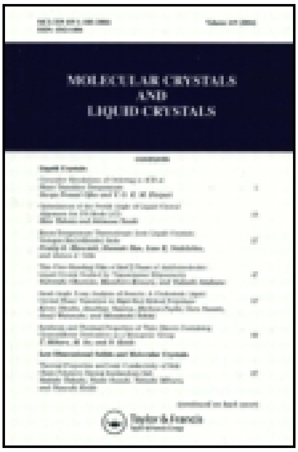

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The adhesion between vegetable fibres and the polymeric matrix remains one of the technological bolts of the development of composites. Indeed cellulose, the principal constituent of vegetable fibres, is not generally compatible with thermoplastic matrices. Many studies thus focus on the improvement of these properties, in particular by the means of physical or chemical treatments of fibres. The objective of this work was the chemical modification of cellulose by epoxidized soybean oil to improve compatibility between the cellulose and the matrix. The effect on the physico-mechanical properties of the PVC/cellulose composites containing 10 to 30% treated cellulose was studied. The resultant composites were characterized various tests (mechanical, thermal and morphological).

Keywords Cellulose; composites; epoxidized soybean oil; interfacial adhesion; poly (vinyl chloride)

Introduction

The combination of woody materials with thermoplastic polymers to yield wood polymer composites (WPC) is gaining more and more attraction in USA and Europe. A wide range of commercial products are already available on the market because they are renewable, biodegradable and environmentally friendly [1].

Biopolymers or synthetic polymers reinforced with natural fibre can be viable alternatives to glass fibre reinforced composites. Though natural fibres have appealing properties they also suffer from some serious setbacks due to their hydrophilic character. This limitation is remedied by several methods like alkaline treatment, grafting functional moieties onto the fibres, introduction of coupling agents or pre-treatment of fibres with suitable agents. An enormous amount of research has been invested in studying the modification of natural fibres and their subsequent characterization in composites [2,3].

In the present work, we have endeavoured to present cellulose reinforced PVC composites and investigated the effect of filler content and fibre treatment on the morphological,

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mechanical and thermal properties of the composites. The cellulose is a hydrophilic glucan polymer consisting of a linear polymer chain of 1,4-β-bonded anhydroglucose units that contains alcoholic hydroxyl groups. These hydroxyl groups form intra-molecular hydrogen bond within the macromolecule itself and with other macromolecules. In order to inactivate these hydrophilic groups, we have used a chemical treatment method for cellulose employing epoxidized soybean oil (ESO). ESO is a nontoxic and degradable plasticizer and can be blended with plastics such as PVC to improve their properties such as melt rheology and tensile strength, etc. [4]

The objective of the present work was to fabricate composites from raw and chemically treated cellulose with PVC and subsequently investigate the effect of chemical treatment on the properties of the composites. To understand why the mechanical properties of the composites prepared from treated and untreated cellulose are different and to gain insights into the effect of fibre treatment on the filler-matrix interfacial adhesion, the morphological features of the fractured surfaces of both raw and treated cellulose-PVC composites were recorded using scanning electron microscopy (SEM). The effect of the filler content on the mechanical and thermal properties of the composites has also been reported.

Experimental

Materials

The polymer used us matrix was the poly(vinyl chloride) type SE-1200 produced by Câblerie Électrique (CABEL) at Algiers in Algeria. It has the following physical characteristics: K-value, 71; powder density, 0.52 g mL^{-1}. The additive used in the preparation of the various formulations was dioctylphtalate (DOP) as plasticizer, a thermal stabilizer system based on Ca-Zn and acid stearic as a lubricant.

Microcrystalline cellulose type Avicel (Art 2330 Merck Darmstadt) from Oran, Algeria, was used as filler; its diameter is lower than 100μm. Epoxidized soybean oil (ESO) type HSE-100 S produced by Betaquimica, SA. It had the following physical characteristics: Density, 6.5 g mL^{-1}; oxirane functionality, 1.0%.

Fibber Surface Treatment

The chemical treatment was carried out according to the experimental protocol reported previously [5]: Microcrystalline cellulose and epoxidized soybean oil were mixed in the ratio of 1:0.33 (by weight). The reaction carried out at 55°C for 30 min in acetone as solvent. Then the mixture is filtered and dried in the oven at 50°C for 24 h.

Preparation of the Composites

Blends based on PVC powder and the various additives (see Table 1) were placed in a mixer and processed at a speed of 2000 rpm at temperature below 80°C to obtain a

Table 1. Formulation of PVC compound

Component	PVC	DOP	Ca/Zn stabilizer	Stearic acid
Content (phr)	100	30	4	0.5

Table 2. Formulation codes of PVC /cellulose composites used

Components Formulations	PVC (wt %)	Untreated cellulose (wt %)	Treated cellulose (wt %)
F0	100	0	0
F10N	90	10	0
F20N	80	20	0
F30N	70	30	0
F10H	90	0	10
F20H	80	0	20
F30H	70	0	30

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 platens. The film was subjected to a compression melding 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 2.

Characterization Techniques

Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectra (FTIR) of untreated and treated cellulose were obtained with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1} in a SHIMADZU FTIR-8400S spectrometer. The samples were analysed using the KBr pellet method.

Scanning Electron Microscopy (SEM). The interfacial interaction cellulose/PVC was analysed by scanning electron microscopy (SEM) in a Scanning Electron Microscope (FEI CONTA 200). The samples to be analysed were prepared by fracturing after frozen them in liquid nitrogen.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed using a thermogravimetric apparatus of type SETARAM TGA 92 from 20 to 700°C at a heating rate of 10°C/min under a nitrogen flow. Approximately 10 mg of PVC/cellulose composites was used.

Tensile Testing. The tensile properties of the composites were measured in a tensile testing machine type Zwick/Roell controlled by a microcomputer according to the standard ISO 527, June 1993 at a crosshead speed of 100 mm/min. Three tensile properties were tested: the tensile strength; the tensile modulus; and the elongation at break.

Results and Discussion

Characterization of Cellulose

FTIR Analysis of the Cellulose Before and After Treatment with Epoxidized Soybean Oil. FTIR analysis can indicate the principal differences between treated and untreated cellulose.

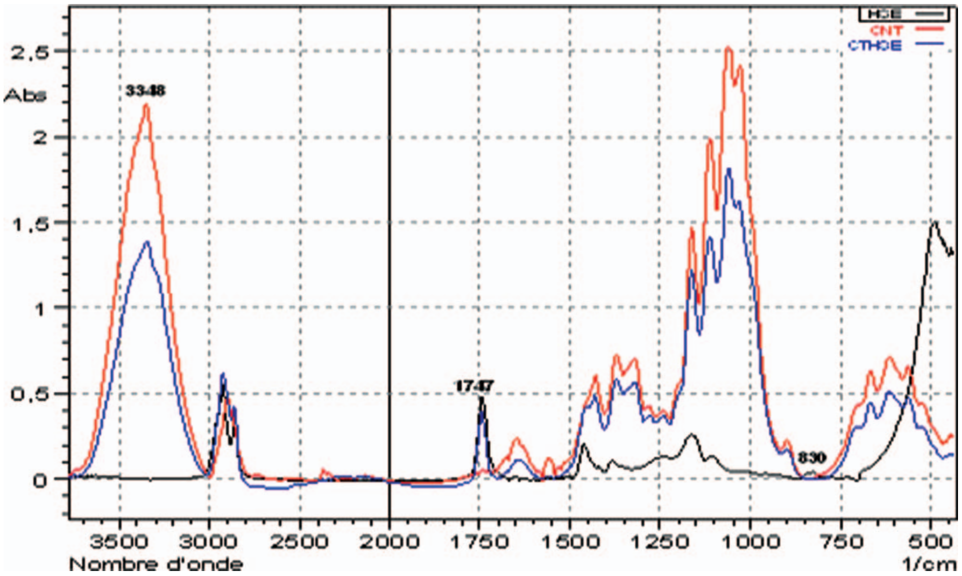
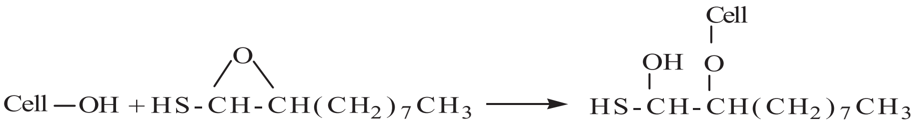


Figure 1. FTIR spectra of cellulose treated and untreated.

Changes and the appearance of new bands can provide information about the effectiveness of the chemical modification. The spectrum presented on the Fig. 1 shows the differences between the absorption bands before and after treatment of cellulose with ESO. It is clear from the spectra of the treated cellulose that there is a reduction of the intensity of the band at 3348 cm^{-1} corresponding to (—OH) functional groups of the cellulose. This reduction is due to the etherification of the hydroxyls groups of cellulose and the oxirane function of the ESO which is confirmed by the disappearance of the epoxy function in the region of 830 cm^{-1} this result is confirmed by Bueno-Ferrer et al. [6]. We also observe the appearance of absorption band at 1747 cm^{-1}, this band corresponds to the vibration of elongation of connection C=O of the ester function existing in the ESO. After FTIR analysis of the treated cellulose, we propose the following reaction mechanism (Scheme 1):



Scheme 1. Reaction between the cellulose and the epoxidized soybean oil.

Characterization of the Composites

Scanning Electron Microscopy (SEM). The results of scanning electronic microscopy (SEM) of fractured surfaces of the PVC/cellulose composites loading at 10% (w/w) are presented on the Fig. 2. The photograph of the SEM of the untreated composites shows the existence of cavities, which can be attributed to weak interactions between cellulose and the matrix. On the other hand the treated composites show a better dispersion of cellulose in the matrix owing to improved interfacial adhesion between cellulose and the matrix.

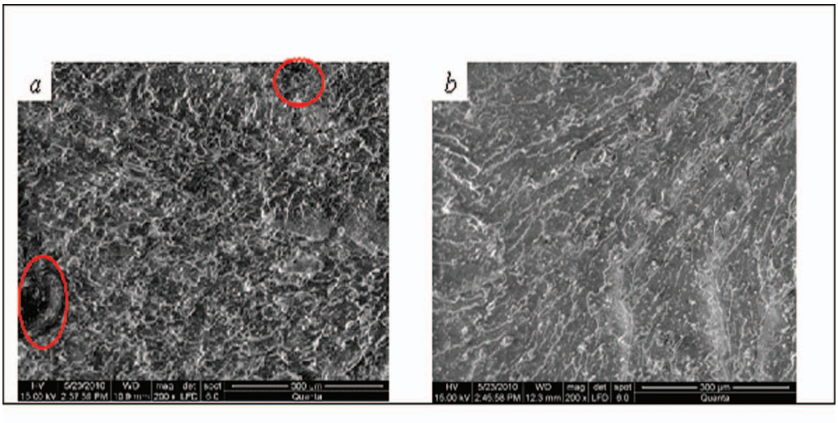


Figure 2. Scanning electron micrographs of fractured surface of PVC/cellulose composite loading at the 10 wt.%: (a) composite untreated (b) composite treated with epoxidized soybean oil.

Hardness. The hardness of a sample is related to its rigidity. It is indicated by the penetration resistance to the needle of a durometer. For composite materials, hardness depends on the distribution of the reinforcement in the matrix. Figure 3 shows the effect of the cellulose loading and the chemical treatment on the hardness of the composites. According to the results we can note that the incorporation of the ESO, at various ratios in PVC, enabled us to obtain more flexible composites. This is due to the reduction in rigidity; we register a decrease of 17% for the formulation F30H compared to the formulation F30N. This

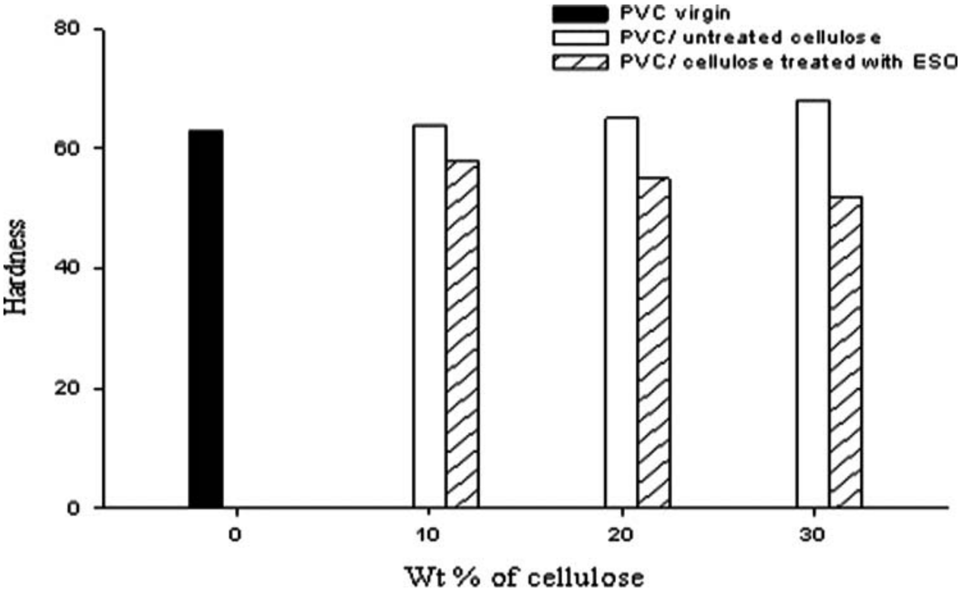


Figure 3. Evolution of hardness Shore D of PVC/cellulose composites according to the loading treated and untreated cellulose.

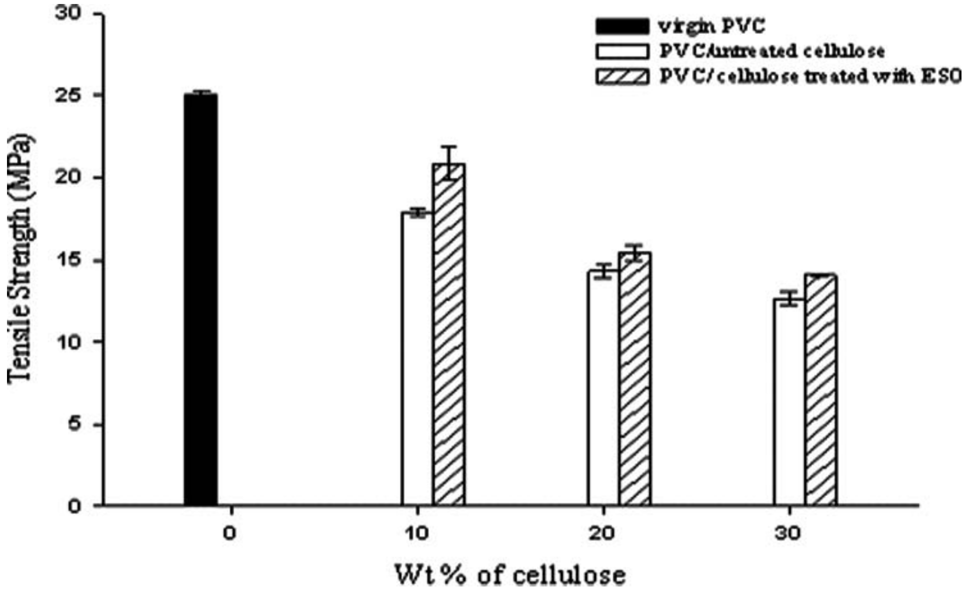


Figure 4. Tensile strength behaviour.

reduction can be conferred to the Epoxidized soybean oil which is one of plasticizers of PVC. Djidjelli et al. [7] found results similar for sisal fibres treated by maleic anhydride.

Tensile Strength. Figure 4 shows the results of tensile strength for poly (vinyl chloride) and composites reinforced with untreated and treated cellulose as a function of fibre content. It is evident from the Figure that the tensile strengths of both raw and chemically treated cellulose-PVC composites decrease gradually with the increase in filler loading. We record a reduction from 25 MPa for the neat PVC to 12.6 MPa for the formulation F30N. Increases in filler content increased the interfacial area and weakened the filler–matrix interaction, resulting in a decreasing trend of the tensile strength. This result is confirmed by several studies such as that of Islam et al. [8]. In order to achieve better mechanical properties of the composites, cellulose was chemically treated with ESO. The treatment provided for an increase in the tensile strength compared to the untreated composites. For example, for the formulation F10H we record an increase of 14.3% compared to F10N. This is due to the improvement of the interactions between cellulose and the matrix and consequently a better transfer of constraint between the two phases. Similar results were found by Sreekumar et al. [9]. They recorded an increase in tensile strength of about 36% for polyester charged with 40% of mercerized sisal fibre compared to the untreated composites.

Elongation at Break. The effect of the load factor and the chemical treatment on elongation at break of the composites is illustrated on Fig. 5. This Figure indicates that the content of the reinforcement is the principal factor affecting elongation at break. Elongation at the break of the composites decreases as the content of cellulose increases. It passes from 180% for virgin PVC to 26.5% for the formulation F30N. This is due to the poor dispersion of cellulose in the matrix what entrains a reduction of interfacial adhesion. This result is similar to that of Zheng et al. [10] who recorded a reduction in elongation at break from 150% for virgin PVC to 3.5% for PVC charged with 25% of bagasse fibre. In the same

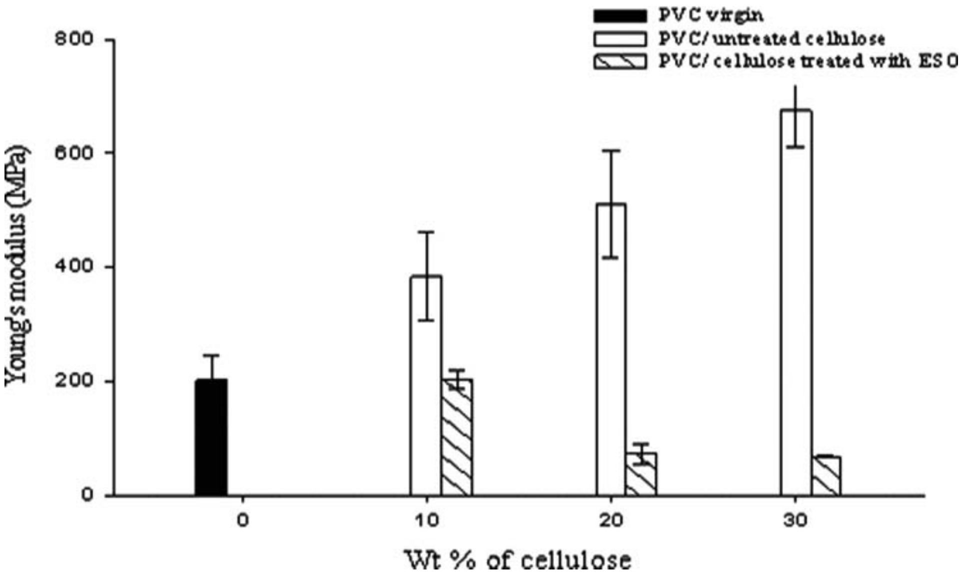


Figure 5. Elongation at break behaviour

context Spasquini et al. [11] observed a reduction in the lengthening from 125% for the virgin PEBD to 20% for the PEBD charged with 30% cellulose.

Treatment of cellulose with epoxidized soybean oil improved the elongation at break. As an example, for formulation F30, we record an increase from 26.5% to 171%. PVC/cellulose composites treated with ESO have almost same elongation at break as virgin PVC for all the formulations. This result can be explained by the reduction in the rigidity of the composites because the ESO is also a plasticizer of PVC.

Young's Modulus. Figure 6 presents the evolution of the Young's modulus according to the modified and not modified cellulose content. The results show clearly that the incorporation of cellulose in PVC yields composites with a higher Young modulus. The modulus increases with cellulose loading. We recorded a rise in the modulus from 202 MPa for the formulation F0 to 675 MPa for formulation F30N and this can be granted to the increase in the rigidity of the composites. These results are in perfect correlation with those of Islam et al. [8] who recorded an increase in the Young modulus from 0.8 GPa for the virgin PP to 2.8 GPa for the PP charged with 20% of untreated coconut fibre. Spoljaric et al. [12] recorded an increase in the Young's modulus from 1.01 to 1.31 GPa after introduction of 10% of microcrystalline cellulose into the PP matrix. The incorporation of treated cellulose in PVC caused a reduction in the Young's modulus compared to the untreated composites. The PVC/treated cellulose composites present modules lower than that of virgin PVC. As an example, for the formulation F30H, we recorded a reduction in the Young's modulus of 66% compared to F0 and a reduction of 90% compared to F30N. This reduction is due to the flexibility brought about by the ESO as a plasticizer for PVC.

Thermogravimetric Analysis. Figure 7 illustrates the thermal behaviour of poly (vinyl chloride). The thermogram TGA permit the determination of the temperature at the beginning of the decomposition of the sample, this temperature is equal to 237°C. As shown in the thermograms ATG/DTG, the decomposition of PVC occurs in two stages. The first stage

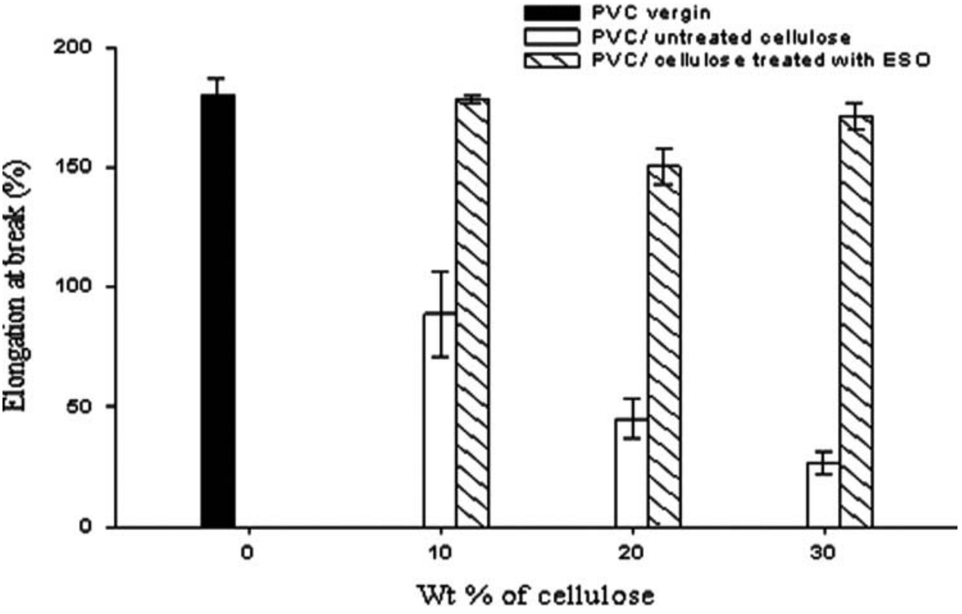


Figure 6. Young's modulus behaviour.

starts at 237°C and ends at 322°C with a maximum temperature of degradation which is about 262°C. During this stage we record a weight loss of 62.2%, which is attributed to the elimination of HCl and the formation of the double bonds along the macromolecular chains of PVC. This yields a new thermally stable polymer (with polyene sequences) that forms in the temperature range from 321.8°C up to 387.5°C. The second stage of degradation ranges

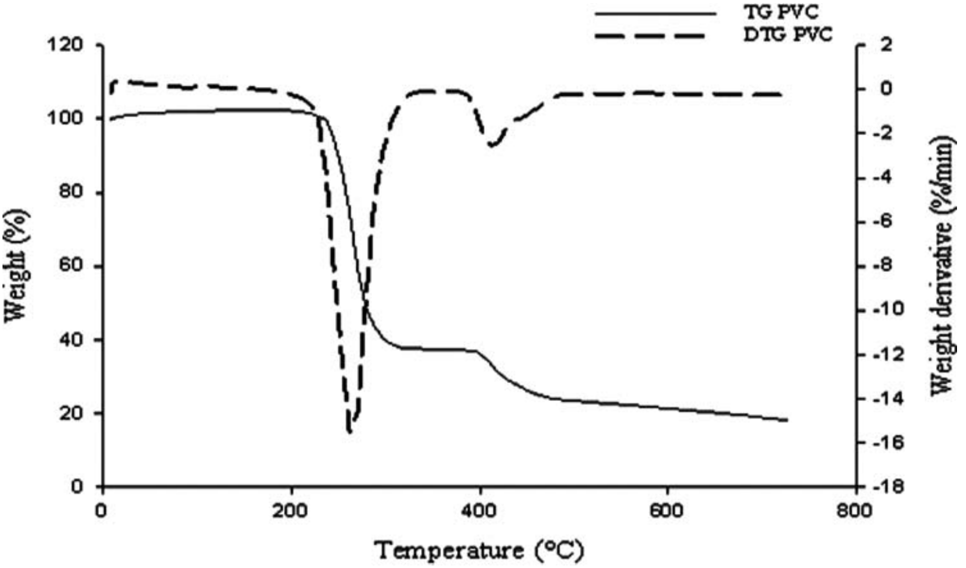


Figure 7. TGA-DTA Thermograms of virgin PVC.

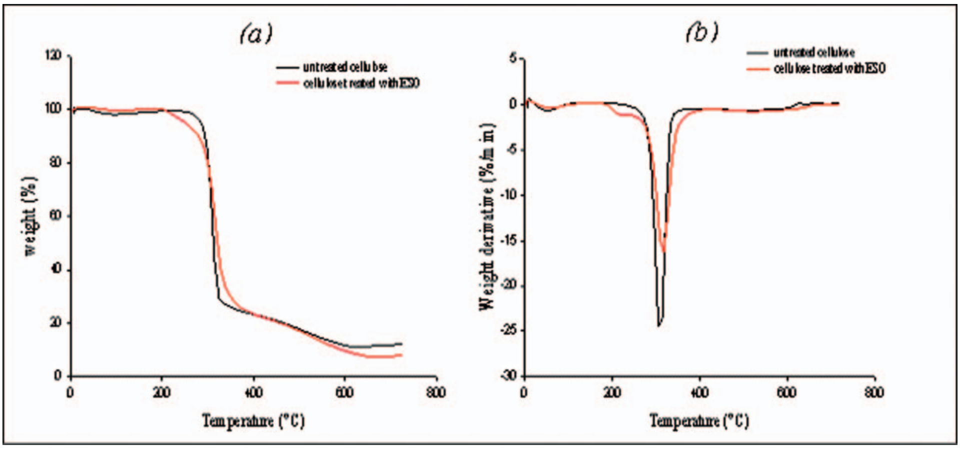


Figure 8. Thermal degradation behaviours of the composites. (a) TGA curves of the formulation F20, (b) DTG curves of the formulation F20.

from 387.5°C and 475.6°C, during which the polyene degrades to form a residue made up of a carbonaceous residue which is stable beyond 475.6°C and which presents 18.23% by weight [13,14].

The effect of the chemical treatment on the thermal behavior of the composites is represented on Fig. 8. According to the thermograms TGA, we notice that the temperatures at the beginning of the decomposition of the composites are almost identical to that of virgin PVC for the formulation F20N. The thermal stability of treated composites is improved compared to the untreated composites, and that is due to the presence of the hydrocarbons chains of ESO which require more energy to break them [15]. The increase in thermal stability can be also attributed to the increase in the compatibility between cellulose and the matrix which gives rise to improved interfacial interactions. These results are well in agreement with those of Nachtigall et al. [16] and those of Joseph et al. [17] who recorded an improvement of the thermal stability of the composites PP/fibre of sisal by using PP-*g*-MA like campatibilisant agent.

By analysing the peaks represented on the thermograms, we observe their displacement towards higher temperatures. Indeed, the maximum rate of degradation recorded for formulation F20H is about 10.9%/min correspondent at a temperature of 284°C. These results confirm the thermal stability of the treated composites compared to the untreated ones which have a maximum rate of degradation of about 11.4%/min corresponding to a temperature of 278°C.

Conclusion

Cellulose filler was modified by treatment with epoxidized soybean oil. FTIR analysis confirmed that a chemical reaction took place during the modification. Apart from the appearance of an absorption band at 1747 cm^{-1}, which correspond to the ester group of ESO, there was also a reduction in the intensity of the peak at 3348 cm^{-1} and the disappearance of the epoxy function in the region of 830 cm^{-1}. This indicates that a reaction between the oxirane function of the ESO and the hydroxyl groups of cellulose took place. The results of scanning electronic microscopy (SEM) show that the chemical treatment improved dispersion of cellulose in the PVC matrix. It also improved the interfacial adhesion. It was conclude that the incorporation of untreated cellulose in matrix PVC caused an increase in Shore D hardness, whereas the cellulose treated by the ESO caused a reduction in this property. The mechanical behaviour of composites PVC/cellulose changed as follows. Tensile strength decreased with the incorporation of untreated cellulose while the ESO treatment by improved this property. Incorporation of untreated cellulose in matrix PVC caused a significant reduction in elongation at break. In contrast, the ESO treatment led to a significant improvement in this property. The Young's modulus of the treated composites decreased with the increase of the cellulose content. The incorporation of the treated and untreated cellulose improved the apparent thermal stability of the composites compared to the virgin PVC, and the treated composites were more stable than untreated ones.

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