The apparatus used was a contact angle system (OCA20), which allowed the determination of contact angle by taking images about 30 s after the deposition of the drop on the surface. 30 s is the necessary time for a drop to reach its equilibrium shape. Sessile drops of about 2 µL for water and 1.5 µL for DIM were deposited on treated and untreated composite surfaces. The contact angle measurements were used to evaluate the composite surface hydrophilicity and wetting characteristics. A minimum of 10 droplets of each liquid were deposited on each sample and then their average was reported. All experiments were carried out under ambient conditions. From the data obtained with pure liquids, the dispersive and polar contributions to the surface energy were determined using the approach proposed by Busscher et al.[12]

Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) technique was used to analyze the interfacial interaction in PVC/cellulose composites by using a FEI CONTA 200 apparatus. Prior to analysis, the samples were prepared by cryo-fracturing.

Tensile test

The strength of the cellulose reinforced PVC composites was determined using a tensile testing machine type Zwick/Roell, tests were carried out according to the standard ISO 527 at ambient temperature and a crosshead speed of 10 mm/min. Five measurements were conducted for each sample, and the results were averaged to obtain a mean value. Three tensile properties were studied: tensile strength, tensile modulus, and elongation at break.

Thermal properties
Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition behavior of PVC/cellulose composites. The thermograms of the various samples were recorded using a thermogravimetric apparatus type SETARAM TGA 92. Tests were done under nitrogen atmosphere at a heating rate of 10 °C/min in a temperature range set between 20 and 700 °C. The weight change was recorded as a function of temperature. Derivative thermogravimetry (DTG) was taken as the maximum temperature acquired from the differentiation of the weight change as a function of time.

Differential scanning calorimetry (DSC)

TA Q-10 thermal analyzer was used for recording DSC traces under nitrogen atmosphere. The test temperature ranged between 0 and 160 °C with a heating rate of 10 °C/min and sample sizes of 3 to 5 mg were used in each experiment.

Dynamic mechanical analysis (DMA)

DMA tests were performed using a TRITON dynamic mechanical analyzer, in single cantilever bending mode at a frequency of 1 Hz, in the temperature range of -40 to 140 °C under an inert atmosphere of nitrogen gas. The testing was carried out on rectangular bars measuring approximately 20 mm in length, 10 mm in width and 2 mm in thickness with a heating rate of 3 °C/min.

RESULTS AND DISCUSSION
FTIR analysis of the cellulose before and after treatment with acetic anhydride

The FTIR analysis indicates the principal differences between untreated and treated cellulose. Indeed, the changes and the aspect of new bands can provide information about the effect of the chemical treatment. The spectra presented in Fig. 1 show the difference between the absorption bands before and after the chemical treatment of cellulose.

The spectrum of chemically treated cellulose shows a reduction in the intensity of the band corresponding to the hydroxyl groups of cellulose at 3348 cm^{-1}. This reduction is due to the substitution of the hydrogen of the hydroxyl groups by acetyl ones.

The appearance of absorption bands at 1755 and 1234 cm^{-1} is observed. These bands are associated to C=O and C-O stretching, respectively, of acetyl components. An increase in the intensity of the peak at 1373 cm^{-1} is also observed. This increment is assigned to the vibration of the methyl groups of the acetyl ones. The intensity of the absorption band located between 1200 and 935 cm^{-1}, attributed to the groups C–O and C-O-C of cellulose, was reduced. This reduction can be explained by the diminution of the polymerization degree of cellulose during acetylation. These results are in good agreement with those obtained by Luz et al.,[11] Guimes et al.,[13] Wei et al.,[14] and Nechita et al.[15]

FTIR analysis confirms the efficiency of the chemical treatment. The acetylation reaction is carried out according to the mechanism illustrated in Scheme 1.

Contact angle measurements

Contact angles (θ) provide useful information about wettability, which is essential in the modification of fiber surfaces. Photographs of

water drops deposited on the surface of both unmodified and modified composites (Fig. 2) illustrate that water had a higher affinity for the untreated composite surfaces than for the treated

ones. In order to determine the surface energy of the composites, we have measured the contact angle of another nonpolar liquid, diiodomethane, deposited on various material surfaces.
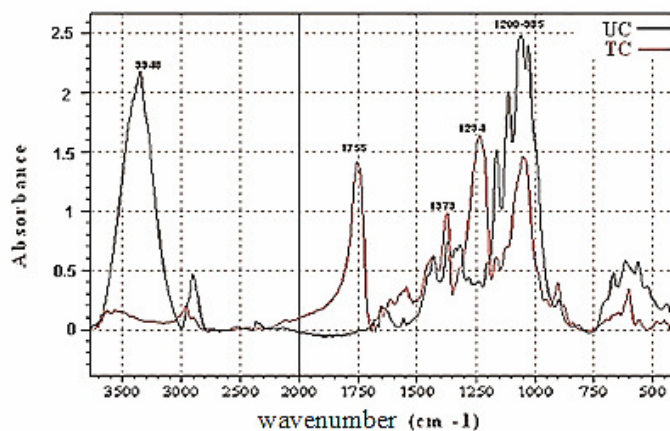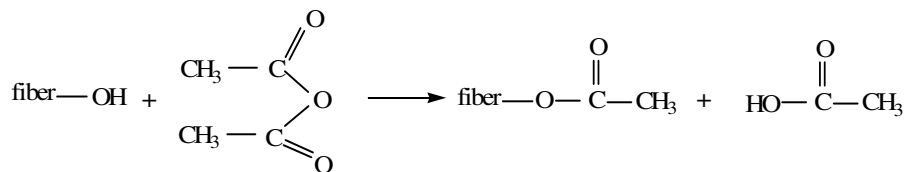

Figure 1: FTIR spectra of treated (TC) and untreated cellulose (UC)

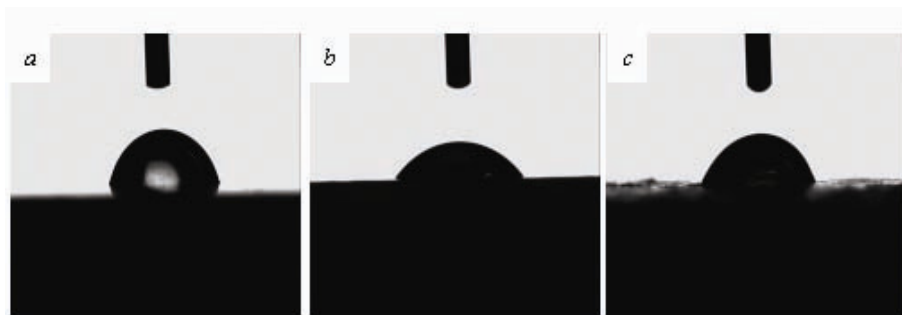Scheme 1: Acetylation reaction of cellulose with acetic anhydride (AA)

Figure 2: Photographs of water drops deposited on the surface of different materials: (a) PVC (F0),
(b) PVC/untreated cellulose (F20U) and (c) PVC/treated cellulose (F20T)

According to the contact angle results, we obtained the surface energy (γ), its polar (γ^p) and dispersive (γ^d) components, which are listed in Table 2.

The results (Fig. 2 and Table 2) revealed that the incorporation of untreated cellulose in a PVC matrix led to a decrease of the water contact angle (θ_{water}) from 75° to 49° and an increase of the

diiodomethane contact angle ($\theta_{diiodomethane}$) from 35° to 58°, causing an increment in total surface energy from 42 to 50 Nm/m. This can be attributed to the hydrophilic characteristic of cellulose, which is hydrated by water molecules and increases the hydrophilic character of the composites.[16]

Table 2
Contact angle (q_{water} and $q_{diiodomethane}$), dispersive component (γ^d), polar component (γ^p) and surface energy (γ) values of PVC matrix and its composites

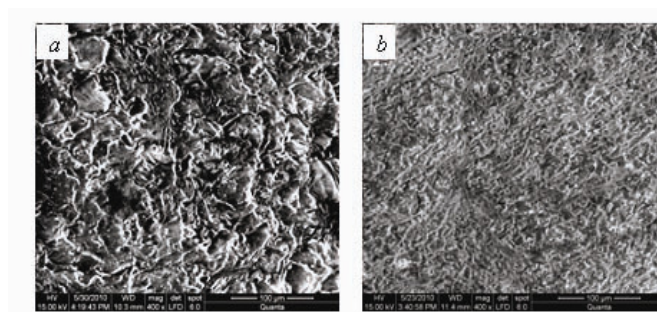| Samples	q_{water}	$q_{diiodomethane}$	Surface energy (γ)	Polar component (γ^p)	Dispersive component (γ^d)
F0	74.7 ± 0.8	38.8 ± 1.2	42	5	37
F20U	48.9 ± 1.8	57.8 ± 1.2	50	32	18
F20T	62 ± 4.1	51.7 ± 1.3	41	17	24

Figure 3: Scanning electron micrographs of fractured surfaces of PVC/cellulose composites with a loading of 20 wt%: (a) untreated composite, (b) treated composite

The analysis of the data shows that the total surface energy of the treated composites is lower than that of untreated ones, which indicates that chemical modification induced dramatic changes in the surface polarity of cellulose by the substitution of hydrophilic OH groups by acetyl ones. The different performances relative to the change in contact angle on treated and untreated composites corroborate the occurrence of chemical modification. This is consistent with the results of FTIR and with those obtained in previous reports.[17,14]

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is a common method to observe qualitatively the level of fiber/matrix adhesion. The SEM analysis of the morphological features of fracture surfaces is an important tool for observing the surface morphology of the composites. Figure 3a and Figure 3b depict the fracture surface of PVC/untreated and treated cellulose composites at 20% weight loading, respectively. The presence of voids and cavities is clearly visible in the untreated composites. This indicates that the level of adhesion between the fibers and the matrix is poor and when stress is applied it causes the fibers to pull out from the PVC leaving behind gaping holes. From Figure 3b, we can observe that the number of the cavities is reduced. This

improvement in the surface morphology can be explained by the better interfacial adhesion and the better dispersion of cellulose in the matrix after chemical treatment.[19,20] An enormous amount of studies have evaluated the bonding between matrix and fiber by means of SEM analysis. In the work of Maya Jacob John et al.,[21] the fracture surfaces of sisal/oil palm fiber filled rubber composites were investigated and the authors observed that the chemical modification of the fibers produced better adhesion. Wang et al.[22] reported a study on the composites obtained by the incorporation of bamboo particles in a PVC matrix. The SEM results revealed that the chemical treatment of the bamboo particles had improved the interfacial adhesion between the filler and the matrix.

Mechanical properties
Tensile strength

Figure 4 shows the results for the tensile strength of poly(vinyl chloride) and composites reinforced with untreated and treated cellulose as a function of fiber content.

It is clear from Figure 4 that the tensile strengths of both raw and chemically treated cellulose/PVC composites decrease gradually with the increase in filler loading. We recorded a reduction from 25 MPa for the neat PVC to 12.6 MPa for the formulation F30U. This lowering is

due to the weak filler/matrix interactions and the bad dispersion of the fiber in the polymer matrix.[23] This result is confirmed by several studies such as that of Nazrul Islam *et al.*,[24] which reported a reduction in the tensile strength from 27.5 MPa for virgin PP to 25 MPa for the composites reinforced with 25% of coconut fiber. Djidjelli *et al.*[25] recorded a decline in this property from 27 MPa for raw PVC to 10 MPa for PVC/sisal fiber composites at a loading of 30%. Gajender Saini *et al.*[26] studied the mechanical properties of PVC/acacia bark flour composite. They noted that the addition of fibers (20%) caused a decrement of about 18% in the tensile strength of the PVC matrix.

The deterioration of the mechanical properties after the incorporation of the filler in the matrix is due to the incompatibility between hydrophilic fibers and hydrophobic polymer. To remedy this problem we have treated microcrystalline cellulose by acetic anhydride.

The chemical treatment of the cellulose improved the adhesion between the fiber and the matrix, which decreased the number of cavities observed by SEM analysis; however it had a detrimental effect on tensile strength. We recorded a slight reduction in the tensile strength for the formulation F30U compared with the untreated cellulose. This decline can be attributed to the high degree of substitution of the OH groups of cellulose by acetyl groups (DS=3),[27] which prevents the formation of the hydrogen bonds. Also, it can be assigned to the decomposition of cellulose during the acetylation caused by the acetic acid used as solvent.[28,29] Gardea-Hernandez *et al.*[30] modified wood fiber by oxalic acid. According to SEM micrographs, it was evident that the treated fibers became smaller than the untreated ones. The authors attributed the morphological changes in the fibers after the esterification process to their degradation, which caused their fragility and consequently the dropping of the tensile properties. In this same context, Zita Dominkovics *et al.*[31] noted a reduction in the tensile strength of the composites after benzylation of cellulose fibers.

Elongation at break

The effects of the load factor and of the chemical treatment of cellulose on the elongation at break of PVC/cellulose composites are illustrated in Fig. 5. This figure indicates that the content of the reinforcing agent is a principal factor affecting the elongation at break of the composites. Indeed, it is observed that the elongation at break of PVC/cellulose composites decreases as the content of treated and untreated cellulose increases. Elongation values decrease from 180% for virgin PVC to 26.5% for the formulation F30U, because of the bad dispersion of cellulose in the matrix, which induces a reduction of interfacial adhesion between cellulose and PVC. We can also explain this reduction by the fact that the fibers hinder the chain mobility of the polymer matrix.[32-34] A similar result was obtained by Yu-Tao Zheng *et al.*,[1] who recorded a reduction in elongation at break from 150% for virgin PVC to 3.5% for PVC reinforced with 25% bagasse fiber. In the same context, Daniel Pasquini *et al.*[35] observed a reduction in the elongation at break from 125% for the virgin LDPE to 20% for the LDPE reinforced with 30% of cellulose. The chemical treatment of cellulose by acetic anhydride produces a slight improvement in the elongation at break of the composites, compared to the untreated ones. This is a consequence of the better dispersion of cellulose in the matrix, as was verified microscopically in Fig. 3.

This amelioration of the elongation can be also attributed to the plasticization behavior of the cellulose acetate phase, thus the polymer chain can slip easily. A similar behavior was also reported by Boukerrou *et al.*,[36] Yu-Tao Zheng *et al.*[1] and S. M. Luz *et al.*[11] They recorded an increase in the elongation at break of the composites after chemical treatment of natural fibers by epoxidized soybean oil (ESO), benzoic acid and acetic anhydride, respectively.

Young's modulus

Figure 6 presents the evolution of Young's modulus as a function of treated and untreated cellulose contents. The results show clearly that the incorporation of cellulose in the PVC matrix gives rise to composites with higher Young's modulus. The modulus increases with cellulose loading. We recorded an increase in the modulus from 202 MPa for the formulation F0 to 675 MPa for the formulation F30U and this can be explained by the increase of the composites rigidity. These results are in perfect correlation with those of Nazrul Islam *et al.*,[24] who recorded an increase in Young's modulus from 0.8 GPa for the virgin PP to 2.8 GPa for the PP charged with 20% of untreated coconut fiber. Steven Spoljaric

et al.[37] registered an increase of Young's modulus from 1.01 to 1.31 GPa after the introduction of 10% of microcrystalline cellulose into a PP matrix.

The incorporation of treated cellulose in the PVC matrix causes a slight reduction of Young's modulus, compared to the untreated composites. This reduction is of about 14% for the formulation F30T compared to F30U, which can be ascribed to the increase in composites ductility and the malleable character of the fiber/matrix interface. Many researchers have obtained a similar result.
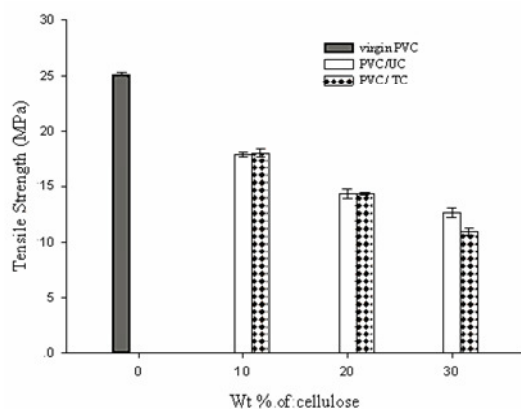
Kaci et al.[38] recorded a reduction of about 27% of Young's modulus of the LDPE/olive husk flour composites, after chemical treatment by maleic anhydride. Tronc et al.[39] recorded a reduction of about 21% of Young's modulus of the HDPE/sisal fiber composites after the esterification of fibers by a mixture of octanoic acid and acetic anhydride. Also, Luz et al.[11] showed that the acetylation of cellulose causes a reduction of about 30% of Young's modulus of PP/modified cellulose composites, compared to the untreated ones.
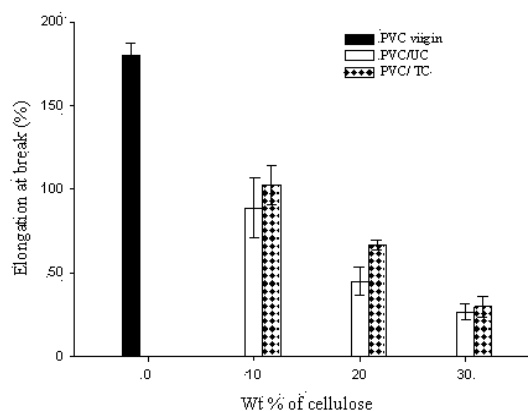

Figure 4: Tensile strength behavior of PVC matrix and its composites

Figure 5: Elongation at break behavior of PVC and PVC/cellulose composites

Thermal properties
Thermogravimetric analysis (TGA)

The thermal behavior of PVC and its composites is shown in Fig. 7 and Table 3. The recorded thermograms allow the determination of the onset decomposition temperature of the polymer matrix, which is equal to 237 °C. As shown in the TGA/DTG thermograms, the decomposition of PVC occurs in two stages: the first stage begins at 237 °C and finishes at 321.8 °C with a temperature of about 262 °C at the fastest degradation. During this stage, a loss of weight of 62.24% is recorded, which is attributed to the elimination of HCl molecules and formation of double bonds along the macromolecular chains of PVC. This leads to a new polymer (the polyene), which is thermally stable in the temperature range 321.8-387.5 °C. During the second stage of degradation situated between 387.5 and 475.6 °C, the polyene is degraded to form a residue made up of carbon

black, which is stable beyond 475.6 °C and which represents 18.23%.[36]

According to the thermograms (TGA/DTG) of the treated and untreated cellulose/PVC composites, it can be observed that the onset decomposition temperature of the formulation F20U is almost identical to that of virgin PVC (an improvement of 1.1 °C is recorded), however for the formulation F20T, one notes a reduction of 3.6 °C compared to F20U. This can be explained by chain scission and cellulose depolymerization during the chemical treatment.[40]

Beyond the onset temperature, the treated and untreated cellulose improved the thermal stability of PVC. By analyzing the peaks represented on the thermograms, we can observe their displacement towards the highest temperatures. Indeed, the maximum degradation rate recorded for the formulation F20U is about 11.37%/min corresponding to a temperature of 279.6 °C.

These results confirm that the untreated composites are more stable compared to the treated ones, which have a maximum degradation rate of about 13.56%/min corresponding to a temperature of 271.9 °C. These results are in agreement with those of Jue Lu *et al.*,[41] who recorded a reduction in the thermal stability of the epoxy/cellulose composites after chemical treatment of cellulose by titanates.
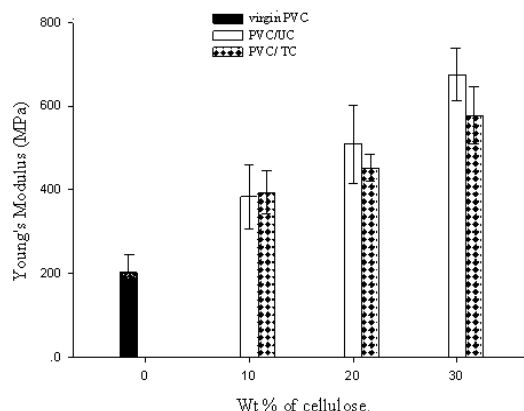

Figure 6: Young's modulus behavior of the different formulations
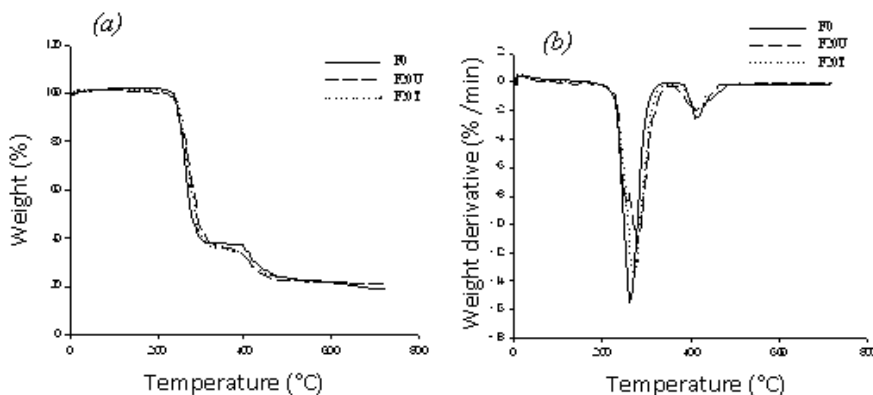

Figure7: Thermal degradation behavior of PVC and PVC/untreated and treated cellulose composites with a loading of 20 wt% (F20U and F20T respectively); (a) TGA curves, (b) DTG curves

Table 3
Thermal behavior of PVC and PVC/cellulose composites

Samples	Onset temperature (°C)	Temperatures at the fastest degradation (°C)	Maximum rate of degradation (wt %/min)	Residue ratio (wt %)
F0	237	262	15	18
F20U	238	279	11	21
F20T	234	272	14	21

The same tendency was noted by Araùjo *et al.*,[42] who reported that the thermal stability of the HDPE/curaua fiber composites compatibilized with polyethylene grafted with maleic anhydride (PE-*g*-MA) was reduced compared with the uncompatibilized composites. The loss in the thermal stability of the composites is attributed to the increase in compatibility between cellulose and PVC matrix, which improves the interfacial interactions and induces contamination phenomena. This is supported by the process of degradation of the composites, which means that

in the same composite the degradation of a component accelerates the degradation of the other one.[43]

Differential scanning calorimetry (DSC)

Figure 8 shows the DSC scans for the PVC and PVC/cellulose composites. According to the DSC results, the (Tg) values and the melting point (Tm) of the various samples are shown in Table 4. It can be observed from Table 4 that the effect of treated and untreated cellulose on the glass transition temperature of PVC was not considerable in DSC analysis. (Tg) did not show apparent changes, there is a slight decrease (1 °C) after the incorporation of both treated and untreated cellulose. These observations can be explained by the presence of two separate phases, which is a consequence of the bad interphase interactions between the untreated cellulose and the PVC matrix[26] and the plasticizing of the interface fiber/matrix caused by the acetylation.[44]

Table 4
DSC results for PVC and PVC/cellulose composites

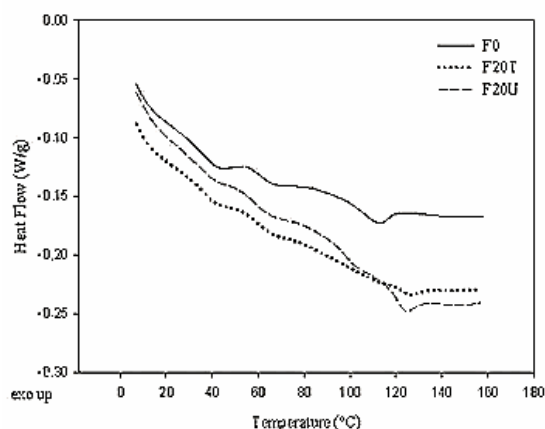| Samples	T g (°C)	T m (°C)
F0	60	113
F20U	59	124
F20T	59	126

Figure 8: DSC scans of PVC matrix, PVC/untreated cellulose composites loading at 20 wt% (F20U) and PVC/treated cellulose composites loading at 20 wt% (F20T)

Table 5
Dynamic mechanical behaviors of the different formulations

Samples	T g (°C)	E' at -30 °C (glassy region) (MPa)	E' at T g (MPa)	E' at 80 °C (rubbery region) (MPa)
F0	65	1030	35	9
F20U	65	1370	65	26
F20T	64	1100	69	21

Similar results have been reported by several researchers. Haihong Jiang et al.[45] did not observe a visible effect of wood flour contents and wood flour treatments on the glass transition temperatures of PVC. Gajender et al.[26] studied the PVC/acacia bark flour composite and concluded that the (Tg) of PVC did not show changes with the introduction of the filler. The melting temperature of PVC matrix is about 114 °C, this endothermic pick is attributed to the crystalline melting region of PVC. Melting temperature (Tm) shifts to higher temperature by adding microcrystalline cellulose, the highest value is obtained by adding treated fibers. This increment in Tm indicates that the crystallinity of the virgin matrix increased upon incorporation of filler, and may be also attributed to the strong interfacial interactions between the PVC matrix and the

treated cellulose. The obtained data are in agreement with the results of Gajender *et al.*[26] and Tao Yu *et al.*[46]

Dynamic mechanical analysis (DMA)

Figures 9 and 10 illustrate the viscoelastic properties of PVC and PVC/cellulose composites. Some data obtained from the storage modulus and tan (δ) curves are presented in Table 5.

Figure 9 shows the effect of treated and untreated cellulose on the storage modulus of PVC. At low temperatures, PVC presents high elastic modulus (E' (-30 °C) = 1.03 GPa). The

increase in the temperature causes a reduction in the modulus. The reduction is drastic at the glass transition temperature, which is estimated at 64.8 °C, this temperature corresponds to the temperature at which the tangent δ is maximum. The storage modulus gives information about the rigidity of the materials. From the obtained results, one notes that the modulus of PVC matrix is high in the elastic region and weak in the plastic one (beyond *T*g). This is ascribed to the carbonaceous chain movements, which are more favored at high temperatures.
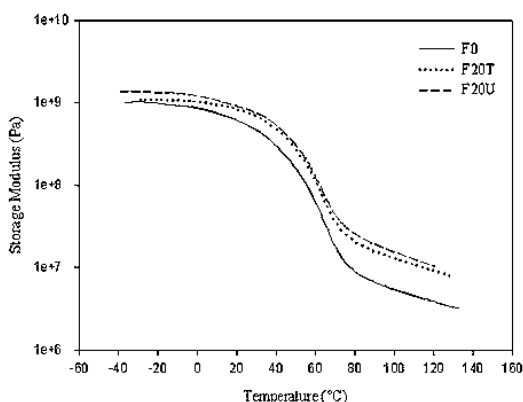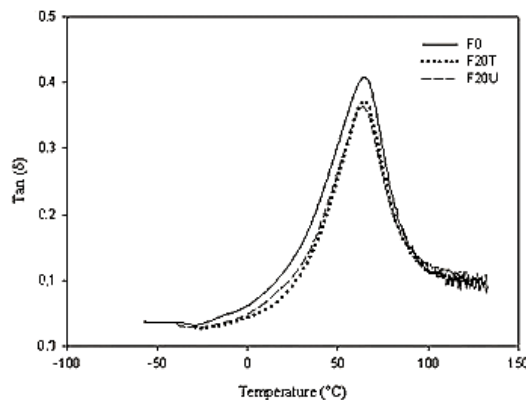

Figure 9: Storage modulus (E') versus temperature of PVC and PVC/untreated and treated cellulose composites with a loading of 20 wt% (F20U and F20T, respectively)

Figure 10: Tan δ against temperatures of virgin PVC (F0), untreated composites with a loading of 20 wt% (F20U) and treated composites with a loading of 20 wt% (F20T)

The incorporation of cellulose in PVC allows obtaining composites with higher modulus. The influence of cellulose appears in both elastic and plastic zones. This result can be attributed to the increment of the composites stiffness due to the high rigidity of cellulose.[3] The increase is more pronounced for the untreated cellulose and this is due to the plasticization by acetylation. According to Figure 10 and Table 5, one can note that the glass transition temperature of the PVC matrix does not change with the incorporation of treated and untreated fibers. These results are in correlation with obvious DSC data. Previous reports revealed that the incorporation of stiff natural fibers into the polymeric matrix significantly increased the storage modulus of the resulting composite, compared with the unreinforced polymer.[3,47]

CONCLUSION

In the present paper, the chemical treatment of cellulose was successfully realized by acetic

anhydride (AA) and was confirmed by FTIR analysis. The acetylation conferred organophilic character to the fiber, which was evidenced by contact angle measurements.

The chemical treatment improved the interfacial adhesion and the dispersion of cellulose in the PVC matrix, which resulted in the improvement of surface morphology analyzed by SEM method. According to the mechanical and dynamic mechanical results, we can conclude that both raw and chemically treated cellulose cause a decline in the tensile strength of virgin PVC. The acetylated fibers have not improved this property, because chemical modification was accompanied by cellulose degradation. On the other hand, the incorporation of stiff natural fibers into the PVC matrix significantly increased Young's and storage moduli of the resulting composites, compared with unreinforced polymer.

The DSC data show that the (*T*g) did not change much as confirmed by DMA analysis but the melting temperature (*T*m) of PVC matrix

shifted to higher temperature after the addition of microcrystalline cellulose. The thermal stability of the composites was improved by the incorporation of both untreated and treated cellulose, compared with the virgin PVC.

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