Research Article

Effects of Filler Contents and Surface Treatments on Morphology, Dielectric and Mechanical Properties of Polyvinylchloride Reinforced with Date Stones

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ABSTRACT

The aim of this paper is to study the influence of fiber content and surface treatments on morphology, dielectric and mechanical properties of date stones (DS) fiber reinforced polyvinylchloride (PVC) composites. Different fiber loadings were added to PVC matrix (ranging from 5-20 wt %). The obtained results reveal that both methods, i.e. chemical treatment of DSs with acetic anhydride and heat treatment, improved the interactions between the two composite components (DSs and PVC) and promoted better dispersion of the filler within the matrix. The ductility which was measured as percentage of elongation at break, decreases as filler loading increases, the same behavior of strength at break was observed. Whereas, the addition of both heat and chemical treated fibers to the polyvinylchloride improve slightly these properties. With increasing the filler content, dielectric constant, dissipation factor and conductivity increased, which was mainly due to the motion of dipolar groups of the interfacial polarization occurring within the composites. However, surface modification of fibers resulted in a decrease of the dielectric properties.

Keywords: PVC; Surface treatments; Morphology; Dielectric properties; Mechanical properties

INTRODUCTION

In recent years, natural fibres reinforced polymers have received much attention, because of numerous advantages encompassing low cost, low density, high specific strength, nonabrasive, non-toxic, biodegradable and their positive contribution to environment protection [1,2].

However, the use of these additives reveals such drawbacks including poor resistance to moisture, degradation at relatively low temperature and the incompatibility with the polymer matrix [3-5].

The incompatibility of components is responsible for the poor interfacial fibre-matrix adhesion and low dispersion of the fibres, which causes a decrease of the pivotal role in transferring the stress from the matrix to the fibres [6]. In order to develop composites with enhanced properties, it is necessary to overcome and resolve the above mentioned problems by applying suitable surface treatments in particular to enhance the compatibility between hydrophilic fibres and the hydrophobic matrix. There are several methods used to modify the natural fibre surface such as: alkali treatment [7,8], organosilane [9-11], plasma treatment and graft copolymerization [1,12] as well as other new

developed methods [13,14]. Flax, jute, bamboo, palm, hemp, bagasse, sisal and wood-fibre are examples of fillers commonly used as reinforcement to the thermoplastic composites [15,16].

The dielectric properties of polymer composite materials have been studied with a view to modify/optimise the properties of polymeric systems for practical applications. The inorganic insulators and dielectrics have been largely replaced by polymers because of their unique ability for specific needs such as dielectric substrates, potting compounds, embedding materials and conformal coating. Hence, the study of the dielectric properties of polymer composites reinforced with lignocellulosic fibres is very important. Although various studies have already been devoted on fibre reinforced polymer composites, only few research works are reported in the literature on dielectric properties of lignocellulosic fibres reinforced PVC composites. The dielectric properties of sisal and oil palm hybrid bio-fibre reinforced natural rubber biocomposites were investigated by Jacob et al. [17]. Hong and Wool [18] developed a new low dielectric constant material suited to electronic materials applications using hollow keratin fibres and chemically modified soybean oil. Paul et al. [19] investigated the electrical properties of low-density polyethylene composites reinforced with short sisal fibres, and a comparative study on the dielectric properties of flax, hemp and oil palm fibres was reported by Shinoj et al. [20] as well as the modelling study of the dielectric constant that was reported by Hung and Frank [21].

Date pits have received less consideration as a source material for the preparation of polymer composites. Algeria is one of the leading countries engaged in planting several million of palm-date trees. Huge quantities of date stones are generated as wastes. The generated stones can be used to reinforce many polymers. The research work dealing with Polymer /date stones composites is rather scarce. Although, some papers have been reported in literature including those of F. D. Alsewailem et al. [22] and A.Ghazanfari et al. [23] investigated the mechanical behavior of HDPE/ date stones composites. While, Hamma et al. devoted to a study of the morphology, thermal and mechanical behavior of composites based on polypropylene and date stones in the absence and presence of (EBAGMA) used as the compatibilizer [24], On the other hand nothing study was reported on the usage of PVC as matrix for date stones. PVC/wood fiber composites are more often applied to windows, doors, decking and roofing shakes. Furthermore, it can be used as connectors, industrial and house hold plugs, switches, panels, insulators. Therefore, it is important to study the mechanical and dielectric behavior of the composites.

The aim of this work was to evaluate the morphology, dielectric and mechanical properties of polyvinylchloride (PVC) filled with DSs at various filler content ratios (10, 20, and 30 wt %) in the absence and presence of treatment. Two methods of treatment of the date stones (DSs) were used: a first method based on chemical treatment of DSs through acetylation reaction; whereas the second one is a heat treatment.

EXPERIMENTAL SECTION

Materials
The polymer used for the preparation of all the formulation is the polyvinylchloride (PVC-type SE-1200). This material was provided by the Algerian company "CABEL" with the following physical characteristics: Kwert, 70.2-72.0; powder density, 0.561 g ml^{-1}; viscosity, 0.99 Cst; thermal stability, 60 min at 180 °C. The additives used were dioctylphthalate (DOP) as a plasticizer, having the following properties: a viscosity ranging from 75 to 85 Cst, a molecular weight of 390 g mol^{-1}, a thermal stabilizer system based on Ca-Zn and stearic acid as lubricant. For the chemical modification of date stones, acetic anhydride was used.

Date stones (DSs) were obtained from Algerian date and were used as filler. It was found that carbohydrates are the largest component of date stones and are composed of cellulose = 16.62 wt %, hemicellulose = 19.35 wt %, lignin = 41.13 wt % and mineral ash =1.5 wt %. The moisture content is 6.46 wt % [24].

Fibres modification
The date stones were initially washed with distilled water, dried in an air oven at 105°C for 24 hours, then crushed and sieved. The particle size of the filler was less than 100 μm.

Chemical treatment
The chemical treatment of DSs fibres was done following a procedure described by Khalil et al. [25]. In this procedure, dry fibres were covered by acetic anhydride with a mass ratio 1:10 in a rounded-shape flask under reflux. After 3 hours of refluxing at 100°C, the anhydride acetic was decanted off and the residue was introduced into acetone at ambient temperature for one hour in order to stop the reaction. After that, the acetone was poured out. The fibres were washed again with fresh boiling acetone with reflux for 3 hours in order to remove the unreacted reagents. The modified fibres were dried for overnight in an oven at 103°C, and then cooled down to room temperature in desiccators.

Heat treatment
Date stones fibres were subjected to heat treatment in a furnace (VMK-1600) at 600°C for 5 hours. After sieving, the majority of particles were found to have an average size in the nanoscale regime.

Preparation of PVC/DSs Composites
Both PVC and PVC/DSs composite with the same concentration of stabilizer and processing additives were mixed in a high mixer at a speed of 2000 rpm at 50°C, then the obtained compounds were introduced in a two-cylinder rotary mixer heated at 140 °C during 3min. The prepared samples were moulded into sheets by hot pressing at a temperature of 170 °C and at a pressure of 250 kN for 3 min. The obtained plates with dimensions of 300×300×2 mm^3 were cooled at room temperature and then cut into normalized specimen for testing. The samples were labelled to describe the amount of DSs and the method of treatment as mentioned in Table 1.

Table 1. The specification of PVC and DSs fillers

Sample label °	PVC (wt %)	Untreated date stones (wt %)	Chemical treated date stones (wt %)	Heat treated date stones (wt.%)
F0 (Pure PVC)	100	0	-	-
F 5 U	95	5	-	-
F 10 U	90	10	-	-
F 20 U	80	20	-	-
F 5 C	95	-	5	-
F 10 C	90	-	10	-
F 20 C	80	-	20	-
F 5 H	95	-	-	5
F 10 H	90	-	-	10
F 20 H	80	-	-	20

Characterization Techniques
Infrared spectra of raw and treated DSs fibres were recorded on a Spectrometer of Perkin Elmer (Spectrum One FTIR) with a resolution of 4 cm^{-1} and an accumulation of 500 scans within the range 400 to 4000 cm^{-1}. FTIR spectra were measured in KBr pellets containing 1% finely grounded samples.

A field emission scanning electron microscope (FESEM) JEOL JSM 840, with an accelerating voltage of 35 kV was used to investigate the morphology of the prepared samples.

Water uptake tests were carried out according to ASTM D 570-99 (ASTM 1999). Three specimens of each formulation were selected and dried in an oven for 24 hours at 50°C until a constant weight was reached prior to the immersion in distilled water for 24 hours. The samples were taken out of the water and the surface was wiped off using blotting paper, and then re-weighed. The amount of water absorbed by the composites was calculated according to the following equation:

$$WA(\%) = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

Where W_0 is the initial weight of the sample and W_1 is the weight of the sample after immersion in distilled water.

Capacitance, resistance and dissipation factor for PVC loaded with different concentrations of treated and untreated DSs, were measured by using a dielectric apparatus type *TETTEX AGZURICH* at fixed frequency (50 Hz) and at temperatures ranging from 20 to 80°C.

The dielectric permittivity ε' of a material represents the ratio of the capacitance of a plane condenser filled with the dielectric to that of the same condenser under vacuum and is calculated from the expression:

$$\varepsilon' = \frac{C \cdot d}{\epsilon_0 \cdot A} \qquad (2)$$

Where C is the capacitance of the condenser with the dielectric, A is the area of the sample covered by the electrode, d is the thickness of the samples and $\epsilon_0 = 8.85 \times 10^{-12}$ Fm^{-1} is the dielectric constant of the vacuum.

The dissipation factor or tan δ is defined mathematically as the ratio of the electrical power dissipated in a material to the total power circulating in the circuit. It is calculated from the equation:

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$$tan \, \delta \; = \; \frac{\epsilon''}{\epsilon'} \qquad\qquad\qquad\qquad\qquad (3)$$

Where ϵ'' is the loss factor and ϵ' is the dielectric constant

The insulation resistance of a material depends on its volume resistance, thus the volume resistivity (ρ) can be calculated by using the equation:

$$\rho \; = \; \frac{R \cdot A}{d} \qquad\qquad\qquad\qquad\qquad (4)$$

Where, R is the volume resistance (Ω) and A is the area of cross-section.

The electrical conductivity (σ) is calculated according to the equation:

$$\sigma \; = \; \frac{1}{\rho} \qquad\qquad\qquad\qquad\qquad (5)$$

Where ρ is the volume resistivity of the sample.

Tensile test of the composites was performed on a universal ZWICK/ROELL.Z.2.5 tester according to ISO 527-1 procedure, at a crosshead speed of 50 mm/min at room temperature. Hardness test was conducted according to NF ISO T51-123 standard using a durometer Shore D with specimen dimension of $10\times10\times0.2$ cm^3, where the value of hardness represents the average of five measurements taken on each sample.

RESULTS AND DISCUSSION

FTIR analysis
Figure 1 show FTIR spectra recorded in the range 4000-400 cm^{-1} of DSs before and after treatments. The assignment of the observed absorption bands shows the presence of functional groups such as hydroxyl, ester, alcohol, aromatic and carboxyl, in agreement with reported data [26, 27]. FTIR spectrum of DSs shows a large absorption band at about 3340 cm^{-1} corresponding to hydroxyl groups and two strong bands at about 2922 cm^{-1} and 2853 cm^{-1} ascribed respectively to asymmetric and symmetric C–H bands in alkyl groups. The stretching absorption band in the region around 1744 cm^{-1} is assigned to carbonyl C=O present in esters, acetyl derivatives, aldehydes and carboxyl groups. The spectrum of untreated DSs exhibits also a band at about 1613 cm^{-1}, which may be attributed either to olefinic double bands ν (C=C) or to ν (C=N) vibration in aromatic region [27], whereas the peak located at 1375 cm^{-1} is attributed to bending vibration of CH$_3$ group [28].

Upon the acetylation (chemical modification) of DSs, the absorption bands observed at 2922, 2853 and 1744 cm^{-1} exhibit a remarkable decrease in the intensity. At the same time, a decrease in the absorption band intensity of the hydroxyl groups at about 3350 cm^{-1}. The acetylation results in the increase of the hydrophobicity of the fibres due to the introduction of acetyl groups (through the substitution of the OH groups of the fibres). Thus, it can be postulated that the degree of moisture adsorption is also accordingly reduced. Hence, the changes in the absorption at 3350 cm^{-1} may be as the result of OH substitution and the decreased in the moisture absorption [29].
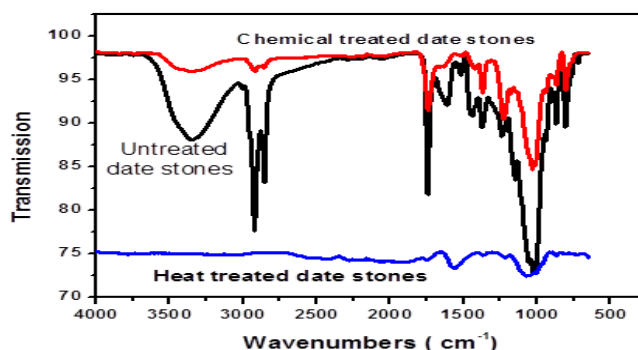

Figure 1: FTIR spectra of treated and untreated DSs

After heat treatment, the IR absorption bands exhibit a lower intensity than that of the raw material. The bands located at 3340, 2922 and 2853 cm^{-1} disappear; which indicates a decrease of hydroxyl groups and aliphatic respectively.

SEM observations

SEM images of fractured surfaces of neat PVC, untreated and modified DSs particles reinforced PVC composites are shown in Figure 2. SEM micrograph of neat PVC (Figure 2a) shows no visible cracks on the surface. In the case of untreated composite sample (Figure 2b), the micrograph reveals that the addition of DSs to PVC matrix results in a big phase segregation morphology. Furthermore, it is observed that the formation of agglomerates indicates clearly the poor dispersion of the untreated DSs within PVC matrix, because of the poor interactions between a polar untreated DSs and the organic matrix [30]. Hence, the raw fibres were not well interlocked with PVC, and the interfacial adhesion between them was therefore negligible. On the contrary, with chemical treatment of DSs with acetic anhydride, SEM micrograph in Figure (2c), exhibits clearly a finer DSs dispersion. This is probably a result of chemical interactions between hydroxyl groups of date stones and acetic anhydride, thus a strong reduction of filler interactions resulting from hydrogen bonding. More uniform dispersion of DSs particles within PVC matrix was further obtained after the heat treatment as illustrated in Figure (2d), resulting from a good compatibility between organophilic treated DSs and organic matrix. Indeed, a decrease in the size of the aggregates is observed which indicates the effectiveness of the applied treatment.
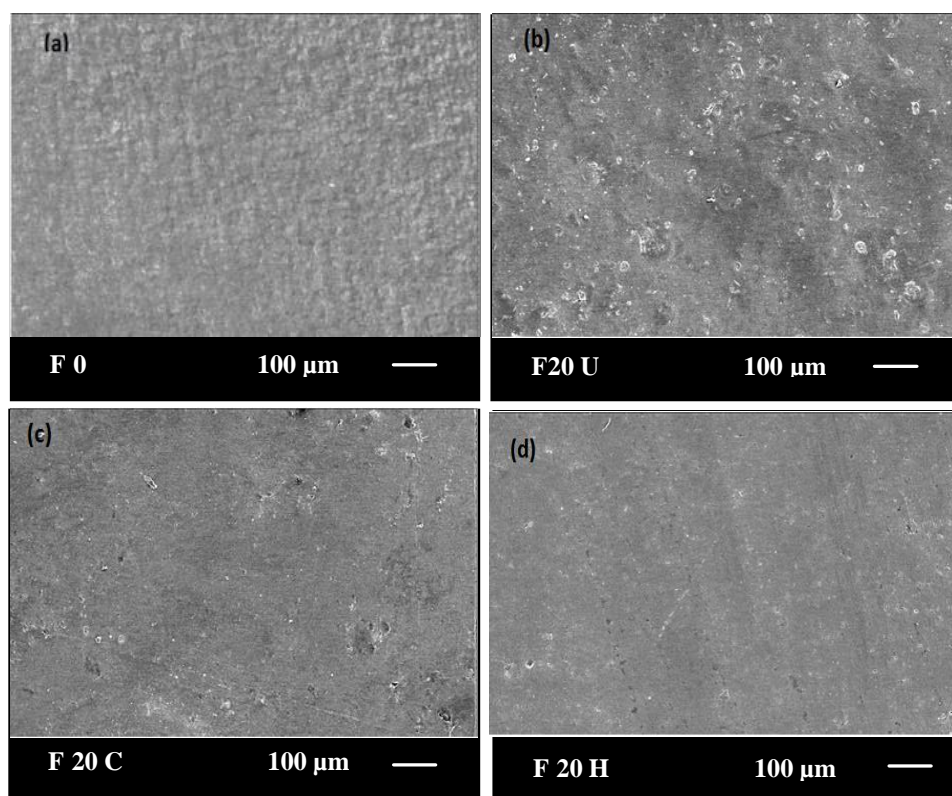

Figure 2: SEM micrographs of PVC composites containing (a) 0.0, (b) 20 wt% untreated (c) 20 wt% chemical treated and (d) 20 wt% heat treated DSs contents

Water absorption behaviour

Figure 3 shows the evolution of water absorption characteristic of the prepared composites at various DSs filler loading. As it can be seen, the water absorption of composites increases with the increase of reinforcing filler. The amount of water absorbed for PVC/untreated DSs is more pronounced than that for PVC/treated DSs, which is due to the high hydrophilic character of the natural filler. The presence of numerous hydroxyl groups, are responsible for the moisture absorption, and the free-OH comes in contact with water to form hydrogen bonding resulting in weight gain in the composites. As DSs loading increases, the cellulose content increases, consequently, resulting in the absorption of more water [31-33]. Additionally, we can observe (in Figure 3) that, for all filler loading, the level of water absorption for treated DSs/PVC composites is less than that for untreated DSs/PVC. This result could be attributed to the lower number of free -OH in cellulose, occurring through acetylation reaction between hydroxyl groups of the filler and anhydride groups of anhydride acetic, which was previously confirmed by FTIR results.
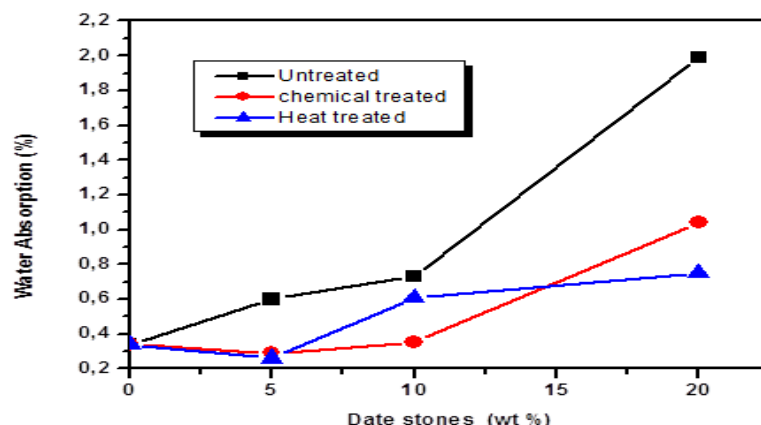
Figure 3: The effect of filler loading on the amount of water absorption of DSs/PVC (untreated and treated) composites

Besides, thermal modification of cellulose results in modifications of lignin and hemicellulose, which means less hydroxyl groups and more C-C double bonds. This leads to an improvement of the adhesion between the fibres and the polymer matrix.

Dielectric properties
The dielectric constant of a material depends on the polarizability of the molecules. The polarizability of non-polar molecules arises from electronic polarization (the application of an applied electric field causes a displacement of the electrons relative to the nucleus) and atomic polarization (the application of an electric field causes a displacement of the atomic nuclei relative to one another). In the case of polar molecules, a third factor also comes into effect which is the orientation of the polarization (the application of an electric field causes an orientation of dipoles) [34-35].

Effect of fibre loading and surface modification
The effect of fibre loading and different surface treatments on both dielectric constant ϵ' and dissipation factor tan δ measured at room temperature for all the samples, is illustrated graphically in Figure 4. The effect of the reinforcement of PVC with DSs consists on the increase of the dielectric constant ε'. Pure PVC is a non-polar hydrophobic material which shows only instantaneous ionic and electronic polarizations [36]. The addition of a hydrophilic lignocellulosic material to the PVC involves the insertion of polar groups into the non-polar material thus resulting in the rise of the polarization related to the dipole reorientation. Moreover, the presence of hydroxyl groups –OH in the cellulose, the hemicellulose and the lignin extends the moisture absorption due to the interaction of –OH groups and water molecules. The total polarization of the composite, being the sum of three contributions: electronic, ionic and dipole reorientation. It is noticed that loss tangent increases further as the fibre content increases due to the increase in the number of polar groups [37]. The variation of conductivity of PVC/DSs composites with respect to fibre loading is depicted in Figure (4c). It can be observed that the change in fibre loading influences the conductivity. As DSs are introduced into the PVC matrix the volume resistivity decreases and the conductivity increases. This is due to the fact that the presence of DSs within the matrix increases the polar groups and the orientation polarization, which facilitates the flow of current through DSs/PVC composites, thereby resulting in a reduction of volume resistivity and marginal increase in the conductivity.

As a result of both chemical and heat treatments, the hydrophilicity of fibres is reduced which leads to the lowering of the orientation polarization and subsequently the dielectric constant. Moreover, it can be seen that, the composite prepared with heat treated DSs exhibits the lowest dielectric constant at 20% fibre loading. The improved interaction between the treated DSs and PVC increases the hydrophobicity of the composite, which, in turn, reduces the orientation polarization. However, the orientation polarization decreases considerably because of the decrease in water content within the fibre, hence the conductivity and the dissipation factor values also decrease.
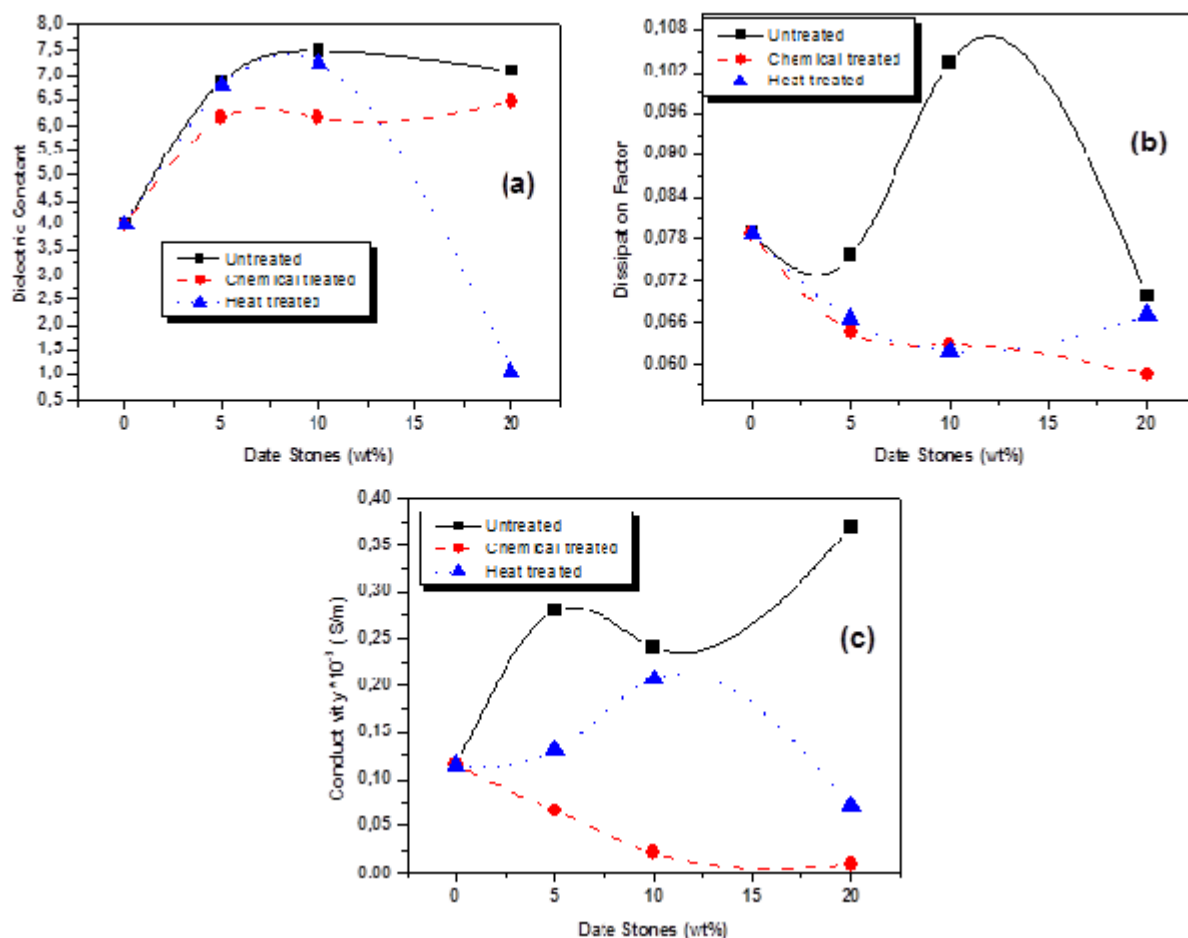
Figure 4: Variation of (a) dielectric constant (b) dissipation factor tanδ (c) conductivity of treated and untreated composites

Effect of temperature on the dielectric properties

The dielectric constant ε' and the dissipation factor tanδ of pure PVC and the composites containing 20% of untreated and treated DSs are presented in Figure 5 as a function of the temperature for a frequency of 50 Hz. From this Figure, it is clear that both ε' and tan δ values increase with the increasing temperature. Same trend was reported by Djidjelli et al. [38]. As temperature increases, the dissipation factor first increases up to a value corresponding to a particular temperature near 42°C and then decreases.

The dielectric constant ε' for the sample F20U which contains a considerable concentration of untreated date stones reveals a much pronounced increase starting from 20°C. On the other hand, with the heat treatment, this sample F20H records less important dielectric constant and thereby can be used for applications in the electronic industry, e.g., the value of its dielectric constant rises from 1.05 at 20°C to 2.25 at 80°C.

The effect of temperature on the conductivity of PVC, untreated and treated composites (with 20% DSs content) at a frequency of 50 Hz is illustrated in Figure (5c). It can be observed that the conductivity initially remains constant especially between 40 and 60°C and then increases with increasing temperature for the sample F20H.
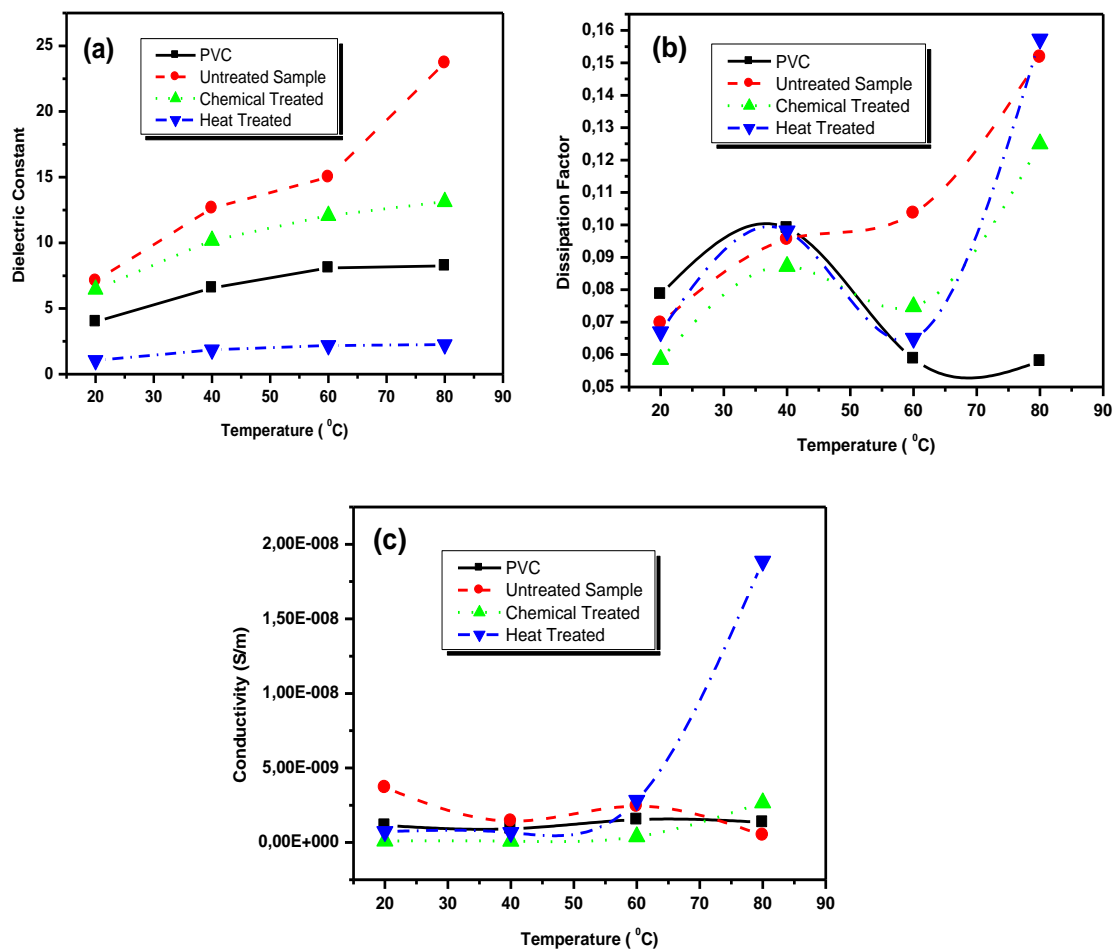
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Figure 5: Temperature dependence of (a) dielectric constant (b) dissipation factor tanδ (c) conductivity for treated and untreated composites

Tensile properties

The tensile strength of the composites is plotted versus the extent of surface modification is illustrated in Figure 6. It is noticed that the tensile strength of DSs/PVC composites decreases with increasing fibre loading. The chemical incompatibility between the matrix and the cellulose fillers results in lowering interfacial adhesion. Hence, the force needed to break these composites is found lower than that for pure PVC. An increase in the fiber content increases the microvoides between the fiber and the matrix, which weaken the fiber−matrix interfacial adhesion [30]. As a result, the values of tensile strength show a decreasing trend with increasing of fiber content in the composite.
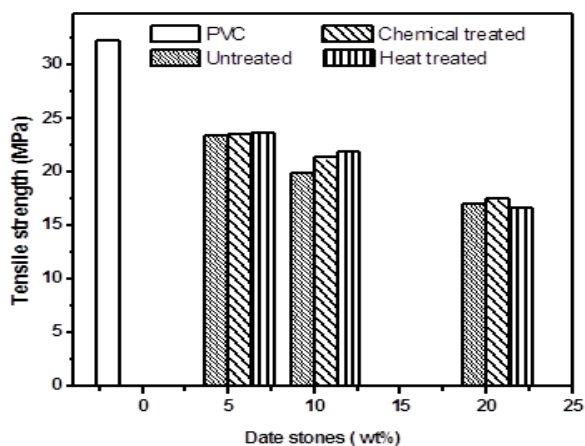

Figure 6: The effect of filler loading on the tensile strength of DSs/PVC (untreated and treated) composites

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The effect of chemical and heat treatments of fibres can be also seen in Figure 6. The composites with treated fibres exhibited a slightly higher tensile strength compared to that of untreated fibres reinforced PVC composites because of increased interfacial adherence. The synergy between fibers and the matrix reinforces material and increases energy necessary to break it [39]. It can be appreciated, that the addition of low fiber content in the matrix leads to its good dispersion. However, with raised concentrations, the particles occupy a more significant volume, which weakens the composites.

Figure 7 show clearly that the elongation at break decreases with increasing fibre content, there is a significant decrease in ductility with increasing filler content. As more filler is added, the mobility of the polymer chains was reduced. It is also found from this Figure that pure PVC exceeds 186 % of elongation at break then reduces to about 121 % when 5 wt % of the filler is added to the composites. The elongation at break is further reduced to less than 71.49 % as the filler concentration increases up to 20 wt%. The chemical treatment of the filler with acetic anhydride presents the same behaviour after heat treatment, which represents a slight increase in elongation at break in comparison with untreated DSs/PVC composites at all filler loading.
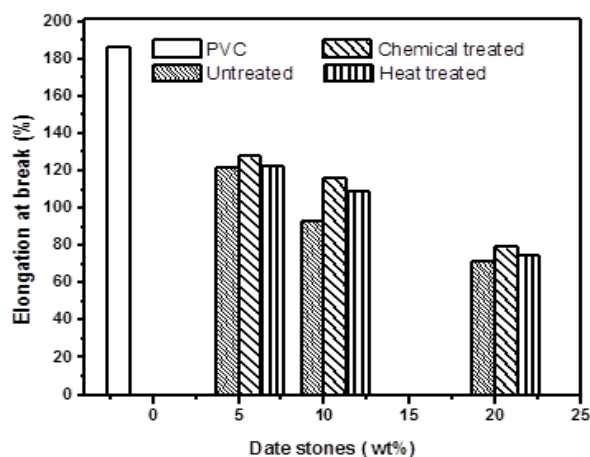

Figure 7: The effect of filler loading on the elongation at break of DSs/PVC (untreated and treated) composites

The improvement of both tensile strength and elongation at break of the treated date stones/PVC composites is due to the good interfacial adhesion between matrix and filler.

Figure 8 illustrates the Young's modulus of untreated and treated DSs fibre reinforced PVC composites. It is observed that, for all composites, the evolution of Young's modulus as a function of filler content exhibited a general tendency to increase. As for the untreated fibres, various authors note the same observation [3]. The nanosized DSs particles, obtained from heat treatment, possess higher specific surface area available for contact with the polymer matrix [40]. The fibres are distributed more homogeneously thus the compatibility between fibres and matrix becomes much important which involves the improvement of stress transfer.
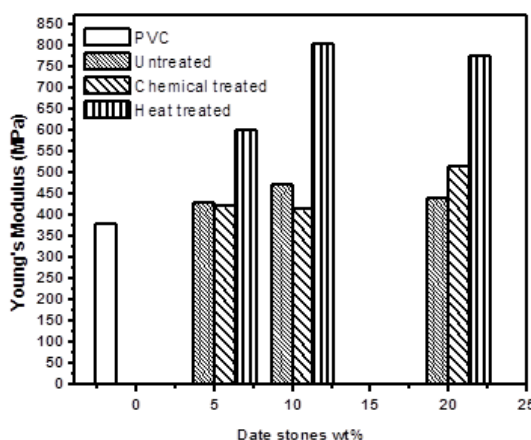

Figure 8: The effect of filler loading on Young's modulus of DSs/PVC (untreated and treated) composites

In general, the tensile properties of plasticized PVC are influenced by many factors, including the poor dispersion of DSs fillers within the matrix, the interfacial defects and the presence of voids within the composites during mixing [38, 41].

Hardness tests

The hardness plays an important role in the evaluation of wear properties and friction resistance [42]. The effect of untreated and treated composites with the content of DSs on the hardness of PVC is shown in Figure 9. It can be observed that the hardness of PVC/untreated DSs composites decreases with the increase of the reinforcement content, due to the softness of DSs compared with the PVC matrix.
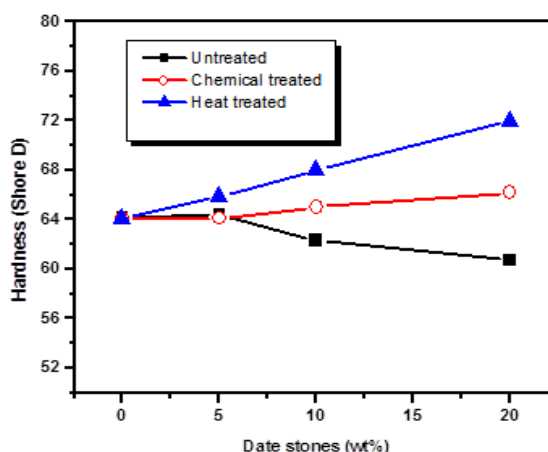

Figure 9: The effect of filler loading on hardness of DSs/PVC (untreated and treated) composites

The addition of treated DSs leads to a significant increase of the hardness compared to pure PVC. This could indicate that a reaction takes place at the interface, especially for PVC reinforced with heat treated DSs, which exhibits relatively higher value of hardness, approximately 74 Shore D when compared to the chemical treated DSs/PVC composites at 20 wt % loading. This could be attributed to the good dispersion of the filler particles within the polymer matrix and the stronger interfacial bonding [43].

CONCLUSION

The aim of this study was to compare the effect of different surface treatments for various levels of loading (5 to 20 wt %) on the properties of date stones / polyvinylchloride composites. FTIR results indicate that the hydrophilic character of date stones decreases after treatment, which was attributed to the substitution of the hydroxyl groups of the fibres throughout acetylation reaction and during heat treatment. This result was also confirmed by water absorption measurements of the prepared composites. Indeed, the rate of water absorption of treated composites is lower than that of untreated composites. The chemical treatment of DSs with acetic anhydride as well as the heat treatment enhances the compatibility between PVC matrix and filler, which creates a strong interfacial adhesion and therefore a better stress transfer between the two phases. This could be explained by the improvement of hardness and tensile properties. The dielectric constant, loss factor and conductivity increased with fibre content. Whereas volume resistivity decreased due to the better net orientational polarisation in DSs reinforced PVC composites. However, the dielectric constants and conductivities of treated composites was less than that of the untreated ones as a result of reduction in orientational polarisation and moisture absorbance.

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