Fabrication of Bio-Plastic Composite Pellets From Agricultural Waste And Food Waste

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Abstract - *This study aims to produce starch bioplastic pellets from food waste such as potato peels. Measuring the ease of flow of the melt is crucial for producing these pellets. The melt flow index (MFI) is measured in this study to evaluate the consistency of the produced pellets and determine the extent of degradation of the plastic because of molding. This study investigates the effect of adding different fillers to the starch matrix on reducing the MFI value. The fillers used in this work are nano chitosan, nano potato peel, and micro cellulose fillers. The fillers were used with different percentages (0.1%, 0.5%, and 1%). The study showed that increasing the percentage of filler reduces the MFI value. Nano chitosan filler had the highest reducing effect on the MFI value than the other fillers.*

Keywords — *MFI for starch bioplastic, Potato peels, Food wastes, Nano chitosan, Cellulose filler.*

I. INTRODUCTION

Biopolymers receive increasing attention from researchers as alternatives for petroleum-based polymers due to their environmentally friendly characteristics and biodegradability; starch-based bioplastics consider one of the most important types of biopolymers; they can be produced from different sources of starch such as, cassava, maize, and potato[1]. However, biopolymers should have comparable processing characteristics to replace petroleum-based polymers. Melt flow index (MFI) is considered a quick and economic indicator to measure the flow properties of polymers, thus identify the processing conditions [2]. MFI is highly affected by polymer physical properties and is used for polymer process quality control[3][4]. Although the higher values of MFI cause ease of melting and processing, they result in lower mechanical properties of composite produced parts. This is due to the lower dispersion of fillers in high viscous matrices. In addition, other processing problems would appear. For the polymers extrusion process, higher MFI would result in low sag resistance. On the other hand, better mechanical properties can be achieved from lower MFI values, with the expense of more energy needed for melting and processing. Therefore, an optimum value should be obtained[5][6]. For the same polymer, MFI varies with the polymer grade. Therefore, in the plastics industry, MFI is considered a very important parameter to determine the suitable polymer grade for a certain processing technique and application. For instance, compression molding for polymer processing usually

requires low MFI values, while injection molding needs a high MFI. Several grades of high-density polyethylene have an MFI ranging from 0.2- 3 gm/10min. While for Low-density polyethylene (LDPE), MFI ranges from 0.3-2.6 gm/10min [7]. Furthermore, the addition of fillers was reported to reduce MFI due to molecular motion restriction and flow resistance induced by the fillers. Hamzah et al. investigated the effect of several nanofillers on cross-linked polyethylene and found that organoclay filler has the highest MFI reduction among other fillers[8]. Likewise, MFI reduction was observed after using halloysite nanotubes as a filler with Low-density polyethylene [9], micro basalt particles were also incorporated in low-density polyethylene, and high-density polyethylene to decrease MFI [10], and graphite micro powder and carbon nanotubes were added to the polylactic acid polymer to decrease it's MFI [11].

On the other hand, micro and nano cellulose were added to cassava starch to form composite films with different percentages ranging between 0 to 2%. They had a noticeable effect on decreasing MFI [1]. Commercial micro cellulose was used as a filler to decrease MFI for food-grade corn starch. The starch and the micro cellulose with percentages from 0 to 1% were extruded and hot pressed for producing composite films[12]. Nanocellulose with various percentages (1,3,5,10,15%) was obtained from red cedar bark to be incorporated into regular corn starch for composite film fabrication [13]. Micro and nano cellulose were prepared from corn stalks and incorporated into starch for the same application as well [14]. Besides, micro cellulose was extracted from wood pulp and utilized for reinforcing potato starch foams [15]. Cellulose fibers were extracted from henequen fibers (with a percentage of 5 to 10%) and added to the poly lactic acid polymer and calcium carbonate into the commercial-grade of cassava starch to form foam composites[16]. Nano cellulose (0 to 1.5 %) was also utilized to reinforce corn starch foam[17]. However, the use of corn starch or cassava starch is not favored since they are considered a rich source of food. In this paper, starch is extracted from potato peels waste and used as a matrix to enrich the concept of valorization of waste. Potato peels are produced every year in large amounts. Therefore, they have been used for several applications like producing lactic acid and biofuels. In addition, they have been used for biopolymer applications. For instance, potato peels and sweet lime pomace were blended to form composite films[18][19]. Three different filters are incorporated with starch extracted from potato peels waste in this study. The fillers used are micro

cellulose extracted from cotton stalks, potato peel nanoparticles, and chitosan nanoparticles. Thus, this article investigates the effect of adding percentages of 0.1, 0.5, and 1% of micro and nanofillers on the MFI of the fabricated starch biocomposite pellets. It also emphasizes the enhanced effect of nanoparticles on decreasing the MFI of starch biocomposite pellets.

II. Materials and methods

Potato peels were used as raw material for starch and potato peel nanofiller. Cotton stalks and shrimp shells were used as starting materials for micro cellulose and chitosan fillers. Cotton stalks waste were purchased from a local farm in El-Minya governorate, Egypt. Shrimp shell waste was purchased from a local market in El-Obour city, Egypt. Glycerol (98%purified) was purchased from Loba Chemie. It was used as a plasticizer, and distilled water was used as a solvent. All the reagents used for the preparation of chitosan nanofiller and cotton stalks micro filler were supplied by Sigma-Aldrich; Hydrochloric acid (HCl, 35–38%), Sodium Hydroxide pellets (NaOH, pure), Acetic Acid (CH_3COOH, 99.9%), and sodium tripolyphosphate (sTPP). The natural polymer composite consists of the matrix (starch) and three different fillers: micro cellulose, nano chitosan, and nano potato peel.

A. Extraction of starch from potato peel waste

Potato peels were collected, cleaned, granulated by a home mix blender. They were soaked in water for [4-5] hr. afterward. The mixture was separated to remove the solid particles of potato peels, and the residual liquid was left until the starch particles participated, as shown in fig 1. The participated starch was washed several times. The starch was dried at 50 °C for 2.5 hr.[20]. 40g of starch was extracted from 800 g potato peels waste.

Fig 1: Extraction starch from potato peel

B. Preparation of chitosan nano filler

Shrimp shells were washed, cleaned, and heated at 110 °C. During heating, NaOH was added to remove the brownish color, then HCL was added several times until the demineralization (DM) occurs. Chitin was produced from this process. The chitin was cleaned with distilled water and allowed to dry at room temperature. Chitosan nanofiller was obtained from chitin by a deacetylation (DD) process. It was achieved by soaking the sample in 50% NaOH at 110 °C. The sample was washed repeatedly while the pH was neutralized and was left to dry at room temperature. 1 g of chitosan was dissolved into 2% acetic acid by making the solution stirring at 300 pm, followed by

adding 11 ml sTPP (0.033 g of sTPP into 100 ml water) to the solution of chitosan dropwise to produce chitosan nano filler[21][22].

C. Preparation of micro cellulose filler

22 g of cotton stalks (5 mm) were cut, as shown in fig 2a. They were shredded into small pieces of (1 to 4 mm) long and 1mm diameter using a home blender, as shown in fig 2b. Subsequently, warm water at 60°C was utilized for 2 hr. soaking for the small pieces. They have filtered afterward and dried in an oven for 2 hr. at 100°C and left at room temperature for 4 days. The weight of the residues was 17.7 g. An alkaline treatment process was then performed to remove hemicellulose and disrupt the lignin structure. The small pieces were treated with 12.5 wt.% NaOH for 2 hr. at 100°C. Afterward, they were washed to achieve neutral pH and dried in an oven for 1 hr. at 100 °C, and residues of 7.7 g were obtained as shown in fig 2c. HCL solution was utilized with a concentration of 3 Moles/Liter for 1 hr. at 90 °C and 500 rpm constant stirring. This was followed by washing to obtain neutral pH as well. Eventually, NaOH was applied with 2 wt. % for 2 hr. at 100 °C. Washing and drying in the oven for 1 hr. were carried out at the end of the alkaline process. A digital thermocouple was used to get feedback on the actual temperature in the solution and regulate the stirrer heating. Cellulose fibers were mixed with water in a beaker, and a homogenizer (CAT x120) was used for 20 min at [16000 to 22000] rpm to reduce the size of the cellulose fiber, as shown in fig 2d [1][2][3].
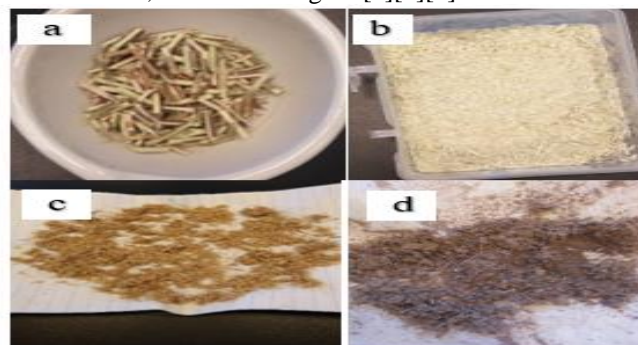

Fig 2: Extraction micro cellulose filler from cotton stalks

D. Preparation of potato peel nanofiller

Potato peels were washed, cleaned up, dried at 110 °C for 2 hr. They were ground by using a home grinder to obtain fine powder particles, as shown in fig 3 [19].

Fig 3: potato filler from potato peels

E. Preparation of bioplastic composite pellets

Starch bioplastic pellets were prepared at lab scale, the ratio of starch: glycerol: water was 40:30:30 (wt.%). Glycerol and water were dissolved at 40 °C[12] . Potato starch extracted from potato peels was added gradually and then mixed at [600-800] rpm with a magnetic stirrer for 2 hr. The mixture was poured in a Petri plate as shown in fig 4a and dried at 140-150 °Cfor 1.5 hr. as shown in fig 4b. After drying, the obtained paste was cut into small pieces, as illustrated in fig 4c, to perform the melt flow index test and measure the MFI for potato starch bioplastic. To study the effect of fillers on the flow characteristics of the composite, the starch bioplastic composite was prepared by adding the three different fillers with (0.1, 0.5, 1% wt. %starch) [23][24].
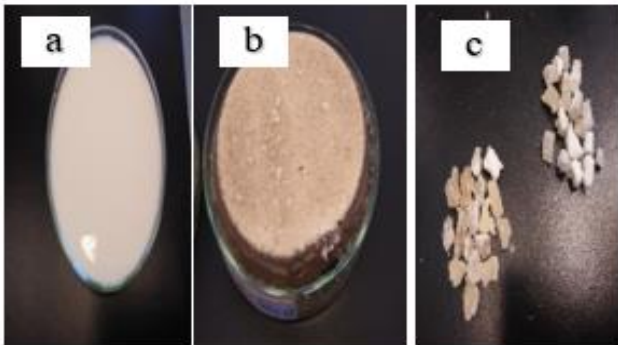

Fig 4: Starch bioplastics paste before and after drying

III. Characterization techniques

A. Melt flow index

The MFI for the prepared starch bioplastic composite was measured using (INSTRON MELT FLOW INDEX MACHINE NO 3210) highlighted in fig 5. The test was carried out at [190 °C, 2.16 kg][4]. Each sample was measured three consecutive times to ensure correct results.

Fig 5: Instron MFI machine

B. Scanning electron microscopy (SEM)

SEM was used to measure the dimension and size of the prepared micro cellulose filler. The particles of micro cellulose filler were glued into a holder using Tissue-Tek O.C.T.TM compound and then fell into the temperature of solid nitrogen under vacuum; they were coated and imaged.

C. Particle size analysis

The particle size of chitosan and potato peel nanofiller was measured using a nano trace wave II machine operating with traditional dynamic light scattering (DLS). The particles of chitosan and potato peels suspension at 4%(w/v) were watered down and ultra-sonicated in an ultrasonic bath, model USC-1400 (40 kHz of ultrasound frequency,135 W RMS power) for 30 min, the temperature condition was at 230 °C, and the used wavelength was 632.8 nm.

IV. Results and discussion

This study gives an initial insight for using micro cellulose, nano chitosan, and nano potato peel as fillers that are added to the starch bioplastic composite and their effect on flow characteristics. The MFI values are shown in Table I. The test was carried out with 0%, 0.1%,0.5% and 1% filler. The results demonstrate that the nanofillers have a higher effect on reducing MFI than the micro filler.

TABLE I
MFI FOR BIOPLASTIC COMPOSITE WITH DIFFRENT FILLERS

Percentage of filler	0%	0.1%	0.5%	1%
cellulose	1.1 gm/ 10min	1.1 gm/10 min	0.98gm/10min	0.62gm/10min
chitosan		1.01 gm/10 min	0.45gm/10min	0.26gm/10min
Potato		0.98 gm/10 min	0.95gm/10min	0.63gm/10min

The MFI was reduced by increasing the percentage of micro and nanofiller. The effect of adding 0.1 % was minimal; it slightly decreased the MFI of the bioplastic composite. Adding 0.5% and1% of both the micro and nanofiller reduced the MFI significantly, reaching almost the MFI of LDPE, which is between 0.3- 2.6 g/10min. LDPE is the most used type of polymer in several packaging applications. It could be easily shaped through extrusion and molding techniques [7]. The suitable grade for extrusion processing is between 0.3- 1 g/10 min.[25]. This ensures that the novel fabricated starch bioplastic composite could be easily extruded and can act as a replacement to LDPE pellets. Besides, this MFI grade also gives high melt strength and good mechanical properties than other MFI grades[5]. The results of MFI in table I can clarify the effect of the nanofiller, especially the chitosan nanofiller. It has a stronger effect on reducing the MFI of starch rather than the effect of the micro filler on decreasing the MFI of the starch bioplastic composite. This can be attributed to the existing strong interfacial adhesion between the nanofiller and the extracted starch matrix; this adhesion was due to the good dispersion of the nanofiller with the matrix [23][24]. This was owing to the size of the chitosan nanofiller (810 nm), as illustrated in fig 6a. The size of the nanofillers allows a large surface for interaction between the matrix and the nanofillers, which leads to a large interface or boundary area between the bioplastic

matrix and the nanofiller [26]. However, this significant MFI reduction was not evident with nano potato peel filler in comparison with chitosan nanofiller, that is due to the large nano size of potato filler which is 5730 nm that was measured using the particle size analysis as shown in fig 6b. The exposed surface area of the nanofiller with the matrix was smaller in the case of nano potato peel filler and hence reducing its interaction with the starch matrix. Another reason for this weak interaction that the used starch matrix was extracted from potato peel also, so the starch matrix contains the percentage of potato peel particles, which is not a new filler. So, the chitosan nanofiller is recommended rather than the potato peel nanofiller in this work, especially for packaging applications. However, one of the important properties of packaging applications is mechanical strength. Chitosan nanofiller has a yield strength of about 0.3 GPa [27], while the micro chitosan filler has a yield strength of 0.02 GPa [28].
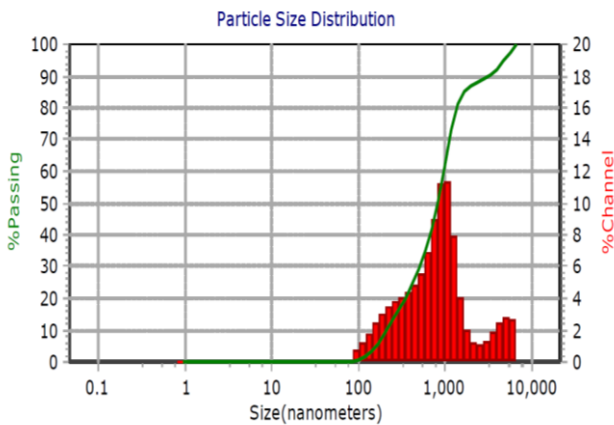

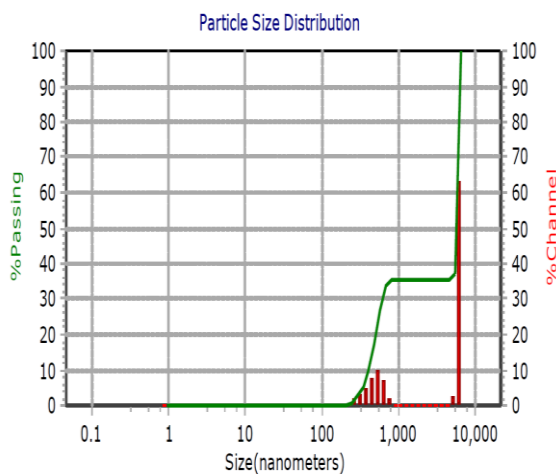**Fig 6a: particle size analysis for chitosan**

Fig 6b: particle size analysis for potato peel

Thus, micro chitosan filler was excluded from this study. Moreover, nano chitosan also has antimicrobial and antibacterial properties. These properties are considered a challenge in the packaging and especially the food industry. Consequently, this paper introduces a novel starch bioplastic composite that is able to prevent food

spoilage and help to increase shelf-life for food during distribution and storage [29] with good mechanical properties due to the presence of chitosan nanofiller. On the other hand, the interaction and coherence between the micro cellulose filler and starch matrix were weaker than the interaction in the case of the chitosan nanofiller due to the smaller surface area of the micro cellulose filler with the matrix[26]. Additionally, the large size of the micro cellulose filler compared to the particle size of the chitosan nanofiller had a smaller effect on the MFI reduction. The SEM images for micro cellulose filler are shown in fig 7, size of particles varied from 170 µm to 700 µm with an average value of 430 µm (±5µm), as illustrated fig 7a. The images also were taken with an amplification of 370 to show the shape of the surface clearly fig. As highlighted in 7b. The magnetified image shows some agglomerations present on the surface of micro cellulose filler, which contributes to the reduction of the interaction between the starch matrix and micro cellulose filler. This explains why the MFI values did not change significantly upon adding micro cellulose filler to the starch.
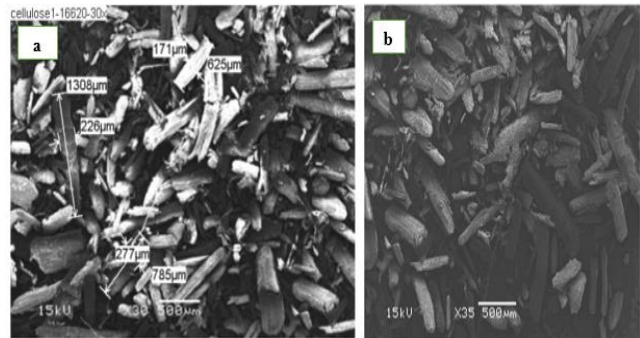

Fig 7a: SEM of micro cellulose filler
Fig 7b: SEM of agglomeration of micro cellulose

V. CONCLUSIONS

The fabricated bioplastic composite can be a successful replacement for LDPE pellets due to its similar MFI to LDPE. The MFI of starch bioplastic can be controlled by adding fillers. Chitosan nanofiller shows a lower MFI value than micro cellulose filler and potato peels nanofiller, which also enhance the mechanical property for the producing composite. Moreover, the antibacterial and antimicrobial properties of nano chitosan will make it suitable for the application of food packaging.

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