



ORIGINAL ARTICLE

Production of biodegradable plastic from agricultural wastes



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Abstract Agricultural residues management is considered to be a vital strategy in order to accomplish resource conservation and to maintain the quality of the environment. In recent years, biofibers have attracted increasing interest due to their wide applications in food packaging and in the biomedical sciences. These eco-friendly polymers reduce rapidly and replace the usage of the petroleum-based synthetic polymers due to their safety, low production costs, and biodegradability. This paper reports an efficient method for the production of the cellulose acetate biofiber from flax fibers and cotton linters. The used process satisfied a yield of 81% and 54% for flax fibers and cotton linters respectively (based on the weight of the cellulosic residue used). The structure of the produced bioplastic was confirmed by X-ray diffraction, FT-IR and gel permeation chromatography. Moreover, this new biopolymer is biodegradable and is not affected by acid or salt treatment but is alkali labile. A comparison test showed that the produced cellulose acetate was affected by acids to a lesser extent than polypropylene and polystyrene. Therefore, this new cellulose acetate bioplastics can be applied in both the food industry and medicine.

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1. Introduction

Biodegradable polymers broaden the range of waste management treatment option over traditional plastics and this is

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supported by the Life Cycle Assessment. The most favored end-of-life disposal options for these materials are domestic and municipal composting instead of landfill which is the worst disposal option. Therefore, biodegradable polymers can make significant contributions to material recovery, reduction of landfill and utilization of renewable resources (Davis and Song, 2006). Because of the difficulty in recovering the conventional polyethylene mulching film after its use, biodegradable films have been developed and commercialized. These are films (usually made of bio-based materials) which, after their use, can be buried in the soil along with the plant remains in order to be decomposed by microorganisms (Demetres et al., 2013).

The U.S.A Department of Agriculture's Bio-Preferred Program took the important step in promoting bio-plastics at the federal procurement level. In 2012, the two most influential commercial biodegradable (and bio-based) polymers were Poly-Lactic Acid (PLA) and starch-based polymers, accounting respectively for about 47% and 41%, of total biodegradable polymer consumption (Petrova and Garner, 2014). Another example is microbial Poly-Hydroxy Alkanoates (PHA) which, for the past many years, have been developed as biodegradable plastics (Ying et al., 2014). PHA has been marketed as environmentally friendly bio-plastics with less CO₂ emissions and sustainability as well as independence from petroleum sources (Chen and Patel, 2012). Also, there were studies of their industrial applications (Viviana et al., 2014).

In recent years, the development of biodegradable packaging materials from renewable natural resources (e.g. crops) has received increasing attention, particularly in EU countries (Davis and Song, 2006) and the use of renewable resources has been revitalized (Tabone et al., 2010; Cateto et al., 2008; Kiatsimkul et al., 2008). If properly managed, this would reduce their environmental impact upon disposal (Davis and Song, 2006) and, also, it would be technically and economically practicable (Tanaka et al., 2008).

Biodegradable plastics, based on cellulose acetate (CA), were studied and the produced plastic decomposed in soil or water within a few years. However, the material can be recycled, also, or incinerated without residue (Alexander, 1993). There were studies of the important properties of CA including mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and di-electric strength (Fischer et al., 2008; Jinghua et al., 2009).

Also, CA could be used for the manufacturing of photographic films, ultra-filtration membranes, fibers and some plastic tools (Cosimo, 2013). Natural plastic is produced in a fluid form and, therefore, it is shaped easily and does not require a large amount of energy. This is to be compared with the conventional plastic which is stored usually as granules and needs a massive amount of energy so that it can be shaped by molding, injection, or extrusion (Xiaoyun and Shuwen, 2013).

Many researchers used acetylation of plant cellulose fiber, such as cotton by-products; rice, wheat, rye and barley straws; and cornhusk and poplar wood fiber for the production of CA. The acetylation process was performed in supercritical carbon dioxide (Nishino et al., 2011), or in an ionic liquid (Cao et al., 2007) and also, by phosphotungstic acid (Guozhi et al., 2013) or by iodine and acetic acid (Cheng et al., 2010).

Because the raw materials have a high impact on the cost of bio-based plastic production, the use of low cost or negative value cellulosic raw materials is attractive, therefore, for industrial CA production. Flax is an ancient crop in Egypt and the amount of flax fibers are roughly seven thousand tons/year (Agricultural Egyptian Government, 2011); these contain 92% cellulose (Textile Learner, 2012). Cotton linters are regarded world-wide as a valuable cellulose raw material for paper manufacture, for the conversion to cellulose derivatives and for regenerated fibers. Cotton linters are by-products which are produced during cottonseed processing. In 1970, the oil mills gained 120 kg of (raw) linters fiber from 1000 kg of cottonseed (=12%) but, in 2009, it was roughly only 6–8.5% and cottonseed represented about 63% of the crop of cottons (Axel, 2009). In Egypt, the estimated amount of the crop of cottons was 82,829 thousand tons from 1990 to 2008

(Assiute University thesis, 2012). Also, cotton linters contain 94% cellulose (Textile Learner, 2012).

This work aims to use low cost cellulosic raw materials for the preparation of CA and, so far, few reports have been proposed on the preparation of CA from flax fiber. Consequently, in this work, flax fibers and cotton linters were used for the production of CA. Moreover, this work investigated and evaluated the obtained CA for crystalline structure, molecular weight, biodegradability, resistance for acids, alkalis and salts.

2. Experimental

2.1. Materials and chemicals

Flax fibers were obtained from Tanta Flax and Oil Company, Tanta, Egypt and cotton linters were obtained from El-Nile Cotton Ginning Company, Minia, Egypt. Fig. 1A and B show the two raw materials. Glacial acetic acid and acetic anhydride were purchased from El-Nasr Pharmaceuticals and Chemicals Company, Cairo, Egypt. Sulfuric acid was used as a catalyst and for the acid resistance test; polyethylene glycol 600 was used as a plasticizer; and acetone was used as a solvent. Sodium hydroxide, lead acetate, ferrous sulfate and tri-sodium orthophosphate were used for testing acids, alkalis and salts to the produced CA's resistance. They were purchased from Sigma-Aldrich Corporation, USA.

2.2. Procedure

2.2.1. Procedures of manufacturing cellulose acetate

Colors, dusts, and fats were removed from flax fibers and cotton linters by washing with water and bleaching with 120 mL of household bleaching agent (5% NaOCl & 5% NaOH), thoroughly washing and, then, was followed by drying. A sample of 35 g of each raw material was used. Acetic anhydride (100 mL), glacial acetic acid (100 mL) and sulfuric acid (10 mL) were mixed and the mixture was cooled to 7 °C. Flax fibers or cotton linters were added slowly to the previous mixture with agitation to bring about the acetylation process; this step produced the primary CA. Hydration of the primary CA (viscous fluid) was achieved by diluting with 30 mL of equal parts of concentrated acetic acid (99.8%) and sulfuric acid (98%) and, then, the primary CA was allowed to age for 15 h. The resulting viscous fluid was centrifuged in order to separate the final product. Plasticizer (polyethylene glycol 600) was added as 25% by volume of the viscous CA with agitation; this formed the final product which was dried in an oven at 60 °C until a constant weight in order to get the product ready for use. Before being shaped, the product was diluted with acetone to bring it into the form of a viscous fluid which could be poured in a mold or on a smooth surface for shaping.

2.2.2. Characterization of the produced cellulose acetate

2.2.2.1. X-ray diffraction (XRD). This test was performed to obtain information about the crystallinity of the produced CA by using an X-ray diffractometer to collect (at room temperature) XRD patterns of the prepared cellulose acetate sample. By using a Philips powder diffractometer with Cu K α radiation ($k = 0.154$ nm), X-ray diffraction (XRD) patterns of the samples were recorded in the range $2\theta = 4-80^\circ$. The



Figure 1 The photos of flax fibers (A) and cotton linters (B) before processing.

instrument was operated at 40 kV and 40 mA. The spectra were recorded with a 2θ step of 0.02° at a scanning rate of $2^\circ \theta/\text{min}$.

2.2.2.2. Fourier Transform Infrared (FTIR). FTIR was used to confirm the structure of cellulose acetate. By using a Nicolet IS-10 FTIR instrument with KBr discs, FTIR spectroscopy measurements were made. The peaks, as given in the chart, indicated that the functional groups were present in the CA sample.

2.2.2.3. Gel Permeation Chromatograph (GPC). The information about the molecular weight of CA was obtained by using Waters 515/2410 Gel Permeation Chromatograph (GPC, Waters, America) and a Styragel column calibrated with polystyrene standards and series 2410 refractive index detector. In the mobile phase, tetrahydrofuran was used at a flow rate equal to 1 mL min^{-1} and at a temperature of 40°C .

2.2.3. Biodegradation tests

2.2.3.1. Biodegradation by composting. Samples (5 g) of the produced CA were vacuum dried for 24 h at 45°C , weighed precisely and, next, buried into the municipal solid waste mixture. Then, they were examined for possible biodegradation. The mixture consisted of leaves, paper waste, cow manure, food waste, composting seeds, urea, wood waste and water (Müller, 2005). The mixture was kept in an oven at 55°C , at which the maximum growth of thermophilic microorganisms occurred. The samples were weighed every three days in order to determine the percentage of weight loss.

2.2.3.2. Bench-scale simulated composting. In this test (ASTM D5988, 2012), the compost consisted of inoculums (cow manure and garden soil). The test was run on three samples and each sample (5 g) was contained in a separate reaction vessel; however, the compost was common batch compost. For characterization, the samples were removed (in triplicate) from the compost at three day intervals in order to determine weight loss. The average weight loss of the three samples was determined and recorded. Also, the temperature of the compost was measured daily and recorded.

2.2.4. Chemical tests

2.2.4.1. Effect of acids. Samples (5 g) of the produced CA were weighed precisely and, then, put into sulfuric acid with concentrations of 10%, 20% and 30%. The samples were dried and weighed periodically for 4 days in order to determine the

percentage of weight loss after each time period. With the objective of making a comparison between the produced CA and two of the other known types of plastics, samples of polystyrene, and polypropylene were exposed to the same test but only for 30% concentration of sulfuric acid.

2.2.4.2. Effect of alkalis. Samples (5 g) of the produced CA were weighed precisely and, then, put into alkali solution (sodium hydroxide) with different concentrations (10%, 20%, 30% and 40%). The percentage weight loss was calculated daily for a period of ten days. With the objective of making a comparison, samples of polystyrene and polypropylene were exposed to the same test by using NaOH (40% concentration).

2.2.4.3. Effect of salts. The CA, produced from either cotton linters or flax fibers, was mixed with solid salt and left for 5 days, with periodic weighing every day, with the objective of determining its resistance to the action of salts. The salts, which were used, were ferrous sulfate, sodium chloride, trisodium orthophosphate and lead acetate. Samples of CA weighing 5 g were used and every day the CA was removed from the salt, thoroughly washed, dried and weighed.

3. Results and discussion

3.1. Preparation of cellulose acetate

The experimental results showed that the yield of cellulose acetate was 81% and 54% from flax fibers and cotton linters respectively (based on the weight of the cellulosic residue used).

In this study, the production yield of CA from cotton linters (54%) was higher than that prepared by iodine-catalyzed acetylation reaction. This gave a production yield of 34% from cottonseed hull and 37% from cotton burr (Cheng et al., 2010). This might have been due to the difference in methods used for the acetylation process and, also, the types of cellulosic residues. Also, the production yield of CA from flax fibers was higher than that from cotton linters and this might have been due to flax fiber being 50–120 cm long (Agricultural Egyptian Government, 2011) compared with cotton linter which was 2–6 mm long (Axel, 2009). Also, Fig. 1A and B (material and methods section) proved, also, that there was no significant difference in the cellulose content of the two residues. Also, this was likely due to the different physical structure of

the cellulose matrix in these materials. The CA, produced from the two residues, was viscous fluid with nearly the same color. Therefore, the acetylation process, used in this work, produced nearly the same CA from the two different types of residues but they differed in the percentage of production yield.

3.2. Characterization of the produced cellulose acetate

3.2.1. X-ray diffraction

Fig. 2A and B represent the typical XRD patterns for CA produced from flax fibers and cotton linters respectively. It can be seen that identical characteristics peaks around 14.6° , 16.49° , 22.68° and 34.5° appear in the two samples but with a small difference in the intensity; this increases in the case of cotton linters. The peak around 22.68° in the curves is ascribed to the typical crystal lattice of cellulose I β (Li and Rennekar, 2011; Nishino et al., 2011; Siqueira et al., 2010), indicating that all samples exhibit the diffuse characteristics pattern of an amorphous phase. The diffraction peak at 22.68° of (002) reflection is sharper and narrower in the produced CA; this indicates the removal of lignin and hemicellulose and results in an increase in the degree of crystallinity and a higher tensile strength (Montane et al., 1998). A shoulder peak at 16.49° of (101) reflection and a weak peak at 34.5° of (040) reflection appear in the spectrum of the produced CA; these are assigned to the cellulose phase. The weak diffraction peak appears around 14.6° in the diffraction pattern of CA in the two samples; these could be indexed with the crystalline peaks of CTAII modification (Sun and Sun, 2002).

3.2.2. FTIR spectra

Fig. 3A and B present the FTIR spectra of CA produced from flax fibers and cotton linters respectively. It can be seen that identical characteristics peaks appear in the two samples; these indicate that the CA, produced either from flax fibers or cotton linters, has the same function groups. The dominant absorption peaks around 3403 and 2916 cm^{-1} are attributed to the stretching vibrations of —OH group and the C—H bond in —CH_2 respectively (Guozhi et al., 2013). Whilst a shoulder peak at 1646 cm^{-1} is attributed to the β -glycosidic bond in glycogen. The peaks in the two CA samples can be observed at 1646 , 1456 and 1223 cm^{-1} ; these are ascribed to C=O and C—H bond in —O(C=O)—CH_3 group, and CO— stretching of acetyl group respectively (Cao et al., 2007; Huang et al., 2011). The observations of these peaks provide evidence of acetylation.

3.2.3. GPC test

Tests were run on the Gel Permeation Chromatograph (GPC) for the objective of investigating the molecular weight distribution. Fig. 4A and B show the individual GPC sample results for a run of 50 min and injection volume of $200\text{ }\mu\text{L}$. The molecular weight distribution curve shows that the produced CA was sufficiently homogenous and the average molecular weight (MP) was 1607 & 1674 Daltons for flax fibers and cotton linters respectively. Therefore, the CA, produced either from flax fibers or from cotton linters, has nearly the same polymeric structures.

3.3. Results of biodegradation tests

Fig. 5A and B show the results of biodegradation from composting and bench-scale simulated composting tests for flax fibers and cotton linters respectively. It is clear from the figure that, in the case of biodegradation tests from composting, CA lost 6% & 4% of its weight after the first three days and, then, the percentage of weight loss continued to increase over time until it reached 44% & 35% after 14 days for CA produced from flax fibers and cotton linters respectively.

Also, the results of the bench-scale simulated composting tests show that the CA lost 5% & 2% of its weight after the first three days. The results show, also, that the percentage of weight loss continued to increase over time until it reached 41% & 32.5% after 14 days. During the biodegradation process, there was, as depicted in the figure, a variation in the temperature of the compost. Therefore, it is clear from these results that the CA, produced from either flax fibers or cotton linters, is biodegradable by the thermophilic microorganisms. In addition, this is confirmed by the increase in temperature of the compost during the incubation period of the thermophilic microorganisms. Also, CA, produced from flax fibers has a slight increase in the rate of biodegradation and, thus, an increased percentage of biodegradation ($\sim 9\%$ weight loss) when compared with that produced from cotton linters. This may be due to the minor variations in the chemical structure of the CA produced from the two residues.

3.4. Chemical tests

3.4.1. Effect of acid on cellulose acetate

Fig. 6A and B show the results from the effects of different concentrations of sulfuric acid at on CA produced from flax fibers and cotton linters respectively.

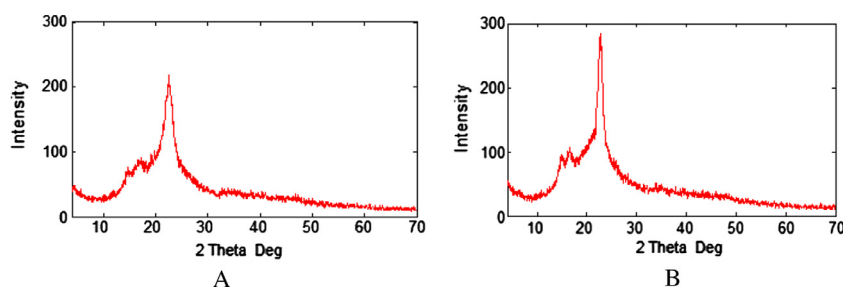


Figure 2 XRD result of the produced CA from flax fibers (A) and cotton linters (B).

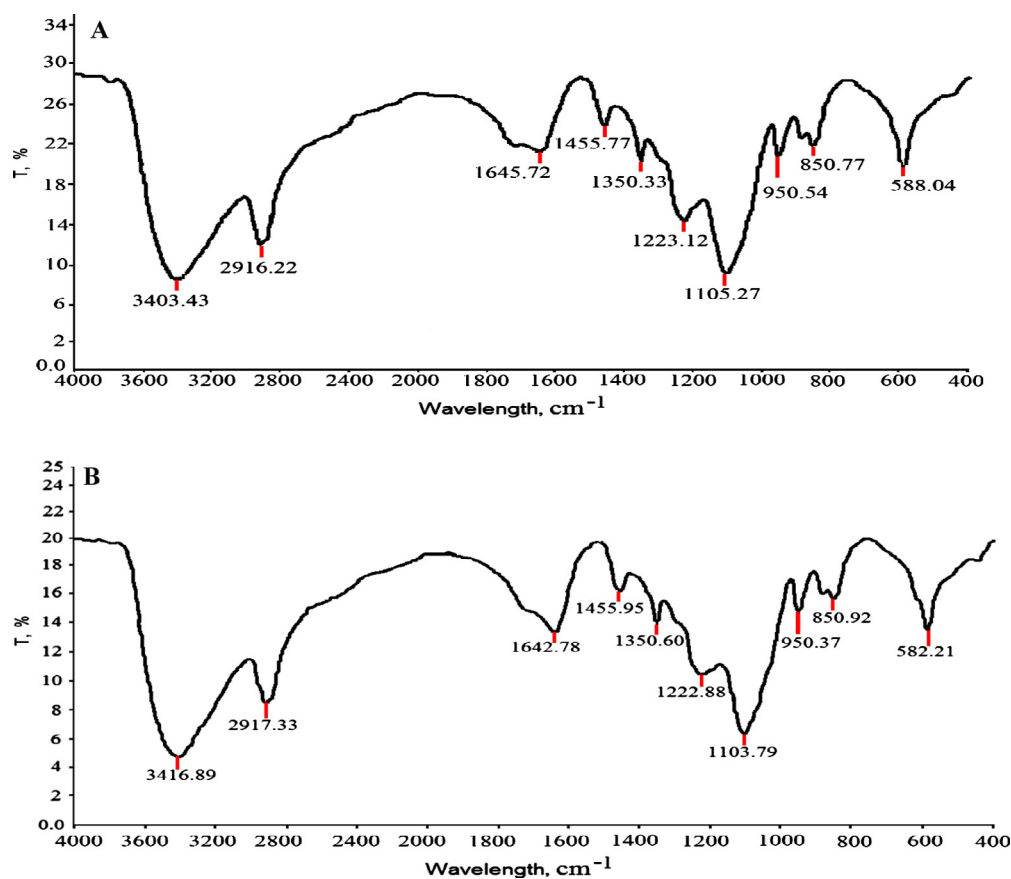


Figure 3 IR spectra of CA from flax fibers (A) and cotton linters (B).

The weight loss of CA, produced from flax fibers, had been increased by increasing the concentration of sulfuric acid from 10% to 20% and, then, the weight loss of CA became reduced at 30% sulfuric acid concentration (Fig. 6A). These results can be explained by the fact that, by increasing acid concentration from 10% to 20%, the acid content increased and, hence, the weight loss increased. However, at 30% acid concentration, there was a reduction in the water content which promoted the ponding rupture by acid.

On the other hand, the percentage weight loss of CA, produced from cotton linters, had been reduced by increasing the sulfuric acid concentration from 10% to 30% (Fig. 6B). Also, sulfuric acid (30%) gave a lower weight loss (1.84%) of CA produced from cotton linters than that (2.92%) from flax fibers. These results could be due probably to the high stability of chemical crystalline structure and ponding of CA from cotton linters.

In general, CA produce from both residues had a very good acid resistance; this was slightly higher than the environmental resistance factor of the commercial CA for strong acid (=3) which meant good resistance (Granta Design Limited, 2014).

The results in Fig. 7A and B illustrate the effect of 30% sulfuric acid on the produced CA compared to polystyrene and polypropylene. As shown from the figure, CA is affected by acid to a much lesser extent, i.e., 2.92% & 1.84% loss in weight for CA (produced from flax fibers and cotton linters respectively) in 30% sulfuric acid (after 4 days) compared to 29.4%, 34.3% for polystyrene and polypropylene respectively

under the same conditions. This means that the prepared CA is more durable than polystyrene and polypropylene.

3.4.2. Effect of alkalis on cellulose acetate

As illustrated in Fig. 8A and B, the weight loss of CA, produced either from flax fibers or cotton linters, increased as the concentration of NaOH increased and, also, it was increased over time. A maximum weight loss of 60.4% & 59.2% was noticed for CA from flax fibers and cotton linters after 10 days treatment with 40% sodium hydroxide solution (compared to 50.1% at 10% concentration NaOH for each residue).

The effect of time was less pronounced for more concentrated solutions since its maximum value had been reached from the beginning of the test (41.5% & 40% loss in weight after one hour for 40% NaOH, compared to 19.8% & 18.4% at the same timing for 10% NaOH) for CA produced from flax fibers and cotton linters respectively. It is clear from the results that the resistance of CA, produced either from flax fibers and cotton linters to alkalis, is nearly the same; however, CA produced from both residues had a poor alkalis resistance when compared to commercial CA which have a good resistance factor (=3) for strong alkalis (Granta Design Limited, 2014). However, the poor alkali resistance was due to the presence of hydrolysable ester bonds in the structure of acetate.

Fig. 9A and B show the results of the comparison test. It is clear from the results that the resistance of CA, produced

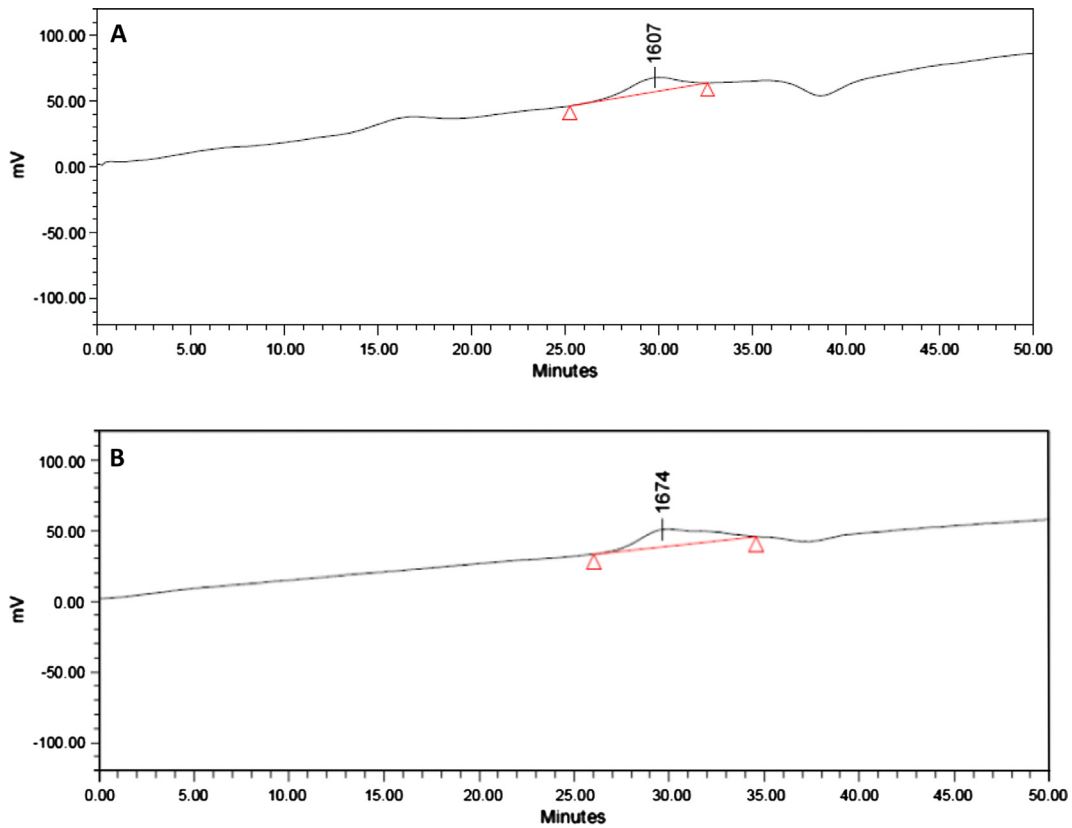


Figure 4 GPC sample results of CA from flax fibers (A) and cotton linters (B).

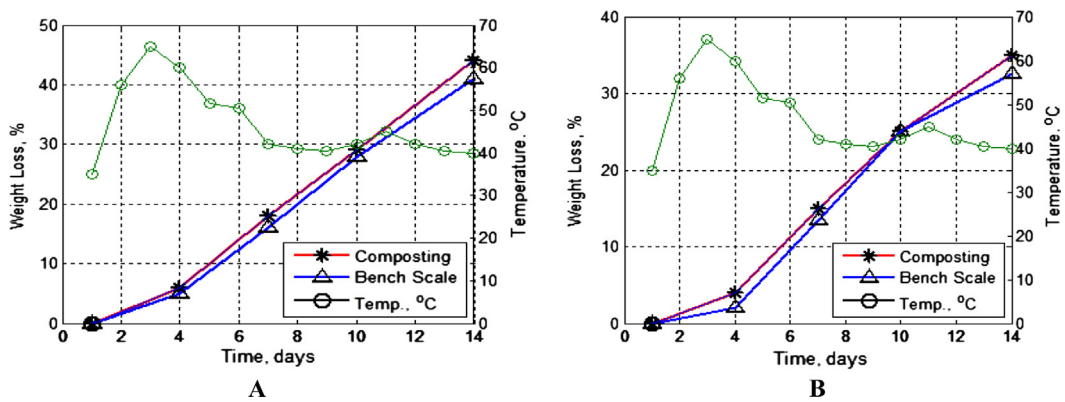


Figure 5 Compost' temperature profile and percentage weight loss due to biodegradation (by composting and bench-scale) of CA produced from flax fibers (A) and cotton linters (B).

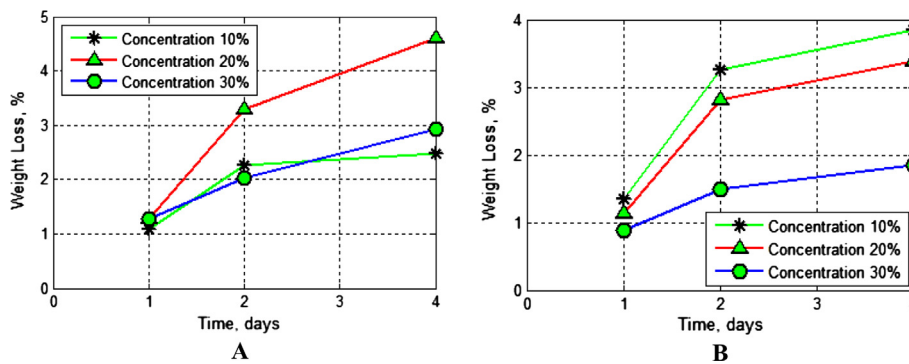


Figure 6 Effect of different concentrations of sulfuric acid on weight loss of CA produced from flax fibers (A) and cotton linters (B).

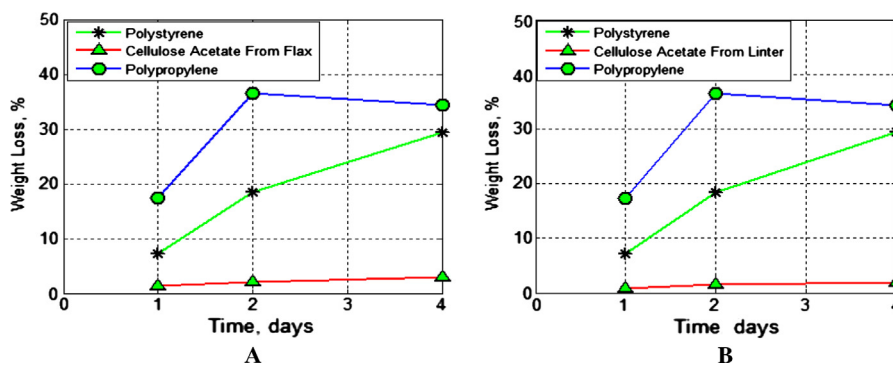


Figure 7 Effect of 30% concentration sulfuric acid on weight loss of CA produced from flax fibers (A) and cotton linters (B) compared to polystyrene and polypropylene.

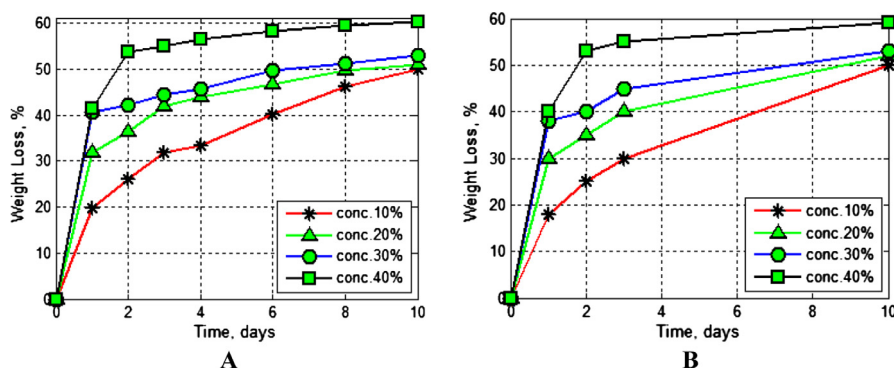


Figure 8 Effect of different concentrations of NaOH on weight loss of CA produced from flax fibers (A) and cotton linters (B).

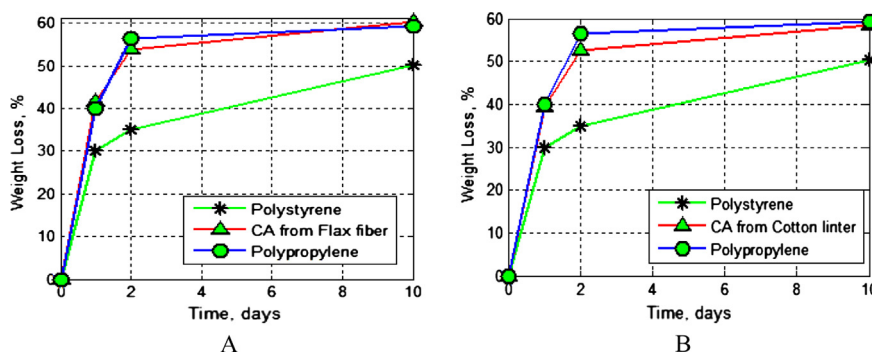


Figure 9 Effect of 40% concentration NaOH on weight loss of CA produced from flax fibers (A) and cotton linters (B) compared to polystyrene and polypropylene.

either from flax fibers and cotton linters to alkalis, is very close to the values of polypropylene but is higher than polystyrene.

3.4.3. Effect of salts on cellulose acetate

The test showed that the solid ferrous sulfate, sodium chloride, tri-sodium orthophosphate and lead acetate had no effect on the produced CA where it did not show any weight loss when mixed with these salts for 5 days. These results were consistent with the environmental resistance factor of the commercial CA for sea water (=5); this meant an excellent resistance factor (Granta Design Limited, 2014). Also, the produced CA could

be an alternative to using polyethylene; this is used commonly for manufacturing containers for salts.

4. Conclusions

The environmentally benign natural cellulose-based CA either from flax fibers or cotton linters was prepared successfully by using sulfuric acid-catalyzed acetylation process and characterized by using various instrumental techniques and environmental properties tests. It was found that CA produced as viscous acetone-soluble fluid and the production yield of CA from flax fibers (81%) was higher than that from cotton

liners (54%). In addition, it was better than that from cotton liners in terms of biodegradation properties (41–44% weight loss after 14 days) but they had nearly the same chemical resistance. Also, the produced CA proved to be comparable with polyethylene and polypropylene with respect to its resistance to 30% sulfuric acid and 40% NaOH. Flax fiber is recommended for the commercial production of CA because of its higher production yield and it is available in large quantities compared with cotton liners; these are used as an ingredient of cattle feed. This acceptable overall performance, shown by this CA, has put it forward as a suitable material for packages, salt containers, fiber and plastic tools manufacture. This CA has the potential to replace or minimize the use of non-biodegradable and petroleum-based materials.

5. Recommendations

Other types of agricultural wastes could be studied for their accessibility to produce CA and a pilot plant could be carried out for CA manufacture from agricultural residues. Also, the effect of different types of plasticizer on the physical and environmental properties of the produced CA could be studied.

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