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Study of the properties of a hybrid composite thermoplastic matrix/vegetable fillers.

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Abstract

The study carried out in this work aimed to develop and characterize hybrid composites based on polychloride of vinyl reinforced with date stone flour (DSF) and starch with PVC%/DSF%/ starch % percentages: 80/0/0, 80/20/0, 80/15/5, 80/10/10, 80/5/15 and 80/0/20 respectively. We were particularly interested in the problem of matrix-filler interfacial adhesion due to different characters of the constituent deferens. Several techniques have been used to characterize the composites developed, and the impact of hybridization on the mechanical and physical properties elaborate materials were studied. The incompatibility and poor interfacial adhesion between the different constituents leads to the appearance of phenomenon of embrittlement of the prepared materials, and consequently the reduction in stress, elongation at break and a reduction in elasticity of hybrid composites. The physical properties that were inspired by the density measurement state that the fillers used give the composites developed a lightness compared to virgin PVC.

Keywords : *Polyvinyl chloride, Date stone flour, Starch, Hybrid composites.*

I. Introduction

Environmental awareness as well as government legislations around the world have encouraged academic and industrial research to develop environmentally friendly composite materials that are durable and biodegradable [1].

Composite materials reinforced with natural fibers are increasingly sought after in various fields such as the industrial sector, particularly in the field of transport and the automobile industry, which require high-performance lightweight materials, recycling possibilities, the minimum of impact on the environment, and a reduction in the cost of materials [2-7].

In our work we were interested in the exploitation of date stone flour with starch as polyvinyl chloride reinforcements. However, the majority of research work has been devoted to the valorization of these nuclei in the form of: activated carbon, supplement in livestock feed, in traditional medicine and for its antimicrobial and antiviral properties, preparation of citric acid and proteins.

Algeria produces nearly 1,100,000 tonnes of dates/year, more than 10% of production is soft dates and the average weight of date stones ranges between 10% and 15% of the weight of dates. These stones are rejected and are considered a by-product of the date industry, they are poorly exploited and represent a loss of biomass deposits [8].

Among the plastic materials most used for the preparation of these composites, polyvinyl chloride (PVC). The latter is one of the most produced plastic materials. Its global production is 35 million tonnes per year. It is used in various sectors and is in third position in production after polyethylene and polypropylene [9,10].

One of the interesting solutions to meet this dual requirement is the hybridization technique [11]. The usage of hybrid polymer composites is increasing day-to-day because of their outstanding properties [12].Hybridization is the fact of using two or more types of reinforcements within the same composite. The term hybrid is defined in several ways in the scientific literature. Some the term hybrid is necessarily associated with a synergy between the reinforcements, which allows an additional improvement in the properties of the composite compared to a simple mixture. The behavior of hybrids can be seen as a weighted sum of the properties of the individual components and presenting a favorable balance between the advantages and disadvantages inherent in these components. Therefore, a balance between cost performance and sustainability. The main objective of this work is the development of PVC/ date stone flour (DSF)/Starch hybrid composites and the study of the effect of hybridization on the mechanical, physical, morphological and rheological properties of the materials developed.

II. Material and methods

PVC (Type 3000H) manufactured by CIRES (USA) (from the plastic calendering company "CALPLAST" in Sétif,

Algeria) was used to prepare the formulations. The added plasticizer was dioctylphthalate (DOP). The industrial-grade heat stabilizer used was a mixture of epoxidized soybean oil (HSE 100S) and NEW STAB 26, with stearic acid as the lubricant. The natural fillers used are date stone flour (DSF) and starch. The starch used is cornstarch, which is bought directly from the shop.

To prepare the DSF, the collected nuclei underwent several pre-processing steps: Pulp- stone separation, the stone are then washed in hot water to remove traces of pulp and all kinds of impurities, followed by drying in the open air and grinding. The diameter of the selected flour particles is less than 63µm.

The PVC resin and the various additives are, mixed in a beaker using a spatula until the mixture becomes homogeneous. Sheets of 0.4 mm in thickness of F0, (formulation based on PVC and these additives), F20A (formulation based on 80% PVC, these additives and 20% starch), F20DSF (formulation based on 80% PVC, these additives and 20% DSF), F10A10DSF (formulation based on 80% PVC, these additives, 10% starch and 10% DSF), F5A15DSF (formulation based on 80% PVC, these additives, 5% starch and 15% FND) and F15A5ND (formulation based on 80% PVC, these additives, 15% starch and 5% DSF), were prepared using a calendar. The temperature along the twin cylinder mixer is maintained at 160°C for a residence time of 15 min. The sheets are, and then cut into the appropriate shape for characterization.

The properties of the PVC/DSF/Starch composites developed are then determined by the tensile test, the Water absorbing test and by measuring the density.

III. Results and discussion

A. Mechanical properties of PVC%/DSF%/ starch % composites determined by the tensile test

Figure 1 represents the variation in the stress at break and the maximum stress of the composites F0, F20DSF, F10A/10DSF and F20A.

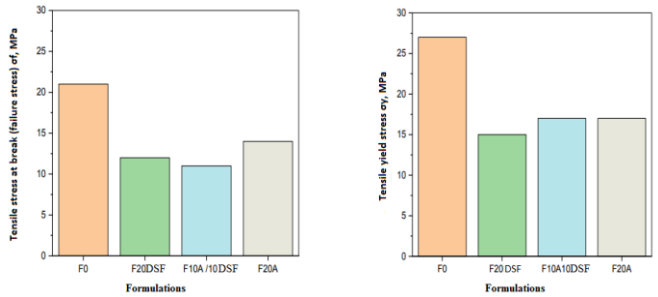

Figure 1. The variation in the stress at break and the maximum stress of the composites

The presence of particles of the fillers used with a hydrophilic nature in the hydrophobic PVC matrix reduces the tensile strength of the composites developed due to the incompatibility and poor interfacial adhesion between the different constituents. The reduction in breaking stress is estimated at 48, 43 and 34% for F10A10DSF, F20DSF and F20A respectively. The estimate of the reduction in the maximum stress of the reinforced composites compared to the virgin matrix is of the order of 44, 37, and 37% for the F20DSF, F10A10DSF and F20A composites respectively. The sharp decrease recorded is consistent with composites reinforced with date stone flour because it is more hydrophilic than starch. This is confirmed by the water absorption test.

Indeed, this loss of stress can be explained by the tendency of the filler particles to group together, forming agglomerates and resulting in poor dispersion, which induces heterogeneities and non uniform stress transfer within the matrix. This result is in agreement with several research studies. Islam et al. [13], recorded a decrease in breaking stress from 27.5 MPa for virgin PP to 25 MPa for composites filled with 25% coconut fiber. Djidjelli et al. [14], recorded a decrease in tensile strength of approximately 63% for PVC loaded with 30% sisal fibers compared to virgin PVC.

The variation in the elongation of the composites F0, F20DSF, F10A/10DSF and F20A is, shown in Figure 2.

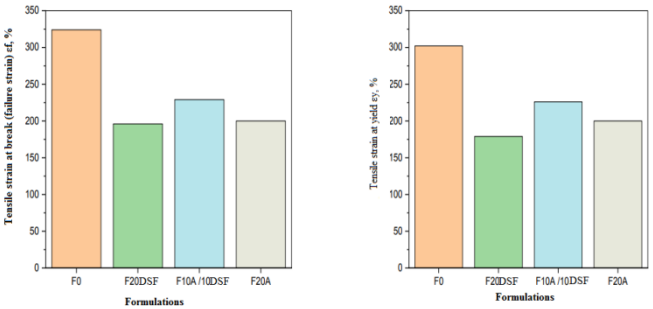

Figure 2. Evolution of the elongation of the developed composites

From Figure 2, we observe a significant drop in the elongation at break of filled composites compared to virgin PVC. This result is explained on the one hand, by the hydrophilic nature of the DSF and FA which absorb more humidity and causes swelling in the polymer matrix, on the other hand due to the volume occupied by the particles of the fillers, the Inter-chain interactions and the mobility of polymer chains are reduced, creating defects in the system and therefore material embrittlement. The phenomenon is more proven by composites reinforced with DSF particles.

S. Kormin et al [15], explained the decrease in elongation of LDPE/starch composites with increasing loading rate by the generation of internal deformation forces and a poor matrix-starch interface.

Figure 3 represents the evolution of Young's modulus of the prepared composites.

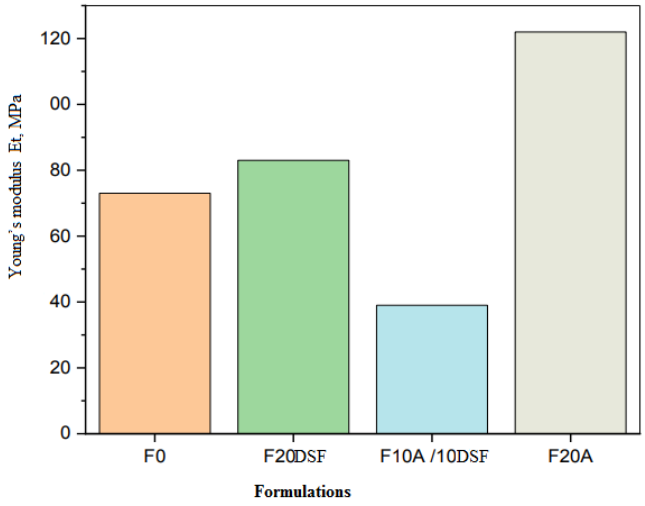

Figure 3. Evolution of Young's modulus of the prepared composites

From Figure 3, we can see that the incorporation of DSF and FA into the PVC matrix increases the rigidity of the material and reduces their elasticity. We also see that the Young modulus is significantly reduced for the hybrid composite.

A. Water absorption test

Water absorption analyzes are carried out to determine the influence of hybridization on the physicochemical properties of the materials produced. The water absorption behavior of the composites is compared to that of PVC resin and the results are reported in the figure 4.

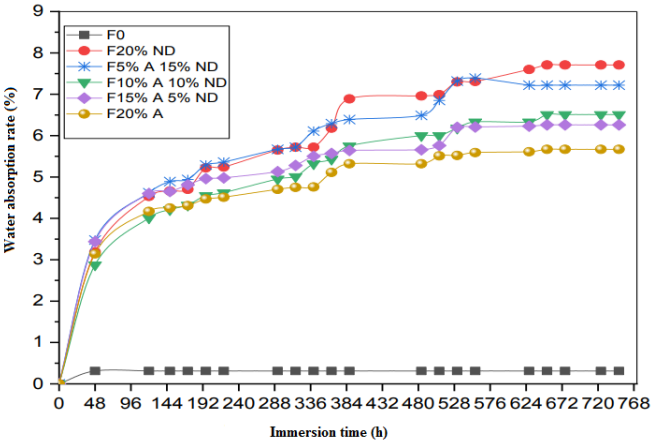

Figure 4. Evolution of the water absorption rate of the different composites developed as a function of immersion time.

The results show that the water absorption of F0 is negligible and does not exceed 0.31% whatever the immersion time due to the hydrophobic nature of this polymer, while the addition of starch or date stone flour with PVC matrix increases the water absorption rate with increasing immersion time in distilled water. This increase is attributed to the increase in the concentration of hydroxyl groups which have a strong affinity with water. This can be explained by the presence of hydroxyl groups in the two fillers used (a major constituent of corn flour and in the kernels of date) S. Sahi et al. [16], A. Hamma et al. [17]. These groups form hydrogen bonds with the water molecules absorbed by these hydrophilic reinforcements. Plus the concentration of OH group in composites is higher, the greater the water absorption rate. We can also attribute this phenomenon to poor filler/matrix interfacial adhesion leading to an increase in microvoids. The results of this test allowed us to reveal the hydrophilic nature of the fillers used and that date stone flour is more hydrophilic compared to starch. Indeed, the F20DSF composites absorbed a higher quantity of water than the F20A composites. This is also confirmed by the increase in the quantity of water absorbed by increasing the rate of date stone flour in the hybrid composites, in fact, the hybrid composites F10A10DSF, F5A15DSF and F15A5DSF) reached their water saturations of 6.51%, 7.22% and 6.26% respectively. From these results, we can say that the rate of water absorption depends on the time and the nature of the charge incorporated in the PVC matrix. These results are in agreement with the results observed by ESPERT.A et al. [18] who found that the hydrophilic nature of plant fillers is responsible for water absorption.

B. The density

The low density of lignocellulosic materials is one of the major advantages of their use as fillers in thermoplastic-based composites. Know the value density of date stone flour and starch makes it possible to predict the mass of a material reinforced by these loads. The results of the density test of the different composites developed F0, F20DSF, F5A15DSF, F10A/10DSF, F15A5DSF and F20A are shown in Figure 5.

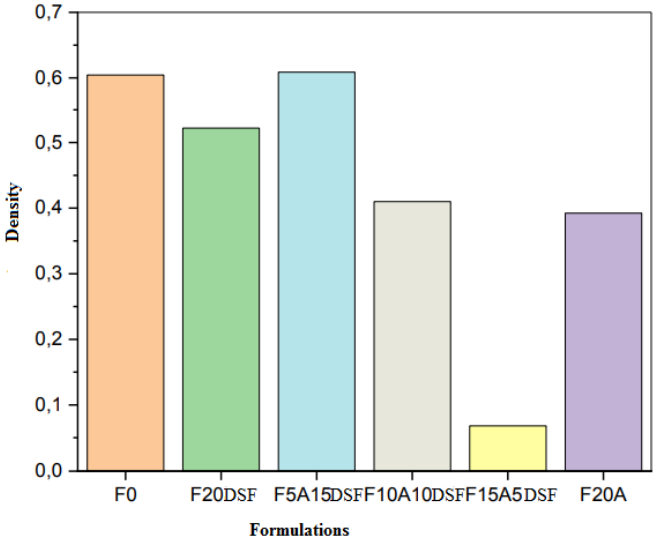

Figure 5. Evolution of the density of the different composites produced as a function of type and filler rate.

In this regard, the incorporation of date stone flour and starch flour into the polyvinyl chloride leads to low density composites compared to PVC virgin. The higher the starch content, the lower the density of the hybrid composites. The highest density value corresponds to the composite loaded with date stone flour. This is attributed to the highly hydrophilic nature of DSF compared to starch and the presence of micro voids in composites due to interfacial incompatibility charge/matrix. These empty microphones will subsequently be, filled with air, increasing the density of its materials Masri T. et al. [19].

A. Conclusions

The study carried out in this work aims to develop composites based on polyvinyl chloride reinforced by hybridization of two fillers: date stone flour and flour of starch with different loading rates ranging from 5 to 20%. The impact of hybridization on the mechanical and physical properties of the materials produced was, studied. The incompatibility and poor interfacial adhesion between the different constituents' leads to a reduction in the stress of hybrid composites compared to the virgin matrix. The lowest value is, recorded for composites reinforced with starch flour.
The phenomenon of embrittlement of the prepared materials induced by the creation of defects in the system, produced by the volume occupied by the particles of the fillers used, leads to the reduction in the elongation at break of hybrid composites. This phenomenon is more obvious for the F 20DSF composite. A reduction in elasticity of the composites induced by the rigid nature of the fillers incorporated in the PVC matrix was observed and manifested by the increase of Young's modulus. This reduction is more significant for hybrid composites.
The increase in the quantity of water absorbed by increasing the rate of date stone flour in the hybrid composites confirms the more hydrophilic character of date stone flour compared to starch. The density of composites is significantly lower than that of virgin PVC, which affirms that the fillers used give the composites produced lightness, or composites filled with starch are the lightest materials.

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