Research Article

Thermophysical Behavior of the Treated Date Palm Tree Leaf- Reinforced Polyvinylchloride/Styrene Acrylonitrile Copolymer/Low-Density Polyethylene Ternary Composite

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ABSTRACT

Date palm tree leaf-reinforced polymer composites are advantageous in terms of being sustainable and low-cost. In the present study, ternary composites of polyvinylchloride (PVC) reinforced with treated date palm tree leaves (TDPL) (10, 20, and 30 wt.%), styrene acrylonitrile (SAN) copolymer, low-density polyethylene (LDPE) were fabricated (PVC/SAN/LDPE) using an extrusion process. TDPL and SAN copolymer were used to improve the interfacial bonding, compatibility, and thermomechanical properties of the composite. Morphological behavioral analysis revealed that the incorporation of SAN copolymer enhanced the compatibility of the blend. Mechanical studies revealed improved tensile strength and hardness of the PVC/SAN/LDPE composite. In addition, the flexural and tensile modulus of the composite increased with increasing date palm leaves (DPL) content. Thermal analysis revealed increased Tid and Tmax, indicating improved thermal stability of the composite. Moreover, scanning electron microscopy revealed that the ternary PVC/LDPE blend modified with SAN copolymer and 30 wt% TDPL exhibited enhanced interfacial adhesive bonding compared with the binary PVC/LDPE blend; this improvement was also supported by the results of thermogravimetric and mechanical behavioral analyses.

Keywords: *Polyvinylchloride (PVC), Styrene acrylonitrile (SAN), Treated date palm tree leaves (TDPL), Mechanical behavioral analyses*

1. INTRODUCTION

Over the past few decades, fibers derived from plants, such as date palm [1], jute [2], and Aloe-vera [3], have garnered much research attention owing to their various economical, technical, and environmental benefits [4]. Natural fibers play important roles in quotidian life, with several uses in the construction sector [5]. Date palm tree leaves (DPL) represent a renewable, a nonabrasive, and an abundant source in not only the Algerian oasis agriculture but also all Saharan countries in northern Africa [6]. These natural fibers have low specific weight and cost yet show comparable strength and hardness to synthetic fibers, offering excellent mechanical characteristics [7]. Indeed, this natural resource can be turned into a value-added product through the manufacture of composites with various plastic materials. As such, DPL may be an interesting and eco-friendly alternative for use as a synthetic filler or reinforcement in advanced composites [8].Various plastic materials in the form of waste at landfill sites lead to environmental pollution [9]. Recycling is one of the simplest approaches to minimize pollution [10]. However, the behavior and properties of the recycled materials are poor, due to low compatibility and adhesion among various plastic materials [11]. Specifically, immiscible polymer blends often exhibit inferior thermal and mechanical properties to neat polymers [12]. Melt blending is one of the most frequently used processes for mixing plastic materials that contain a percentage of polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC) [13–15].

A remarkable strategy to overcome the drawbacks of compatibility and adhesion is the introduction of small quantities of a third component used as a compatibilization agent, which serves as the bridge linking the polymer–polymer interfaces for blend compatibilization, and/or bio-reinforcement to the polymer matrix [16,17], which may markedly alter the mechanical characteristics of the polymer blends. In this regard, styrene acrylonitrile copolymer (SAN), polyethylene-graft-maleic anhydride (PE-g-MAH) [18] and styrene-ethylene-butylene-styrene-graft-maleic anhydride (SEBS-g-MA) [19] have been used to improve the interfacial compatibility of polymer blends and composite systems [20].

Recently, green composites have attracted much attention and have found numerous applications, thanks to their improved mechanical, morphological,

and thermal properties [21]. To fabricate good green composites, it is important to enhance the bonding adhesion among plastic polymer blends and natural fibers [22]. Another important strategy for improving the behavior of green composites is to enhance the compatibility between the natural reinforcement and polymer matrices. Alkaline modification has been frequently applied to enhance the interfacial bonding as well as the bonding between the matrix and fibers by reducing non-cellulosic parts, leading to the significant improvement of fiber surface [23]. To this end, the objective of the present study was to fabricate a green composite using PVC reinforced with untreated or treated DPL, SAN copolymer, and low-density polyethylene (LDPE) via melt blending extrusion. Furthermore, different behaviors of the fabricated green composites were investigated.

2. EXPERIMENTAL

Raw materials

LDPE pellets (melting point = 129°C, the specific enthalpy of melting = 106 J/g) and PVC 4000 M with a K value 67- 72, and Bis (2-ethylhexyl) terephthalate (DOP) were supplied by the "National Petrochemical Company (ENIP)" in Skikda, Algeria. Ca/Zn stearate was purchased from Nanjing OMYA Fine Chemical Ind. Co. Ltd. (Nanjing China). SAN copolymer with acrylonitrile (AN) content of 32 wt.%, sodium hydroxide (NaOH) and acetic acid (CH3COOH), were purchased from Sigma Aldrich, France. Date palm tree leaves, were collected from the local Sidi-Okba oasis of southern Algeria.

Preparation of DPL samples

Extraction procedure of the DPL: In this study, the collected DPL were immersed into a big glass beaker filled with deionized water at 75 °C for 2 h to remove the dust, wax and impurities. DPL were dried by sunshine in 5 days. These dried DPL were crushed by a coffee blender and sieved into different particle sizes (<1mm).

Alkali modification of the DPL: Pre-treatment was conducted by soaking the DPL in a 2L glass beaker filled with NaOH solution (5 %. wt.) for 1 h at 80°C. Finally, the sample was fully washed with deionized water and then neutralized with the acetic acid solution. The TDPL were then filtered and dried at 60 ° C for 2 days.

Preparation of the DPTL/PVC/SAN/LDPE composites

The PVC with (5%. wt. of Ca/Zn and 20%. wt of DOP), SAN and LDPE were added slowly at the same time in a laboratory twin screw extruder, with a processing temperature ranging from 165°C and a speed of 60 rpm. The temperature of the melt blending was increased to 170° C to make a homogenous blend. Dried DPTL was added slowly to this polymer blend during melt mixing. The composite sample was cooled to room temperature and ground using Grind Machine. The composite samples were obtained using the compression molding press at 170° C under a pressure of 200 bar for 5 min. The sample code and designation of the composites are presented in Table 1.

Table 1. The sample code and designation of the blends and composites

Sample code	Designation				
	PVC	SAN	LDPE	DPL (phr)	
	(phr)	(phr)	(phr)	Untreated	Treated
BC0	20	-	80	-	-
BC1	20	10	80	-	-
BC2	20	10	80	10	
BC3	20	10	80		10
BC4	20	10	80	30	-
BC5	20	10	80	-	30

3. CHARACTERIZATION

Morphological properties: Fracture Surfaces of the blend and composites were prepared by liquid nitrogen freezing before being manually broken down., thin gold coating. Images were recorded with an SEM, model JEOL JSM-6031.

Thermogravimetric analysis (TGA): Thermal decomposition of the blend and composites were performed on a thermogravimetric analyzer (TGA/ DSC STARE, Mettler Toledo/ TA Instruments) in the temperature range of 20 to 600°C at 10 °C/min heating rate under nitrogen atmosphere.

Mechanical tests: Tensile and flexural behaviors of the blend and composites were measured using an MTS Synergy RT1000 machine under ambient conditions. Tensile samples were tested according to ISO: 527-2 at a crosshead speed of 3 mm/min. Three-point flexural samples were conducted according to ISO:14125 at a crosshead displacement speed of 1.5 mm/min. At least five samples were tested for each formulation.

4. RESULTS AND DISCUSSION

Morphology of the PVC/SAN/LDPE composite: Figure 1 illustrates the fracture surface microtopography of the blends and composites containing 10 and 30 wt.% DPL at low and high magnifications. The voids in the BC1 blend matrix and BC2 composite can be observed in Figure 1. The interface between the raw DPL fibers and the PVC/SAN/LDPE blend matrix was poorly bonded, and the raw DPL fibers did not adhere to the PVC/SAN/LDPE blend matrix due to numerous impurities distributed on the DPL surface, in addition to the formation of lignin and wax layers. Moreover, there were no large interfacial gaps and voids in the BC3 and BC5 sections, indicating that the alkaline treatment of DPL could strengthen the interfacial bonding in the composite system, potentially improving its mechanical properties Bessa et al [24]. This improvement of compatibility resulted from the reduction of hemicellulose and lignin content due to alkalization. Meanwhile, the compact structure also prevented the dispersion of water molecules and reduced water uptake of the composites.

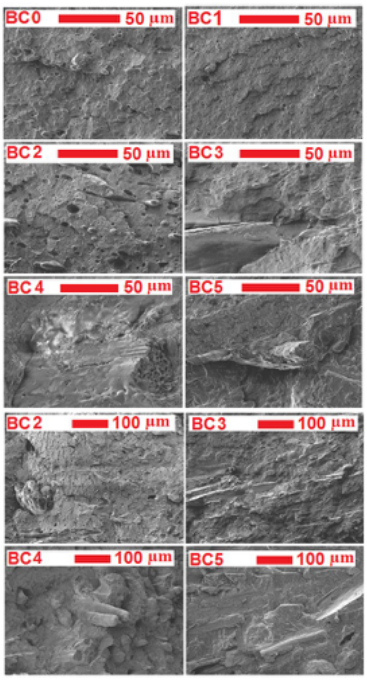
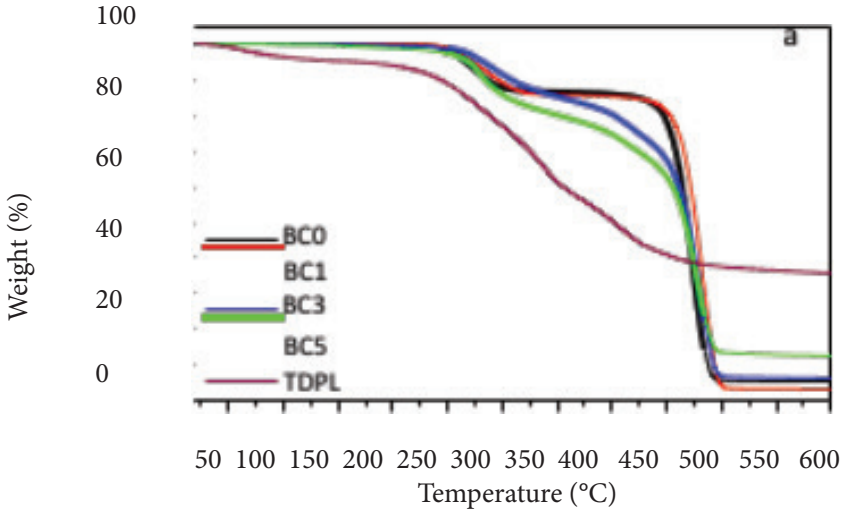


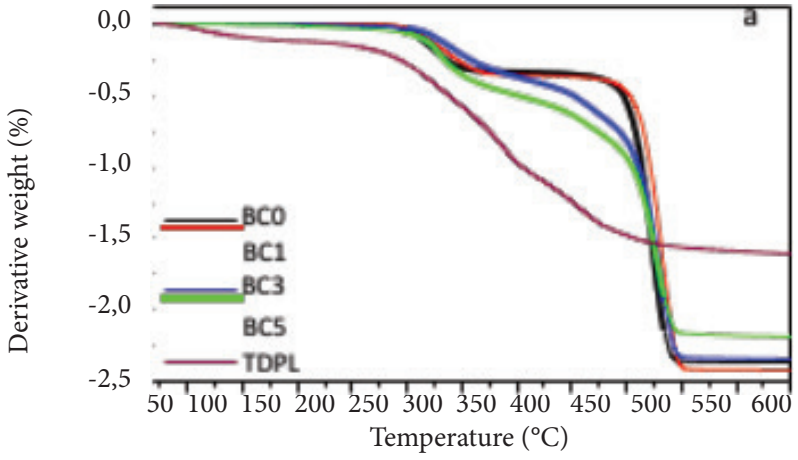
Figure 1. SEM micrographs of the PVC/SAN/LDPE blend and composites.

Thermal properties of the PVC/SAN/LDPE composite:

The blends and composites showed similar thermal degradation patterns (see Figure 2a-b); as such, thermal decomposition occurred in two stages between 239°C and 299°C for the former and between 300.05°C and 500°C for the latter. The values of the first decomposition temperature (T5%); decomposition temperatures for 10%, 20%, and 50% weight loss; and decomposition temperature for the maximum weight loss (Tmax) obtained from the derivative thermogravimetric curves are presented in Table 2. The BC0 blend underwent thermal degradation at the T5% value of 279°C, and the BC1, BC3, and BC5 composites and the DPL fibers underwent thermal degradation at the T5% values of 298°C, 291°C, 273°C, and 243°C, respectively. The introduction of SAN polymer into the PVC/LDPE blend did not alter the decomposition pattern but significantly enhanced the thermal stability and increased Tmax toward the highest value for thew blend matrix. Therefore, SAN copolymer altered the maximum weight loss decomposition behavior and improved the thermal stability of the PVC/ LDPE blend.

The TGA curve of the TDPL showed an initial weight loss between 50 and 110 °C associated with the removal of water and all almost primary volatile components. The degradation of alkali modified DPL showed only one step at about 310 °C which corresponded to cellulose and hemicellulose degradation since most of the lignin and residues were removed after alkaline modification. Comparing the BC3, BC5 composites with the B0 blend matrix, indicated that the composite underwent faster thermal degradation because of the presence of the fiber effect which composes the cellulose, hemicellulose, and lignin, and these latter compositions degrade over a wide range of different temperatures compared to the blend matrix. The char yield is directly related to the potential flame retardation in polymers. This latter indicates that an increase of the lignocellulosic filler content can reduce the formation of combustible gases, lowering the thermal degradation exotherm and so hindering the thermal conductivity of the combustion processes. Similar observations were reported by Bessa et al. [24].


100
80
60
40
20
0
Weight (%)
a
BC0
BC1
BC3
BC5
TDPL
50 100 150 200 250 300 350 400 450 500 550 600
Temperature (°C)


0,0
-0,5
-1,0
-1,5
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-2,5
Derivative weight (%)
a
BC0
BC1
BC3
BC5
TDPL
50 100 150 200 250 300 350 400 450 500 550 600
Temperature (°C)

Table 2. The decomposition temperature of the blends and composites

Sample	T5% (°C)	T10% (°C)	T20% (°C)	T50% (°C)	Residue left (%)
BC0	244.84	284.76	449.12	467.77	3.88
BC1	253.26	298.91	454.84	477.54	3.23
BC3	264.53	310.22	403.28	471.65	6.57
BC5	261.05	286.98	348.16	469.57	12.92
TDPL	239.12	241.67	287.17	403.13	36.25

Mechanical properties of the PVC/SAN/LDPE composite: The tensile and flexural, hardness and elongation at break properties of the blends and composites containing 10wt.% and 30 wt.% DPL fibers are plotted in Figures (3-5). Alkaline modification can effectively improve the mechanical performance of the composites, especially the tensile and flexural modulus. Compared with the BC0 blend, the tensile and flexural strength of the BC1 blend were increased by 25.80 % and 9.89 %, respectively. The results show the influence of the SAN on the mechanical behaviors of the PVC/LDPE blend. The incorporation of the SAN into the PVC/LDPE blend promotes the phase dispersion of the PVC and LDPE and also improves the interfacial bonding. As a result, the SAN copolymer used here is compatible with PVC. A similar behaviors were also observed by Xu et al [25].

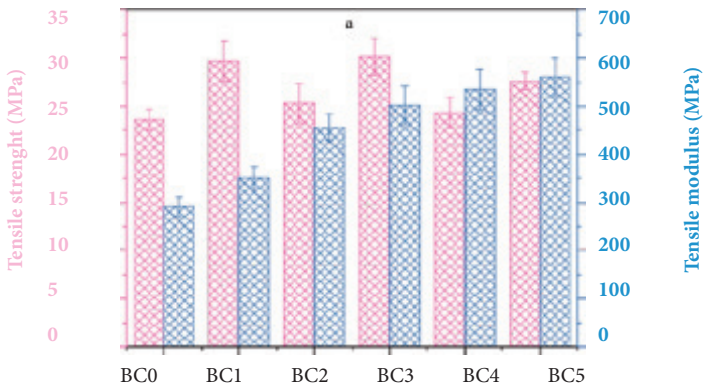

Figure 3. Tensile properties of the PVC/SAN/LDPE composites.

Figure 3 indicates that the alkali treatment has a greater influence on the tensile modulus of the TDPL than the raw DPL reinforced composite. The tensile modulus of the BC3(501.65 MPa) and BC5(560.24 MPa) composites are significantly different from that of BC2 (456.36 MPa) and BC4 (534.65 MPa), indicating that the use of the alkali treatment can effectively improve the interfacial bonding between the DPL fiber and the PVC/SAN/LDPE matrix. When the fiber loading was 30 wt.%, the tensile modulus of sample BC4 and Sample BC5 were 534.65 MPa and 560.24 MPa, respectively that of PVC/SAN/LDPE blend.Compared with the BC1 blend matrix in figure 4, the flexural modulus of the BC2, BC3, BC4, and BC5 were increased by 32.71%, 37.03%, and 64.30.5%, and 84.64 %, respectively. This result revealed that the SAN copolymer and TDPL strengthened the intermolecular interactions, thus increasing the hardness of the PVC/SAN/LDPE composite through crosslinking. The effect of the DPL content on the flexural modulus of the composite is obvious. When the TDPL fibers were used as a reinforcement, their flexural properties were superior to those of the composite using raw DPL fibers. As a result, the SAN copolymer works as a compatibilizer of the PVC/LDPE blend, and alkali solution can be used as an alternative to various treatments, which can effectively improve the interface compatibility during the preparation of the composite material.

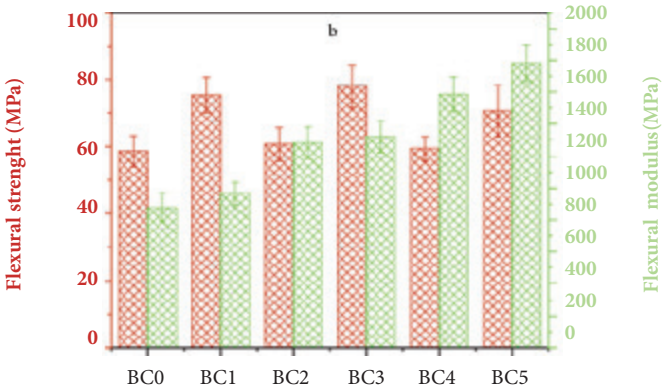

Figure 4. Flexural properties of the PVC/SAN/LDPE composites.

The hardness increases with an increase in TDPL content up to 30wt.% but decreases slightly in raw DPL reinforced composites at10 wt.%, 20 wt.%, and 30wt.%. The increase in raw DPL creates complications in its suitable blending. As shown in figure 5, a significant decrease of the elongation at break was observed with increasing DPL fibers concentration. The agglomeration of raw DPL fibers at higher loading leads to irregular agglomerate dispersions in the blend [23], which results in a decrease in surface resistance to the penetration. This latter affects the hardness and elongation at break results of the PVC/SAN/LDPE composites.

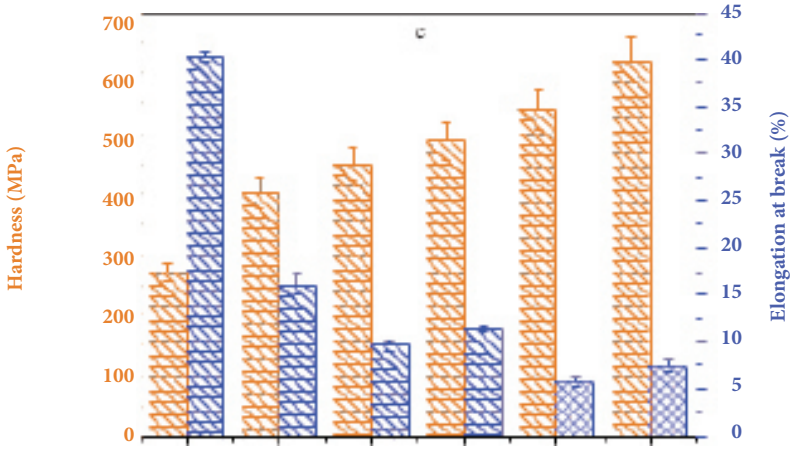

Figure 5. Hardness and elongation at break of the PVC/SAN/LDPE composites.

5. CONCLUSION

In the present work, the PVC/SAN/LDPE blend, DPL fibers reinforced composites were prepared. The results indicate that the addition of the SAN copolymer as a compatibilizer enhanced the thermophysical behaviors of the PVC/LDPE blend. The SAN copolymer helps the formation of chemical bonds between PVC and LDPE polymer, and the TDPL fibers enhanced the interfacial compatibility between the DPL and PVC/SAN/LDPE blend matrix. As a type of compatibility agent, the TDPL fibers and SAN copolymer provided a synergistic effect for preparing environmentally friendly PVC/SAN/LDPE composite with excellent thermophysical behavior.

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