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Communications

Novel Thermoplastic Materials Based on the Outer-Shell Oxypropylation of Corn Starch Granules

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The study of the plasticization of corn-starch granules through the bulk oxypropylation of their outer shell produced a novel biphasic material consisting of a low glass transition temperature component surrounding the granules' inner core, which could be hot pressed to form films of the granules dispersed into a thermoplastic matrix. The success and extent of these chemical modifications and the properties of the ensuing composites were assessed by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, and contact angle measurements. This approach has the additional advantage of being simple and "green".

Introduction

The interest in polymers from renewable resources has recently gained exponential momentum,[1] and, within that broad family, starch constitutes one of the most attractive sources of novel materials for several good reasons, which include its ubiquitous availability (albeit from different vegetable sources) in very large quantities at modest prices, the possibility of plasticizing it with a number of common additives,[2] including natural compounds,[3] and the relative ease with which it can be chemically modified.[4]

The hydroxypropylation of starch has been thoroughly investigated in aqueous and organic media.[5] These studies have focused on the role of various reaction parameters in the overall degree of substitution and its distribution at specific individual oxygen atoms of the saccharide units of both amylose and amylopectin.[5] The major effects of appending oligo(propylene oxide) grafts onto the starch macromolecules are their internal plasticization, which facilitates considerably the gelatinization of these materials, and the associated modifications in their pasting behavior and rheological properties.

Over the past several years, one of the authors has been involved in a systematic research program dealing with the bulk oxypropylation of various OH-bearing natural polymers, including sugar beet pulp,[6] chitin and chitosan,[7] cork,[8] and lignin.[9] In all these systems, the solid substrate is activated with a Brønsted or Lewis base and thereafter mixed in an autoclave with variable amounts of propylene oxide (PO). The oxianions generated on the substrate macromolecules induce the PO anionic polymerization through a "grafting from" process that is always accompanied by some PO homopolymerization. The oxypropylation parameters were varied in these studies to optimize the formation of the ensuing viscous polyols, which were recovered as such, without the need of any further operation such as separation procedures or the removal of any components. This "green" procedure provided a series of OH-bearing macromonomers that have been, and are being, exploited for the processing of novel polymeric materials from renewable resources.

In a different vein, we recently applied these principles to cellulose fibers, but limited the oxypropylation to their outer "sleeves", which thus became thermoplastic, while their inner core retained its stiff semicrystalline properties.[10] This partial transformation led to the possibility of preparing original composites by pressing the outwardly mollified fibers into a continuous film.

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To the best of our knowledge, the bulk oxypropylation of starch using this approach has not been previously described, and the present paper provides a preliminary report of its successful implementation.

Experimental Section

Materials. The corn starch used in this study was Amidex 3001 (28% amylose and 72% amylopectin), supplied by Corn Products Brasil, Ltda. PO (99%), KOH, and 1.4-diazabicycle[2.2.2]octane (DABCO) were purchased from Acros, Synt, and Aldrich, respectively, and used as received.

Oxypropylation of Corn Starch. The procedure for the partial oxypropylation consisted in impregnating ~2 g of corn starch with 10 mL of an ethanol/KOH or an ethanol/DABCO solution for 12 h at room temperature, before evaporating the ethanol and soaking the activated starch with the appropriate quantity of PO in a 100 mL stainless steel autoclave kept under a nitrogen atmosphere. The closed autoclave, equipped with a stirrer, a thermocouple, a manometer, and a controlled heating system, was then heated at 5° $\min^{-1}$ to the desired temperature, while the corresponding pressure increase was monitored. In some systems, the onset of the oxypropylation reaction was revealed by a rapid increase in both temperature and pressure, and the subsequent swift return to atmospheric pressure signaled its final stage, associated with the total consumption of PO. In other instances, the reaction was too slow to generate a detectable temperature increase, and the reaction time (related to the progressive pressure decrease) therefore became the relevant parameter in terms of the extent of PO consumption. At the end of all the experiments, the autoclave was allowed to cool to room temperature before being opened. The variables explored in the preliminary study were the [OP]/[starch-OH] molar ratio (1 and 3), the catalyst (KOH or DABCO), with a [cat]/[starch-OH] molar ratio of 0.1, and the temperature, which was varied between 135 and 170 °C. Each product was submitted to a Soxhlet extraction with *n*-hexane in order to separate the PO homopolymer from the oxypropylated starch.[6] This operation was carried out with the specific purpose of assessing the quantitative behavior of the different systems tested and was not necessary in the context of the actual use of the materials, since we found that modest amounts of PO oligomers could be left in them without affecting their properties, as in previous studies on other substrates.[6−10]

Product Characterization. Fourier transform infrared (FTIR) spectra were taken with KBr pellets (1:100 w/w) using a BOMEN MB102 spectrometer. X-ray diffractograms were recorded with a Carl-Zeiss-Jena UDR6 diffractometer. The scattered radiation was detected in the angular range of 5−40° (2θ) at a speed of 2° $\min^{-1}$. The extent of crystallinity was estimated by the height ratio between the diffraction peak (B-type starch at 17°) and the baseline.[11] A Leo scanning electron microscope (SEM) was used to examine the morphology of fractured surfaces prepared in liquid nitrogen. Differential scanning calorimetry (DSC) thermograms were recorded between −100 and 180 °C with a Shimadzu TA-50WSI apparatus, operating at a scanning rate of 10 °C $\min^{-1}$ in a nitrogen atmosphere. Thermogravimetric analyses (TGA) were conducted in the temperature range of 25−1000 °C with a Shimadzu TA-50 calorimeter, working at 20 °C $\min^{-1}$ in a nitrogen atmosphere. Static contact angles were measured with an OCA Dataphysics contact angle system, using various liquids of different polarity, namely, water, formamide, ethylene glycol, and diiodomethane. The dispersive and polar contributions to the surface energy were then calculated using Owens and Wendt's approach.[12]

Results and Discussion

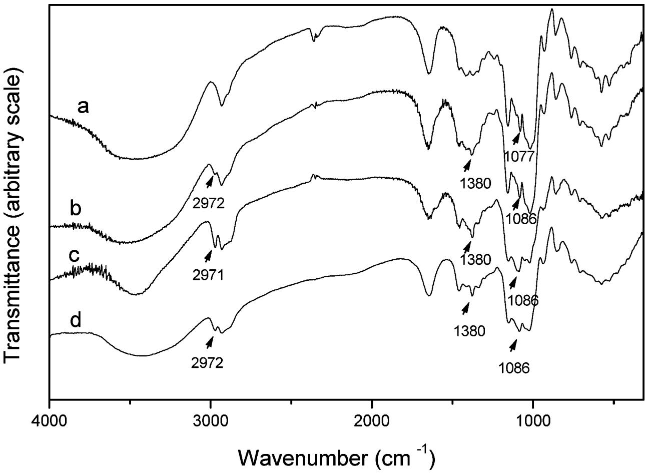

Figure 1. FTIR spectra (KBr pellets) of **1** (a), **2** (b), **3** (c), and **4** (d) (see Table 1 for sample numbering). All treated samples had been previously submitted to an extraction with *n*-hexane to remove the PO homopolymer.

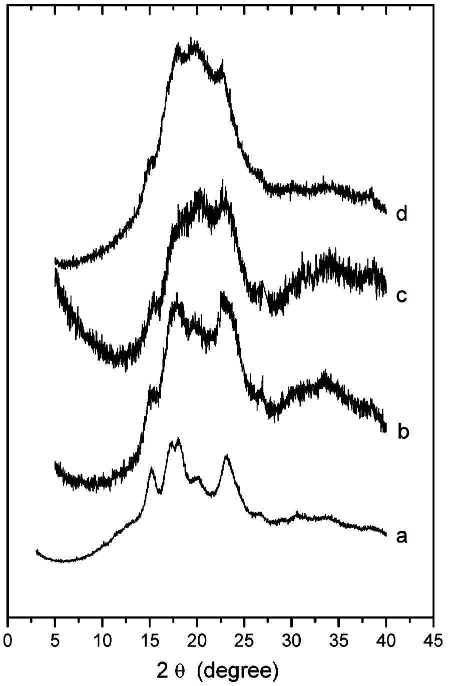

Figure 2. X-ray diffraction patterns of corn-starch samples. See legend of Figure 1 for details.

As expected, all the products extracted with *n*-hexane displayed the typical FTIR, DSC, and ^{1}H NMR features of commercial low-molecular-weight PO macrodiols. As with previous studies on other substrates,[6−10] the number-average molecular weights of these oligomers ranged between 400 and 1000. The FTIR spectra of a typical selection of the corn starch samples before and after modification induced by their partial oxypropylation, the latter after the removal of the PO homopolymer, are shown in Figure 1. The relevant features here are (i) the overall absorption increase in the aliphatic CH stretching region (2800−3000 cm^{-1}), with the appearance of a new peak around 2970 cm^{-1} associated with the methyl groups of the grafted PO units; (ii) the increase and shift in absorption within the C−O stretching region (1000−1100 cm^{-1}) associated with the ether moieties borne by those units; and (iii) the new peak at 1380 cm^{-1}, confirming the presence of CH_3 groups. The spectral intensity change as a function of the oxypropylation extent, also related to the kind of base employed to activate the hydroxyl groups, can also be observed in Figure 1.

Figure 2 shows the X-ray diffractograms of the same oxypropylated corn starch samples, compared with that of the

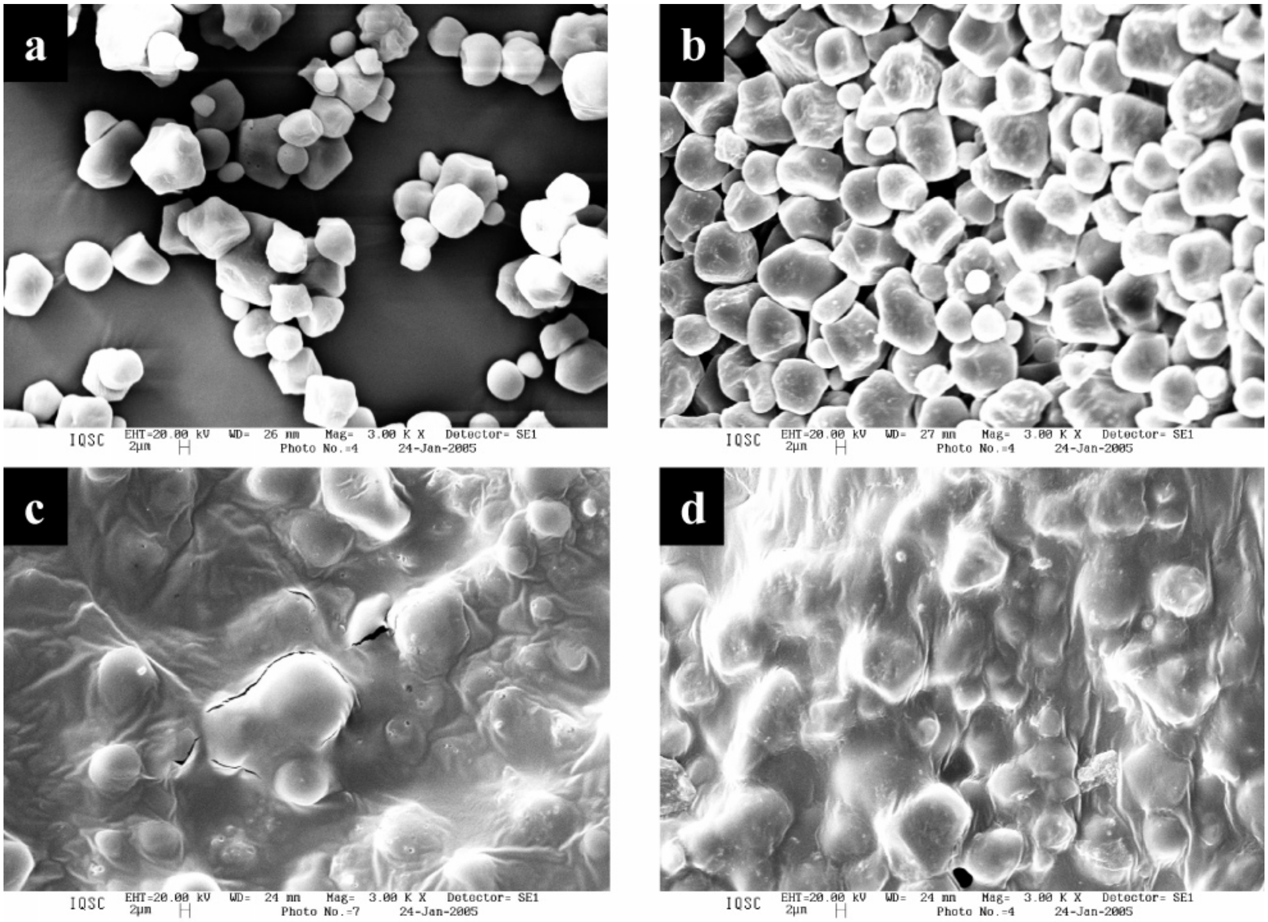

Figure 3. SEM micrographs of corn-starch samples (magnification 3000×). See legend of Figure 1 for details.

Table 1. Values of the Weight Gain, T_g Range, CI, and Onset of Thermal Degradation Temperature of Corn-Starch Samples before and after Partial Oxypropylation

sample	[PO]/[starch-OH]	weight gain (%)	T_g range (°C)	CI %	temperature at 2% weight loss (°C)
1 unmodified				31	299
2 ethanol/KOH	1	27		16	226
3 ethanol/KOH	3	52	−45 to −20		235
4 ethanol/DABCO	3	52	−45 to −20		232

Table 2. Contact Angle (deg) and Surface Energy (mJ m^{-2}) of the Corn-Starch Samples before and after Partial Oxypropylation[a]

	contact angles						
sample	water	formamide	ethylene glycol	diiodometane	γ_S^p	γ_S^d	γ_S
1	50	31	43	31	21.9	26.9	48.8
2	58	50	52	43	19.6	21.8	41.4
3	82	74	77	48	5.3	22.3	27.6
4	78	64	74	46	6.8	24.0	30.8

[a] The sample numbering corresponds to that of Table 1.

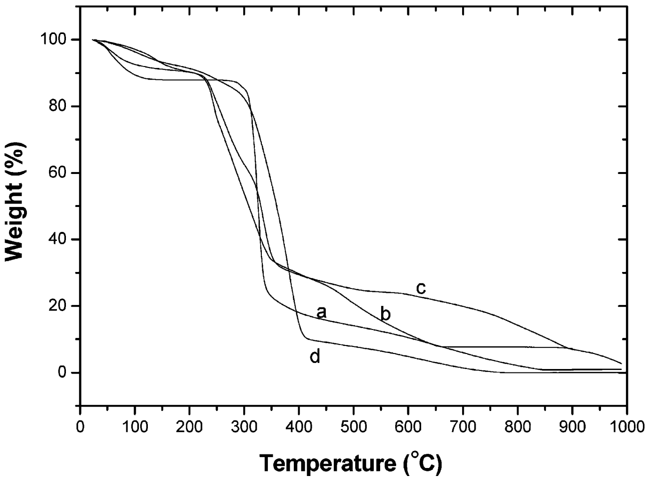

Figure 4. TGA tracings of corn-starch samples. See legend of Figure 1 for details.

pristine substrate, and Table 1 gives the corresponding calculated crystallinity index (CI). The observed changes clearly reflect the transformation of part of the corn starch into a more amorphous oxypropylated derivative.

The SEM micrographs of these materials (Figure 3) show the presence of a thermoplastic envelope around the modified granules. It was observed that, after hot pressing, these materials showed a high interfacial adhesion giving rise to a continuous morphology, unachievable with the unmodified material. These pictures also show that the granular structure of starch was partially preserved after the various reactions.

The thermal behavior changed after the partial oxypropylation, as shown by the thermograms in Figure 4. The extent of the first mass loss, from room temperature to about 130 °C, associated with the evaporation of the water present in the starch samples, decreased considerably as the extent of oxypropylation increased, that is, their hydrophilic character decreased correspondingly. Table 1 shows additionally that the introduction of poly(propylene oxide) (PPO) grafts induced a decrease in the degradation temperature of the modified starch materials, as indeed expected given the higher thermal fragility of that polyether. However, the different profiles of these thermograms above 300 °C are not correlated with the extent of oxypropylation, and we have no explanation for this behavior.

Table 1 also gives the glass transition temperature (T_g) values obtained from the DSC thermograms of these modified starches. Only the samples obtained with the higher amount of PO actually displayed a clear-cut transition, albeit within a fairly wide temperature range. This is in tune with the well-known difficulty in detecting a glass transition in starch samples of different origin and composition. The introduction of a sufficient number of PPO branches on some of the starch macromolecules generated some internal plasticization, which manifested itself with a broad glass transition between −20 and −45 °C.

The contact angles measured with different liquid drops deposited on the compressed samples and the corresponding calculated surface energy components are given in Table 2. These results confirm that the oxypropylation reaction occurred mostly at the surface of the corn-starch granules, because the decrease in the polar component (γ_S^p) reflects the presence of PPO moieties, whose structures are sensibly less polar than those of amylose and amylopectin. The contact angle with water increased from 50° for the pristine starch surface to about 80° for the samples with the higher extent of oxypropylation, confirming their increased hydrophobic character already suggested by the TGA tracings.

Conclusions

The original process investigated in this preliminary study provided a simple route to a novel thermoplastic starch composite material in which the proportion of chemically plasticized starch (matrix) relative to the amount of granule residue (reinforcing element) can be readily modulated by adjusting the operating conditions. It is important to emphasize that no solvent is used in this process and that no separation or purification procedure is required for the ensuing material to be utilized.

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