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A valorization of agricultural waste for the preparation of an environmentally sustainable material

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Abstract

The valorization of agricultural waste is a critical area of research aimed at transforming what is often considered waste into valuable eco-friendly materials. This study has two objectives: firstly, to design a composite material based on a thermoplastic matrix (PVC) reinforced with vegetable fibres, which is chemically treated with acetic anhydride to improve the fibre-matrix interface. Secondly, to study the effect of this treatment on the physico-mechanical properties of resulting materials. The composites developed have been characterized by various analysis techniques, namely: tensile, hardness, water uptake and density tests. The recorded results show that increasing the load rate of the chemically treated fibre tends to decrease the elongation and breaking stress of the composites and increase their hardness and stiffness.

Keywords: Polymeric materials, Polyvinyl chloride, natural fiber, Acetic anhydride.

1. Introduction

For almost a century, the study and design of composite materials have attracted great interest in the many and varied fields of modern chemistry. Natural fiber composites occupy an important place in the history of technology. The development of plant resources provides a highly attractive alternative to environmental, ecological, social and economic problems, the growing problem of waste, environmental legislative standards and the depletion of fossil resources [1]. The search for sustainable green technologies has led scientific research to focus on the development of green composite materials based on cellulosic plant fibers. This new category of materials is characterized by properties such as high rigidity, low cost, low density and environmental friendliness, since they are derived from renewable and biodegradable resources. It also requires little energy to produce, and offers good thermal and acoustic insulation [2]. However, the lack of adhesion with polymer matrices is a difficulty that may prevent the widespread use of plant fibers in composites. The hydrophobic nature of most synthetic polymers and the hydrophilic nature of cellulosic fibers adversely affect interfacial adhesion [3]. To overcome this problem, it is generally necessary to modify the surface of the fibers to improve their adhesion to the polymer matrix. It has been shown that appropriate treatment of cellulosic fibers can result in compatibility with the polymer matrix, improving composite quality and reducing moisture absorption [4].
Chemical modification of the fiber surface enables coupling between highly hydrophilic cellulose fibers and hydrophobic polymers. There are various chemical treatments for natural fibres: alkaline treatment, acetylation, benzylation, treatment with silane, etc [5].
Among natural fibers, date karnel flour fibers are attracting increasing attention from researchers. However, the majority of research work has focused on adding value to these pits in the form of activated charcoal, as a supplement in livestock feed, in traditional medicine and for its antimicrobial and antiviral properties, and in the preparation of citric acid and proteins [6].

2. Method

2.1 Materials

Date kernel flour (DKF) with a particle size ≤ 300 µm, density of 0.72 and a relative humidity of 12% [7]. The date kernel used come from different varieties of Algerian dates. Polyvinyl chloride (PVC) used is the SE1200 type, supplied by CABEL ‘Câblerie électrique’ of Algiers, Algeria. This polymer has the following physical properties: K-Wert, from 70.2 to 72.0 with a density of 0.521.

2.2.1 Pre-treatment of date kernel flour

Date kernel flour was pre-treated several times, as mentioned in our previous study [7]:
- Several washes with ordinary water to remove as many impurities as possible, followed by a wash with distilled water,
- Drying in the open air for 48 hours,
- Drying in an oven at 60°C for 24 hours,
- Grinding with an electric grinder to obtain a finer grain size,
- Sieving with a series of sieves to obtain a particle size of 100 µm.

2.2.3 Acetylation of DKF

DKF was dissolved in distilled water at room temperature. The pH was adjusted with 1 M NaOH to 8.0-8.5. 8 g of acetic anhydride was added to the blend and then mechanically stirred for 30 min. The blend was washed with distilled water three times and dried at 35 °C.

2.2.4 Samples preparation

The different materials with varying fiber content from 0 to 30% (table 1), were prepared using calendering and compression molding working with 170°C of temperature and with pressure of 300 kN. Plates of 250×250×2 mm^3 are obtained, which will be used for cutting samples in the form of dumbbells.

Table 1. Weight compositions of the various PVC/DKF and PVC/TDKF formulations.

Formulations / Compositions (%)	F10	F20	F30
DKF	10	20	30
TDKF	10	20	30
PVC	90	80	70

2.2.5 Density test

The density of the samples was determined by measuring the Archimedes' buoyancy exerted on the volume of sample immersed in distilled water at a known temperature. It was determined using a Model DSM Density Meter**.**

2.2.6 Water absorption test

The water absorption test is carried out according to ASTM D7031-04. The samples immersed in distilled water at room temperature with stirring. The samples are weighed every 24 hours until their mass is stabilized. The

variation of mass is given by the following formula:

$$\Delta m\ (\%) = \frac{m-mo}{m}.100 \quad (1)$$

Δm : the water absorption (%),
m : the final mass of the sample
m_0 : the initial weight of the sample

2.2.7 Hardness test

Measurement of shore D hardness in accordance with standard NF T51-109 using a Shore D durometer was carried out at CABEL 'Câblerie Electrique' in Algiers, Algeria. The test consisted of subjecting the pointed steel needle of a shore D durometer to a force tending to push it onto 5×5 cm² plates with a mass of 5g. The durometer measures between 100 and 0 (100 maximum hardness, zero penetration, 0 maximum penetration). Penetration is indicated by a direct reading on the durometer after 15 seconds.

2.2.8 Tensile test

The mechanical behaviour of the composites elaborated was determined using an MTS Criterion tensile testing machine, in accordance with standard NFC 32-200 using computer-controlled TXW-type software. The tests were carried out at a pulling speed of 50 mm.min-1. The machine gives the force F as a function of elongation ($L-L_0$), where L_0 is the initial length of the specimen. The machine is connected to a computer, which performs all the necessary calculations and plots the stress-strain curves using software such as Test X pertV10.11. Five specimens were tested for each formulation. These tests were used to determine Young's modulus, strain and stress.

3. Results and discussion

3.1 Density test

Figure 1 shows that the incorporation of DKF in the PVC leads has not affect the density materials compared to PVC. This result is explained by the low density of the DKF. Comparing the results of the density test on the PVC/DKF composites elaborated with those on the PVC/TDKF composites prepared for the same loading rates, it can be seen that the incorporation of DKF into the PVC has no effect for loading rates of 10% and 20%. At a filler content of 30%, the density is lower than that of untreated composites.

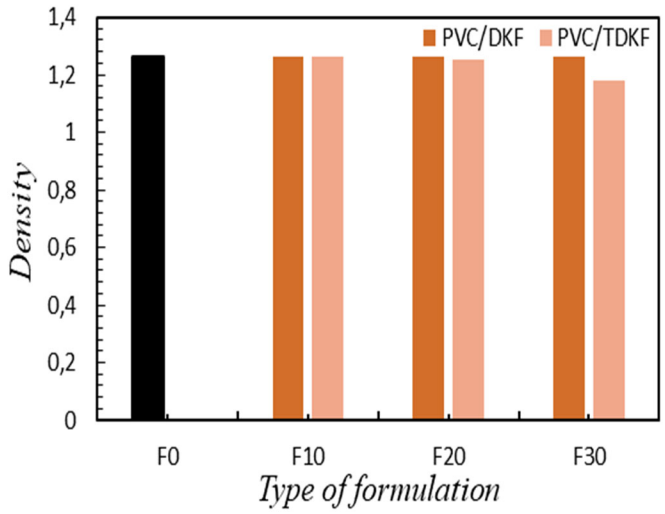

Figure 1. Density of PVC and (PVC/DKF and PVC/TDKF) composites for different formulations.

3.2 Water absorption test

The water uptake of pure PVC and PVC/DKF and PVC/TDKF composites are shown in Fig. 2. Moisture uptake increased with immersion time and rapid moisture uptake was observed for all samples within the first few days of immersion, but this decreased slowly with time. The decrease in the rate of moisture uptake with time of immersion could be due to the higher absorption of water molecules by fibre. When all of the available hydroxyl groups are used up in this way, the water absorbed became less. It was found that the water absorption of LDPE/TDKF composites is less than for those prepared with DKF. This is due to the fact that DKF is more hydrophilic that TDKF [7]. For the pure PVC, there was a very low water absorption which is of the order of 0.038 %, which is due to the hydrophobic nature of this polymer.

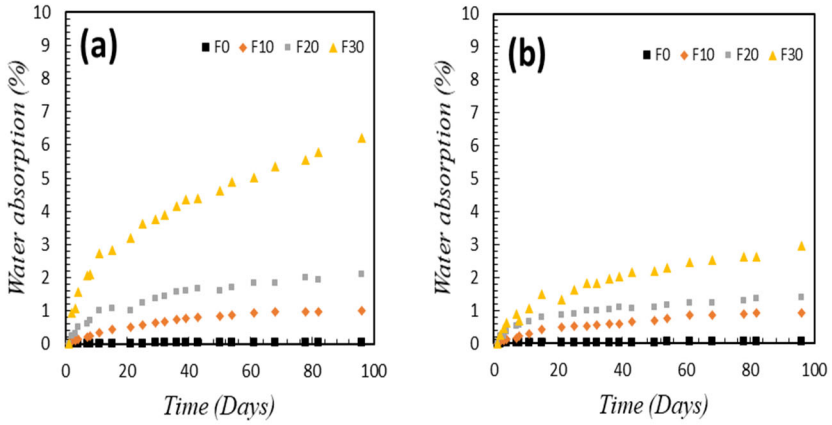

Figure 2. Water absorption of PVC, (a): PVC/DKF and (b): PVC/TDKF composites

3.3 Hardness test

The evolution of the hardness of PVC/DKF composites as a function of the filler content is shown in Fig. 3. It can be seen that the hardness increases with increasing filler content in the matrix. These results are to be expected, since date stone flour has a hardness that increases the hardness of PVC/DKF composites. An increase of 4.61%, 6.15% and 7.69% is recorded for composites filled with 10, 20 and 30% TDKF respectively, compared with virgin PVC.

Comparing the Shore hardness results of the PVC/DKF and PVC/TDKF composites, it can be seen that the composites filled with TDKF show a higher hardness than those filled with FNDB. For a loading ratio of 20%, the hardness increased from 66 to 69 for the PVC/DKF and PVC/TDKF composites respectively. This increase is explained by the good dispersion of the fiber in the matrix with a reduction in voids and stronger fiber-matrix interfacial adhesion [5]. These results are in agreement with other research work [8-10].

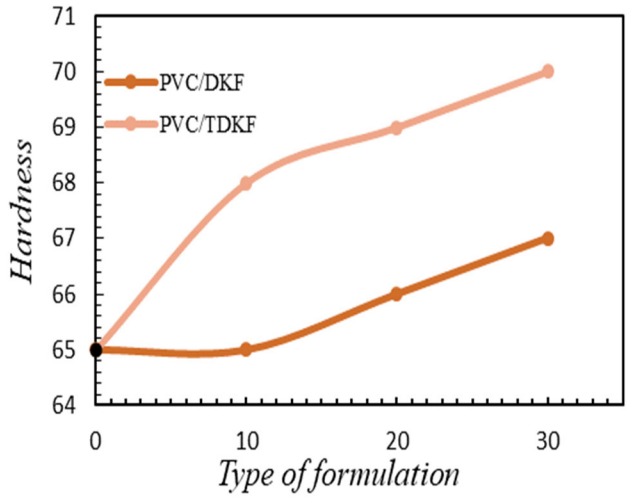

Figure 3. Hardness of PVC and PVC/DKF and PVC/TDKF composites with 10, 20 and 30% load.

3.4 Tensile test

3.4.1 Tensile strength

After chemical treatment with DKF, a decrease in stress was observed for all three formulations compared to composites prepared with DKF. This can be attributed to the degradation of the cellulose during acetylation, which subsequently results in depolymerisation of the cellulose and a loss of crystallinity leading to a drop in its mechanical properties [5, 11]. The problems of cellulose degradation after chemical modification are commonly described in the literature and are problematic when cellulose is used as a reinforcement in composite materials [12]. Another point to note is that the conditions used (temperature, reaction time and swelling agent) can themselves lead to fiber degradation [11]. This result is similar to that found by Luz et al. [13], who recorded a decrease in the tensile strength of PP/cellulose composites from 26.2 to 24.5 MPa and from 25.8 to 20.1 MPa for a filler content of 10 and 20% respectively, after acetylation. This result was attributed to the shape and size of the fibers obtained after chemical modification, as the fibers before acetylation had a fibrous appearance, whereas acetylation resulted in globular and amorphous particles.

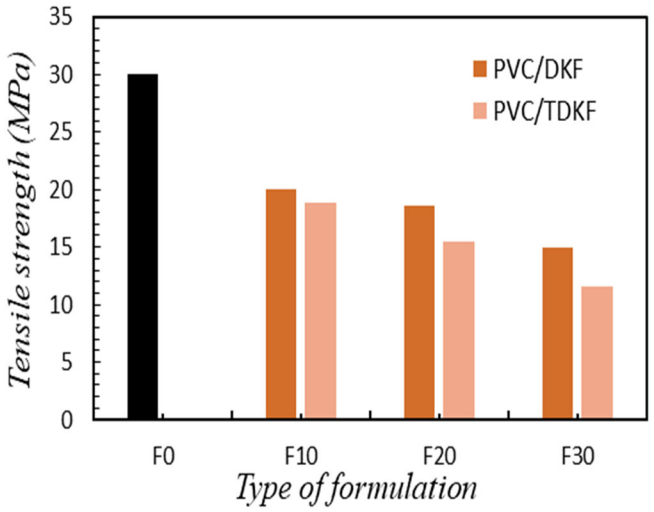

Figure 4. Tensile Strength of PVC and (PVC/DKF and PVC/TDKF) composites for different formulations.

3.4.2 Young's Modulus

Figure 5 shows the evolution of the Young's modulus of PVC and PVC/FNDB and PVC/FNDT composites with 10, 20 and 30% filler. Generally speaking, it can be seen that the introduction of filler into the PVC matrix significantly increases the stiffness of the composites. In fact, composites elaborated with treated and untreated date kernel flour record higher Young's moduli than PVC.

A comparison of the Young's moduli of the different composites shows that incorporating treated date stone flour into PVC results in an increase in Young's modulus compared with composites prepared with untreated flour. Similar results have been found by several researchers. Abdul Khalil et al [14] studied the evolution of the Young's modulus of polyester/coir fibre composites and recorded an increase in this parameter after acetylation of the coir fibres. They explained this result by an improvement in adhesion between the fibres and the polyester matrix due to acetylation. Indeed, the fibre is made more hydrophobic by such a modification and it can be used to prevent delamination at the interface of the fibre with the polyester matrix.

Kalaprasad et al. [15] reported a 14.89% increase in Young's modulus of polyethylene/sisal/glass fibre hybrid composites after chemical modification of these fibres with acetic acid. This result is attributed to the increased hydrophobicity of sisal after treatment.

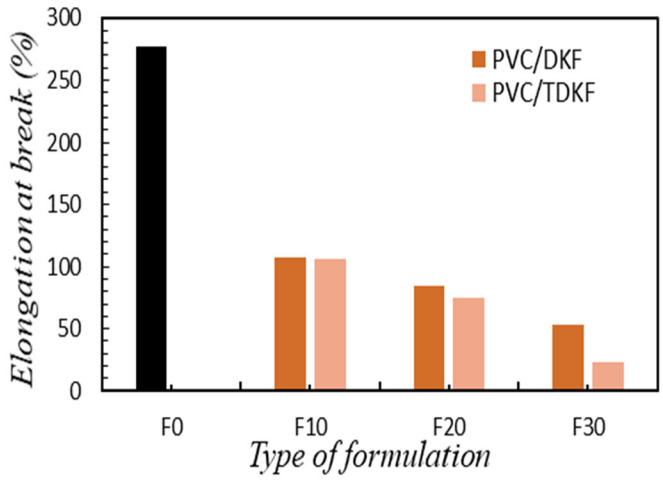

Figure 5. Young's Modulus of PVC and (PVC/DKF and PVC/TDKF) composites for different formulations.

3.4.3 Elongation at break

Figure 6 illustrates the trend in elongation at break for PVC and PVC/DKF and PVC/TDKF composites with 10, 20 and 30% load. It can be seen that the trend for all the formulations as a function of the type and level of filler is characterised by a significant drop in elongation compared with virgin PVC. As for elongation, it falls from 277.55% for PVC to 107.69% and 106.57% for PVC/ DKF and PVC/ TDKF composites (10% filler) respectively.

Comparing the results for the elongation at break of the different composites, it can be seen that acetylation of date stone flour did not affect the elongation at break of the composites at 10% load. However, for the composites loaded with 20% and 30% TDKF, a slight decrease was recorded compared with the composites loaded with DKF, with elongation falling from 52.92% to 22.76% for the PVC/DKF and PVC/TDKF composites (at 30%) respectively. This result is similar to that found by Abdul khalil et al [14], who found that acetylated coir fibres show a decrease in elongation compared to unmodified fibre for the same loading ratio. They explained this decrease by improving fibre-matrix adhesion (to give composites greater stiffness) or because acetylated fibres are more brittle after acetylation.

Vinod et al [16] studied the elongation at break of composites filled with chemically treated Ziziphus mauritiana fibres and found lower values than those prepared with untreated fibres. They explained this result by the better hardness and stiffness obtained thanks to the strong adhesion between the treated fibre and the rubber matrix. Higher extension is obtained from low interfacial adhesion as seen for untreated composites.

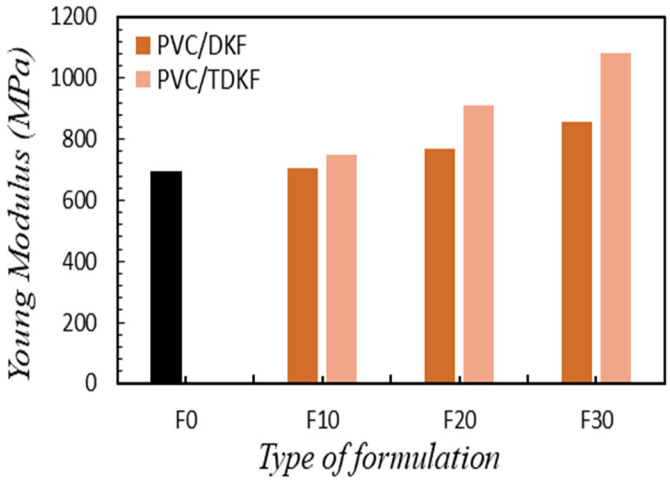

Figure 6. Elongation at break of PVC and (PVC/DKF and PVC/TDKF) composites for different formulations.

4. Conclusion

The analysis of the various experimental results has enabled us to draw the following main conclusions:
Characterization of PVC/NDF composites
- Acetylation of DKF did not affect the density of composites at low loading rates (10% and 20%) compared with composites prepared with untreated flour; however, a decrease in density was recorded for loading rates of 30%.
- The study of mechanical properties showed that:
- The stress and elongation at break of PVC/DKF composites decreased with increasing filler content compared with virgin PVC. These two properties also decreased for PVC/TDKF composites compared with those prepared with DKF.
- The Young's modulus of the composites increased with increasing filler content. An improvement in this property was recorded after chemical treatment with DKF.
- The hardness of the composites increased after acetylation of DKF.

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