Carbohydrate Polymers 77 (2009) 526–529

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Preparation and characterization of cross-linked starch polyurethanes

A.L. Da Róz [a], A.A.S. Curvelo [a], A. Gandini [b,*]

[a] Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, CEP13560-970, São Carlos, São Paulo, Brazil
[b] CICECO and Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 16 December 2008
Received in revised form 19 January 2009
Accepted 23 January 2009
Available online 11 February 2009

Keywords:
Starch
Oligoether diisocyanate
Networks
Elastomers

ABSTRACT

This study describes the preparation and characterization of new starch cross-linked polyurethanes produced by the reaction of native cornstarch with a propylene oxide toluene diisocyanate oligomer. Infrared analysis confirmed the occurrence of the reaction and solubility and swelling tests showed that it had led to cross-linked structures. These products were totally amorphous and displayed elastomeric properties associated with two T_gs at −60 and 35 °C.

1. Introduction

The use of renewable resources to prepare novel materials has attracted growing attention in the last decade. Polysaccharides are among the most intensively studied precursors, particularly cellulose, chitin and starch, because they are abundantly available almost everywhere, renewable, biodegradable, cheap, and can be chemically modified into a variety of macromolecular structures with a wide range of properties and applications (Belgacem & Gandini, 2008).

Starch is found in numerous basic agricultural products and, apart from its essential role as a foodstuff, it has been traditionally exploited as such, or after minor modifications, in important industrial processes, e.g., as an additive in papermaking and as an adhesive (Carvalho, 2008, chap. 15). Its structure is made up of two polysaccharides, viz. amylose and amylopectin. Amylose is a linear polymer of anhydroglucose units linked through α-1-4 glucosidic bonds. Amylopectin is a branched polymer constituted by a backbone structure like amylose with 4–5% of its units bearing β-1-6 glucosidic linkages generating amylose-like branches. The proportions of each polymer in native starches vary appreciably in starch from different species and even within a given vegetable, albeit to a minor extent (Carvalho, 2008, chap. 15).

The development of new starch-based materials has spurred much interest in recent years (Carvalho, 2008; Wurzburg, 1997; Alfani, Iannace & Nicolais, 1998). Two distinct approaches have been tackled in this context, viz. the preparation of "thermoplastic starches" (TPS) by plasticization, with or without blending with another polymer (i.e., physical modification of the natural polymer), and the synthesis of chemically modified starches (Tomasik & Schilling, 2004). Given the predominant presence of hydroxyl groups in starch, as in all polysaccharides, the focus of attention for these chemical modifications has obviously been on their transformation with various reagents, including esterification and etherification (Carvalho, 2008; Wurzburg, 1997; Alfani, Iannace & Nicolais, 1998). The destruction of some or most of the hydrogen bonds induced by these reactions, is responsible for the decrease in crystallinity and in the extent of the granulate structures of starch. More importantly, the modifications produce distinct changes in the properties of the ensuing polymers, and give rise to a wide range of materials, including cross-linked structures, which are among the more frequently sought products of these treatments (Carvalho, 2008; Wurzburg, 1997; Alfani, Iannace & Nicolais, 1998).

The use of diisocyanates to prepare starch–polyurethane networks has received very little attention. Alfani et al. (1998) synthesized starch-based polyurethanes using a polycaprolactone triol and an aliphatic diisocyanate. These materials showed a relatively high glass transition temperature and a thermal stability lower than that of starch. Desai, Thakore, Sarawade and Devi (2000) synthesized polyurethane elastomers using polypropylene glycol, starch and toluene diisocyanate. The DSC curves showed two glass transitions, indicating phase separation. Ha and Broecker (2002) synthesized polyurethanes containing different proportions of potato starch, using polycaprolactone diol, 1,4-butanediol and diphenylmethane diisocyanate as reagents. The starch granules were well dispersed in the continuous polyurethane phases without shape modification and their incorporation up to 20 wt%, improved the elon-

---

* Corresponding author. Tel.: +351 234 370735; fax: +351 234 370084.
E-mail address: agandini@ua.pt (A. Gandini).

0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.01.035

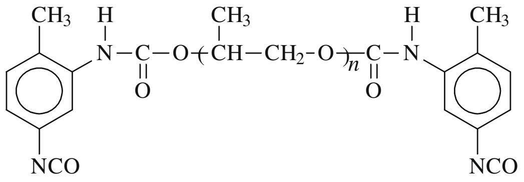
gation and the tensile strength of the samples. Above this content, however, these properties decrease rapidly, because of phase separation. On the whole, these studies showed some contradictory results and involved rather complex systems, which conspired against a thorough treatment.

The purpose of this investigation was to begin a more systematic approach, starting with a simple context involving the reaction of starch with an oligoether bearing two terminal aromatic isocyanate moieties.

2. Experimental

2.1. Materials

The starch used in this work was a hybrid cornstarch containing 28% of amylose (AMIDEX 3001), kindly provided by Corn Products of Brazil. The polypropyleneoxide toluene diisocyanate (Biocol BS40) was a generous gift from the Resibras Company (Portugal). Its structure is shown below (*n* = 22):



The catalyst dibutyltin dilaurate (Aldrich) was used as received. The solvents used here were dried over calcium hydride before use.

2.2. Cross-linking reactions

The preparation of the cross-linked starches was carried out in a nitrogen-filled glove box. Typically, a mixture of 0.5 g of starch swollen in 20 mL of dry dimethylsulfoxide (DMSO) was maintained under magnetic stirring for 30 min at room temperature, before adding 12 g of the polypropyleneoxide toluene diisocyanate (PTD) to give a [NCO]/[OH] molar ratio of ~1.4, and catalytic amounts of dibutyltin dilaurate. The reaction was left under stirring at room temperature between 10 and 24 h, before ending it by the addition of 2 mL of methanol and 200 mL of a 7/3 v/v methanol/water mixture. In other runs, the same procedure was applied, but the [NCO]/[OH] ratio was varied to give values of 0.75, 0.63, 0.50 and 0.25, respectively. The ensuing precipitates were soxhlet extracted with tetrahydrofuran (THF), to remove the excess PTD, and oven dried at 60 °C to constant weight.

2.3. Materials characterization

The solubility of the unmodified starch, the cross-linked starches and the PTD were tested (i) in DMSO at 100 °C for 2 h, followed by 17 h at room temperature and (ii) in THF at room temperature for 17 h. The swelling ratio of the cross-linked materials was determined by measuring the sample size before and after swelling and by their mass ratio.

Fourier Transform Infrared (FTIR) spectra were taken with a FT-GO BOMEM MB-102 instrument using KBr pellets with a KBr/sample w/w ratio of 100:1.

Thermogravimetric analyses (TGA) were performed with a SHIMADZU TGA-50 unit, with a nitrogen flow of 20 mL/min, and scanning between room temperature and 800 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed with a SHIMADZU DSC-50 calorimeter, under a nitrogen flow of 20 mL/min. The first run, necessary to condition the sample, ranged between room temperature and 110 °C, at a heating rate of 10 °C/min, whereas the second and third were carried out between −100 and 150 °C, at a heating rate of 5 °C/min.

Scanning Electron Microscopy (SEM) images were acquired with a model 440 Leo microscope. The samples were agglutinated with a carbon ribbon adhesive, dried under reduced pressure at 90 °C for 10 h and thereafter coated with a 20 nm gold layer. Wide Angle X-ray Scattering (WAXS) analyzes were conducted using a Rigaku X-rays diffractometer operating at a rate of 2 °/min, with an angular range of 3–40°.

Prior to the water absorption measurements, the samples were dried at 80 °C to constant weight. They were then conditioned in hermetic containers with 43%, 53% and 75% relative humidity at 25 + 2 °C using saturated salt solutions of K_2CO_3, $Mg(NO_3)_2{\cdot}6H_2O$ and NaCl, respectively, according to ASTM E 104. The amount of water absorbed, expressed in weight percentage (*W*), was determined by weighing the samples periodically until a constant weight was attained.

3. Results and discussion

Typically, the products arising from the reaction of starch with TDP, after extraction with THF to remove the unreacted macrodiisocyanate, showed a very large weight gain, e.g., from 0.5 to 6.7 g, which indicated the occurrence of the coupling (Table 1).

The characteristic infrared spectrum of native starch is shown in Fig. 1A, with its prominent broad peak around 3400 cm^{-1} associated with the hydroxyl groups. After the cross-linking reaction, major changes were observed in the spectrum of the product after the extraction with THF (Fig. 1B), namely, (i) a decrease in the

Table 1
Weight gain and equilibrium moisture absorption (*W* in weight%) as a function of the relative amount of PDT used for the cross-linking reaction.

Sample identification	Yield* (%)	*W*		
		43% rh	53% rh	75% rh
Unmodified starch	–	7.5	11.8	12.8
[NCO]/[OH] = 1.4	99	0.2	2.8	3.5
[NCO]/[OH] = 0.75	61	0.3	3.4	4.0
[NCO]/[OH] = 0.63	43	0.6	4.1	4.7
[NCO]/[OH] = 0.50	34	1.1	4.6	8.3
[NCO]/[OH] = 0.25	02	4.3	5.7	12.0

* The term yield is used here to indicate the percentage of starch OH groups converted into urethane moieties.

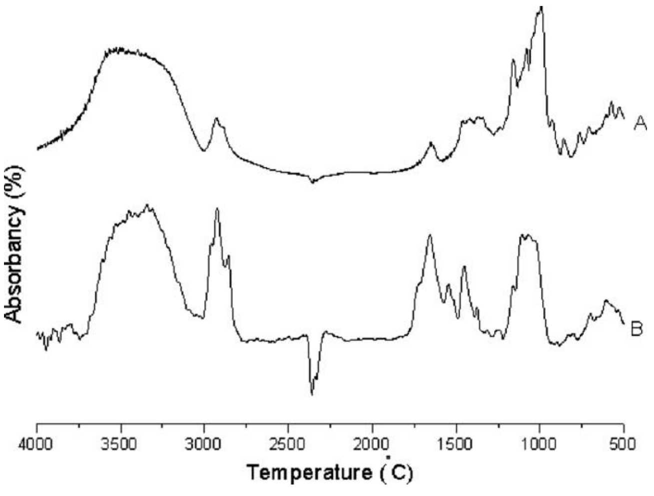


Fig. 1. FTIR spectra of the unmodified starch (A) and of the sample cross-linked with [NCO]/[OH] = 1.4 (B).

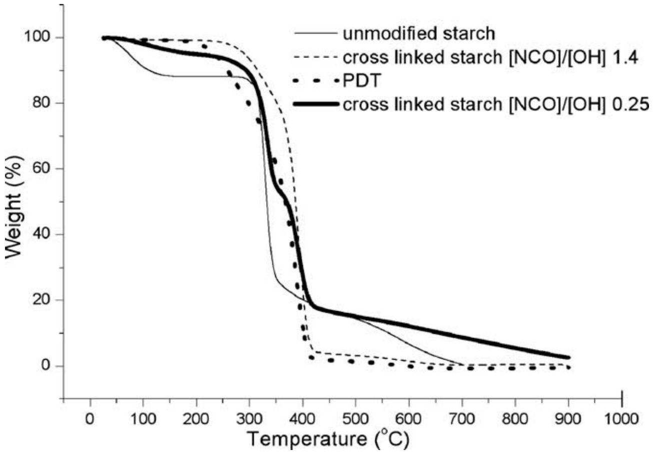


Fig. 2. TGA tracings of the unmodified starch, PTD, and of the sample cross-linked with [NCO]/[OH] = 1.4.

intensity of the OH band and its shift to lower frequencies, indicating their partial replacement by the NH functions of the urethane moieties formed in the reaction; (ii) the appearance of a new peak at 1710 cm^{-1}, corresponding to the carbonyl groups of the urethane moieties; (iii) the presence of a new peak at 2970 cm^{-1}, characteristic of the C–H stretching in methyl groups associated with the propylene oxide units. These differences clearly confirmed that the reaction between at least some of the starch OH functions and the terminal NCO groups of PTD had indeed taken place.

By definition, cross-linked polymers are insoluble in all media, but swell when immersed in liquids bearing structural affinities with them. The extent of this swelling with a given solvent depends inversely on the cross-link density of the network. In this context, on the one hand, the unmodified starch was soluble in hot DMSO, whereas PTD showed complete solubility in THF at room temperature; the modified and THF-extracted starches, on the other hand, were completely insoluble in both media, which proved unambiguously their cross-linked nature.

The extent of swelling of these networks depended on the solvent used. The sample immersed in DMSO grew by about 50%. The weight gain of the network, associated with this swelling was about 1.9 times. The polymer did not dissolve at all during this test, as proved by the fact that pouring the DMSO into an excess of acetone did not produce any precipitate. The sample immersed in THF showed a higher degree of swelling, namely almost 80% and its weight increased by a factor of five, again without any polymer dissolution.

It was moreover observed that the well-known hydrophilic character of starch was greatly reduced by the formation of these networks. In fact, the exposure of the samples to atmospheres with relative humidity of 43%, 53% and 75% gave moisture absorption values at equilibrium of 7.5%, 11.8% and 12.8%, respectively, with the native starch and, on average, of 0.2%, 2.8% and 3.5%, respectively, with the urethane networks after THF extraction (Table 1). This major change was attributed to both the replacement of the

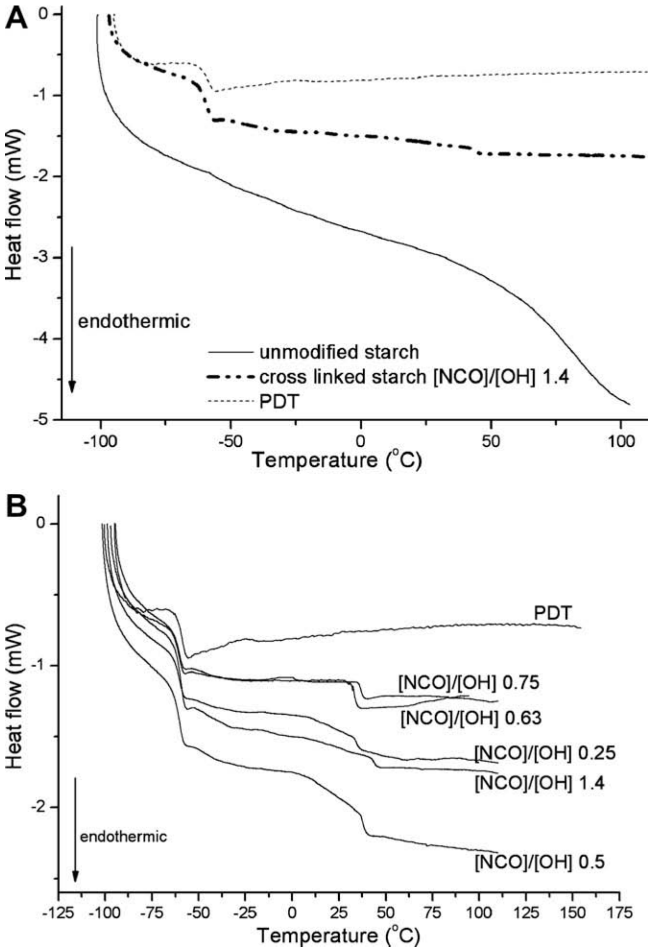


Fig. 3. DSC tracings of the unmodified starch, PDT and of the variously cross-linked samples.

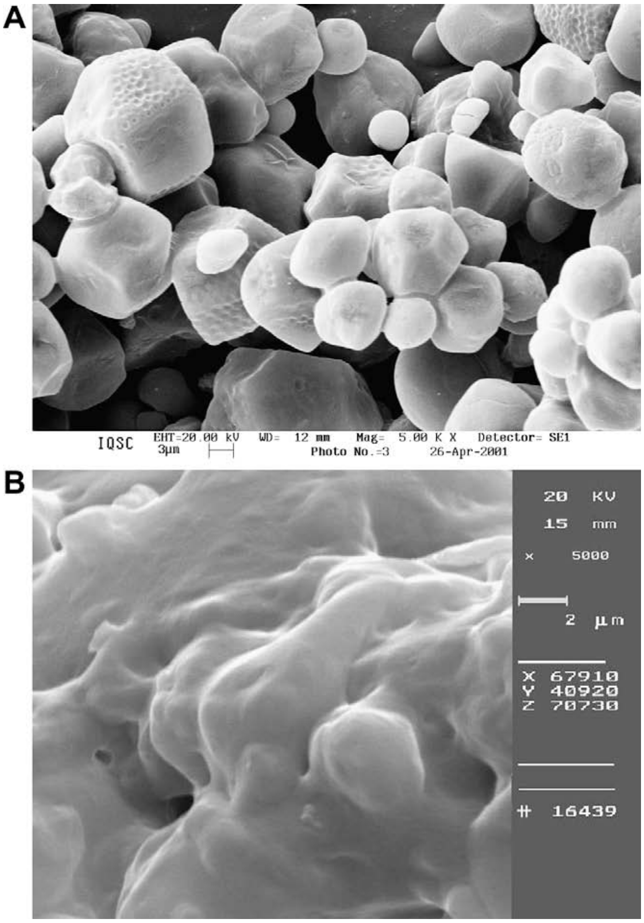


Fig. 4. SEM micrographs at 5000× of unmodified starch granules (A) and of the sample cross-linked with [NCO]/[OH] = 1.4 (B).

Table 2
Glass transition temperatures and the associated changes in heat capacity of PDT and the cross-linked starch samples.

Sample identification	T_g (°C)	ΔCp (J/g°C)	T_g (°C)	ΔCp (J/g°C)
PDT	−60	0.70	–	–
[NCO]/[OH] = 0.25	−60	0.38	31	0.10
[NCO]/[OH] = 0.50	−60	0.47	38	0.10
[NCO]/[OH] = 0.63	−60	0.48	35	0.13
[NCO]/[OH] = 0.75	−60	0.49	32	0.18
[NCO]/[OH] = 1.4	−60	0.50	37	0.23

very polar OH groups by the aromatic urethane moieties and the lower polarity of the oligopropylene oxide (PPO) chains.

The thermogravimetric behavior of the native starch (Fig. 2) showed, after the characteristic moisture loss up to 100 °C, a degradation onset at 310 °C with an endset at 349 °C and an overall mass loss of 93% at 600 °C. PTD started degrading at 230 °C and showed 100% weight loss at 700 °C. Fig. 4 shows the TG tracing of a network sample prepared with [NCO]/[OH] = 1.4, after THF extraction. Its thermal degradation begun around 350 °C and ended at 410 °C with a weight loss of 99% at 450 °C. This behavior was entirely in tune with the fact that these networks contained more than 90% of PPO chains with respect to the modified starch, and it was therefore to be expected that their thermal degradation would be essentially the same as that of PDT. As the proportion of chemically incorporated PDT decreased, the TG traces displayed a progressively higher contribution of the starch degradation features (Fig. 2).

Fig. 3A shows the typical DSC tracing of native starch, with its characteristic absence of a T_g signal, as often reported for this natural polymer. Fig. 3A also displays the DSC behavior of PDT, with a clear-cut T_g at −60 °C (ΔCp = 0.70 J/g °C) typical of PPO oligomers, and that of the [NCO]/[OH] = 1.4 starch network, which showed two well-defined T_g at −60 and 37 °C, with a ΔCp of 0.50 and 0.23 J/g °C, respectively. Fig. 3B completes this study with the thermograms of all the modified samples compared with that of PDT.

The transition at −60 °C was clearly associated with the relaxation of the grafted PPO chains, which were sufficiently long to display the same rotational mobility as their free PDT counterparts. The smaller changes in the baseline at ~35 °C (Fig. 3A and B) could be attributed to a possible glass transition of the starch macromolecules in the network (Table 2).

The X-ray diffractograms of the cross-linked derivatives indicated the exclusive presence of essentially amorphous domains, in contrast with that of the unmodified starch, which showed a crystallinity index close to 0.50 with the diffraction bands of its A-type crystalline structure, typical of this natural polymer as found in cereals. This loss of macromolecular organization seemed entirely plausible, in view of both the perturbing effect of the cross-linking and the loss of OH groups and their hydrogen-bond aptitude.

The cross-linking reaction also produced a radical change in the starch morphology, since its pristine discrete granular structure (Fig. 4A) was completely destroyed by the chemical modification (with [NCO]/[OH] = 1.4), which left a homogeneous soft mass (Fig. 4B). All other cross-linked samples reflected the same phenomenology.

4. Conclusions

The reaction of cornstarch with a low-T_g macrodiisocyante led to the production of amorphous elastomeric networks swelling in DMSO and THF and possessing a reduced hydrophilicity. These materials could be employed as matrices for composites in which cellulose fibers, i.e., another renewable resource, would provide improved mechanical properties without the need of surface treatment, given the highly similar structure between starch and cellulose. Such biodegradable composites would constitute promising substitutes for petroleum-based counterparts, e.g., in packaging applications. In addition to their biodegradability, associated with the predominant starch component, another interesting aspect related to these novel networks has to do with the possibility of recycling them, taking advantage of the well-known thermal reversibility of the urethane moieties at temperatures, which in the present context are well below the onset of the network degradation. Work is in progress to extend this preliminary investigation to a more thorough approach, including the use of other reagents and assess their applications, biodegradability and recyclability.

Acknowledgement

The authors wish to thank FAPESP for financial support.

References

Alfani, R., Iannace, S., & Nicolais, L. (1998). Synthesis and characterization of starch-based polyurethane foams. *Journal of Applied Polymer Science, 68*, 739–745.
Belgacem, M. N., & Gandini, A. (Eds.). (2008). *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier.
Carvalho, A. J. F. (2008). Starch: Major sources, properties and applications as thermoplastic materials. In M. N. Belgacem & A. Gandini (Eds.), *Monomers, polymers and composites from renewable resource*. Amsterdam: Elsevier.
Desai, S., Thakore, I. M., Sarawade, B. D., & Devi, S. (2000). Structure-property relationship in polyurethane elastomers containing starch as a crosslinker. *Polymer Engineering and Science, 40*, 1200–1210.
Ha, S., & Broecker, H. C. (2002). Characteristic of polyurethanes incorporating of starch granules. *Polymer, 43*, 5227–5334.
Tomasik, P., & Schilling, C. H. (2004). Chemical modification of starch. *Advances in Carbohydrate Chemistry and Biochemistry, 59*, 175–403.
Wurzburg, O. B. (1997). Introduction. In O. B. Wurzburg (Ed.), *Modified starches – properties and uses* (3rd ed.). Florida: CRC Press.