



Study of the properties of thermoplastic composites filled with date palm waste

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Abstract : Green polymer composites were prepared by adding 5 wt% of treated date palm tree waste as a filler to linear low-density polyethylene (LLDPE) and polystyrene (PS) matrices. A green treatment was applied using a gum Arabic solution, after which the filler was characterized, and the rheological, thermal, and mechanical properties of the resulting composites were investigated. A comparison of the composites with the original polymers showed no changes in the Vicat softening temperature (VST). The differential scanning calorimetry (DSC) results of the PS composites showed similar results, while the DSC results of the LLDPE composites were quite different, especially for the fiber/LLDPE composites. The Young's modulus, tensile strength at break, and the elongation at break were affected by the addition of the filler.

Keywords : Date palm, Gum Arabic, Green composites.

Introduction

Polymer composite materials consist of a polymer, which named a matrix phase, reinforced by another material that named a filler. Polymer composites are commonly used in many applications such as automotive and furniture industries. However, they are difficult to dispose of which is a growing issue. Growing awareness of environmental issues has encouraged the use of natural materials as the reinforcing agents to produce green polymer composites to be a potential solution because they are economical, environmentally friendly, recyclable, biodegradable, and readily available. Previously published papers reported the development of green polymer composites using agricultural waste as natural materials; for example, sunflower husk [1], banana [2], baggage [2], groundnut shell [3], kenaf [4], jute [5] and sisal [2,6].

For environmental considerations and sustainability, utilizing renewable locally sourced natural materials is of great interest. In Saudi Arabia and most Arab countries, date palm trees (*Phoenix dactylifera* L.) are an important crop, and a large quantity of natural fiber from date palm is wasted each year. Upcycling of its waste for producing green polymer composites is very attractive economically and environmentally. Treatment of the filler surfaces is necessary process to improve the interfacial adhesion between the hydrophilic polar filler surface and nonpolar hydrophobic polymer,

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In previous studies, chemical treatment of the used parts of date palm to produce polymer composites have been reported [7-10].

This study aims to develop a green treatment process of the date palm waste surface, using a gum arabic solution as a natural treatment to prepare a green polymer composite and investigate their properties.

Experimental

Polystyrene (PS) and linear low-density polyethylene (LLDPE) were used as polymeric matrices. The polymers were supplied by the Saudi Basic Industries Corporation (SABIC). For the LLDPE, the series is 118 and grade is 118N. This grade is produced without any additives and is suitable for general purpose packaging. For PS, the brand name SABIC® PS325 was used, and is suitable for general use.

Two types of date palm wastes were used as fillers: leaflets and fibers (Figure 1(a)). The leaflets are the sharp needles of the date palm leaves, while the fiber is the brownish sheath that surrounds the tree trunk. Powdered date palm waste was used as the filler and the waste material was collected from a local farm in Saudi Arabia. The plant material was cut, pulverized, and sieved to particle size of $\leq 600 \mu\text{m}$.

The treatment process was performed by washing the desired amount of sieved powder with distilled water, followed by washing with gum arabic (GA) solution in an electric mixer. The mixture was subsequently sonicated, passed through a mesh, and dried for a few days under sunlight. The color of the fiber is dark brown, and the leaflet is reddish (Figure 1(b)).

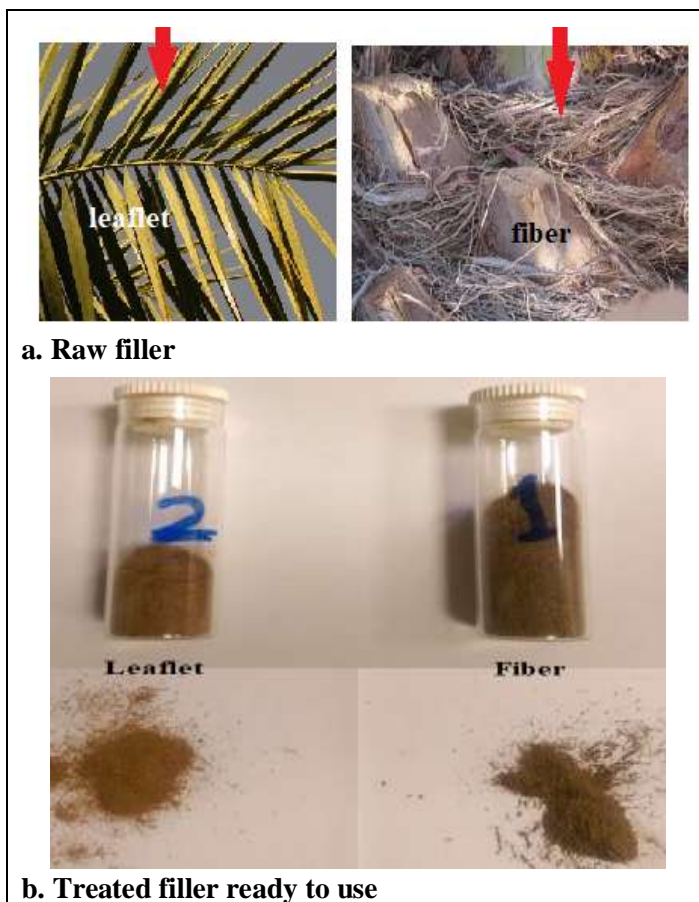


Figure 1. Fillers before (a) and after treatment and preparation (b).

The samples of the original polymers and their composites were prepared using a two-roll pressing machine at $190 \text{ }^\circ\text{C}$ to form of sheets with a thickness of 3 mm. The samples were labeled as follows: PE, PEf,

PEI, PS, PSf, and PSI for the LLDPE, LLDPE/fiber composite, LLDPE/ leaflet composite, PS, PS/fiber composite, and PS/leaflet composite, respectively.

Two techniques were used to characterize the treated and raw fillers. Fourier transform infrared (FT-IR) spectra were recorded from 400 to 4000 cm^{-1} using a Perkin-Elmer spectrophotometer. The samples were prepared as KBr pellets containing the powder samples. A scanning electron microscope (SEM, Quanta 250) was used to study the surface morphology of the filler powder.

The rheological, thermal, and mechanical properties of the prepared samples were investigated to study the effect of filler addition on the final properties of the composites by comparing these properties to those of the original polymers. The various properties were measured as follows:

- The viscosity at various shear rates was measured using a capillary rheometer.
- The tensile tests were performed using a Zwick/Roell tensile machine, following ASTM D 638. The test speed was 5 mm/min. The clamps used during the tests had a self-concentric alignment and were manually adjusted using mechanical springs. The grip to grip separation at the start position was 65.00 mm and the gage length at the standard travel distance was 25 mm. All tests were conducted at a room temperature (23 °C) and relative humidity of approximately 55%.
- The Vicat softening temperature (VST) was measured at a load of 10 N at 50 °C using a CEAST 6521 (CeastSpAPianezza, Italy) HDT Vicat tester. Thermal transitions were determined using differential scanning calorimetry (DSC, Q2000 V24.11 Build 124 Universal V4.5A TA instrument). A Fritsch grinder was used to prepare the powdered samples for DSC analysis. The weight of sample was approximately ≈ 2 mg, and the heating scan was performed to 200 °C.

Results and Discussion

Figure 2 shows the FT-IR spectra of the raw and treated fillers. Absorbance peaks of the raw fiber appeared at 3415, 2920, 2851, 1619, 1460, and 611 cm^{-1} , whereas for the raw leaflet the peaks at 3424, 2922, 2853, 1622, 1432, 1257, and 611 cm^{-1} . These bands were assigned to the OH stretching band of cellulose, CH stretching band of cellulose and hemicellulose, aromatic ring of lignin, C=O stretching band of lignin, and C–H out-of-plane of cellulose [11-14], respectively. After the treatment, no significant changes were observed except for the shifting of a few absorbance peaks presented in the figure

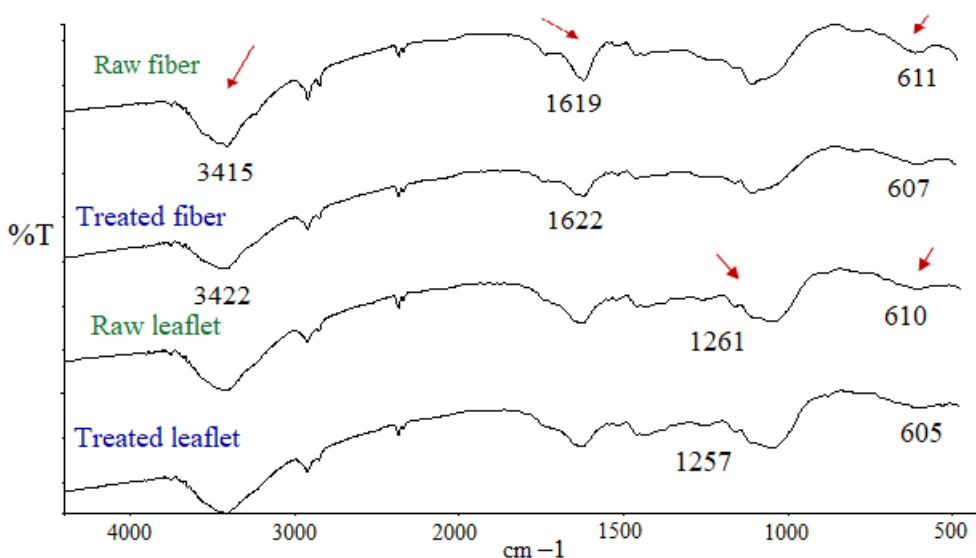


Figure 2. FT-IR spectra of raw and treated fillers.

Figure 3 shows the SEM images of the raw and treated filler. The surfaces of the leaflets became rougher after treatment because the surface was distorted in the form of large and deep cracks. Distortion in the fiber surface after treatment can also be seen; these distortions manifest themselves in the form of large, deep cracks (Figure 3(a) and 3(b)). These surface defects could act as active sites and provide binding sites for the polymer chains. Furthermore, the particles of the treated fillers varied in size and exhibited irregular shapes. These factors could influence their distribution throughout the polymeric matrix, adhesion between these particles and the polymer, and, consequently, the final properties of the composites (Figure 3(c)).

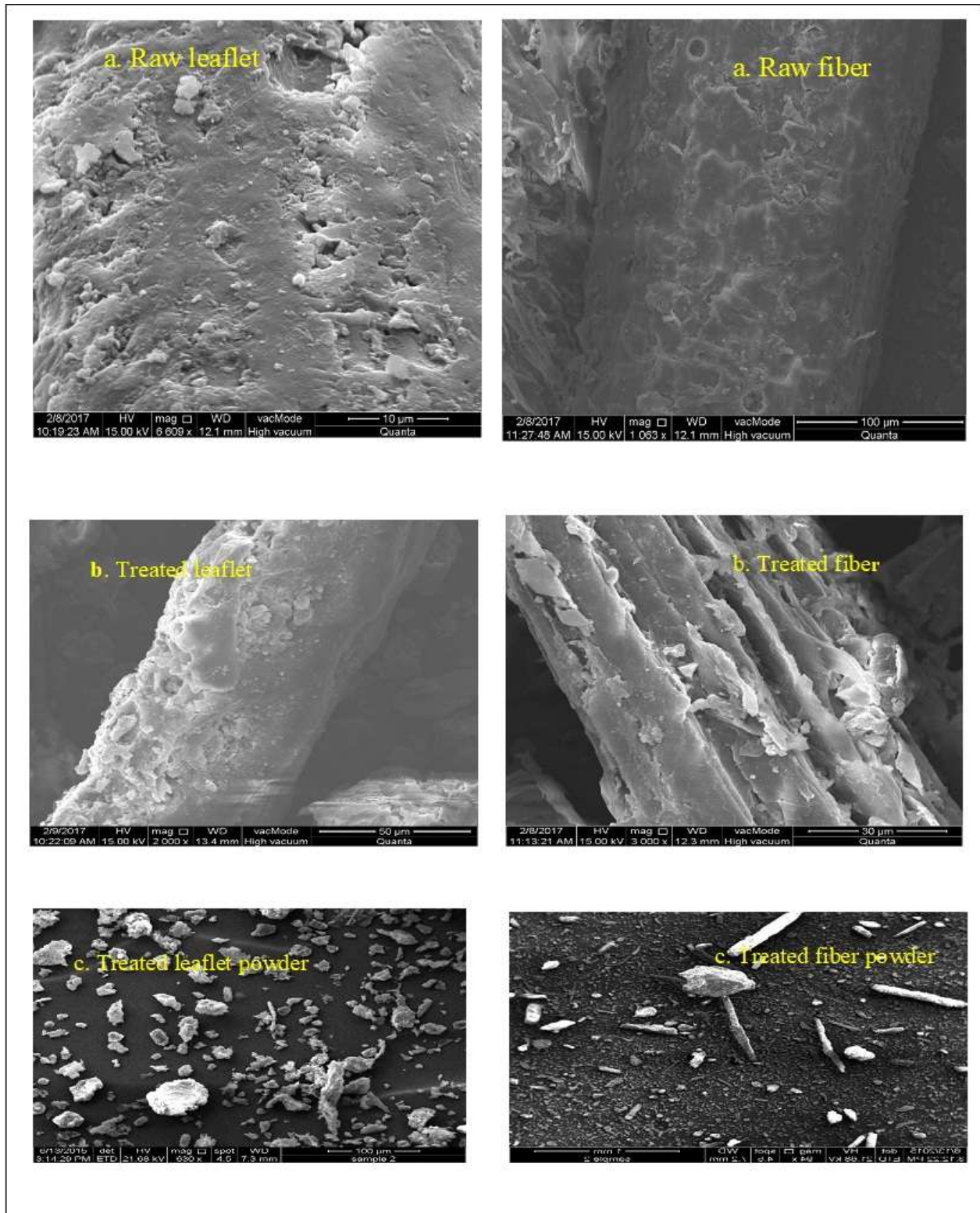


Figure 3. SEM images of raw and treated fillers.

The rheological properties were studied in terms of viscosity. Figure 4(a)–(c) show the plots of the viscosity as a function of shear rate for the original polymers and the prepared composites. Overall, the viscosity decreases with increasing shear rate, indicating non-Newtonian viscosity [15,16]. Comparing PEf with PE, a considerable increase in the viscosity of PEf was observed at low shear rates ($10 - 10^2 \text{ s}^{-1}$) because the presence of the fiber fillers may hinder chain segment movement in the melt flow [17]. However, as the shear rate increased, the viscosity continued to decline, likely because the filler particles slide within the polymeric matrix, which is caused by polymer flow orienting the particles in the flow direction. Comparing PEI with PE, the viscosity decreased at low shear rates then became similar at high shear rates. This is likely because the non-Newtonian behavior increased at low shear rates after adding the filler particles, but the contribution of the polymeric matrix overcame the effects of the filler with increasing shear, leading to decreased viscosity (Figure 4 (a) and (b)).

For PS and its composites, as shown in Figure 4(c), no significant changes in the viscosity of PSf was observed compared to PS, although the viscosity increased slightly in the PSf. This suggested insufficient filler loading (5 wt%) which affected the mobility of the polymer chains[15].

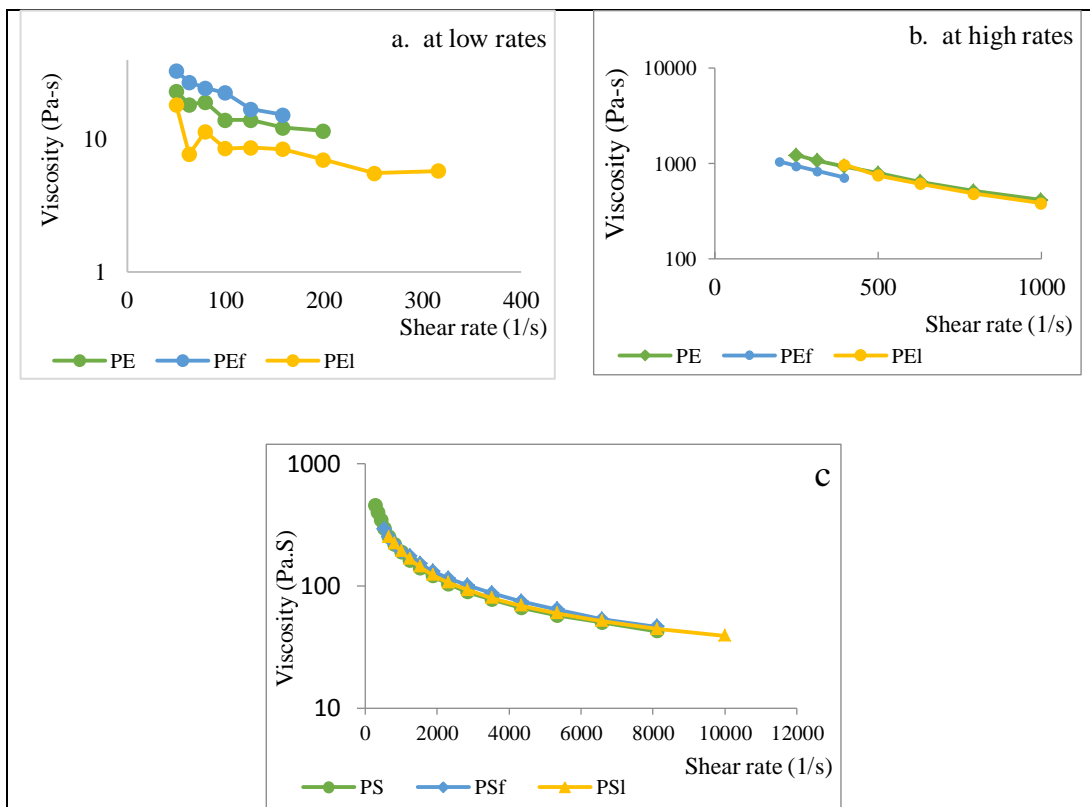


Figure 4. Viscosity versus shear rate of the original polymers and their composites.

Figure 5 shows the results of the mechanical properties in terms the tensile strength at yield, tensile strength at break, elongation at yield, elongation at break, and Young's modulus. Overall, a considerable reduction in the elongation at break was observed for all composites (PEf, PEI, PSf, and PSI), especially for PEf and PEI, compared to the original polymer. A similar trend in the tensile strength at break was observed for the PEf, PEI, and PSI composites, whereas a negligible decrease for the PSf sample was apparent. In contrast, a significant increase was recorded in the Young's modulus of all composites. Neither the elongation at yield nor tensile strength at yield were recorded for the original LLDPE sample or its composites and are not shown. Negligible changes in the elongation at yield and tensile strength at yield for the PS composites compared to those of the PS sample were observed. The load is usually transferred from the matrix to the filler[18], making interfacial adhesion between the filler and polymer essential for affecting the mechanical properties. Many previous studies attribute the reduction in tensile strength to poor adhesion between the filler and polymer [10]. Although this factor could be controlled by treating the surfaces of the filler particles[18,19], many other factors must be considered to explain the results mentioned above. Irregular particle size and shapes of the filler

particles, as observed in SEM images, negatively contributed to the random distribution throughout the polymer matrix, causing voids, formation of cracks [17,18] and poor adhesion. Improper loading of the filler is another important factor [17,18]; besides, the processing parameters as reported by Kutty and Nando“Processing parameters like nip gap, friction ratio and mill roll temperature have a profound influence on the fiber orientation and hence on the mechanical properties.” [20].Furthermore, differences in the behaviors of the LLDPE and PS composites can be attributed to the nature of the polymer itself, whereas differences in the mechanical properties between the leaflet filled polymer composites and fiber filled polymer composites can be attributed to differences in the components of the cellulose content.



Figure 5. Mechanical properties of the original polymers and their composites.

The thermal properties of the tested materials are shown in Figures 6–8. Figure 6 shows the Vicat softening temperature (VST) values of the original polymers and their composites. The VST did not change with addition of the filler, whether fiber or leaflet, suggesting insufficient loading of the filler to cause changes in the VST.

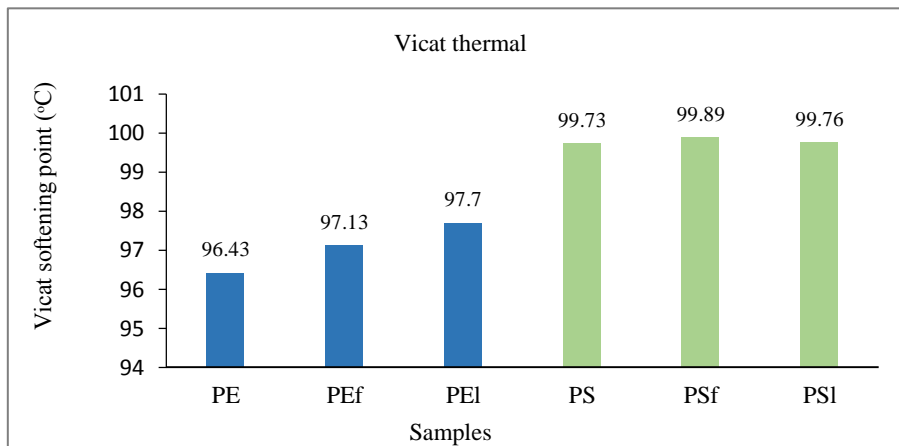


Figure 6. Vicat thermal of the original polymers and their composites.

Figure 7 shows the differential scanning calorimetry (DSC) thermograms of the LLDPE sample and its composites. The DSC curve of PE contains two peaks; a melting endothermic peak at 120.28 °C with an enthalpy of melting (ΔH_m) of 114.4 J/g and exothermal transition at 105.09 °C with an enthalpy (ΔH_c) of 111.5 J/g. The first peak shifted slightly towards lower temperature by approximately 1 °C in the DSC curve of the PEI sample (119.7 °C), associated with a sharp drop in ΔH_m (103.7 J/g). In addition, a shift towards higher temperature by approximately 5 °C was observed in the PEf sample, (125.20 °C), associated with a sharp increase in ΔH_m (179.5 J/g). This indicates that the PEf sample is more thermally stable than the unfilled PE polymer. The second peak of PE can be attributed to the crystallization of the polymer. This peak remained unaffected after addition of the leaflet particles as a filler of the PEI sample with a decreasing ΔH_c value by approximately 29 J/g. This is in contrast to the PEf sample whose peak increased (112.03 °C), associated with a considerable increase in ΔH_c (190.5 J/g). The increase in ΔH_c of the PEf sample indicates that its crystallinity increased with the addition of the fibrous filler, wherein the fibers acted as nucleating agents during crystal growth. A similar process was observed in a previous study regarding vetiver fibers where they acted as a nucleation agent during the nucleation stage [17].

Figure 8 shows the DSC curves for PS and its composites. As shown in the PS curve, a single peak at 98.80 °C was observed and can be attributed to the glass transition temperature. This peak shifted to 100.08 °C and 100.20 °C in the PSf and PSI samples, respectively. These peak shifts suggest that the fillers do not affect the thermal stability of PS.

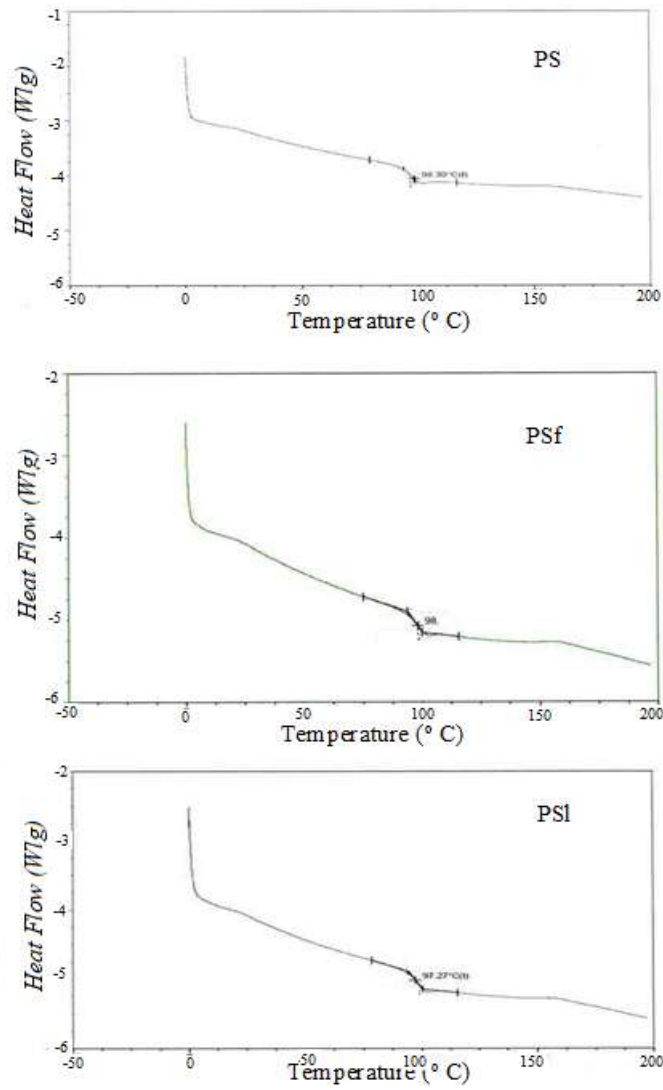


Figure 7. DSC thermogram of the original LLDPE and its composites.

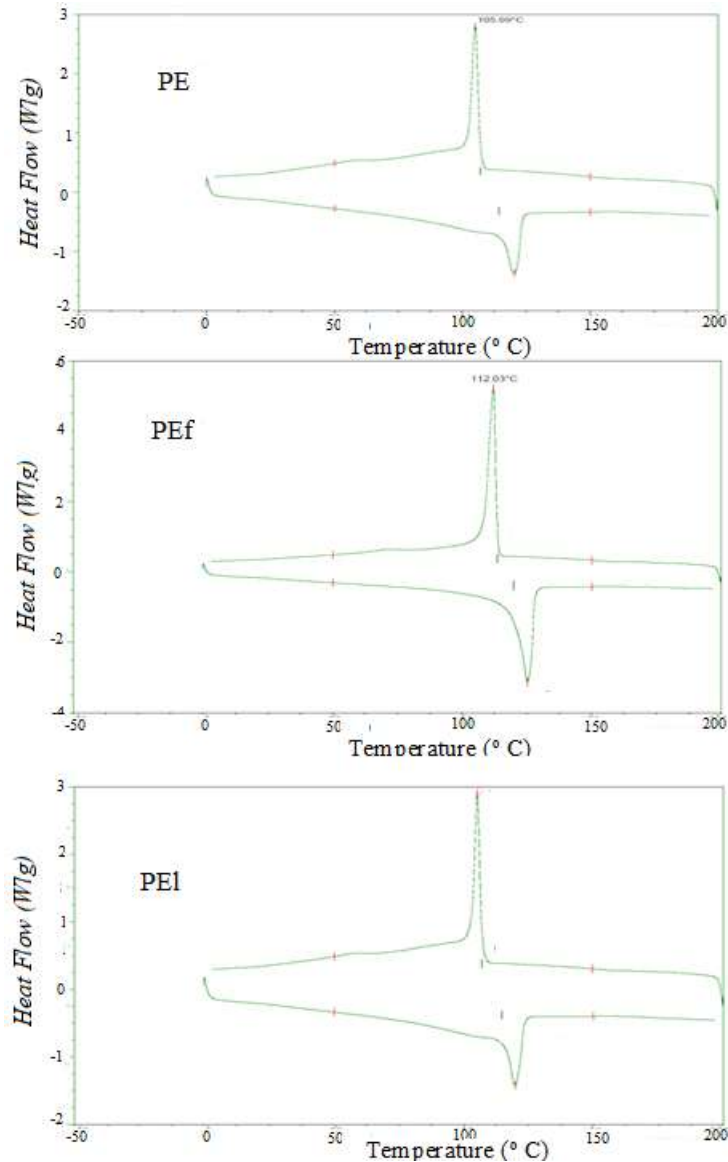


Figure 8. DSC termogram of the original PS and its composites.

Conclusion

Date palm waste was treated naturally with GA solution for use as a filler in the preparation of green composites of LLDPE and PS. Comparing the rheological, thermal, and mechanical properties of the resulting composites with the original polymer samples, the following could be concluded:

- The effect on viscosity depended on the polymer and filler type.
- No significant change was observed in the VST of the composites of both polymers.
- DSC analysis of the PS composites showed negligible changes compared to the original polymer, while the DSC analysis for the LLDPE composites showed that these materials were affected by filler addition.
- The Young's modulus, tensile strength at break, and elongation at break were affected by filler addition.
- In terms of the effect of filler type, differences between the leaflet and fiber fillers were observed because of the differences in the cellulose content of these materials.

Further studies are required for additional variables, such as treatment conditions, filler loading, and other properties of composite systems such as degradable properties to obtain a clearer picture concerning the best conditions to prepare composites for various applications.

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