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Synthesis and characterization of starch-modified polyurethane

M. Barikani *, M. Mohammadi

Department of Polyurethane and Nanopolymers, Faculty of Science, Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Islamic Republic of Iran

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Abstract

Corn starch was reacted with urethane prepolymer in order to modifying starch and preparing new hydrophobic copolymers. These copolymers were prepared by two-step reactions. The polycaprolactone terminated hexamethylene diisocyanate (HDI) (as prepolymer) was prepared by introducing diisocyanate on both ends of PCL at a molar ratio of 1:2 (PCL:HDI). The grafting was performed by addition of polycaprolactone based prepolymer to starch solution of DMSO with different weight ratio of starch and prepolymer. The samples were characterized and examined by FTIR and ^{1}H NMR spectroscopy, DSC analysis, and scanning electron microscopy (SEM). By introducing NCO groups onto the PCL terminals, the FTIR spectrum shows a new sharp peak, representing the NCO groups and formation of prepolymer. By grafting this prepolymer onto starch a NH and urethane band were appeared. The effect of prepolymer percentage on hydrophobicity was measured through contact angle and it was found that increases with increasing amount of prepolymer. Glass transition temperature (T_g) is also affected with increasing amount of urethane linkages. Surface morphology of modified starch was studied by SEM. It was observed that the surfaces of modified starch are rougher and disordered than the surface of unmodified starch particles. This confirms the grafting and modification of starch. This modified starch can be used as filler in biodegradable starch based polymers.

Keywords: Starch; Grafting; Polycaprolactone; Diisocyanate; Modification

1. Introduction

Biodegradable materials derived from renewable resources have been carried into the center of public interest for environmental protection and sustainable development (Cao, Zhang, Huang, Yang, & Wang, 2003). Biodegradable polymers are, however, suitable in many commodities and medical applications, such as packaging, surgical implants, controlled release, and drug delivery systems, but their use is still limited due to their high cost or their low performances (Aminabhavi, Balundgi, & Cassidy, 1990).

Modification of the physical and chemical properties of these materials, through reaction or blending with other biodegradable and nonbiodegradable polymers, is often necessary to meet the required performances (Iannace, Ambrosio, Huang, & Nicolais, 1994; Iannace, DeLuca, Nicolais, Carfagna, & Huang, 1990; Iannace, Ambrosio, Huang, & Nicolais, 1995). As a biopolymer from agricultural resources, starch with multi-hydroxyl groups has been considered as an alternative material in developing degradable plastics because of its biodegradability, derivability, availability and low cost (Whistler, 1984). However, the applications of pure starch materials are limited because of its water sensitivity and brittle property, so by itself cannot satisfactorily replace the functional and physical properties of nondegradable polymers (Kweon, Cha, Park, & Lim, 2000).

The synthesis of biodegradable PUs is a relatively recent issue in PU chemistry. It is well known that polyester based PUs are much more susceptible to biodegradation than PUs derived from polyether diols (Huang, 1989). Biodegradable urethanes were also synthesized by using

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* Corresponding author. Tel.: +98 21 44580081; fax: +98 21 44580021.
E-mail address: M.Barikani@ippi.ac.ir (M. Barikani).

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polyester segments, such as lactic acid (Harkonen, Hiltunen, Malin, & Seppala, 1995; Owen, Masaoka, Kawamura, & Sakota, 1995) poly (3-hydroxybutyrate) (Hori, Suzuki, Okeda, Imai, & Sakaguchi, 1992), and polyethylene adipate (Sreenivasan, Jayabalan, & Rao, 1991). Polyurethanes obtained by reacting aliphatic and aromatic diisocyanates with poly (caprolactonediol)s of various molecular weights were treated with microorganisms and enzymes. There is a correlation between flexibility and biodegradability. In general, the more flexible the PUs, the more susceptible to biodegradation (Huang, Macri, Roby, & Benedict, 1981).

A successful method of increasing biodegradability is to develop biopolymer-based materials (Huang, Koenig, & Huang, 1993; Meister, Aranha, Wang, & Chen, 1993). Cellulose, starch, proteins, lignin, and polysaccharides are naturally occurring polymers obtained from renewable sources. They are readily biodegradable and tend to degrade in biologically active environments like soil, sewage and marine locations where bacteria are active (Alfani, Iannace, & Nicolais, 1998). Starch which is the second largest biomass produced on earth, has been widely used in blends with nonbiodegradable and biodegradable polymers either to lower the total cost and/or to improve the biodegradability of the material (Kim & Lee, 2002; Sun & Sun, 2002; Vargha & Truter, 2005). The hydroxyl functionality of this biopolymer allows chemical reactions with conventional diisocyanates or urethane prepolymer.

This article reports on the results of synthesis and characterization of starch-modified polyurethane. A prepolymer was synthesized by the step-growth polymerization (Barmar, Barikani, & Kaffashi, 2004) of polycaprolactone diol (CAPA, $M_n = 2000$) with a proper amount of hexamethylene diisocyanate (HDI). The prepolymer was then grafted onto starch and the final polymer was characterized. The effect of starch content on T_g, morphology and hydrophilicity was studied.

2. Experimental

2.1. Materials

Polycaprolactone (Capa 225) with number-average molecular weight of 2000 was obtained from Interox Chemical Co Ltd. and dried under vacuum at 50 °C for 24 h prior to use. Hexamethylene diisocyanate (HDI) (Merck) was used without any further purification. Dimethyl sulfoxide (DMSO) (Merck) was purified by distillation under reduced pressure over CaH_2 and stored with molecular sieves (4 Å). Corn starch (Borhan pooya chemie) was dried in a vacuum oven at 90 °C for 48 h and dissolved in dry DMSO before use.

2.2. Preparation of prepolymer

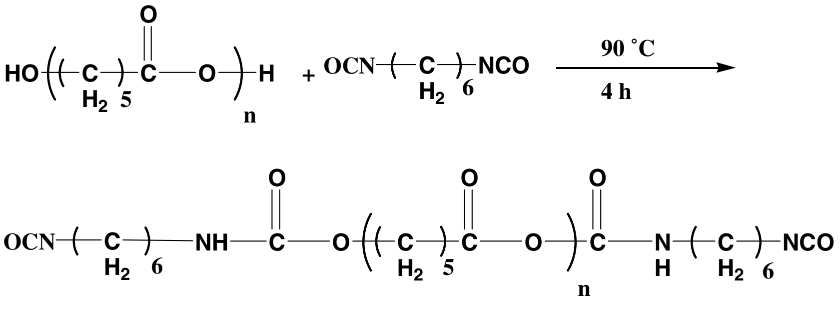
A 250 ml round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and pipette outlet was used as a polymerization reaction vessel [21]. Reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture and forming a blanket of gas. Polycaprolactone diol (Capa) was charged into the dried flask and the system was heated to 90 °C, while stirring. Then HDI was added to Capa slightly with a dropper funnel. The reaction mixture was heated at 90 °C for 4 h to obtain NCO terminated prepolymer. The prepolymer reaction sequence is shown in Scheme 1. Final prepolymer was kept in a closed container under nitrogen gas blanket for further reaction with starch.

2.3. Preparation of starch solution

Corn starch was dried in a vacuum oven at 90 °C for 48 h before preparation of solution, then the required amount of starch (10 g) was added to 100 ml anhydrous DMSO in a round-bottomed flask equipped with mechanical stirrer, condenser and thermometer. The mixture was heated to 50 °C for at least 36 h while stirring. Forming of a clear solution shows complete dissolving of starch.

Table 1
Weight percent of prepolymer and starch used in the reaction

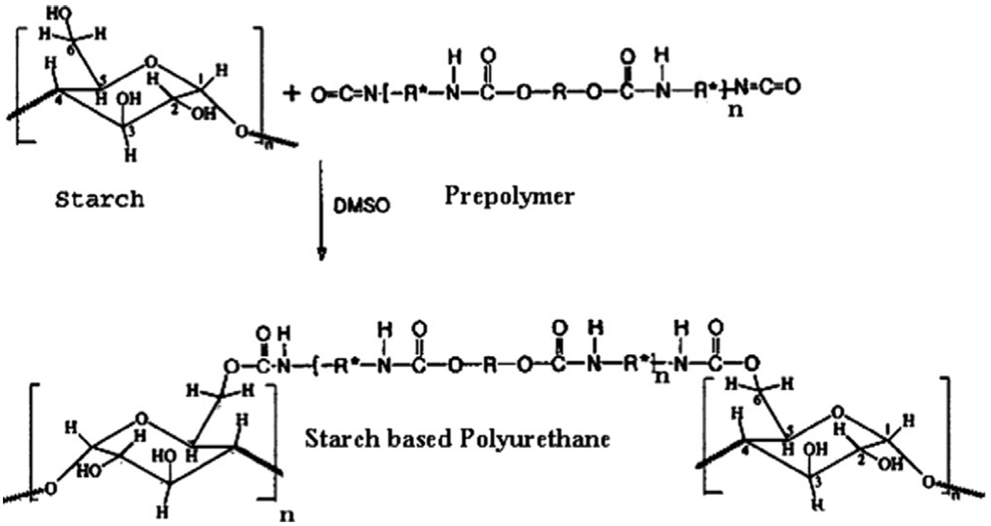
Sample no.	Prepolymer (%)	Weight ratio (prepolymer/starch)
1	2	1:49
2	5	1:19
3	10	1:9
4	17	1:5
5	25	1:3



Scheme 1. Preparation of polycaprolactone based prepolymer.

2.4. Preparation of starch grafted prepolymer

Vacuum dried corn starch (10 g) was dissolved in anhydrous DMSO (100 ml) and, separately, polycaprolactone based prepolymer was dissolved in anhydrous DMSO (10 ml solvent for 1 g of prepolymer). A 500 ml round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and Dean–Stark trap was used as a reaction vessel (Seyed Mohaghegh, Barikani, & Entezami, 2006). Required amount of starch solution was placed into the flask. The reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture. The prepolymer solution was slowly added to starch solution through Dean–Stark trap and the system was heated to 85 °C, while stirring for 30 min. The mixture was then



Scheme 2. Preparation of starch based polyurethane.

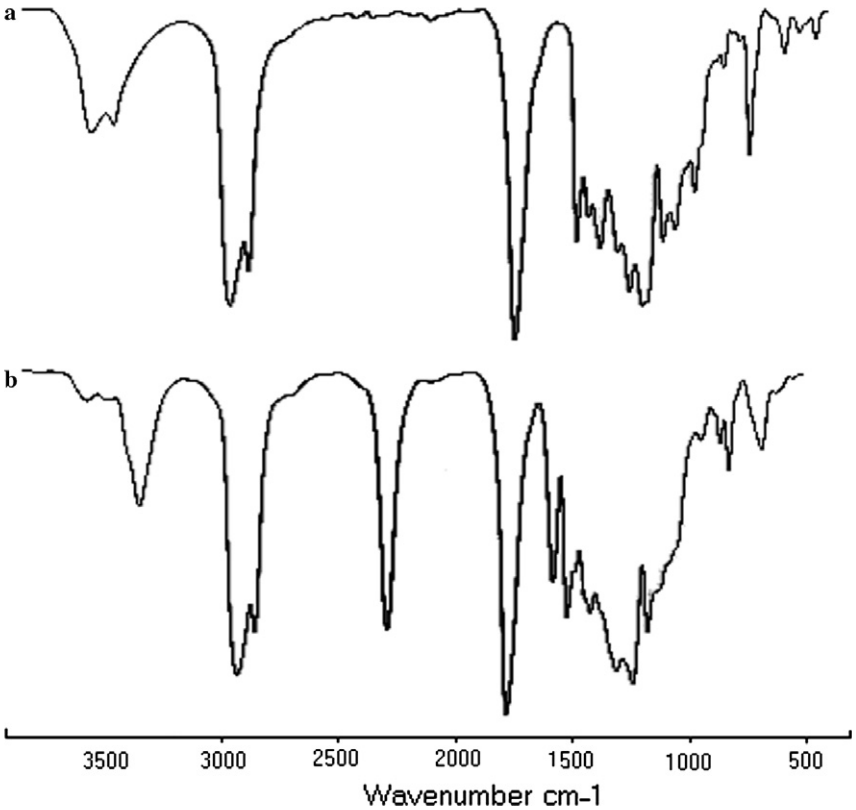


Fig. 1. FT-IR spectra of prepolymer with Capa 225 and HDI.

stirred for 3 h at the same temperature. The reaction mixture was cooled to room temperature, and then excess methanol was added to the mixture. The precipitate was recovered by filtration. The unreacted prepolymer was removed by repeating the solvent–nonsolvent procedure. The final product was kept for 72 h in vacuum oven at 80 °C. The weight percent of prepolymer and starch used in this reaction are given in Table 1 and the reaction sequence is shown in Scheme 2.

2.5. Characterization

IR measurements were performed on a Bruker IFS 48 Fourier transform infrared (FT-IR) spectrometer. The ^{1}H NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO)-d_6 solution using a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ) are given in ppm with tetramethylsilane as a standard. Contact angle was measured by G10 (KRUSS) instrument through sessile drop method. DSC analysis was recorded on a Stanton Redcraft STA-780 (Rheometric Scientific). Samples were heated from room temperature to 250 °C at a heating rate of 20 °C/min. A Cambridge scanning electron microscope (S360) was used to observe the surface morphology of the copolymer. The samples were fractured after immersion in liquid nitrogen and the materials was coated with a thin layer of gold by Bio-Rad, E5200 Auto sputter coater before the observation.

3. Results and discussion

3.1. IR spectroscopy of prepolymer

The prepolymer which having isocyanate terminals at both ends, was prepared by the reaction of polycaprolactone and diisocyanate at the molar ratio of 1:2 for Capa:HDI. The reaction is briefly shown in Scheme 1. This prepolymer was used as the intermediate for the starch based polyurethane. The FT-IR analysis was applied to characterize the prepared prepolymer (Fig. 1). FT-IR spectra of unreacted polycaprolactone showed a strong hydroxyl peak around 3442 cm^{-1} and a sharp peak at 1724 cm^{-1} for the internal ester groups. By introducing NCO groups onto the polycaprolactone terminals a new sharp peak at 2270 cm^{-1} representing the NCO groups and 1525 and 3387 cm^{-1} for the newly formed amide–NH groups were shown. At the same time the hydroxyl peak around 3442 cm^{-1} almost disappeared in the prepolymer spectra.

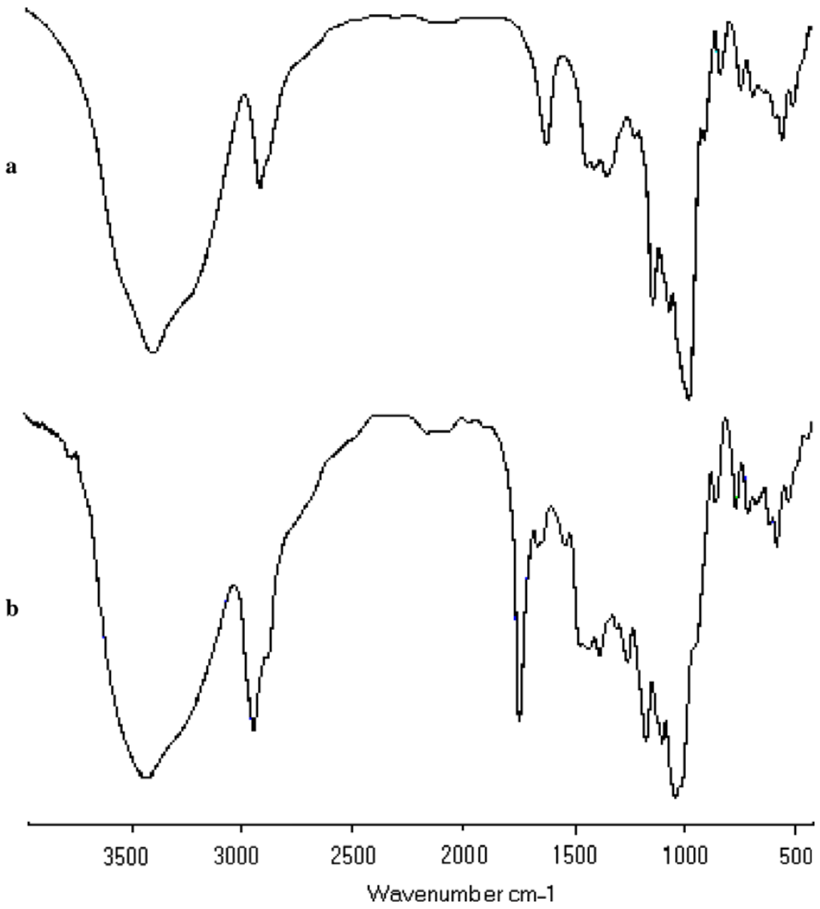


Fig. 2. FT-IR spectra of (a) starch, (b) starch-modified polyurethane.

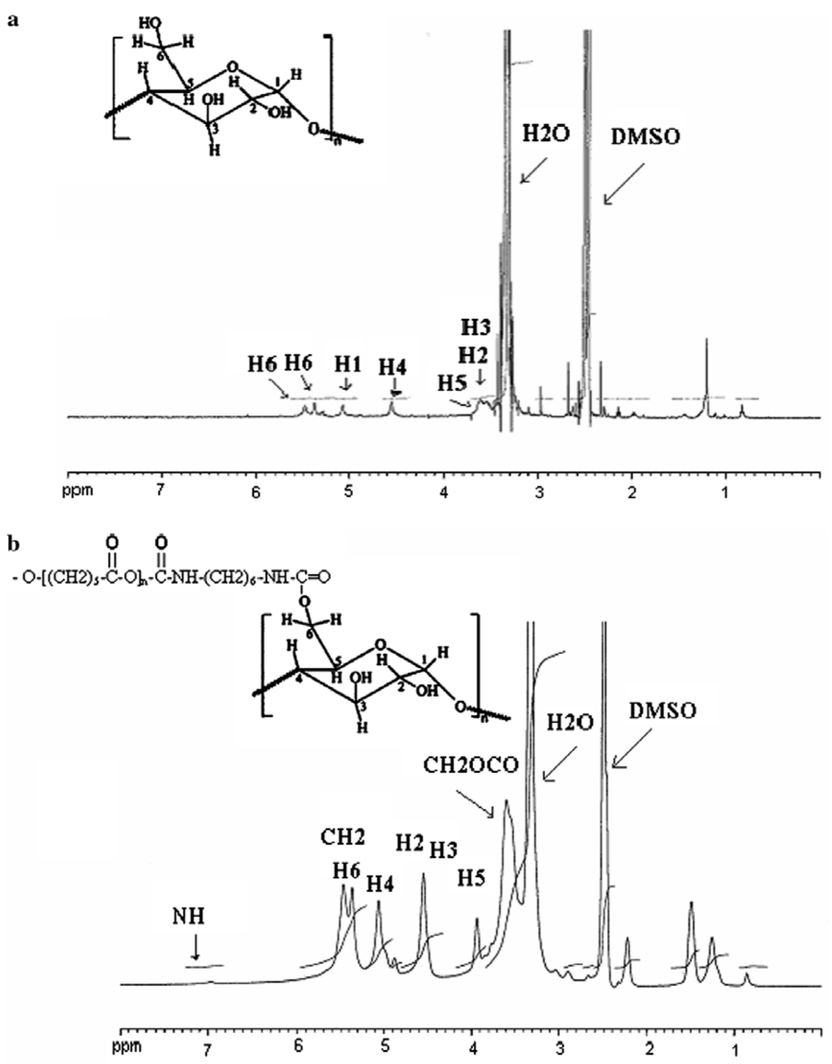


Fig. 3. ^{1}H NMR spectra (a) starch, (b) starch-modified polyurethane.

3.2. Starch-modified polyurethane

The starch-modified polyurethane with different percentage of starch by using polycaprolactone terminated hexamethylene diisocyanate prepolymer was achieved. The reaction is briefly shown in Scheme 2, and the weight percent of prepolymer and starch used in the reaction are given in Table 1. Chemical reaction of starch with prepolymer gives chance for a reaction between OH group in the repeat unite of starch with NCO group of prepolymer producing final polyurethane. This reaction takes place between more reactive OH groups in starch and one end of NCO group of prepolymer till all free prepolymer chain react at least in one end. Then the second stage of reaction start by free starch OH group and prepolymer NCO group of the other end. It is clear that the reaction rate of the second stage is much lower than the fist stage due to less mobility of the polymer chains. The FT-IR and ^{1}H NMR spectra of the starch-modified polyurethane are shown in Figs. 2 and 3, respectively. In Fig. 2, the corn starch

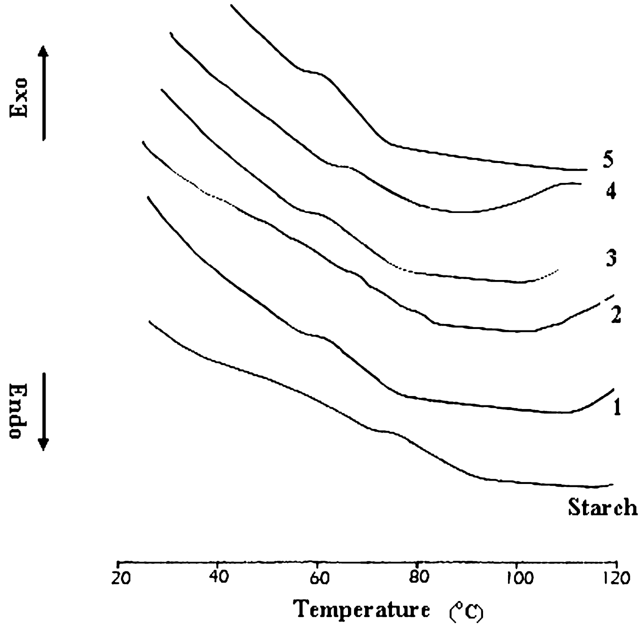


Fig. 4. DSC thermograms of starch compared with starch-g-copolymers.

Table 2
The variation of contact angle with % of grafted prepolymer on starch

Sample no.	Prepolymer on starch (%)	Contact angle (θ)°
Starch	0	0
1	2	87
2	5	88
3	10	91
4	17	105
5	25	107

showed a typical broad hydroxyl peak at 3410 cm^{-1}, a sharp C—H stretching peak at 2927 cm^{-1} and C—O stretching between 937 and 1156 cm^{-1}. By grafting prepolymer onto starch, the FT-IR spectra showed a new peak at 1734 cm^{-1} indicating urethane C═O band and 1540 cm^{-1} for the urethane–NH. The NMR spectra also confirmed the grafting of prepolymer onto starch (Fig. 3). The signal of the urethane proton (NHCOO) was observed at 7.10–7.91 ppm. Some new peaks were observed at 3.77–4.88 ppm and 2.63–3.03 ppm assignable to protons of the CH_2, CH_2O, CH_2OCO and CH_2N support the formation of starch-modified polyurethane.

3.3. Thermal properties

Calorimetric curves of the starch-modified polyurethane as a function of prepolymer content are reported in Fig. 4. The glass transition temperature of these polymers decrease with increasing percentage of prepolymer, and higher T_g's are related to greater amount of starch in the initial composition. This is the first evidence that starch participates in the chemical reaction, becoming part of the macromolecular structure. The decrease of T_g suggest that the molecular mobility of the starch is increased by the addition of prepolymer. In addition, the T_g variation of grafted copolymers not only depend on the amount of grafted prepolymer, but also to the crosslinking effect of prepolymer between two chains of starch and strong hydrogen bonding between molecules which affected on chain mobility of starch-modified urethane in different ways.

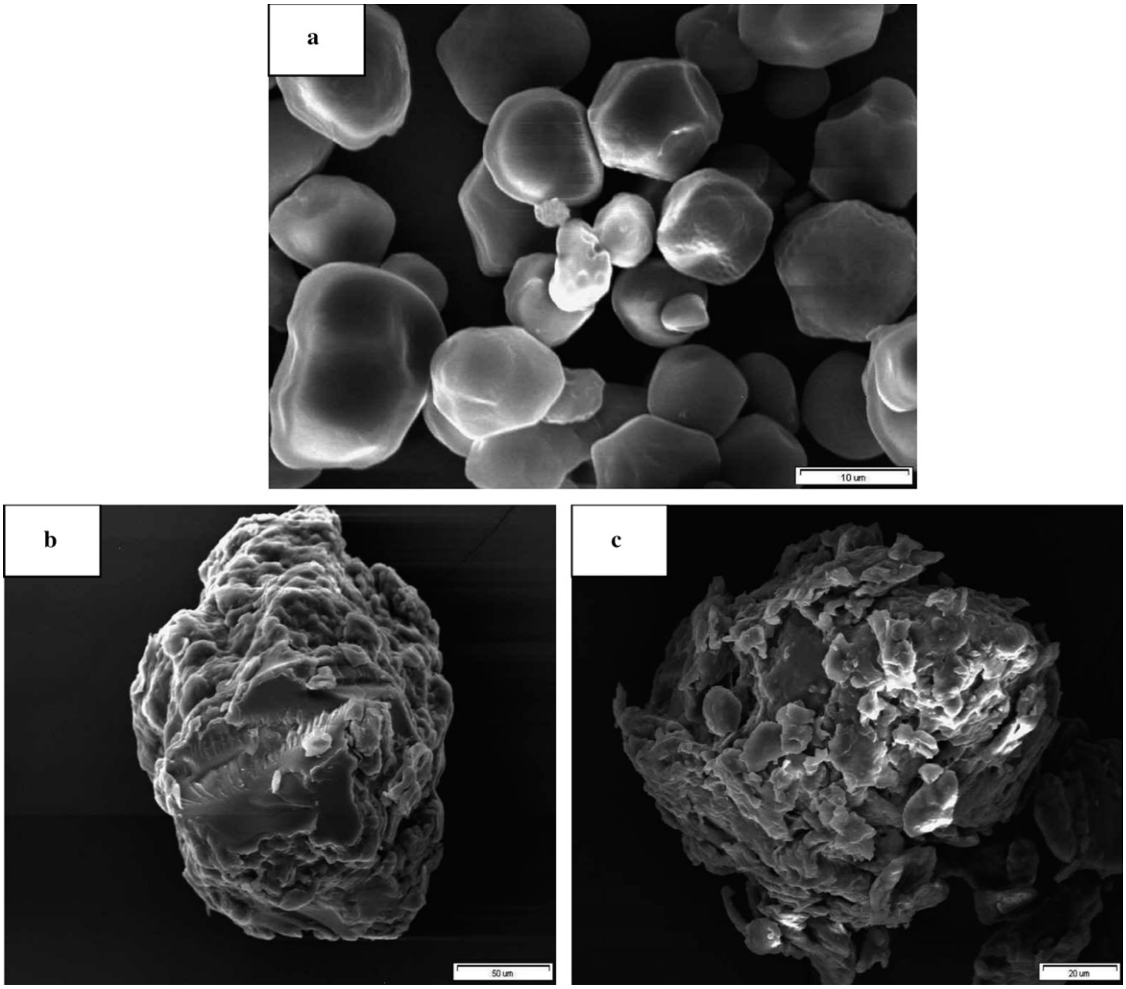


Fig. 5. SEM micrographs of (a) starch, (b) starch-modified urethane, (sample no. 3); (c) (sample no. 5).

3.4. Measurement of contact angle

Hydrophilicity was evaluated by measuring the contact angle formed between water drops and the surface of the modified samples using contact angle measuring system G10 (KRUSS). For this purpose, the drops of water were mounted on 3 different areas of the surface with a microsyring. Results are mean value of three measurements on different parts of the samples. Photos of water drops on the samples were performed from monitor. The contact angle measurements (θ) of starch grafted PU with different percentage of starch are shown in Table 2. As it can be seen, there is a remarkable difference between starch and starch-modified polyurethane with different weight percent of starch or prepolymer, where increases from 0° for starch to 107° for grafted PU with 25% prepolymer. This means that hydrophilicity of starch decreases with grafting by urethane prepolymer.

3.5. Scanning electron microscopy (SEM)

Surface morphological analysis of starch and starch-modified polyurethane were confirmed by scanning electron microscopy (SEM) and is presented in Fig. 5. The scanned surface reveals that starch granules were completely coated by a tightly adhering polyurethane layer. This also confirms the strong adhesion between the polyurethane and the surface of the starch granules and is an evidence of grafting between the starch and polyurethane. It is obvious that the smooth surface of the starch, converted to a completely rough surface which is a good property for use it as a filler in biodegradable starch based polyethylene (Thakore, Desai, Sarawade, & Devi, 2001). This may improve compatibility and better dispersion of starch in PE matrix.

4. Conclusion

An attempt was made to prepare new hydrophobic starch-modified urethane by reaction between a urethane prepolymer and corn starch. The prepolymer was synthesized by the reaction of polycaprolactone diol and hexamethylene diisocyanate. The reaction products were characterized and confirmed by ^{1}H NMR and FT-IR spectroscopy, DSC analysis, and scanning electron microscopy (SEM).The effect of prepolymer percentage on hydrophobicity was measured through contact angle and it was found that it increases with increasing amount of prepolymer. Glass transition temperature (T_g) moved toward the lower temperature with increasing amount of urethane linkages. The scanned surface reveals that starch granules were completely coated by polyurethane. This confirms the strong adhesion between the polyurethane and starch granules. This modified starch can be used as filler in biodegradable starch based polyethylene due to better dispersion and compatibility.

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