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Polypropylene and some Esterified Plants' Fibers Bio-based Composites

Eiman M. Eltyeb, Abuelgasim A. A. Mohammed, and Nawal M. Suleman*

Department of Chemistry, Faculty of Education, University of Khartoum, Omdurman, Sudan.

*Corresponding Author: nawal.mahgoub@uof k.edu

Abstract

This study aimed to synthesize bio-based composites from polypropylene and some esterified plants' fibers extracted from khimp *(leptadenia pyrotechnica*) as well as leaves, and fibers of the date palm tree (*Phoenix dactylifera* L.). 24 composites in form of sheets were synthesized by injection molding technique using a modified manually operated injection molding machine. A mixture of xylene / toluene (1:1) was added to composites matrices. Properties like density, melting range temperature, melt flow rate, molecular weight, melt viscosity and water absorption capacity were determined for each synthetic composite. The study employed ordinary laboratory tools. Specifications have been selected to give MFR values between 0.15 and 25. The study proved that the synthesized composites are of good process ability, physical and thermal properties and have more densities than polypropylene itself.

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INTRODUCTION

Polymers are fundamental part of the modern world, used in everything from coffee cups to cars to clothing. In medicine, too, their importance is growing for purposes as diverse as cardiac pacemakers, artificial heart valves, and biodegradable sutures [1]. Recently synthetic thermoplastics are considered to be important starting materials for industry; due to their characteristic features. However, they have negative impact on the environment including a challenge to wastewater treatment and pollution of groundwater and surface water. Synthetic polymers are recognized as major solid waste environmental pollutants. Another problem is disposal of agricultural plastic wastes [2-4]. To provide greener environment there is a greater need for sustainable technologies and more friendly alternatives [5]. The environmental, safety and economic challenges required the alternation of petrochemical based polymers with bio-based ones [6,7]. Due to its properties such as high impact strength, high tensile strength, good chemical resistance, low density (0.92 g/cm^3), and also rather low cost, polypropylene is used widely in industrial applications. Recently, progresses in improving polypropylene composites: materials have widened remarkably the demands for new applications of this material. However, treatment of a large quantity of waste polypropylene issued from industrial processing, agricultural activities, and household garbage, create a new situation with many opportunities for the searchers [8]. Composite is the term used to describe light, durable and astonishingly tough constructional material, consists of two components at least these being a synthetic resin and a strong fiber [9]. Plants fibers have many advantages over synthetic fibers such as low cost, low density (1.4 cm^3), suitable stiffness and mechanical properties and also high disposability, renewability and biodegradability [10-12]. The future need for natural fibers is predicted to increase both in historic and in new applications [13]. Natural fibers such as cellulose nanoparticles extracted from kenaf and bamboo fibers have been extensively used to produce biodegradable composites depending on their properties [14-16]. But the cost of fiber reinforced polymers is the killer disadvantage in almost all cases [17]. The main objective of this study is synthesis and characterization of bio-based composites from polypropylene and esterified plant's fibers from khimp and date palm tree.

MATERIALS AND METHODS

Materials

Plants' samples (Khimp, leaves and fibers of date palm tree) were collected from their local areas in

Sudan. Crude fibers extracted previously by differential extraction method, and esterified with citric and adipic acids. All chemicals used are of analytical grade. Poly propylene (9003-07-0, Sigma-Aldrich), bentonite clay (from India Mart), (citric acid, adipic acid, ethanol, sulfuric acid, acetic anhydride sodium hydroxide and hydrochloric acid) (from BDH, India). Toluene (108-88-3, Sigma-Aldrich) and Xylene (1330-20-7, Sigma-Aldrich).

Preparation of composites

Composites were prepared by injection molding technique where the compositions of polypropylene in the range (75 to 90 wt%) and esterified fibers were varied in the range from 10 to 25 wt%. A technique that developed by Joseph [18] was modified; the esterified fiber was mixed with a viscos slurry of polypropylene in toluene/xylene mixture (1:1 ratio). The slurry was prepared by adding 40 mL toluene/xylene mixture to the polypropylene (the weight of polypropylene was differed according to the range) and heating at 120 °C, then the esterified fiber was added and the matrix was subjected to the manually operated injection molding machine. Composites sheets (in circle shape) with dimension (101.6 mm x 2 mm) were prepared. Other composites were synthesized by the same procedure with polypropylene in the range (75 to 90 wt%) as well as esterified fibers were varied in the range from 10% to 20% and clay amount was fixed at 5 wt%.

Characterization of composites

Density

According to ASTM D792-91. Using test method A in which a previously weighted composite sample added in a measuring cylinder containing distilled water and the volume of composite sample determined [19].

Melting points

Melting point for each composite was determined using melting point apparatus. The test carried out according to ISO 3146:2000, Method A [20].

Melt flow rate (MFR)

The melt flow rate was determined according to the national standard methods. Temperature range (125-300 °C) and different applied dead loads from 0.0325 to 21.6 kg giving pressures from 0.46 to 30.4 kg/cm^2. Specifications have been selected in such a way to give MFR values between 0.15 and 25 for reliable results [20].

Melt viscosity

Calculated from the melt flow rate.

Molecular weight

Determined from melt flow rate [21].

Water immersion test:

The composite sample was immersed in 100 mL distilled water for 24 hours. The sample weight before (m_o) and after 24 hours of immersion (m) were recorded [22].

RESULTS AND DISCUSSION

Preparation of composites

Plants' fibers are renewable, inexpensive, completely or partially recyclable and biodegradable. In natural fiber composite materials, natural fibers are used as reinforcing agents [23]. According to literature review, Arutun [24], microorganisms produce enzymes that more easily digest aliphatic polyesters derived from 6–12-carbon di-acid monomers than those produced from other monomers and for this reason citric and adipic acids were used as esterification agents in this study. The injection molding technique used in the synthesis of the target composites was very simple (**Figure** 1.) Addition of toluene/xylene mixture decreased the melting point of polypropylene from 230 to 120 °C and this was very important decreasing due to the permeability of addition of the esterified fiber; if this mixture not used; the esterified fiber can ever never be suiting the melting point of the polypropylene. The amount of polypropylene, esterified fiber and bentonite (in some composites) were presented in **Tables** 1 to 4. The synthetic composites were presented in **Figures** 2 to 5.

Characterization of composites

Density

The test sample should be a single piece of the material under the test of any size and shape that can conveniently be prepared and tested, provided that its volume shall be not less than 1 cm^3 and its surface and edges shall be made smooth. The thickness of the sample should be at least 1 mm for each 1 g of weight. A specimen weighing 1 to 5 g usually will be found convenient. According to these criteria stated by the Annual Book of ASTM Standards, Vol 14.02. The thickness of the tested samples was 2 mm and the weight was 3 g. (**Table** 5). Portions of a sample may differ in density because of difference in crystallinity, thermal history, porosity, and composition (types or proportions of resin, plasticizer, pigment, or filler) [4]. This statement can clarify the difference among densities of the synthetic composites. In composites synthesized from sample one (esterified by adipic acid)

the densities increased gradually by increasing the esterified fiber content but this observation was not fixed for other composites. In presence of bentonite as filler the density increased and decreased randomly for the same reason. It can conclude that filled or reinforced grades of polypropylene have significantly higher density depending on their formulation and this in agreement with a previous study [25].

Melting range temperature

The melting range temperature of 24 composites has been determined experimentally by ISO 3146:2000, Method A [20]. The resulted melts for all composites under study were thick liquids; A melting range of 5 °C or more indicates that a compound is impure (as in case of composites under study which contain more than one component) [26].

Melt flow rate (MFR)

In agreement with ASTM D1238 criteria stated by Aron Sh. and Saini D.R. part I, 1986; MFR was determined for all composites using the melting range temperature for each of them (illustrated in **Table** 5) with dead load 2.16. It considered reliable results. Despite the fact that MFR is generally considered as a measure of the rheological behavior and process ability of the polymers, it has been shown over the years to correlate with final product properties (**Table** 6).

Melt viscosity

The Melt flow rate is a measure of the viscosity of the plastic material when exposed to heat above the melting temperature. The relationship for long-chain branched samples were fitted by a straight line given as:

$$[\eta] : 0.996 - 0.189 \log MFR \quad (1)$$

Where:
[ŋ] : Melt viscosity
MFR : Melt flow rate

Average molecular weight

As the melt flow rates for all composites were determined by the equation described by dark:

$$\text{Log (MFR)} = (0.454 \times 10.5)\, M_w - 0.12713 \quad (2)$$

Where:
M^-_w : Average molecular weight

Average molecular weights for 24 synthetic composites under investigation were calculated.

Water immersion test

The synthetic composites were insoluble in water. However; water immersion test demonstrate that all composites absorbed amount of water over time. Water absorption capacity (WA) was determined according to the equation described by Rasika. L. K. N. et.al. [22] as follow:

$$WA\ (\%) = [(m - m_o) / m_o] \times 100 \quad (3)$$

Where:

WA (%) : water absorption capacity.
m_o : weight of dry sample; and
m : weight of sample after immersion in distilled water for 24 hours.

Figures (6-9) represent the water absorption capacities for 24 composites under study.

Figure 1. A Modified Manually Operated Injection Molding Machine.

Table 1. Composites prepared from sample one (khimp) fiber esterified by adipic acid.

Entity code	Polypropylene (g)	Esterified fiber (g)	Bentonite (clay) (g)
1- a	18	2	-
1- b	17	3	-
1- c	16	4	-
1- g	17	2	1
1- h	16	3	1
1- i	15	4	1

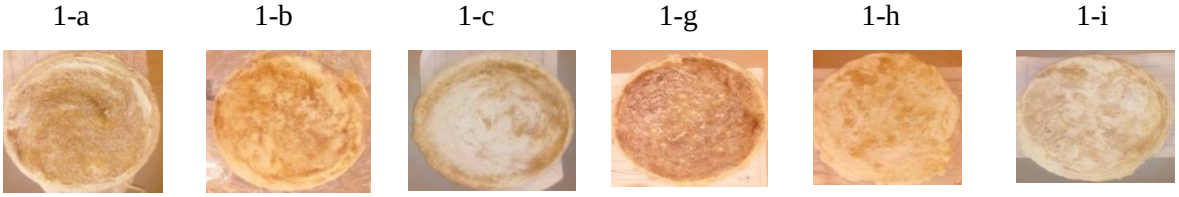

Figure 2. Composites prepared from sample one (khimp) fiber esterified by adipic acid.

Table 2. Composites prepared from sample one (khimp) fiber esterified by Citric acid.

Entity code	Polypropylene (g)	Esterified fiber (g)	Bentonite (Clay)/ (g)
1- d	18	2	-
1- e	17	3	-
1- f	16	4	-
1- j	17	2	1
1- k	16	3	1
1- l	15	4	1

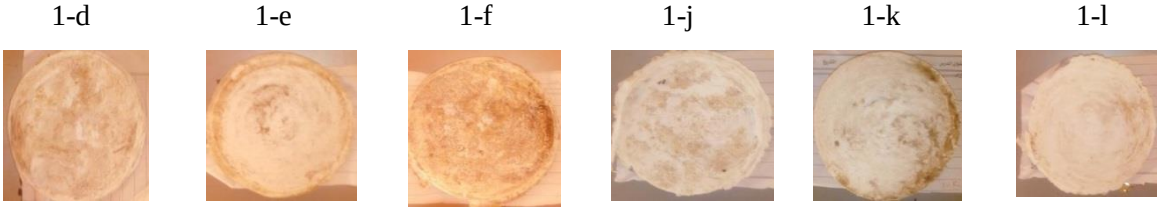

Figure: 3. Composites prepared from sample one (khimp) fiber esterified by adipic acid.

Table 3. Composites prepared from sample two (date palm leaves) fiber esterified by Citric acid.

Entity code	Polypropylene (g)	Esterified fiber (g)	Bentonite clay (g)
2- d	18	2	-
2- e	17	3	-
2- f	16	4	-
2- j	17	2	1
2- k	16	3	1
2- l	15	4	1

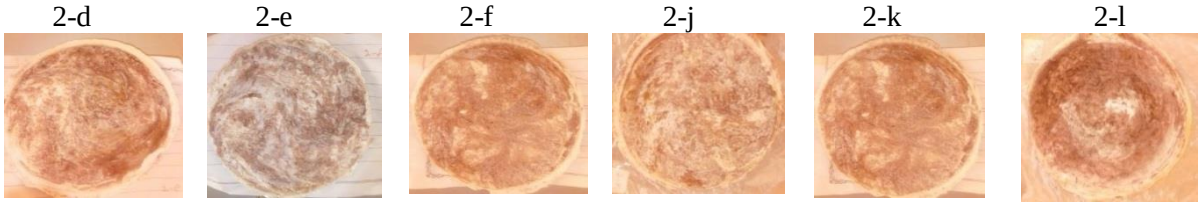

Figure 4. Composites prepared from sample two (date palm leaves) fiber esterified by citric acid.

Table 4. Composites prepared from sample three (fiber of date palm) fiber esterified by adipic acid.

Entity code	Polypropylene (g)	Esterified fiber (g)	Bentonite clay (g)
3-a	18	2	-
3- b	17	3	-
3- c	16	4	-
3- g	17	2	1
3- h	16	3	1
3- i	15	4	1

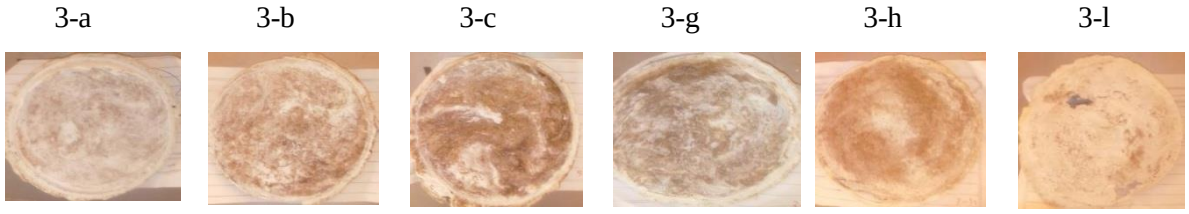

Figure 5. Composites prepared from sample three (fiber of date palm) fiber esterified by adipic acid

Table 5. Characteristics of 24 composites under investigation.

No	Composite entity code	Density (g/cm^3)	Melting range (°C)	Melt flow rate	Melt viscosity	M^-_w
1	1-a	1.100	173 – 178	13.75	0.781	2.6×10^5
2	1-b	1.288	170 – 176	7.53	0.830	1.9×10^5
3	1-c	1.318	167 – 175	10.31	0.805	2.2×10^5
4	1-d	1.094	170 – 191	12.23	0.791	2.4×10^5
5	1-e	1.468	169 – 196	11.60	0.795	2.3×10^5
6	1-f	0.950	167 – 198	11.05	0.799	2.3×10^5
7	1-g	1.060	165 – 188	10.92	0.800	2.3×10^5
8	1-h	1.110	160 – 185	6.87	0.840	1.8×10^5
9	1-i	0.960	158 – 180	3.01	0.906	1.1×10^5
10	1-j	1.580	163 – 190	21.17	0.745	2.9×10^5
11	1-k	1.220	160 – 189	8.14	0.824	2×10^5
12	1-l	1.040	160 – 174	9.17	0.814	2.1×10^5
13	2-d	0.900	175 – 180	11.20	0.798	2.3×10^5
14	2-e	1.320	180 – 190	10.07	0.806	2.2×10^5
15	2-f	0.980	177 – 184	9.10	0.785	2.1×10^5
16	2-j	1.110	173 – 176	11.24	0.780	2.3×10^5
17	2-k	1.400	170 – 180	12.64	0.758	2.4×10^5
18	2-l	1.180	168 – 180	9.47	0.812	2.1×10^5
19	3-a	1.370	180 – 184	11.72	0.794	2.4×10^5
20	3-b	1.380	178 – 185	11.01	0.800	2.3×10^5
21	3-c	1.000	176 – 185	5.80	0.852	1.7×10^5
22	3-g	1.000	175 – 190	8.70	0.820	2.1×10^5
23	3-h	1.010	173 – 190	2.30	0.920	0.8×10^5
24	3-i	1.00	170 – 185	8.90	0.787	2.1×10^5

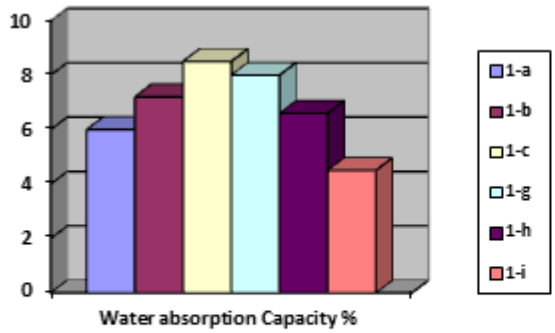

Figure 6. Composites Water Absorption Capacities of Sample 1 Esterified by Adipic Acid

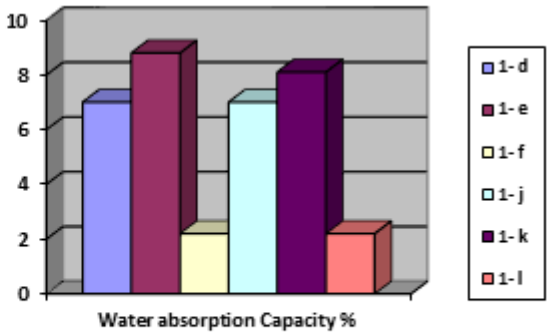

Figure 7. Composites Water Absorption Capacities of Sample 1. Esterified by Citric Acid

Table 6. Product properties affected by an increase in the melt flow rate.

Property	Effect
Tensile strength	Slight decrease
Yield stress	Slight decrease
Rigidity/stiffness	Slight decrease
Toughness	Slight decrease
Modulus of elasticity	Slight decrease
Creep resistance	Slight decrease
Hardness	Slight decrease
Impact strength	pronounced decrease
Resistance to low temperatures	pronounced decrease
Solubility and swell ability	Slight increase
Permeability	Slight increase
Resistance to environmental stress cracking	Pronounced decrease

CONCLUSION

Synthesis of bio-based composites is consider to be a hot research area in order to minimize plastic waste and for this reason this study was conducted. Heterogeneous esterification of the extracted plants' fibers was modified. Incompatibility of polypropylene melting point with melting points of esterified fibers (reinforcement agents) was avoided by adding xylene / toluene mixture. The manually operated injection molding machine was designed by our research team. Determination the MFR of all composites played a vital role in calculation of their molecular weights and melt viscosities, sample with code 1-j has the higher molecular weight. In agreement with the literature review; all synthetic composites have more densities than polypropylene itself. Composite with code 2-k consisted of 80% polypropylene, 15% fiber of date palm leaves esterified with citric acid and 5% of bentonite had the most water absorption capacity among the other composites.

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