Carbohydrate Polymers 79 (2010) 731–737

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Convenient method for preparation of hydrophobically modified starch nanocrystals with using fatty acids

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ARTICLE INFO

Article history:
Received 1 August 2009
Accepted 30 September 2009
Available online 9 October 2009

Keywords:
Nanoparticles
Biopolymers
Hydrophobic starch nanocrystals
Fatty acid

ABSTRACT

Biodegradable nanoparticles of starch were prepared by an acid treatment process. The obtained starch nanoparticles were hydrophobically modified by using octanoyl, nonanoyl and decanoyl chloride in the aqueous media under mild condition. The structure of the resulted polymers characterized with FT-IR spectroscopy and DS-values calculated by elemental analysis experiment. Thermal characteristic of the modified starch nanoparticles was investigated using TGA technique. By introducing fatty acids, onset temperature for modified starch nanoparticles has increased and starch nanoparticles showed greater thermal stability. Also wettability tests showed that the surface characters of starch nanocrystals have changed during modification and modified starch nanocrystals have higher affinity toward organic solvents rather than aqueous media. DSC studies showed that the starch crystalline structure has not changed during reaction.

1. Introduction

Starch is a biocompatible, biodegradable and nontoxic polymer, existing in nature as the major storage polysaccharide in higher plants. Native starches are a blend of two polyglucans, amylose and amylopectin. Amylose is the linear fraction consisting of α-D-glucopyranose linked through α (1 → 4) linkages and has a molecular weight of 10^5–10^6 g/mol (Angellier, Molina-Boisseau, & Dufresne, 2005; Dufresne & Cavaillé, 1998; Namazi, Mosadegh, & Dadkhah, 2009). Amylopectins, with molecular weights between 10^6 and 10^7 g/mol, are branched fractions containing short chains linking linear chains via α (1 → 6) linkages. Native starch occurs in the form of discrete and partially crystalline granules exhibit a so-called onion like structure with more or less concentric growth rings that are readily visible by optical and electron microscopy. Acid treatment allows revealing the concentric lamellar structure of starch granules by dissolving region of low lateral order. The water insoluble and highly crystalline residue obtained from waxy corn starch granules have been found to be composed of nano scale crystals (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005a; Angellier, Putaux, Molina-Boisseau, Dupeyre, & Dufresne, 2005b; Dufresne, Cavaillé, & Helbert, 1996).

Recently, these have been a growing interest in hydrophobically modified derivatives of polysaccharides for different applications. The amphiphilic nature imparted upon polysaccharides after hydrophobic modification give them a wide and interesting applications spectrum, for instance as rheology modifier, emulsion stabilizer, surface modifier and as drug delivery vehicles.

Polysaccharide nanocrystales which bear three hydroxyl groups in each glucose residue offers the possibility of various reactions. They have also been founded to be excellent reinforcement (Angle's & Dufresne, 2000, 2001; Azizi Samir, Alloin, & Dufresne, 2005; Dufresne, Dupeyre, & Vignon, 2000; Dufresne, Kellerhals, & Witholt, 1999; Dufresne & Vignon, 1998).

Chemical modification of starch nanocrystales have been reported with various reagents such as isosyanate, anhydrides and fatty acids in organic solvents. Modification also has been done via graft polymerization of caprolacton, poly ethylene oxide and etc. (Namazi & Dadkhah, 2008; Thielemans, Belgacem, & Dufresne, 2006).

In contrast to the recent progress in starch and starch nanocrystals chemistry which is in particular stimulated by the use of heterogeneous reaction condition, there are developing efforts for doing reactions in homogenous condition (Aburto, Alric, Borredon, & Cedex, 1999; Billmers & Tessler, 1994; Chi et al., 2008; Fang, Fowler, Sayers, & Williams, 2004; Fang, Fowler, Tomkinso, & Hill, 2002) that is more effective in some cases. Therefore our interest was focused on modification of starch nanocrystals via homogenous reactions. The aim of this investigation was the hydrophobically modification of inexpensive, naturally occurring starch nanocrystals and investigation the properties of the obtained modified starch nanoparticles in aqueous media instead of using organic solvents such as toluene. To this end, starch nanocrystals were prepared and characterized then starch nanocrystals were modi-

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doi:10.1016/j.carbpol.2009.09.033

fied with long-chain fatty acids with grafting onto the carbohydrate backbone.

2. Experimental

2.1. Materials

Waxy corn starch was purchased from Fluka and was dried at 110 °C for about 10 h to remove absorbed moisture. Octanoic acid (C8), nonanoic acid (C9) and decanoic acid (C10) as well as thionyl chloride were purchased from Merck. All other chemicals and solvents were analytical grade and were used as received.

2.2. Measurements

2.2.1. FT-IR

The FT-IR analysis was performed using a FT-IR Bruker-Tensor 270 spectrometer. The starch nanocrystals and also modified starch nanoparticles were mixed with analytical grade KBr at a weight ratio of 5/200 mg.

2.2.2. Elemental analysis

Elemental analysis was used to establish the DS-values of modified starch nanoparticles. Samples of solid polymer were ground to a powder and dried at 100 °C for 24 h, then analyzed on a Carlo Erba EA 1108 CHN S–O instrument to measure the carbon and hydrogen content in the modified starch nanocrystals samples. The DS-values were calculated from the % carbon contents.

2.2.3. XRD

The pattern of X-ray diffraction of the samples was obtained by Siemens diffractometer with Cu-Kα radiation at 35 kV in the scan range of 2θ from 2–50°.

2.2.4. Transmission electron microscopy

Transmission electron microscopy (TEM) observations were performed using a LEO 906 microscope with a 80 kV voltage and micrographs were recorded on Kodak film.

2.2.5. TGA

TGA carried out on D. T. G. 60 AH Shimadzu instruments. Thermal degradation behavior of samples was studied thermo gravimetric analysis TGA at a heating rate of 20 °C/min.

2.3. Methods

2.3.1. Preparation of starch nanoparticles

Starch nanocrystals were prepared by acid hydrolysis of waxy maize starch according to previously described method. (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). Briefly, native waxy corn starch granules were mixed with 3.16 M H_2SO_4 solution at a starch concentration of 15 wt.% in a 500 ml Erlenmeyer flask. The suspensions were then continuously stirred at 100 rpm under 40 °C. After 5 days of hydrolysis, the suspensions were washed by successive centrifugations in distilled water until neutrality was achieved. At last, the starch nanocrystal precipitate was ultrasonically homogenized in an aqueous solution and then the obtained starch nanocrystals suspension was lyophilized as loose powder.

2.3.2. Modification procedures

2.3.2.1. Preparation of acid chlorides from fatty acids. The synthesis of acid chlorides was carried out in a round-bottomed flask having two necks. Fatty acids (0.1 mol) were added to the flask and placed in a water bath maintained at 35–40 °C. Then 10.0 g (0.15 mol) of thionyl chloride was added to flask slowly with shaking. The reaction mixture was refluxed in the water bath for 5 h. In order to trap the hydrogen chloride and sulphur dioxide formed during reaction, a beaker containing a cold (10 °C) aqueous sodium hydroxide (1.0 N NaOH) solution was placed at the outlet of the condenser. The reaction mixture was first distilled at atmospheric pressure to remove unreacted thionyl chloride, HCl and SO_2 and it was further distilled at a reduced pressure to collect the liquid acid chlorides.

2.3.2.2. Synthesis of acylated starch nanoparticles by using fatty acids. Starch esterification was carried out in two steps as described previously (Fang et al., 2004). In the first step, starch nanocrtstals dispersed in the reaction medium (water) were alkali treated at room temperature with mechanical stirring under an atmosphere of N_2 for 10 min and in the second step, 0.5 mol equivalents of the required acid chloride was added drop wise and the reaction mixture was stirred for 20 min. Upon completion of the reaction, the mixture was neutralized to pH 7 with acetic acid, and the modified starch nanoparticles were isolated by precipitation in methanol (150 ml). The product was collected by filtration. One gram of the modified starch nanocrystal was put into a 50 ml methanol in a bottle then the mixture was stirred at 20 °C fore 12 h and then filtrated. The remaining solids washed with methanol for three times. The above process was repeated once again. The filtrates were collected together and dried in vacuum, weighed and were kept in a desiccator.

3. Results and discussion

3.1. Esterification of starch nanocrystals

The modified starch nanoparticles substrates were synthesized with using fatty acid chlorides in a homogenous condition, resulting in compositions with chemical grafting. Pathway was used, as represented by the reaction shown in Fig. 1. This method is interesting and very convenient method that utilizes water as a nontoxic and an inexpensive solvent presented by Fang et al. (2004).

3.2. FT-IR analysis

The FT-IR spectra of the unmodified starch nanocrystals and the modified starch nanocrystals with fatty acids have shown in Fig. 2. The main characteristic peak of starch nanocrystals are the stretching and bending vibration of hydrogen bonding OH group of starch accurate 3276 and 1650 cm^{-1}, respectively. The stretching vibration of C—O bonding in C—O—H and C—O—C group in the anhydrous glucose ring appeared at 1150, 1077 and 990 cm^{-1}. The characteristic peak of C—O—C ring vibration in starch located at 760 cm^{-1}.

Also the FT-IR spectra of resulted products obtained from esterification reaction, Fig. 2B–D, showed the combination of both starch nanocrystal's and fatty acid's characteristics and the existence of a carbonyl absorption band can be assigned to formation of fatty acid modified starch nanocrystals. The carbonyl absorption band appeared at 1739, 1742 and 1740 cm^{-1} for octanoyl, nonanoyl and decanoyl starch nanocrystals, respectively. Evidence for the absence of any contaminating fatty acid chlorides and acid is gained by the lack of any absorbance in the region 1710 cm^{-1} associated with the carbonyl stretch of unreacted fatty acid and 1780 cm^{-1} corresponding to carbonyl group of fatty acid chlorides.

3.3. DS-values and yields of products

The DS for a starch derivative is defined as the number of hydroxyl (OH) groups substituted per D-glucopyranosyl unite possesses

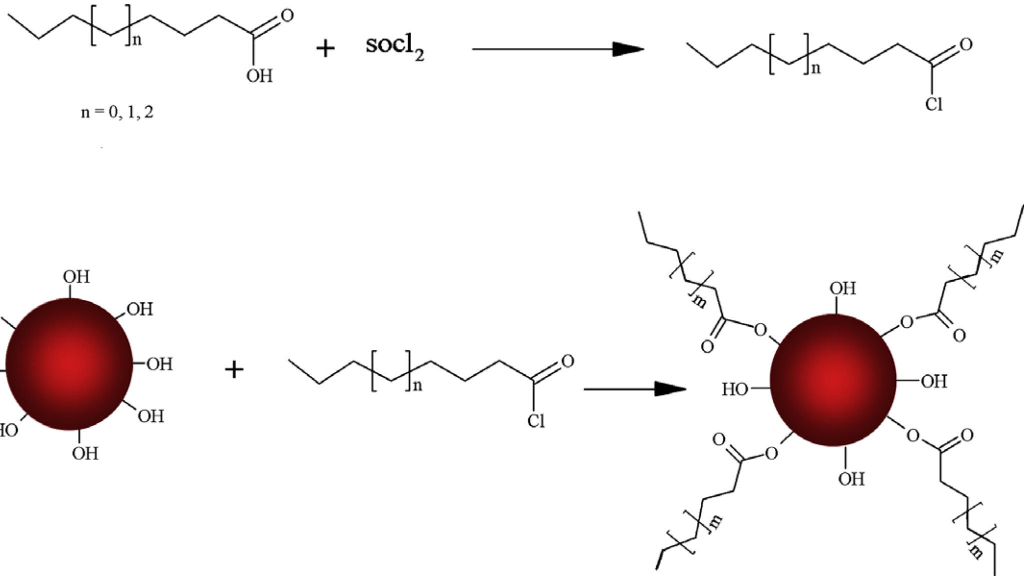

Fig. 1. Typical process for esterification reaction of starch nanocrystals.

three reactive hydroxyl groups, so the maximum possible DS-value is three. The DS-values of modified starch nanoparticles were calculated on the base of measured %C from elemental analysis results. The obtained results for %C and calculated DS-values are presented in Table 1. Native, pure and anhydrous starch nanocrystal contains by weight 44.44% carbon. The results in Table 1 show that the carbon content of all samples were higher than 44.44% indicating an increase in carbon density resulting from successful esterification. Also the yield of products were determined from the weight of recovered modified starch products and calculated on the basis of 100% theoretical conversion of acyl chloride to ester. The results are shown in Table 1.

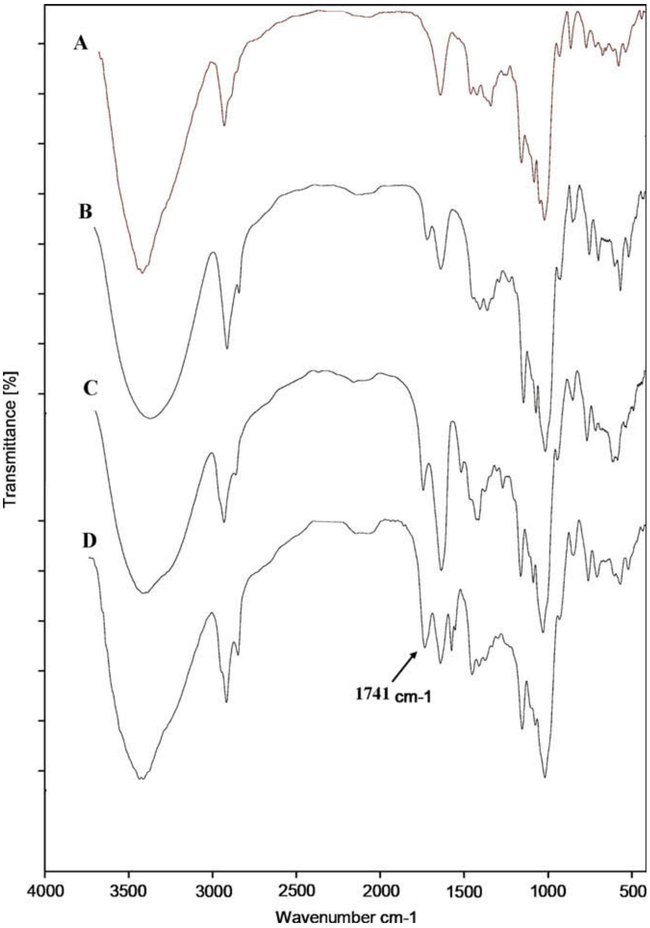

Fig. 2. FT-IR spectrum of (A) unmodified starch nanocrystal (B) decanoyl starch nanoparticles (C) nonanoyl starch nanoparticles (D) octanoyl starch nanoparticles.

3.4. Wettability test

In general, the introduction of hydrophobic fatty acid groups into the molecular structure of starch nanocrystals would alter their surface properties. Wettability can be defined as the tendency of one solvent to spread on a polymer surface in the presence of one or more immiscible solvent. Wettability is known to be one of the basic parameters in determining the physical, chemical and several functional properties of polymers. It can study qualitative by a simple and valuable experiment. In this method modified materials should mix with two immiscible solvents having different polarities to observe the affinity between these two substances. In our experiments, the distilled water and chloroform were used as the solvent system giving rise to two phases, the upper one corresponding to water ($d = 1$) and lower one to chloroform ($d = 1.47$). The reference experiment consisted of putting the same amount of unmodified starch nanoparticles in the mixture. Obviously, native starch nanoparticles were not able to migrate into chloroform and remained in water medium due to its higher affinity with water. Even after shaking the container, we observed that starch still remained in the aqueous medium (Fig. 3A).

Therefore, it was concluded that unmodified starch nanoparticles displayed a higher affinity for a polar solvent such as water.

Table 1
Characterisation of modified starches based on elemental analysis.

Sample	C%	DS	Yield (%)
Starch nanocrystal	44.1	–	–
Octanoyl starch nanoparticle	47.60	0.13	54
Nonanoyl starch nanoparticle	46.79	0.09	59
Decanoyl starch nanoparticle	46.80	0.08	41

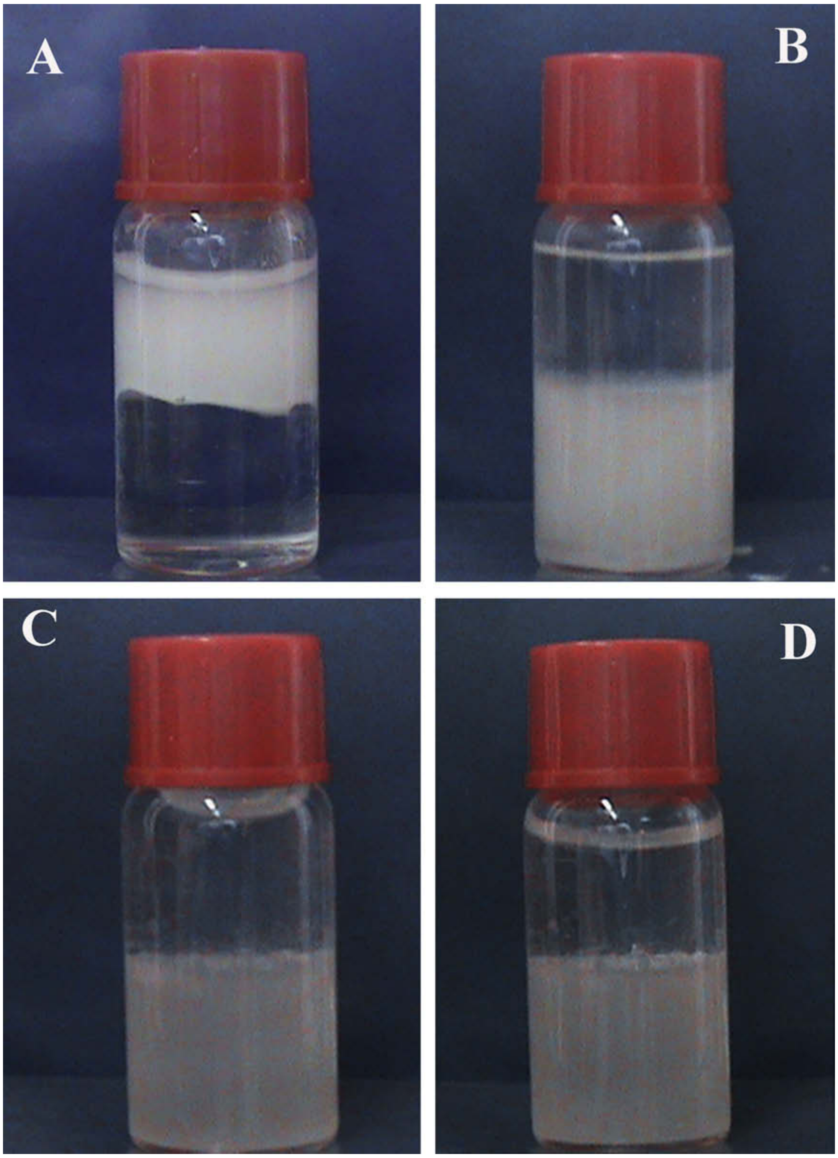

Fig. 3. Wettability tests of (A) unmodified starch nanocrystals in distilled water (B) octanoyl starch nanoparticles (C) nonanoyl starch nanoparticles (D) decanoyl starch nanoparticles in chloroform.

By adding modified starch nanoparticles to the mixture and shaking it, we clearly noticed that they migrated toward the chloroform (Fig. 3B–D), suggesting the lower polar nature after chemical modification of starch nanoparticles by fatty acids.

3.5. Morphological investigation

Transmission electron microscopy were utilized for observation of morphological changes at first during starch nanocrystal formation and then through starch nanocrystal modification by using fatty acids. Also the TEM micrograph corresponding to starch nanocrystal, octanoyl, nonanoyl and decanoyl modified starch nanocrystals have shown in Fig. 4. After acid treatment process of native waxy corn starch granules, the granules have been destructured and degraded to be nanocrystales with a size range of 70–100 nm (Fig. 4A).

TEM micrograph of modified starch nanocrystals by fatty acid (Fig. 4B–D) show that after surface chemical modification it seems that the size of modified starch nanoparticles have increased slightly in comparison of that unmodified starch nanocrystals.

3.6. XRD and DSC investigation

Starch is a biosynthesized polymer containing semi-crystalline granules with varying polymorphic types and degree of crystallinity. Polymorphism of the α-glucans is one of the main characteristics of the crystalline parts in starch granules. Because native starch granules contain crystalline regions as shown by their unique X-ray diffraction patterns (XRD). Therefore, granular crystallinity also can be studied with X-ray diffraction technique.

The crystallinity of unmodified starch nanocrystal and modified starch nanocrystals with fatty acids were discussed on the basis of their X-ray diffractions patterns. Fig. 5 shows the comparison of X-ray diffractograms of unmodified and modified waxy corn starch nanoparticles. It is generally considered that A-type starches such as waxy corn starch nanocrystals exhibit two peaks at about 15° and 23° 2θ, and an doublet at 17° and 18° 2θ (Fig. 5A). However, after chemical modification in homogenous condition in the case of octanoyl, nonanoyl and decanoyl starch nanoparticles neither the crystallization peak of fatty acids nor that of starch nanocrys-

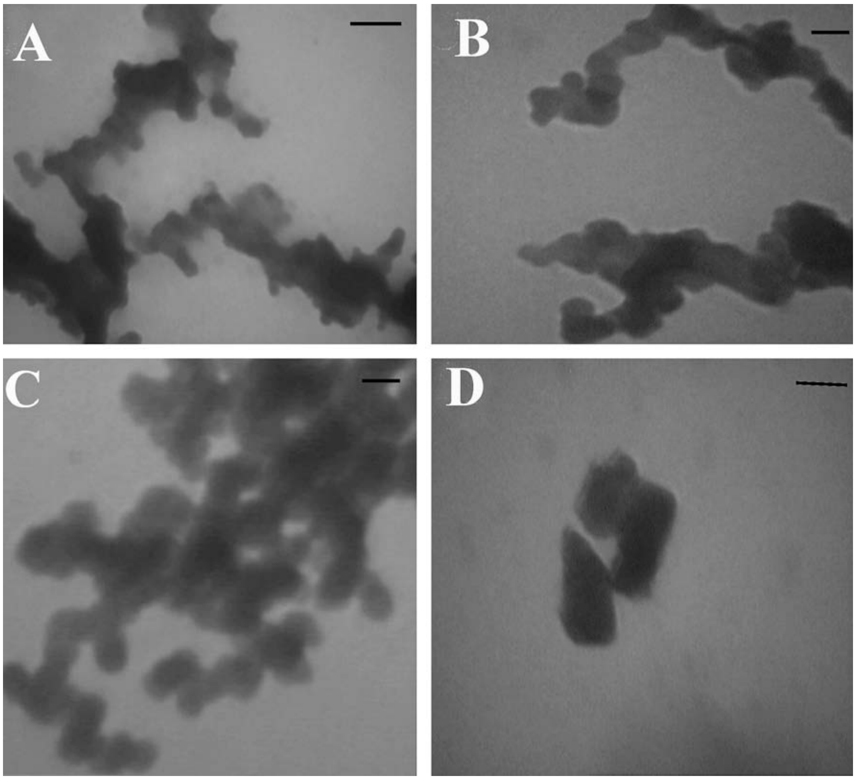

Fig. 4. TEM micrograph of (A) starch nanocrystals (B) decanoyl starch nanoparticles (C) starch nanoparticles (D) nonanoyl starch nanoparticles; scale bar: 100 nm.

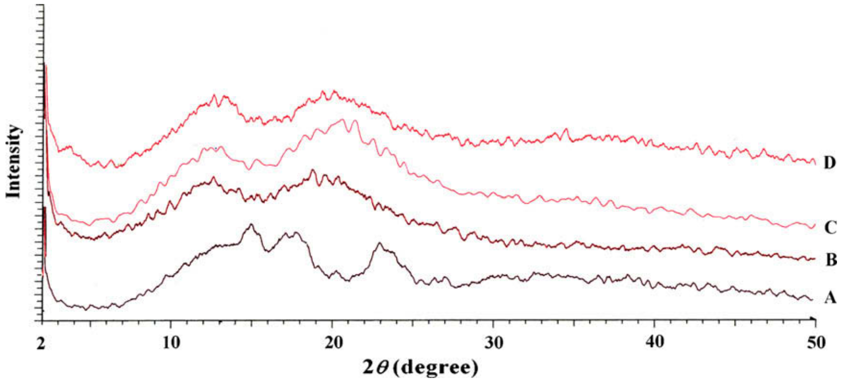

Fig. 5. X-ray diffraction patterns of (A) unmodified starch nanocrystals and (B) octanoyl starch nanoparticles (C) nonanoyl starch nanoparticles (D) decanoyl starch nanoparticles.

tals were observed but two broad peaks around 9–15° 2θ and 16–24° 2θ have appeared.

In order to have better view to the investigation of obtained result of XRD spectrum, the DSC analysis was carried out on one of the products and also on unmodified starch nanocrystals. The typical DSC curves for starch nanocrystals and nonanoyl modified starch nanocrystals are presented in Fig. 6. As shown starch nanocrystals have a peak in region between 112 and 240 °C related to melting of starch nanocrystal's crystalline phase with starch nanocrystals decomposition occurring above 240 °C. The nonanoyl modified starch nanocrystals did not show a separate melting signal in its DSC thermograms The absence of an additional signal of crystalline phase in DSC curve and XRD spectrum is an indication of the absence of a crystalline phase of fatty acids at the starch nanocrystals surface and also existence of peak in region between 112 and 240 °C is related to melting of crystalline phase in DSC curve of modified starch nanocrystals which show that the crystalline structure of starch nanocrystales have been preserved during

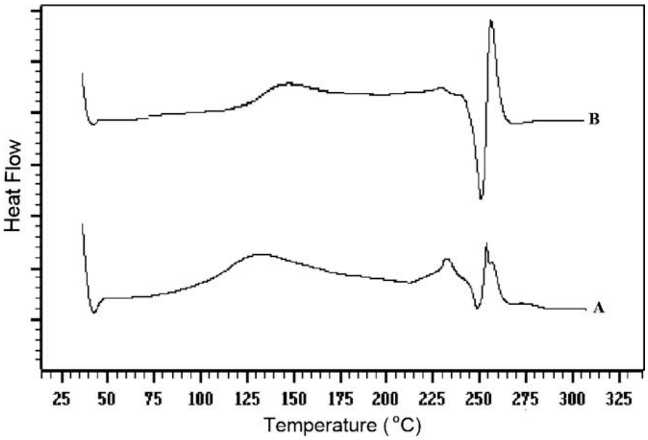

Fig. 6. DSC thermograms of (A) unmodified starch nanocrystals and (B) nonanoyl starch nanoparticles.

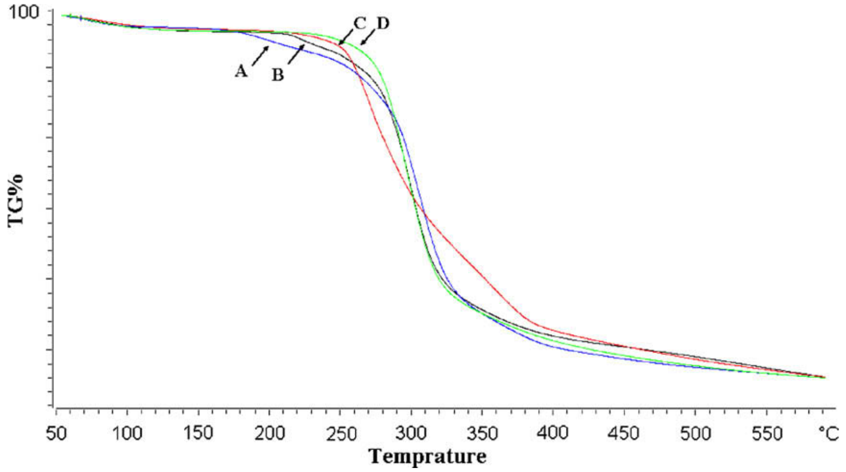

Fig. 7. TGA thermograms of (A) starch nanocrystals (B) octanoyl starch nanoparticles (C) decanoyl starch nanoparticles (D) nonanoyl starch nanoparticles.

esterification reaction in alkaline aqueous medium. DSC observation is in agreement with pervious results reported in the literatures (Wang & Wang, 2002). However, XRD spectrums of products show only two broad peaks. Such phenomenon has been observed in similar works that authors mentioned it can be attributed to the coating of starch nanoparticles with a grafted layer, which provides a diffusing layer around the nanoparticles (Labet, Thielemans, & Dufresne, 2007; Thielemans et al., 2006).

3.7. Thermal properties

3.7.1. TGA

The thermal stability of the starch nanocrystals, octanoyl, nonanoyl and decanoyl modified starch nanocrystals have been investigated by using TGA technique. The TGA curves of related materials have shown in Fig. 7. On the TGA curves, one can see that the degradation process of them occurred in two steps. The first range (50–200 °C) is associated with the loss of water, whereas the second range (200–600 °C) corresponds to the degradation of starch and its derivatives. Also Table 2 provides TGA data for the unmodified starch nanocrystals and also the modified starch nanoparticles. The data include the 10% degradation temperature of peak, $T_{0.10}$, a measure of the onset temperature of the degradation of peak, 50% degradation temperature, $T_{0.50}$, the mid-point of the degradation process. The collected data show that the thermal stability of the fatty acid modified starch nanocrystals, as evaluated by $T_{0.10}$, have increased in comparison of that unmodified starch. Nanocrystals that this greater thermal stability of modified starch nanoparticles is probably due to the lower amount of remaining hydroxyl groups after acylation.

4. Conclusion

In summary, starch nanocrystals were hydrophobically modified with octanoic acid, nonanoic acid and decanoic acid by mild esterification using acyl chlorides in aqueous media. The evidence for the occurrence of chemical modification was checked by FT-IR spectroscopy. The wettability test clearly showed that the described chemical modifications have changed the character of starch nanocrystals surface. Also comparison of TGA curves of modified and unmodified starch nanocrystals indicated that the modified starch nanoparticles have greater thermal stability and finally, DSC studies showed that the starch crystalline structure has not changed during reaction.

Table 2
Collected data from TGA thermograms.

Sample	$T_{0.1}$	$T_{0.5}$
Starch nanocrystals	245	304
Octanoyl starch nanoparticles	260	303
Nonanoyl starch nanoparticles	272	302
Decanoyl starch nanoparticles	260	305

Acknowledgments

We thank Department of Physics and Department of Material Engineering in the University of Tabriz for XRD analysis and SEM 3Images and SUT for TGA analysis. Authors also greatly acknowledge the University of Tabriz for the financial supports of this work.

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