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Chemical modification of starch with hexamethylene diisocyanate derivatives

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Abstract

Chemical modification of potato starch in a two-step process has been presented. At the first stage the starch modifiers, i.e. isocyanate derivatives were synthesised by the equimolar reaction between hexamethylene diisocyanate (HMDI) and monoalcohol or monoamine. Proton NMR analysis has revealed that the prepared modifiers contain monoisocyanate compounds with respectively urethane or urea bonds, as the main products. Synthesis of HMDI-derived modifiers was followed using DSC method and the reaction products were characterized by the FTIR spectroscopy. At the second step starch was modified with the synthesised HMDI derivatives, in *N*-methylpyrrolidone slurry. Some properties of the obtained starch polymers were investigated and compared, i.e. efficiency of substitution, IR spectra, hydrophobic/hydrophilic features, DSC thermograms (melting temperatures) as well as moldability (hot press melt flow).

Keywords: Thermoplastic starch; Urethane starch derivatives

1. Introduction

In recent years a great emphasis has been put on the research of alternative biodegradable materials, which could at least partially replace commodity polymers based on petrochemical basis.

Starch, as a common and a relatively inexpensive biopolymer, is an attractive raw material to develop degradable plastics. It is composed of two different types of polymers: a nearly linear amylose and branched amylopectine. The processing of native starch is often followed by disrupting its granular structure (Nashed, Rutgers, & Sopade, 2003). When heated in the presence of water the starch granules swell, lose crystallinity and amorphous interior of granule diffuses into solution (Stepto, 2001).

Starch itself cannot satisfactorily replace the functional and physical properties of conventional plastics since starch-based plastics exhibit water sensitivity and a weak mechanical characteristics (Lu, Tighzert, Dole, & Erre, 2005). The mechanical properties of starch materials depend to a great degree on the amylose/amylopectin ratio (De Graaf, Karman, & Janssen, 2003). However, the thermoplastic starch can be an interesting alternative for synthetic polymers where long-term durability is not required and a rapid desintegration is an advantage (Van Soest, de Wit & Vliegenthart, 1996). Previously reported methods to overcome the mentioned drawbacks were based on manufacturing of composites of starch with reinforced fibres (Dufresne & Vignon, 1998) or clays (Huang, Yu, & Ma, 2004) and by blending or grafting with hydrophobic polymers (Kweon, Cha, Park, & Lim, 2000). Another possibility of chemical modification of starch is the derivatization of the hydroxyl groups of polysaccharide chains to create low molecular branches via ester, ether, or urethane bonds.

The properties of starches modified by chemical derivatization depend greatly on the degree of substitution (DS) and the length of the introduced alkyl chain. The higher

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DS and the longer aliphatic chain the better are the hydrophobic properties.

In the literature there are some contributions on chemical modification of starch with isocyanates. For example such reactions are reviewed by Tomasik and Schilling (2004). However, the modifications of starch towards hydrophobic thermoplastic starch derivatives with higher degrees of substitutions are reported in only few cases (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005; Engelmann, Bonatz, Bechthold, & Rafler, 2001). The reaction medium was usually an inert organic solvent, e.g. benzene, toluene, pyridine (Wolff, 1951) or dimethylene sulfoxide (Engelmann et al., 2001). These solvents form a constant boiling mixture with water, that offers an additional advantage, as moisture has a tendency to transform the isocyanates into the substituted ureas (Wolff, 1951).

Engelmann et al. (2001) used aliphatic isocyanates synthesised previously from acyl chlorides in toluene for preparation of wrinkled pea starch carbamates. In other work an effect of temperature on the reaction rate between the aromatic isocyanate (phenyl isocyanate) and corn starch granules has been determined (Wolff, Watson, & Rist, 1952). The reaction rate increased along with elevation of temperature, however the reaction proceeds quite satisfactorily even at 25 °C (Wolff, 1951).

An interesting approach comprises a surface modification of the superficial OH groups of starch by coupling the reaction with e.g. phenyl isocyanate, which could change certain properties of material without changing its bulk characteristics (Carvalho, Curvelo, & Gandini, 2005). The result was a decrease of the hydrophilic character of the starch surface.

In this paper results of investigations of potato starch modified via the addition reactions with alkyl monoisocyanates prepared from hexamethylene diisocyanate (HMDI) and monoalcohol or monoamine in a polar solvent, *N*-methylpyrrolidone (NMP), are presented. The presence of additional urethane or urea bonds in short modifying branches can affect the properties of urethane starch derivatives, as compared to those found for polymers obtained with usually applied monoalkyl isocyanates modifiers (Engelmann et al., 2001). The influence of the type of modifier as well as the degree of substitution on some physicochemical and thermal properties, including the moldability of starch polymers was evaluated.

2. Experimental

2.1. Materials

Dried potato starch (superior standard, PPZ Trzemeszno, Poland) containing ca. 3 wt% of water was used for modifications. HMDI (98%), *n*-butylamine (99.5%) and *N*-methylpyrrolidone (NMP) (99%) purchased from Fluka (Steinheim, Germany), methanol (98%) and *n*-butanol (98%) products of POCh (Gliwice, Poland) were used as received.

2.2. Methods

2.2.1. Preparation of urethane- and urea-derivatives of HMDI

After placing of HMDI into a reaction flask an equimolar amount of methyl alcohol, butyl alcohol or butylamine was added dropwise. The reaction temperature was kept below the boiling point of the added substance for 2 h (urethane derivative) or 15 min (urea derivative). The crude products were subsequently used for starch modification.

2.2.2. Modification of potato starch

Potato starch was slurried in NMP in 250 ml reaction flask equipped with thermometer, mechanical stirrer, and a reflux condenser. Starch/NMP slurry (20/80% w/w) was initially heated at 90 °C for 0.5 h under nitrogen atmosphere. The appropriate molten monoisocyanate derivative was then added to the flask, and the system was heated at 115 °C for 6 h (for reaction towards starch derivatives with urethane–urethane bonds) or 4 h (towards starch with urethane–urea bonds). The modified starches were washed three times with methanol and after decantation dried at 60 °C to a constant mass.

2.2.3. Elemental analysis

Euro EA Series (Euro Vector CHNS-O Elemental Analyser, Milan, Italy) was used to perform an elemental analysis. The degree of starch substitution was determined on basis of the nitrogen content.

2.2.4. FTIR spectroscopy

Nexus Thermo Nicolet Corp. (Madison, WI, USA) equipped with ATR (Golden Gate) attachment was used. Powder polymer samples were used for analysis (32 scans, 400–4000 cm^{-1}).

2.2.5. Differential Scanning Calorimetry (DSC)

The Q100 DSC (TA Instruments Inc., USA) was used for starch derivatives characterisation (10 °C/min, from 20 to 260 °C). Samples were weighted (~8 mg) into aluminum pans and hermetically sealed before analyses. The analysis was repeated in triplicate. The reactions between HMDI and butyl alcohol or butylamine, respectively, were performed in the open aluminum pans under the isothermal conditions (25 and 30 or 100 °C). The mixtures of components with weight ~30 mg were investigated. The measurements were also repeated in triplicate.

2.2.6. NMR spectroscopy

The 400 MHz ^1H NMR spectra were measured on a Bruker DPX spectrometer (400 MHz) using deuterated chloroform as a solvent (HMDI/butyl alcohol) or deuterated DMSO (HMDI/butylamine) and tetramethylsilane as a shift reference.

2.2.7. Estimation of swelling index

Dry modified starch sample (0.5 g) was carefully poured with distilled water in a 10 ml measuring cylinder. After soaking for 24 h, volume of the swollen polymer was recorded.

2.2.8. Hot press moulding

Dry modified starch sample (0.5 g) was placed between two poly(ethylene terephthalate) film sheets and pressed at 160 °C under 12 MPa for 3 min using self-made press.

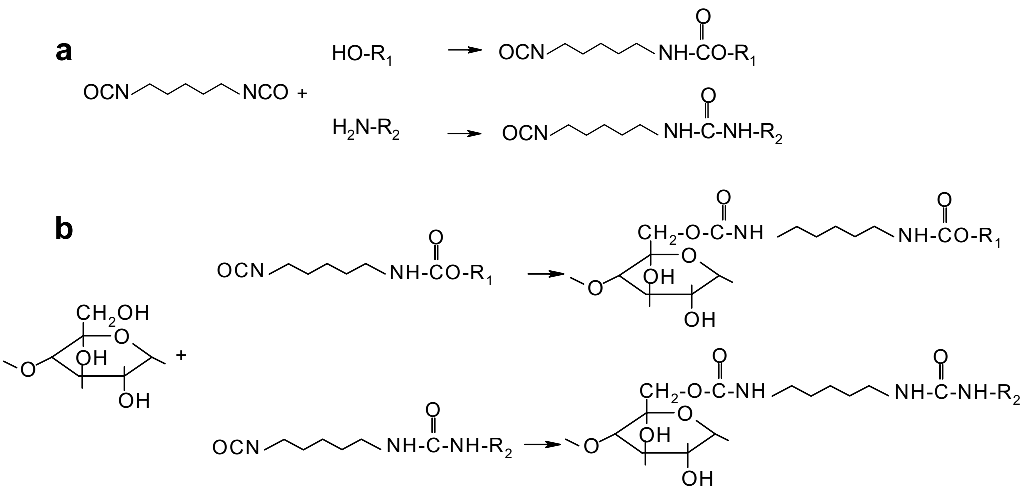

Fig. 1. (a) Reaction between HMDI and mono alcohol or primary amine, respectively, urethane- or urea-derivatives are formed. (b) Reaction between starch polysaccharide unit and HMDI/mono alcohol or HMDI/mono amine modifiers; urethane bonds are formed (for sake of clarity substitution of one of three hydroxyl groups is presented).

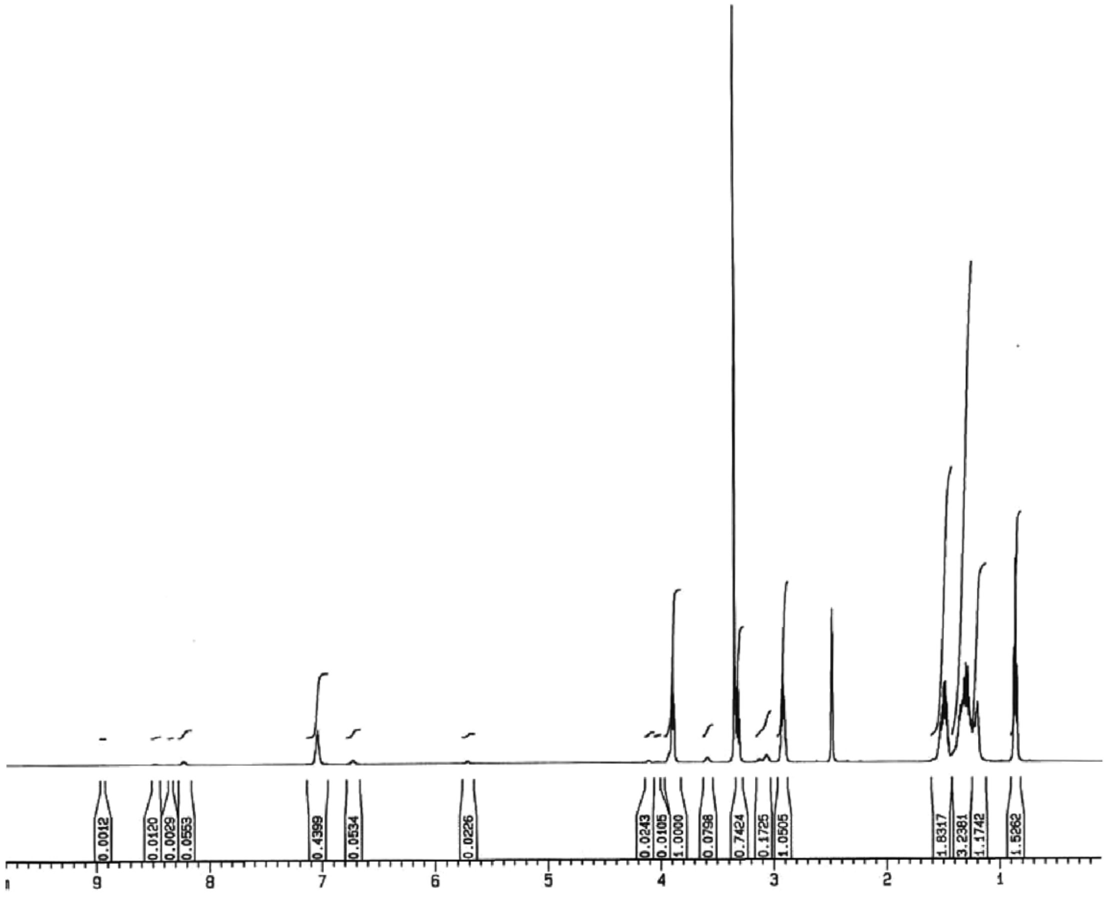

Fig. 2. ^{1}H NMR spectra of HMDI/*n*-butyl alcohol derivative.

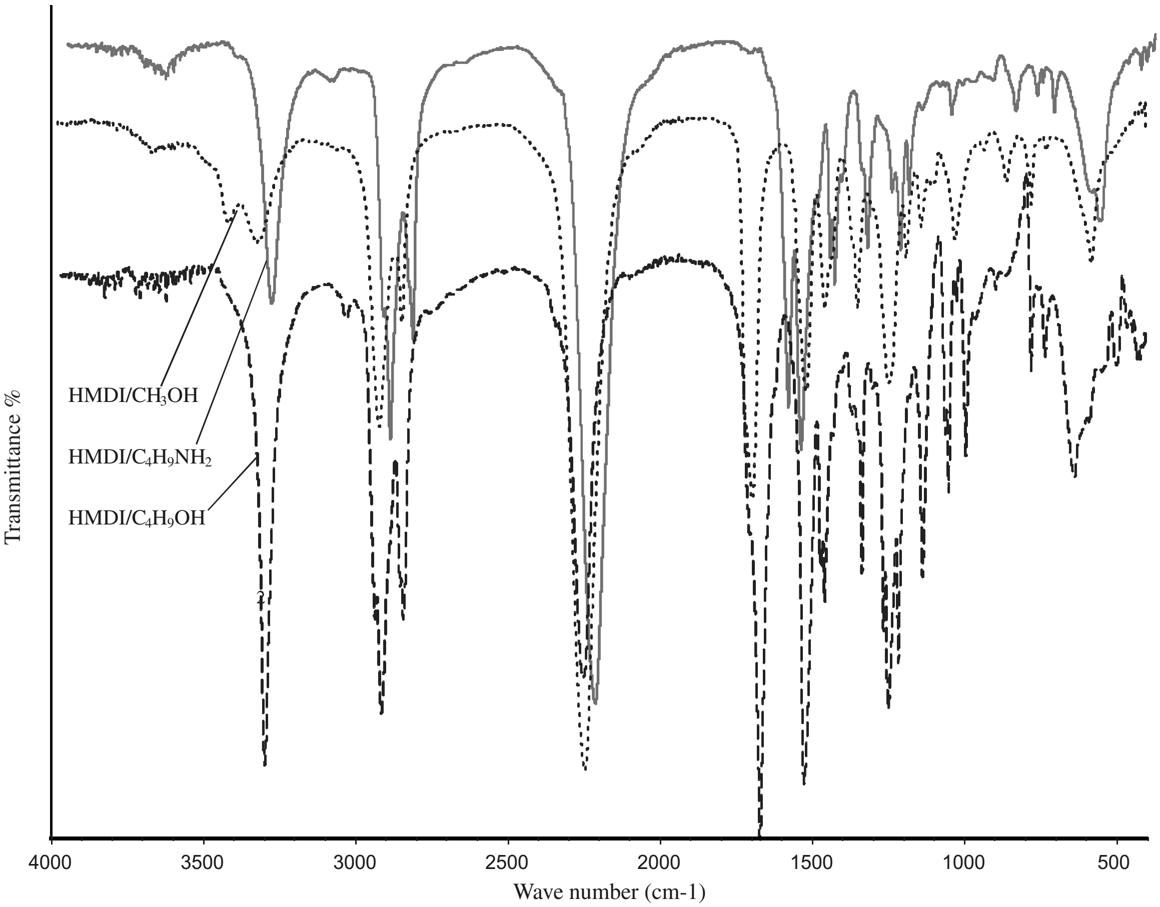

Fig. 3. FTIR spectra of urethane- and urea-derivatives of HMDI.

Table 1
FTIR characteristic bands of monoisocyanate starch modifiers

Modifier	NH	CH_2/CH_3	N=C=O	NH–(C=O)
$HMDI/CH_3OH$	3329	2935	2254	1699
$HMDI/C_4H_9OH$	3322	2934	2251	1683
$HMDI/C_4H_9NH_2$	3317	2918	2257	1618

The average diameter of press-shape material was measured in cm.

3. Results and discussion

3.1. HMDI derivatives as starch modifiers

Starch modification presented in this paper is a two-step process. At the first stage the starch modifier is synthesised. The modifiers were prepared in the reaction between hexamethylene diisocyanate and monoalcohol or monoamine. HMDI was used because it is relatively environmentally friendly (Ohkita & Lee, 2004). Urethane- or urea-monoisocyanate derivative, respectively, was obtained (Fig. 1a). In the second stage urethane–urethane or urethane–urea starch derivative was synthesised (Fig. 1b).

In order to control the content of monoisocyanate derivatives of HMDI in the starch modifiers, proton NMR spectra were recorded (Fig. 2). As HMDI is a difunctional reagent, the disubstituted derivatives may also be formed. ^1H NMR spectroscopy allowed to determine the ratio of mono-/disubstituted derivatives. The main products of both controlled syntheses (HMDI/*n*-butyl alcohol and HMDI/*n*-butylamine) are the monosubstituted derivatives (ca. 80% wt of HMDI monoisocyanates) (Wilpiszewska & Spychaj, 2007). HMDI derivatives were also characterised by FTIR spectroscopy. Fig. 3 shows FTIR spectra of urethane- and urea-derivatives of HMDI. The characteristic bands for the NCO groups are observed in the range of ~2250 cm^{-1}. Other characteristic IR bands are collected in Table 1.

The reaction rate between isocyanate and the hydroxyl groups on one side and isocyanate and the primary amine groups on the other side differ substantially as can be seen from Fig. 4. It presents DSC thermograms measured during the isothermal synthesis of HMDI derivatives performed directly inside DSC pans at 25 °C. Additionally, the thermograms of the isocyanate derivatives synthesis at elevated temperature (100 °C for HMDI/*n*-butanol and 30 °C for HMDI/*n*-butylamine, respectively) are presented. It is evident that the reaction rate of the isocyanate group with the primary amine group is significantly higher than that with the hydroxyl group. This is consistent with other literature sources (Wirpsza, 1991).

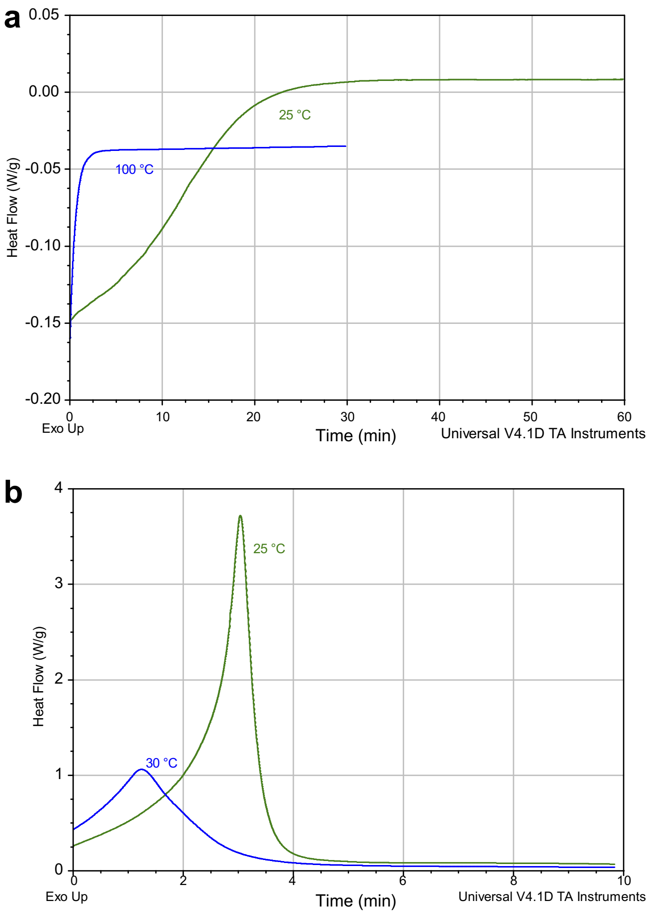

Fig. 4. DSC thermograms measured during syntheses performed directly in DSC pans for: (a) HMDI/*n*-butyl alcohol at 25 and 100 °C. (b) HMDI/*n*-butylamine at 25 and 30 °C.

3.2. Chemical modification of starch with monoisocyanate derivatives of HMDI

Some physicochemical properties and results of moldability tests for the starch polymers obtained after the modification with HMDI/methanol and HMDI/*n*-butanol are collected in Table 2, whereas similar data for starch modified with HMDI/*n*-butylamine are presented in Table 3.

The degrees of substitutions (DS) evaluated on the basis of elemental analysis (for nitrogen content) are lower than

Table 2
Characteristics of starch modified with HMDI/CH_3OH and HMDI/C_4H_9OH monoisocyanate derivatives

Modifier	Degree of substitution (DS)		Efficiency of substitution [%]	Swelling index in water [cm^3/g] 25 °C	Pressed disc diameter [cm]
	Theoretical	Experimental			
HMDI/CH_3OH	1	0.8	85	5.0	6.5
	2	1.6	78	2.5	7.4
	3	2.8	93	3.5	6.5
HMDI/C_4H_9OH	1	0.6	64	2.0	3.0
	2	1.8	92	2.1	6.0
	3	1.1	38	2.1	3.5

Table 3
Characteristics of starch modified with HMDI/$C_4H_9NH_2$ monoisocyanate derivative

Degree of substitution (DS)		Efficiency of substitution [%]	Swelling index in water [cm^3/g] 25 °C	Pressed disc diameter [cm]
Theoretical	Experimental			
1	0.7	69	2.0	4.0
2	1.8	89	2.2	5.7
3	2.2	73	2.0	4.0

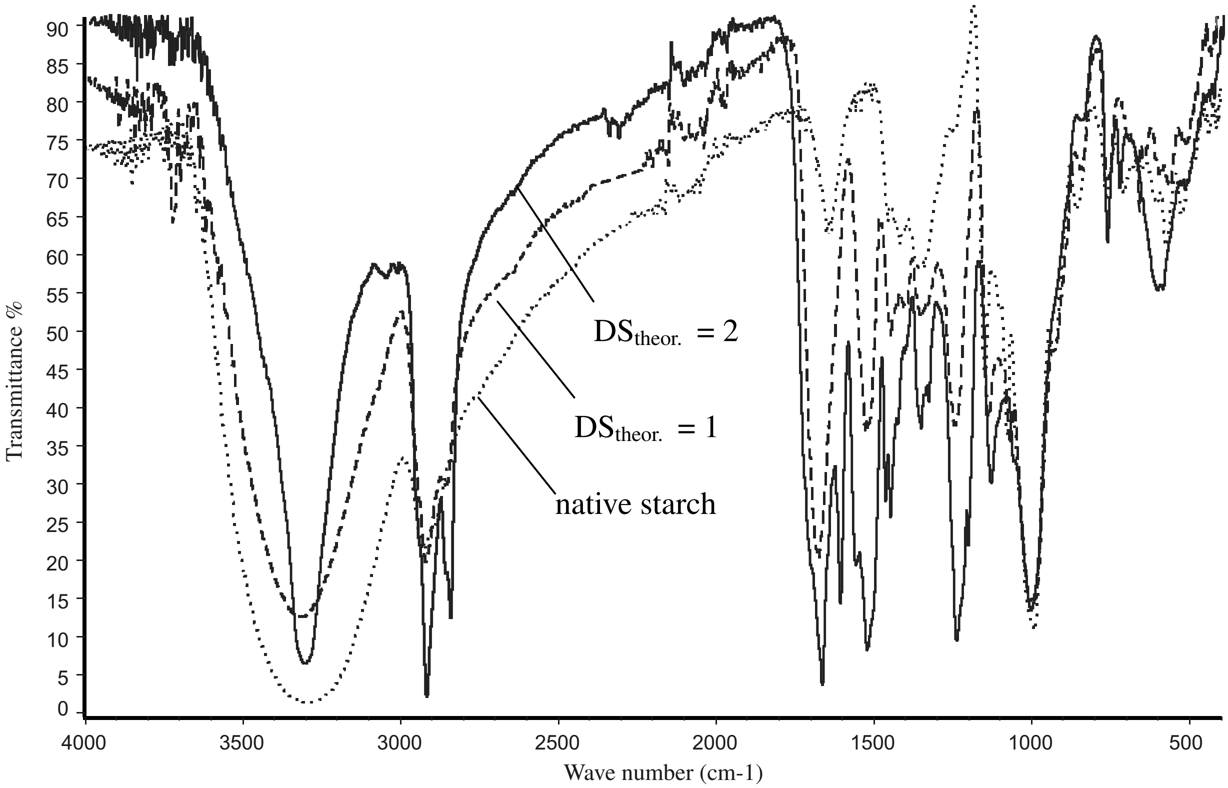

Fig. 5. FTIR spectra of starch modified with HMDI/*n*-butyl alcohol for various degrees of substitution.

those calculated on a stoichiometric basis of the reagents, as it may be seen in Tables 2 and 3. Generally, the reaction efficiencies of starch modification with HMDI derivatives were between 64% and 93% and the final DS values have changed in a range from 0.6 up to 2.8, whereas the stoichiometric molar ratios of modifier/glycosidic unit from 1.0 up to 3.0, respectively (Tables 2 and 3).

As it was mentioned earlier, an essential disadvantage of conventional thermoplastic starch materials is their sensitivity to water. In order to evaluate the hydrophobic/hydrophilic properties of the modified starches, their swelling indices in water were compared. It is known from the literature that the higher degree of substitution and the longer aliphatic chain of the modifying monoisocyanate, the stronger is a hydrophobic character of the final starch-derived material (Engelmann et al., 2001; Engelmann, Bonatz, Bechthold, & Rafler, 2002). Our experimental results (Tables 2 and 3) show that the swelling indices of starches modified with shorter alkyl chain modifier – HMDI/CH_3OH decrease with higher DS value, whereas a rather low and almost constant data (2.0–2.2 g/cm^3) are found for polymer samples after the reaction with monoisocyanates bearing longer aliphatic chains (HMDI/*n*-butyl alcohol and HMDI/*n*-butylamine). Some qualitative differences between our results and those from literature are justifiable because the swellability index is a bulk sensitive parameter, whereas other authors use the surface sensitive parameter, i.e. contact angle measurements for comparison (Carvalho et al., 2005; Engelmann et al., 2001, 2002). The prepared starch–urethane derivatives exhibited also a limited solubility or swellability in polar organic solvents (methanol, acetone, dimethyl sulfoxide, *N*-methylpyrrolidone). That was also a reason why the NMR measurements of urethane–starch derivatives in solution have not been performed successfully.

The starch–urethane derivatives were characterised by FTIR spectroscopy. In all starch–urethane derivatives was observed an intensive band for the OH (and NH) groups in the range of 3300 cm^{-1}, similarly like for potato starch. However, with increasing degree of substitution the intensity of OH/NH band in this region decreases, moreover the peak becomes narrower (Fig. 5). Other differences of the characteristic bands for modified starch polymers, e.g. located in the range from 1536 to 1547 cm^{-1} (amide) and the appearance of carbonyl group (1618–1694 cm^{-1}) can be found.

The thermal features of starch–urethane polymers were characterised by DSC and a hot press-moulding test. The melting temperatures for starch polymers modified with HMDI/methanol decrease with increasing of the DS values ($T_m = 127$ °C for DS = 1 and $T_m = 99$ °C for DS = 3) (Table 4). For other investigated starch derivatives no direct

Table 4
Melting temperature (DSC) of starch polymers after modification with HMDI monoisocyanate derivative

Starch modified with HMDI/CH_3OH		Starch modified with HMDI/CH_4H_9OH		Starch modified with HMDI/$CH_4H_9NH_2$	
DS_{theor}	T_m [°C]	DS_{theor}	T_m [°C]	DS_{theor}	T_m [°C]
1	127	1	116	1	115
2	111	2	108	2	129
3	99	3	118	3	122

correlation between the melting temperatures and DS values was observed. On a basis of moldability tests (Tables 2 and 3) it was found that the starch modified with urethane (HMDI/butyl alcohol, DS = 2) and the urea monoisocyanate derivatives (HMDI/butylamine, DS = 2) exhibit acceptable melt flow features (ca. 5.7–6.0 cm in diameter).

4. Conclusion

Starch–urethane polymers were prepared via chemical modification of potato starch with urethane- and urea-derivatives of hexamethylene diisocyanate with efficiency of substitution usually above 70%. From applied point of view, the starch polymers with the degree of substitution in a range of 1.6–1.8 (for theoretical DS = 2) exhibit acceptable bulk hydrophobic properties (swellability in water in a range of 2.0–2.5 cm^3/g) and melt flow features in hot press test. These modified polysaccharides can be considered as good candidates for manufacturing through reactive extrusion process.

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