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Thermal and Physical Properties of Hybrid Composites Made from Used PET Bottles and Date Palm Fibers Filled with Unsaturated Polyester

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Abstract. Recycling polyethylene terephthalate (r-PET) bottles is a sustainable solution for reducing the accumulation of r-PET in landfills. The primary goal of this study is to determine the viability of combining fibers derived from waste r-PET bottles (r-PET) and date palm fibers (DPF) to produce hybrid unsaturated polyester (UP)-based composites. Hand lay-up was used to make the UP/r-PET/DPF composites, which had 10%, 20%, and 30% r-PET and date palm fibers by weight, with equal weights of the two. Recycled r-PET bottles and date palm leaflets were cut into 5–10 mm lengths and incorporated into the UP matrix. The composites were characterized by their flexural, morphological, thermal, dynamical mechanical, and water absorption characteristics. The thermal behavior of the composites improved when r-PET and DPF were added at high temperatures. However, the composites' flexural strength and storage modulus decreased due to their non-uniform distribution, which made it hard for the fillers to adhere to the UP matrix. SEM micrographs of the composite's fracture surfaces showed that the amount of agglomeration eventually increased as the filler loading increased. Lastly, the composites showed significant resistance to water absorption with lower proportions of DPF and r-PET fibers.

Keywords: Date Palm Tree Fiber, Unsaturated Polyester, Recycled r-PET

INTRODUCTION

Unsaturated polyester (UP) is a thermoset polymer used extensively in the construction, automotive, and aerospace industries. The advantages of UP include its good mechanical properties, low cost, and simplicity on handling (Costa et al. 2016; Sapuan et al. 2020).

In the past few decades, both basic and applied research on composites made from natural resources has garnered considerable attention. The desire to protect the environment and extend the useful life of products has led to the development of more composites made from renewable resources (Almi et al. 2015; Bourmaud et al. 2017; Ramesh et al. 2013). Plastic industries are growing in emerging countries such as

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Algeria, but their waste management policies and practices have room for improvement (Maou et al. 2023b). Plastic pollution has become a major public environmental concern (Chauhan et al. 2019; Montanes et al. 2019). Since the early 2000s, cheaper natural fibers have replaced some synthetic fibers in bio-based polymer composites, and their use has steadily increased. Date palm fiber (DPF) was one of the first fibers to be used in polymer composites in Saharan countries, especially Algeria (Maou et al. 2023a).

Maou et al. (2019) developed a biocomposite based on DPF, a local material. They found that adding DPF enhanced the composite's mechanical properties as the percentage of fibers increased. The thermal stability of the composite also increased with higher DPF content.

Using this plant fiber in a differently, Meftah et al. (2020) found that adding DPF and dune sand made a UP composite with good mechanical and thermal properties.

Recycled plastic fibers, such as r-PET, can be mixed into UP with different loadings and average PET fiber lengths. This method shows strong potential for use in various technical applications (Dehas et al. 2018).

Recently, many researchers have focused on making polymer composites that are strengthened with hybrid fibers (Gupta and Srivastava, 2016). Nevertheless, there has been little use of r-PET and plant fibers to produce a hybrid polymer composite material that takes advantage of the good mechanical and thermal properties of r-PET, as well as the availability, environmental friendliness, and low energy consumption of DPF.

A study by Várdai et al (Várdai et al. 2019) is the only one we know of to examine the use of hybrid fiber composites in combination with a polymer. The authors reported how PET affected the mechanical properties of polypropylene (PP)/wood composites. The work showed a good way to find more uses for these composites. Our work aimed to make eco-friendly hybrid composites out of DPF and r-PET fibers. We studied how adding DPF and r-PET fibers to UP/r-PET/DPF composites affected their flexural, morphological, thermal, dynamical mechanical, and water uptake properties. Further, we used cheap and naturally abundant waste products, such as DPF and r-PET, as reinforcements for the new hybrid composites, which can be used in a variety of structural applications.

MATERIALS AND METHODS

Materials

Orthophthalic unsaturated polyester resin and methylethyl-ketone peroxide (MEKP) were purchased from LORN Chemicals Company, Algeria.

DPF was obtained from the agricultural waste of date farms in Sidi Okba, Algeria. The DPF was washed, and cut to average lengths of 5–10 mm. The fibers were dried in a laboratory oven at 50°C to a final moisture content of 3-4%.

The chemical composition of date palm fibers from the leaf is shown in Table 1 (Maou et al., 2021).

Table 1. The chemical composition of raw DPFs

Lignin (%)	Hemicellulose (%)	Cellulose (%)	Ash (%)
29± 7.5	20 ± 2	42±5.1	9±1.4

The r-PET fibers derived from post-consumer PET bottle recycling were washed and cut to average lengths of 5–10 mm. The materials used in this study are presented in Figure 1.

Fabrication of UP/r-PET/DPF Composites

The DPF and r-PET fibers were added to UP resin to make the hybrid composites. The composites were elaborated via the hand lay-up technique.

First, the DPF, r-PET, and UP resin were mixed manually in different weight ratios, and then the mixtures were mixed with 2 %wt methyl ethyl ketone peroxide. Immediately, the mixtures were poured into a 200 mm ×200 mm ×2 mm steel mold. Wax was used to facilitate an easy removal of the composites from the mold after curing reaction. The samples were cut and designed using a CNC milling machine for flexural and dynamical, mechanical experiments, (see Figure 2).

Fig. 1: (a) UP, (b) r-PET fibers, and (c) DPF fibers.

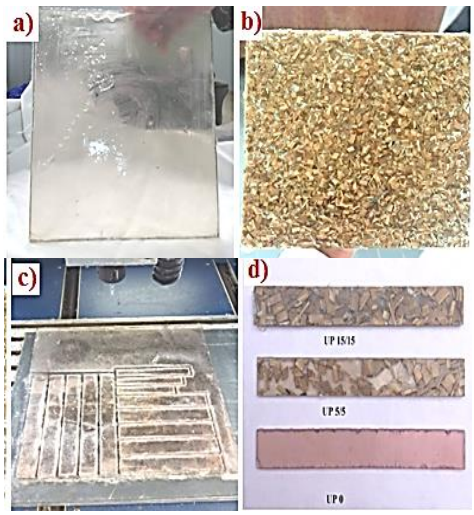


Fig. 2: (a) UP (b) UP/r-PET/DPF composite (c) computer numerical control (CNC) milling machine (d) specimens for flexural testing.

Characterization

Mechanical Characteristics

Flexural testing was carried out according to ASTM D 790 standards using an MTS testing machine.

Morphological Analysis

A Jeol JSM-6031 scanning electron microscope (SEM) was used to look at the shape of the composites.

Thermal Properties

The thermograms of the polymeric matrix and the composites were recorded using an SDT Q600 (TGA/DSC) simultaneous thermogravimetric analyzer and differential scanning calorimeter (TA Instruments, Inc) under N2 conditions, from room temperature up to 600°C using a heating rate of 10°C/min.

Dynamical mechanical analysis (DMA): The dynamical mechanical properties of the samples were evaluated using the DMA Q800 model (TA instruments, Inc) at a heating rate of 5 °C/min in the temperature range of 25 - 150 °C at a fixed frequency of 1 Hz. The dimensions of the specimen were 60 mm x 10 mm x 2 mm.

Water Absorption Test

The percentage of water uptake in the composites was measured every 24 hours for a total of 35 days (Ikladious et al., 2019); the water uptake was determined by the difference in weight between the samples soaked in water and the dry samples using Eq. (1).

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \qquad (1)$$

where M_t is the water uptake percentage and, W_0 and W_t are the mass of the dry weight of the sample and the weight at any specific time t, respectively.

RESULTS AND DISCUSSION

Flexural Properties

The flexural modulus and flexural strength of UP and composite samples are summarized in Table 2. As can be seen from Table 2, all composites have lower flexural strength than pure UP. This deterioration in flexural strength in composites is due to the incapacity of fibers randomly distributed in the UP matrix to resist transmitted stresses and Inadequate interfacial adhesion causes gaps between the fiber and the UP resin, resulting in brittle composite.

The flexural strength of UP was decreased from 58 to 24 MPa by adding 5 %wt DPF and 5 wt% r-PET. Similar observations of decrease have been reported by (Nuzaimah et al., 2019) and (Jayamani et al., 2018), the flexural strength of virgin UP was decreased from 98 to 24 MPa by adding 5 %wt waste rubber and from 70 to 42 MPa by adding 5 %wt chicken feather fibers, respectively, into UP matrix.

As shown in Table 2, the addition of 20 wt% date palm fiber and 20 wt% r-PET fiber (equal wt%) to UP increased the composite's strength. However, the incorporation of 30 wt% date palm fiber and r-PET fiber (both of them were in equal wt%) decreased strength due to the non-uniform distribution and fiber agglomeration, which generated a poor stress transfer mechanism.

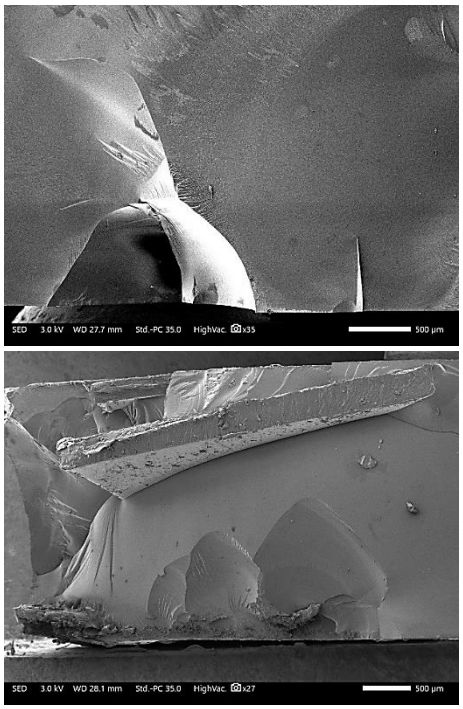
Table 2. Mechanical properties of UP and its composites.

Materials	Flexural strength (MPa)	Flexural modulus (MPa)
UP	58±2.10	1781±101
UP/r-PET5/DPF5	24±1.22	3054±277
UP/r-PET10/DPF10	23±2.33	3100±288
UP/r-PET15/DPF15	18±1.44	1800±105

Contrary to what was shown in Table 2, the flexural modulus was increased by the incorporation of fibers. For example, By adding 10, 20, or 30% of the weight of fibers, the flexural modulus of UP was increased from 1781 MPa to 3054 MPa, 1781 MPa to 3100 MPa, or 1781 MPa to 1800 MPa, respectively. According to Sawpan et al (Sawpan et al. 2012) and Ahlawat et al. (Ahlawat et al. 2019), this increase is attributed to stiffer reinforcement in the UP matrix.

Morphological Analysis

Figure 3 displays SEM micrographs of the broken surfaces for composites with UP matrix and DPF/r-PET fiber contents of 10 wt. %, and 30 wt. % (both of them were equal weights).



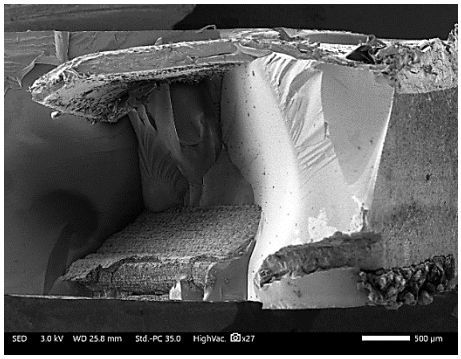


Fig. 3: SEM micrographs of fracture surface of UP/r-PET/DPF composites; (a) virgin polyester, (b) 10 % DPF/r-PET, and (c) 30 % DPF/r-PET.

The increase and decrease of flexural strength were consistent with the morphological features of the broken surfaces as depicted in Figure 3. In particular, as the DPF/r-PET fiber concentration increased, holes and fissures formed between the fibers and the UP matrix. Virgin polyester micrograph (Figure 3(a)) showed a hole-free broken surface, confirming that the sample had the maximum value of flexural strength. A composite with 10 % fibers has greater flexural strength than other composites. This high flexural strength is due to the small hole and gap shown in Figure 3(b). More voids and gaps can be seen as the fiber content increases, as shown in the micrograph of 30% fibers in Figure 3(c). The non-uniform distribution and fiber agglomeration contributed to poor interfacial adhesion between fibers and UP matrix, significantly reducing the flexural strength of composites with 30 % fiber.

Thermal Properties of UP/r-PET/DPF Composites

TGA was used to examine the thermal behavior of the UP matrix and the UP/r-PET/DPF composites. Weight loss from 25 °C to 600 °C was determined using TGA and DTG curves (Fig. 4). (a, b).

Table 3. Thermal properties of UP and its composites.

Sample	Decomposition Temperature (°C)		CY (%)
	T10%	T50%	
UP (100)%	326.90	380.26	6.89
UP/r-PET/DPF (90/5/5)%	306.24	383.09	10.98
UP/r-PET/DPF (70/15/15)%	303.70	381	11.95

Table 3 displays the degradation temperatures and the char yield. Just one deterioration stage was seen in the pure UP and its composites. Virgin UP was more stable than composites at low temperatures. Nonetheless, the composites performed somewhat better than the virgin polyester in terms of stability at elevated temperatures.

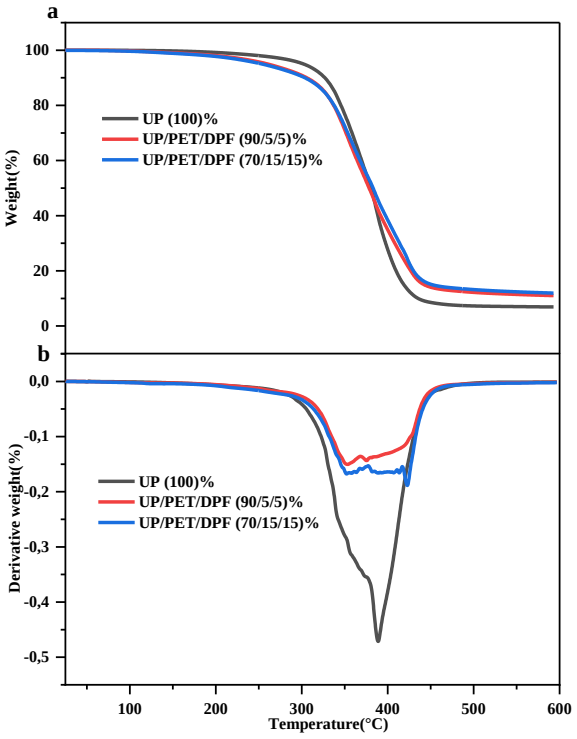


Fig. 4: Thermal stability of the virgin UP and UP/r-PET/DPF composites as determined by (a) TGA, and (b) DTG.

Dynamic Properties of UP/r-PET/DPF Composites

Storage Modulus (E')

E' is closely associated with a material's rigidity. Figure 5a depicts E' as a function of temperature. The DMA findings revealed a higher E'—suggesting greater stiffness—for virgin polyester DPF/r-PET composites. Results showed that the value of E' has been shifted less for UP/r-PET/DPF composites (2219 MPa and 1741 MPa for 10% and 30% fiber composites, respectively) than for virgin polyester (i.e., 3494 MPa) at low temperatures. It is important to note that the decrease in storage modulus shown above is in line with with what other researchers have found in fiber/thermoset composites (da Luz et al., 2018; Tao et al., 2020). The Insufficient interfacial adhesion between DPF/r-PET fibers and the polyester matrix can explain this observation. The samples exhibited a significant decrease in E' over the temperature range of 65 to 110 °C. These temperatures are in the Tg range, indicating the material's phase change from the glassy to the rubbery state.

Loss Modulus (E")

E" is closely associated with "internal friction". Figure 5b depicts the variation of E" pure polyester and in UP/r-PET/DPF composites as a function of temperature. The E" peak for UP70/PET15/r-PET15 shifts to the highest transition temperature region, most likely due to the restricted segmental mobility of the amorphous UP chains at the fiber-matrix interface.

Damping Factor (Tan δ)

Tan δ is a damping factor defined as the ratio of E' to E''. A high Tan δ value implies that the material has an elastic component. A low value indicates good elasticity, as the mobility of the molecular chains decreases at the fiber/matrix interface. Figure 5c depicts the temperature dependence of Tan δ values in UP/r-PET/DPF composites.

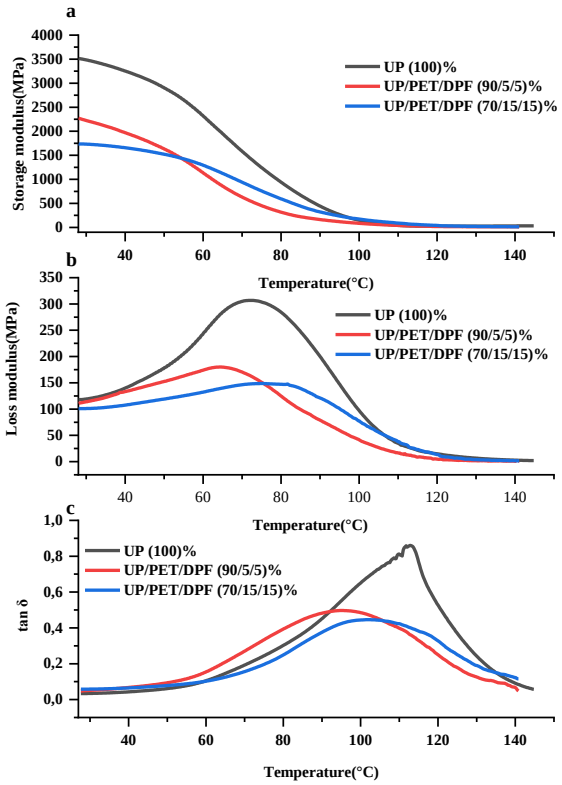


Fig. 5: (a) Storage modulus (E'), (b) loss modulus (E") and (c) the damping factor (Tan δ) for the virgin UP and UP/r-PET/DPF composites as a function of temperature.

As shown on the graph, the Tg of the composites reached an early level before virgin polyester. Tg is the temperature at which the damping reaches its maximum value. As displayed in Figure 5c, the maximum Tan δ values for 10% and 30% r-PET/DPF fiber composites were 0.494 and 0.444, respectively. This is a better result than that of Dehas et al (Dehas et al., 2018)., who found that Tan δ = 0.6 for UP filled with 8 wt% and 2-3 mm fiber length of r-PET. The maximum decrease in damping was found for 30% of the fibers. The area of the Tan δ peak for the composites was broader than that of the

virgin UP. This property implies that the composite has molecular relaxations not seen in virgin UP. In addition to the components, molecular mobility at the fiber/matrix interface contributes to polymer damping. When the r-PET fibers are longer, the good affinity between the ester structures in the unsaturated polyester and fiber surface promotes good adhesion to the matrix. However, the resulting composite is less stiff because the flexibility of the r-PET fiber induces a plasticizing effect.

Water Uptake Behavior of the UP/r-PET/DPF Composites

The effects of water uptake as a function of time (day) for each sample immersed in water at room temperature (25 °C) for 35 days are presented in Fig. 6. One of the most significant disadvantages of natural fibers is their high hydrophilicity. Incorporating r-PET leads to hydrophobic composites, promoting lower water absorption. The virgin UP had a relatively low water absorption rate (<0.5%), indicating its hydrophobic nature. Moreover, the percentage of water absorption for the UP/r-PET/DPF composite increased with increasing amounts of the DPF/r-PET fibers.

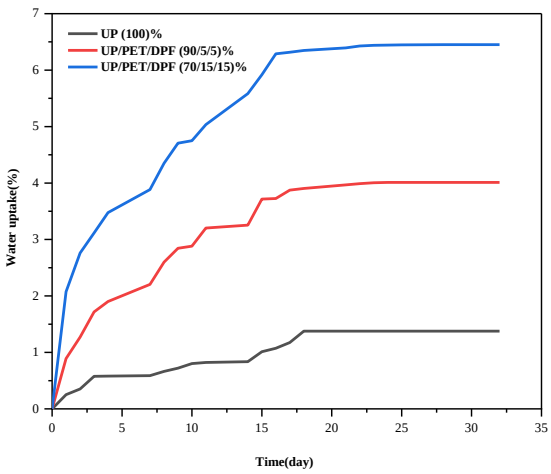


Fig. 6: Water uptake of the virgin UP and UP/r-PET/DPF composites

CONCLUSIONS

This paper studied how adding date palm fiber and polyethylene terephthalate fiber to a UP/r-PET/DPF composite affected its flexural, morphological, thermal, dynamical mechanical, and water absorption properties. Firstly, we successfully produced unsaturated polyester-based date palm fiber/ polyethylene terephthalate fiber hybrid composites.

The flexural strength of the UP/r-PET/DPF composite decreased with higher fiber content. The decrease in flexural strength was caused by poor interfacial bonding between DPF/r-PET fibers and the UP matrix. SEM micrographs proved that the inhomogeneous distribution of DPF/r-PET fibers within the UP matrix may have played a role. On the contrary, the flexural modulus increased proportionately with higher proportions of DPF/r-PET fibers. An obvious increase in flexural modulus occurred in the UP/r-PET/DPF composite. This enhancement of flexural modulus was related to the composite's improved elastic behavior; the fibers impart better flexibility on the composite. Generally, the composite developed with DPF/r-PET fibers and the UP matrix has high stiffness. The thermal degradation of the UP matrix and composites occurred in a single step; at higher temperatures, the composites were slightly more stable than the UP matrix. These results indicate that using DPF and r-PET as fibers in developing UP/r-PET/DPF composites yield promising results. This result represents one approach to ensure the recycling of DPF/r-PET, which will help protect and preserve the environment.

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