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New Biodegradable Material Obtained by Acid Hydrolysis of Starch Followed by Grafting of Acrylamide in Presence of *bis*-Acrylamide

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This work focuses on the development and characterization of new biodegradable material based on corn starch. This material is obtained by acid hydrolysis of starch followed by a grafting of acrylamide in the presence of *bis*-acrylamide. The results of Fourier transform infrared showed the successful hydrolysis of starch and grafting. The viscometer rheological study showed that a grafted starch pseaudoplastique behaviour. X-ray diffraction showed a decrease in crystallinity and graft analysis by scanning electron microscope confirmed the structure of this modification. Thermogravimetry analysis shows an improvement in thermal stability.

Keywords: Starch, Acrylamide, Hydrolysis, Grafting, Film, Casting.

INTRODUCTION

We have witnessed in recent years a strong growth of the plastic materials of natural origin. These materials were a first generation of bioplastics. The second generation of the end of the 90 s and saw the incorporation of naturally occurring materials for applications in plastic packaging with the prominence of the biodegradability of these plastics. This second generation will leave room in future years to a third generation that involve sectors such as construction, electronics and automotive. It will also focus on the use of materials from renewable sources, but this time for durable applications highlighting recycling at end of life.

Most of natural origin currently existing materials have, in general and require limited properties or being chemically modified or being mixed with other materials or reinforced polymers to improve mechanical properties such as or to reduce sensitivity to moisture. Starch is the most common substance of the reservation, after cellulose in higher plants synthesized from solar energy. It is present in a large number of agricultural commodities such as cereals (30 to 70 %), tubers (60 to 90 %), legumes (25 to 50 %) and some fruit [1]. Starch is a natural polysaccharide semi lens that is growing interest in food and non-food applications.

The applications of starch are many and varied in many non-food industries *e.g.*, pulp and paper production, pharmaceuticals, cosmetics, textile *etc*. It has also become in recent years an interesting raw material for the production of plastics biodegradable. There are twenties, materials starch was introduced on the market, but by the context and Economic Policy unfavourable and their properties are too low, they have failed to settle commercial scale. The starch may be physically transformed through treatment using pressure, temperature, shearing action as tools to provide properties totally different from those present in the native condition [1]. It has a semi-crystalline structure and acid hydrolysis of the native grain provides a highly crystalline insoluble residue [2].

Grafting is one of the chemical methods employed for improving the properties of the starch. However, much attention has been made in the synthesis and study of reaction conditions for grafting starch with a variety of monomers such as acrylamide [3-5], methacrylamide [6], acrylonitrile and methacrylonitrile [7].

Our work focuses on the development and characterization of a new material based on hydrolyzed starch, grafted with acrylamide in the presence of *bis*-acrylamide. The samples prepared are characterized by different analytical techniques to study their behaviour, rheological, morphological and thermal.

EXPERIMENTAL

Corn starch (soluble, Sigma-Aldrich), HCl (C = 37 %, d = 1.18 Prolabo) NaOH (M = 40 g/mol, C = 98 %, Prolabo) acrylamide (M = 71.08 g/mol, BIOCHEM chemopharma), N,N-methylene-*bis*(acrylamide) (M = 156 g/mol, Aldrich),

potassium persulfate ($K_2S_2O_8$) M = 270.322 g/mol, BIOCHEM chemopharma), ethanol (C = 96 %, d = 0.803 g/mL, M = 84.01 g/mol Sigma-Aldrich), sodium carbonate (M = 105.988g/mol, BIOCHEM Chemopharma).

Hydrolysis procedure: First, we put 10 g of starch in a solution of HCl (0.5N) and stir at 60 °C for 1 h. The next action is to precipitate the starch in 500 mL of ethyl alcohol and neutralizing by the sodium carbonate, then washed with distilled water and filtered repeatedly. The next action is to precipitate the starch in 500 mL of ethyl alcohol and neutralizing the sodium carbonate and then washed with distilled and filtered water repeatedly. Mostafa [5] showed in his study that the grafting of starch with acrylamide succeeded better with a hydrolyzed starch with HCl concentration equal to 0.5 and 1 N.

Grafting reaction and preparing film: The grafting is a chemical reaction which consists in grafting the hydrolyzed starch on the acrylamide. This step provides a new starch. In the absence of grafting, rather we speak of hydrolyzed starch. We mixed 10 g of hydrolyzed starch with 5 g of acrylamide, 0. 133 g of *bis*-acrylamide, 0.04 g persulphate of potassium persulfate ($K_2S_2O_8$) and 40 mL of distilled water and allowed to stir at around 40-50 °C for 1 h under an inert gas.

Mostafa [5] proved that the temperature of grafting should not exceed 50 °C whereas the duration of reaction must exceed 1 h. Abdollahi and Gomes [8] have shown that grafting of acrylamide in the presence as initiator $K_2S_2O_8$ can be done at 40 °C without the use of catalyst TEMED.

Finally, we add a few drops of a dilute solution of NaOH (0.1 N) to decrease the viscosity of the suspension. We shed it in petri dishes, placed in an oven at 40 °C for 48 h and film thickness of transparent ≤ 1 mm obtained

Infrared spectroscopy Fourier transform: Analysis of our samples was performed using a spectrometer of Fourier transform infrared brand "Perkin Elmer spectrum one instruments" at room temperature with a resolution of 4 cm^{-1}.

Viscosimetery: To determine the rheological behaviour of the individual suspensions, we use a viscometer "Thermo HAAKE VT 550" quilt system that monitors and characterizes fluid in rotation mode. A temperature controller type (HAAKE DC 30).

As for test samples, they are obtained by setting a magnetic stirring volume of distilled water (20 mL) to which is added an amount of 0.2 g of material (powder) already prepared. To ensure a good homogenization, the suspension obtained is subjected to a continuous magnetic stirring for 0.5 h at 90 °C.

Scanning electron microscopy (SEM): The microstructures of the various samples were analyzed with a scanning electron microscope type "JEOL JSM-6360LV scanning electron microscope".

Thermal analysis (TGA): The analysis of our material was carried out in an apparatus for DSC/TGA coupled type NETZSCH STA409 PC/PG. A quantity of 10 mg of sample was analyzed. The scans are performed from 20 to 550 °C at a rate of 10 °C/min.

X-ray diffraction: The X-ray diffraction analysis (XRD studies) was carried out using a diffractometer PANALYTICALKV. The voltage, current and the wavelength of the X-ray source was 45 kV, 40 mA and 1,5418 Å. Samples were analyzed on XRD between 2° and 70°.

RESULTS AND DISCUSSION

Native starch and hydrolyzed starch: Infrared analysis was carried out on native starch [Fig. 1(A)] and hydrolyzed starch [Fig. 1(B)] by direct absorbance through KBr tablet. The infrared spectrum of the native starch is a very broad range of high and intensity characteristics 3500-3100 cm^{-1} valence vibrations of hydroxyl groups bung correspond to the content of hydroxyl groups contained in starch.

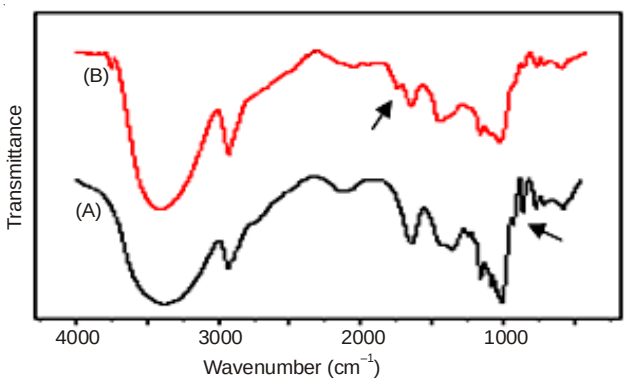

Fig. 1. FT-IR spectrum of the (A) native starch, (B) hydrolyzed starch

In comparison between the native starch and hydrolyzed starch, we observed a shift of the band 3388 cm^{-1} in the case of native starch to 3420 cm^{-1} in the case of the hydrolyzed starch and the appearance of a peak at 1260 cm^{-1} due to deformation of the OH groups and the reduction of peak 928 cm^{-1} indicating the COC bond α (1-4) in the starch. The acid hydrolysis can't be performed at random, preferably it should be at the terminal connections of the chains (COC bond α (1-4)), especially those adjacent the non-reducing end units [9].

Starch graft: FTIR spectroscopy of hydrolyzed starch (B) acrylamide (C) and the grafted copolymer (D) are shown in Fig. 2. The hydrolyzed starch is a broad peak at 3420.07 cm^{-1} of the stretching vibration of OH, a small peak at 2927.24 cm^{-1} attributed to the stretching vibration of CH. The peak of band a 1647.75 cm^{-1} for the water molecule and a peak of 1021.8 cm^{-1} for the stretching vibration COC bond.

In the case of starch-grafted acrylamide, a broad band of OH group hydroxide of starch and NH amide group are presented in overlapping chains, lead to a peak 3431.82 cm^{-1} and the disappearance of peaks 1670.19 cm^{-1} and 1608.43 cm^{-1} attributed to the CO stretching vibration in $CONH_2$ acrylamide suggesting the existence of grafting.

Viscosimetry results: Fig. 3 shows the flow curves of suspensions: (B) hydrolyzed starch, (C) acrylamide and (D) starch-g-acrylamide. The flow chart shows the three suspensions for non-Newtonian behaviour (shear thinning or pseudoplastic); apparent viscosity decreases with the shear rate [1].

It is observed that the viscosity of the acrylamide is higher compared to the viscosity of starch and hydrolyzed starch-g-acrylamide. Both materials have the same shape, which means that the graft does not affect the rheological behaviour of the starch.

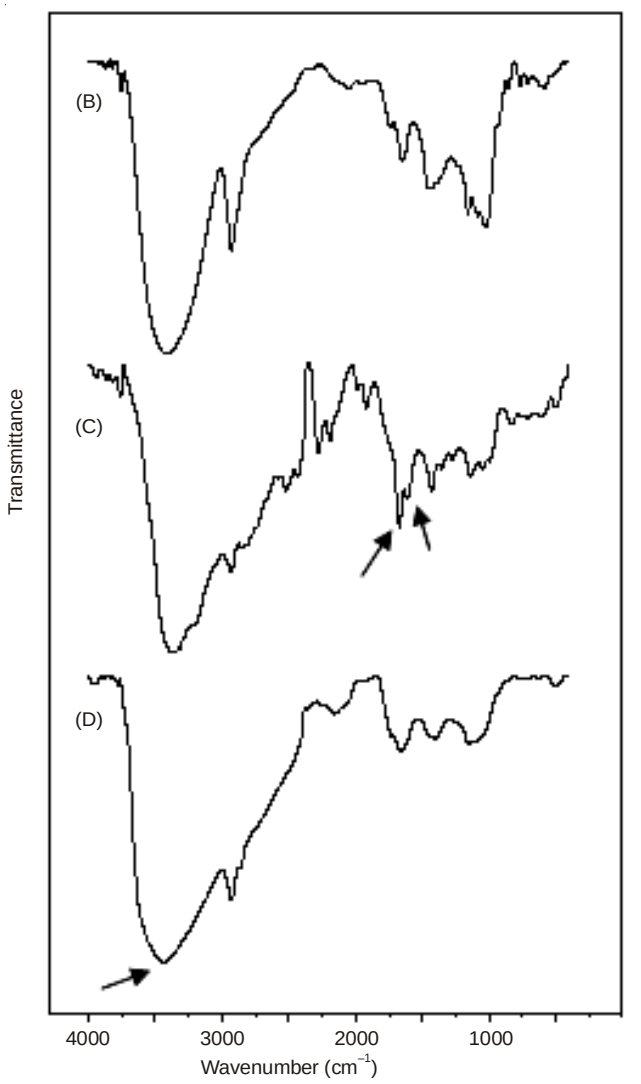

Fig. 2. FT-IR spectrum of (B) hydrolyzed starch, (C) acrylamide and (D) grafted copolymer

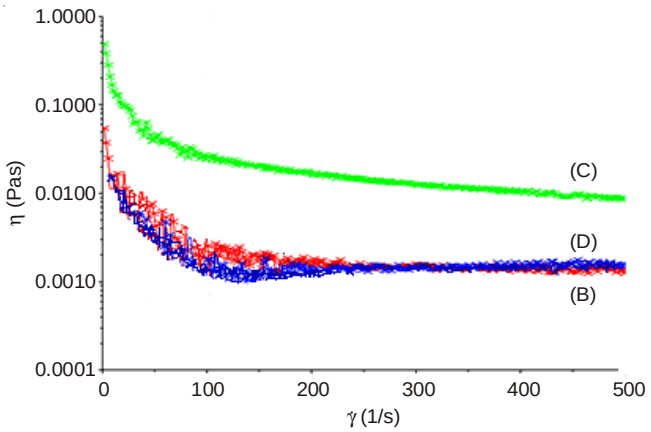

Fig. 3. Curves of flow of (B) hydrolyzed starch, (C) acrylamide and (D) grafted copolymer

SEM characterization: In Fig. 4 the scanning electron micrograph of the film of native starch has a smooth surface [Fig. 4(A)], whereas the acrylamide has a crystal structure [Fig. 4 (B)]. The graft copolymer showed a change of morphology of the surface because the grafting of acrylamide to starch [Fig. 4(C)].

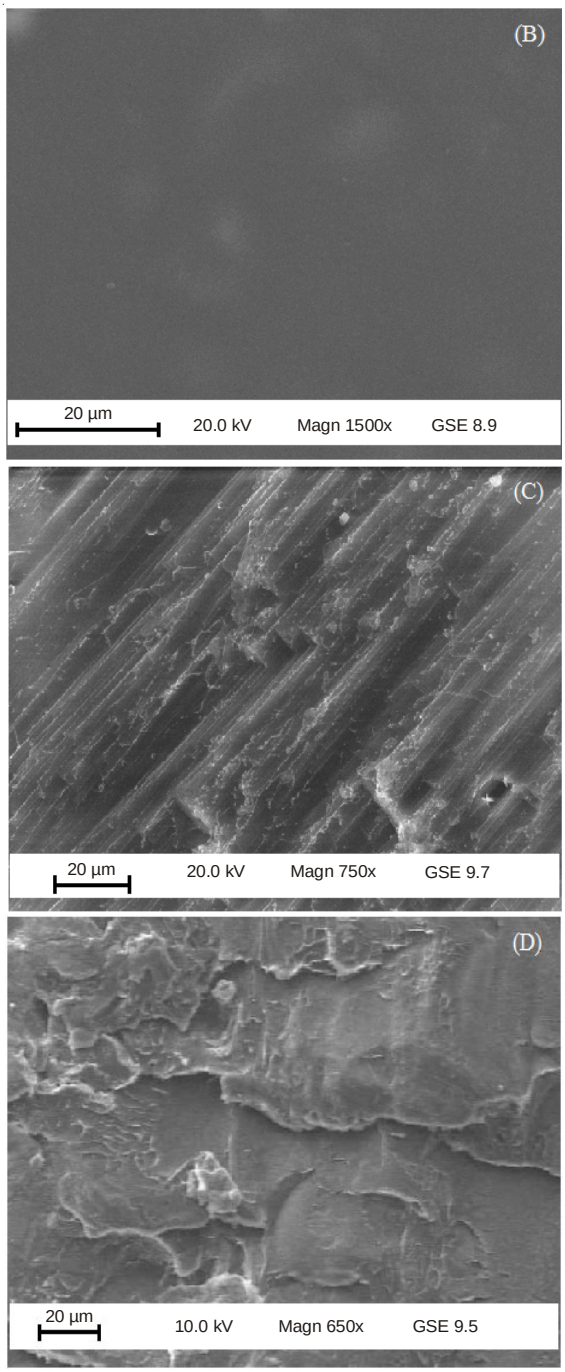

Fig. 4. Scanning electron micrographs of (B) hydrolyzed starch film, (C) acrylamide and (D) grafted copolymer

X-ray diffraction: The XRD pattern of hydrolyzed starch (A), acrylamide (C) and grafted copolymer (D) is shown in Fig. 5. The diffraction pattern of hydrolyzed starch showed semi-cristalline structure with peaks at 15, 17, 20, 24, 26,31, 34 and 36 at the angle 2θ, indicating a typical pattern of corn starch. The pure acrylamide is crystalline in nature [Fig. 5(C)].

During the grafting reaction, the grafted copolymer semi-crystalline structure affected largely the X-ray diffraction pattern [Fig. 5(D)] and a new structure of amorphous nature is observed, it is the change brought on the starch by the grafting. The grafting by microwave makes by Singh *et al.* [10] gives a crystal copolymer, same result was found by El-Hamshary *et al.* [11].

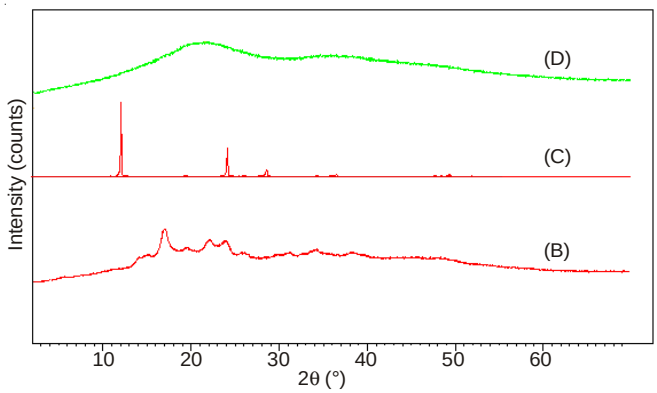

Fig. 5. Spectrum of diffraction of X-rays of (B) hydrolyzed starch, (C) acrylamide and (D) grafted copolymer

It is the reverse of what one found and that is due to the presence of *bis*-acrylamide which gives long and flexible chains to copolymer.

TGA characterization: The thermograms of the thermogravimetric analysis (TGA) and the speed of thermal decomposition (DTG) shown in Fig. 6 of the films prepared, hydrolyzed starch (B), acrylamide (C) and grafted copolymer (D) reveal weight loss of samples of 10 mg, when they are subjected to a heat flow in the temperature range from room temperature to 500 °C.

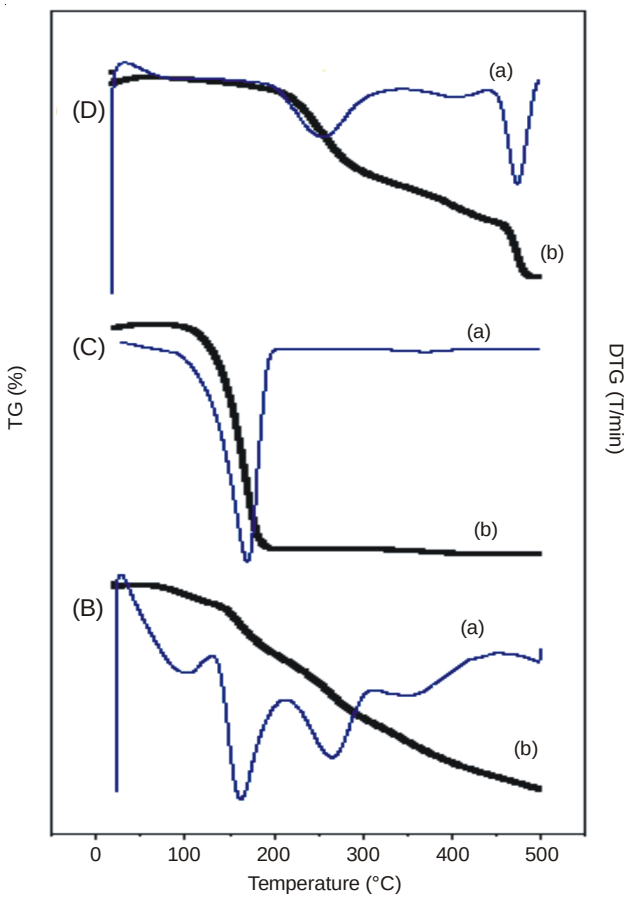

Fig. 6. Thermograms (DTG) (a) and (TGA) (b) films prepared (B) hydrolyzed starch, (C) acrylamide and (D) grafted copolymer

The results of thermogravimetric analysis (Fig. 6) were used to characterize the thermal stability of the starch after grafting of acrylamide. Hydrolyzed starch shows a three steps characteristic thermogram at 109.2 °C, 159.7 °C maximum weight loss occurred at 250.7 °C was due to degradation of the starch back-bone. Acrylamide (C) is totally degraded to 169.7 °C and the grafted copolymer (D), in addition to the above zones of weight loss, has two extra zones of weight loss (418.4 and 503.9 °C), due to the grafted acrylamide chains. The works of Singh *et al.* [10] and Mishra *et al.* [12] have produced the same results.

Conclusion

The native starch was hydrolyzed and grafted by the acrylamide in the presence of *bis*-acrylamide. The spectral analysis confirmed the hydrolysis and the grafting of the starch. The rheological study noted the maintenance of the behaviour pseudoplastic of the starch after its grafting. The results of the SEM and XRD explained the structural modification whereas the TGA showed the good thermal stability of copolymer.

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