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Carbohydrate Polymers 45 (2001) 189–194

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

A first insight on composites of thermoplastic starch and kaolin

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Received 23 September 1999; revised 26 January 2000

Abstract

In this work we have studied the utilization of kaolin as filler reinforcement for thermoplastic starch in order to improve its mechanical properties. The composites were prepared with regular cornstarch plasticized with glycerin and reinforced with hydrated kaolin. All the components were pre-mixed and processed in an intensive batch mixer at 170°C. Compounds with 0, 10, 20, 30, 40, 50 and 60 phr — parts of kaolin per hundred parts of thermoplastized starch — were prepared. The mechanical tests were performed from dumb-bell shaped specimens conditioned in ambient for 14 days. The material were also evaluated by DSC, TGA analysis and water sorption experiments. The composite filled with 50 phr kaolin showed an increase in the tensile strength from 5 to 7.5 MPa. The modulus of elasticity increased from 120 to 290 MPa and the tensile strain at break decreased from 30 to 14%. Scanning Electron Microscope of fractured surface revealed the occurrence of strong bonding between kaolin and the matrix. Besides the good mechanical properties, the utilization of these clays leads to an increase in the water resistance of thermoplastic starch compounds also. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermoplastic cornstarch; Glycerin; Kaolin; Composite

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1. Introduction

The research in biodegradable polymers started in 1960s, but gained importance only in 1970s, with the use of granular starch as filler in plastics (Griffin, 1977, 1978). Starch-containing polyethylene films have been marketed using this technology until today. Recently, new technologies employing starch synthetic polymers blends has gained more interest due to the improved characteristics and possibility to increase the proportion of starch in these blends (Röper & Koch, 1990; Shogren, Fanta & Doane, 1993). In this technology, the grain structure is totally disrupted (Otey & Westhoff, 1979, 1982). Starch was also modified by grafting with vinyl monomers (e.g. methyl acrylate) onto the starch backbone, yielding thermoplastic materials that can be injection molded or extruded into films with properties similar to low density polyethylene (Willett, Jasberg & Swanson, 1994).

The ultimate technology on the use of starch for biodegradable polymers is the utilization of thermoplastic starch (Lay et al., 1990; Röper & Koch, 1990; Shogren et al., 1993; Willett et al., 1994). These materials are produced from totally disrupted starch granule by processing at high temperature, under shear and in the presence of plasticizer. The research on starch-based biodegradable plastic is nowadays focused to develop consumer items for one way use from substantially pure starch and to exclude synthetic polymers from the formulation (Shogren et al., 1993).

However, the pure thermoplastic starch has some limitations: it is mostly water-soluble and has poor mechanical properties. The resistance to water may be improved by adding certain synthetic polymers (Bastioli, 1995), cross-linking agents such as Ca and Zr salts (Shogren, Fanta & Doane, 1998) and lignin (Baumberg, Lapierre, Monties & Della Valle, 1998). To improve the mechanical properties, the use of natural materials like cellulosic fibers (Wollerdorfer, 1998) and minerals (Reis, Cunha, Allan & Bevis, 1997) has been considered, without interfering in the biodegradability of the composites.

Hydroxylapatite-reinforced starch/EVOH composites are described as new materials for biomedical applications, where significant improvement of mechanical properties was achieved with the use of hydroxylapatite (Reis et al., 1997).

Kaolin, a natural mineral, is a hydrated aluminosilicate used in compositions of rubber, plastics and paints. Due to its high surface and the presence of polar groups, it is normally used in association with polar matrix without prior surface treatment (Schwartz & Goodman, 1982).

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0144-8617/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0144-8617(00)00315-5

Vegetal biomass is a renewable resource that has a production potential of estimated 155 billions of ton a year (Narayan, 1994). Polymers obtained from biomass, even when modified are still biodegradable and may be used with advantages for the production of short life products that can be composted. This kind of application needs not only biodegradable or compostable materials but also low cost materials.

In this work, we report the properties of thermoplastic starch composites prepared using glycerin as plasticizer and kaolin as reinforcement agent. The compositions studied were based on thermoplastic starch with 30% of glycerin, compounded with kaolin in proportions of 10, 20, 30, 40, 50 and 60 phr (parts of kaolin per hundred parts of thermoplastic starch).

2. Materials and methods

The preparation of the thermoplastic starch (matrix) — kaolin composites, as well as the materials and techniques used in this work are described below. The composites were characterized by thermal analysis, water sorption experiments, Scanning Electron Microscopy and by mechanical tests.

2.1. Materials

Regular cornstarch (28% amylose) supplied by Corn Products Brasil Ltd. with 11% of moisture was used in the preparation of the composites. The kaolin used is a hydrated aluminosilicate with average particle size of 0.5 μm, apparent density of $0.2\ \mathrm{g\,cm^{-3}}$, with the typical composition, 37% Al_2O_3, 42% SiO_2, 1% Fe_2O_3, 15% H_2O and other minority elements (supplied by Itatex). Glycerin reagent grade and K_2CO_3 analytical grade were used without previous purification.

2.2. Matrix and composites

A pre-mixture of all components (starch and glycerin plus the kaolin in composites) in polyethylene bags were mixed until a powder was obtained. In all compositions, 30% w/w of glycerin to starch (dry basis) was used. Preliminary experiments performed in our laboratories indicated that the glycerin content should be in the range of 20–40% (without added water). Lower amounts produces difficulties in the processing and higher amounts lead to glycerin's exudation. The amount of kaolin was calculated, as parts of kaolin per hundred parts of thermoplastic starch (phr) on dry basis. The composites were prepared with the following kaolin contents: 0, 10, 20, 30, 40, 50 and 60 phr.

The composites were prepared in a batch mixer Haake Rheomix 600 connected to a torque rheometer, equipped with roller rotors. The mixture of all components was loaded in the pre-heated mixer chamber at 170°C. This temperature represents the optimization between melt viscosity with minor degradation. The rotors were operated at 80 rpm and the discharge was performed after 8 min of mixing.

2.3. Specimen preparation and mechanical tests

The mass obtained from the mixer was hot pressed at 160°C to obtain plates of 10 × 10 cm with 2.5 mm thickness. These plates were conditioned at 22–25°C with relative humidity in the order of 60–70%.

The tensile tests were performed to determine the ultimate tensile strength (UTS), the secant modulus at 1% strain ($E_{1\%}$) and strain at break (ϵ_r). These tests were performed according to ASTM D 638M (1990) from six specimens that were cut with a dumb bell shaped cutter and conditioned for 14 days at 23–27°C at 43% relative humidity. The stress–strain test was performed in a testing machine Instron model 5500 R, operated with a velocity of $50\ \mathrm{mm\,min^{-1}}$.

Moisture content determinations were performed by drying the samples at 105°C until a constant weight was reached.

2.4. Scanning electron microscopy (SEM)

The fragile fracture surfaces of the composites were studied in a scanning electron microscope LEO 440. The tungsten filament was operated at 8.0 kV. The fractures were produced from samples frozen in liquid nitrogen. The samples were coated with 250 Å gold.

2.5. Water sorption

The samples dried at 110°C for 36 h were conditioned in 43 and 100% relative humidity at 25 ± 2°C. The 43% relatively humidity was obtained using a saturated solution of K_2CO_3 (according to ASTM E 104 (1985)) and the 100% relative humidity (saturated) was obtained using a closed vessel containing water in its interior. The amount of water absorbed was determined after three days.

2.6. Thermal analysis

Differential scanning calorimetry (DSC) was carried out in a Shimadzu DSC 50. Samples of approximately 25–40 mg were placed in aluminum pans. The analyses were performed under nitrogen flow ($20\ \mathrm{ml\,min^{-1}}$) at a heating rate of $5°\mathrm{C\,min^{-1}}$. The samples were heated at temperatures above its T_g (150°C) and quenched in liquid nitrogen prior to the final analysis. This procedure allows the thermoplastic starch to be frozen to the amorphous state. The graphic determination of glass transition temperature was done taking the temperature correspondent to the half-variation in the calorific capacity that occurred in each transition ($T_g^{1/2}$).

Thermogravimetric analysis was performed in a Shimadzu TG-50, at a rate of $10°\mathrm{C\,min^{-1}}$ from ambient temperature to 900°C. The analyses were performed under nitrogen atmosphere with flow rate of $20\ \mathrm{ml\,min^{-1}}$.

Table 1
Data of modulus ($E_{1\%}$), UTS and elongation (ϵ_r) for the thermoplastic starch–30% glycerin and for its composites with kaolin

Kaolin content (phr)	$E_{1\%}$ (MPa)	UTS (MPa)	ϵ_r (%)
0	125 ± 4	5.0 ± 1.0	31 ± 11
10	163 ± 3	5.3 ± 0.3	26 ± 5
20	162 ± 14	5.7 ± 0.2	24 ± 3
30	200 ± 12	5.9 ± 0.4	18 ± 3
40	225 ± 16	6.0 ± 0.4	15 ± 3
50	293 ± 16	7.4 ± 0.3	14 ± 1
60	254 ± 22	6.0 ± 0.8	12 ± 3

3. Results and discussion

3.1. Mechanical properties

The results of tensile tests, modulus ($E_{1\%}$), elongation (ϵ_r) and the UTS for thermoplastic starch and kaolin–thermoplastic starch composites are presented in Table 1.

For better visualization of the effect produced by the amount of kaolin in the tensile properties, these results are also showed in a graphic presentation (Fig. 1).

The tensile tests display an important increase of 135% in the modulus and an increase in tensile strength of 50% for the 50 phr composition. As expected, a decrease in elongation was also observed. Both modulus and tensile strength have its maximum for the composition with 50 phr, while the elongation decreases almost monotonically. The maximum for the modulus and for the tensile strength corresponds to the maximum quantity of mineral filler that may be incorporated, or wetted by the matrix. Above this point, increase in the amount of filler increases the fragility of the composite. Two different regions in the elongation pattern were observed. From 0 to 20 phr the elongation drops from 31 to 24% and from 40 to 60 phr the decrease is in the range of 15–12%. At 30 phr we have a transition zone, where elongation drops are more pronounced.

The 50 phr composite seems to represent the best composition for these materials, where the modulus and tensile strength showed an increase with respect to the matrix of around 130 and 50%, respectively. Beyond this value the amount of matrix is not sufficient to wet kaolin and the composite became fragile.

3.2. Scanning electron microscopy

SEM micrographs at 250 and 1000 × magnification of fragile fractured surface for the composite with 30 phr kaolin are showed in Fig. 2a and b, respectively. It is possible to see a very good dispersion of kaolin, as there is no smooth areas or large agglomerates. The adhesion between the matrix and kaolin is also very good and the particles of kaolin are recovery by the matrix, even after the fracture.

3.3. Water sorption

The results of water sorption experiments in 43% and saturated relative humidity are shown in Table 2.

The sorption of moisture by thermoplasticized starch (30% glycerin) reached 5.0 and 27% after three days at 43 and 100% relative humidity, respectively. The presence of kaolin decreases the water uptake of the composites, this decrease being more pronounced until 20 phr. From this concentration to 60 phr, the sorption remains almost

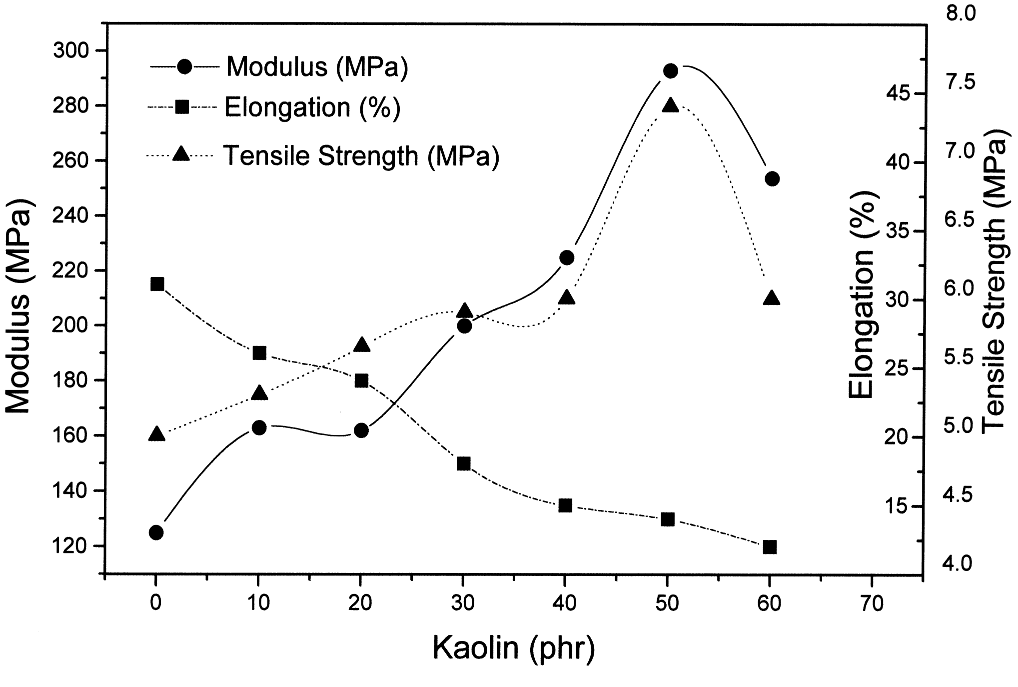

Fig. 1. Modulus, ultimate tensile strength and elongation for the thermoplastic starch and its composites.

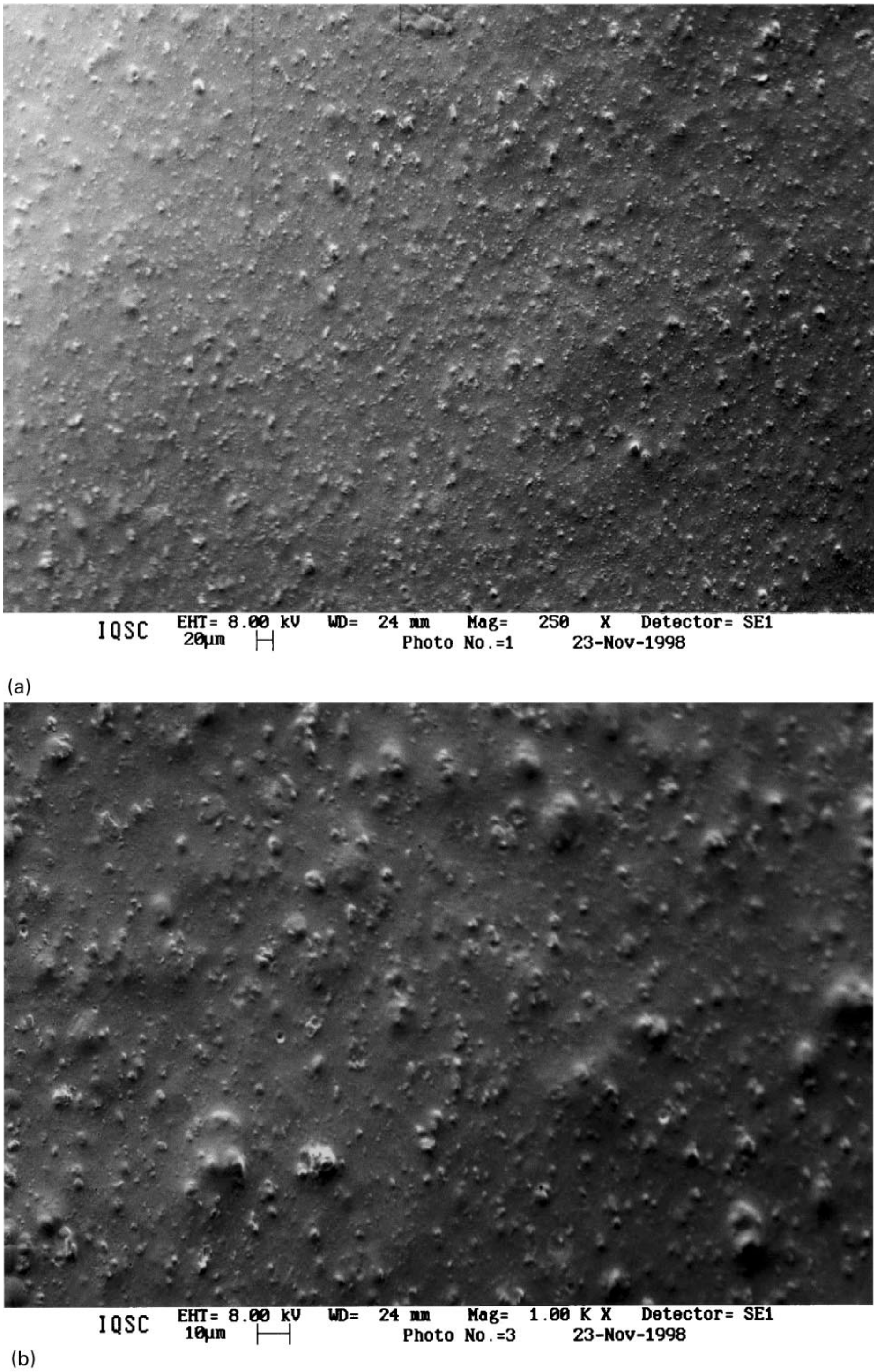

Fig. 2. SEM micrographs at: (a) 250× magnification; and (b) 1000× magnification of fragile fractured surface the composite with 30 phr of kaolin.

constant (1.7 and 14% at 43 and 100% relative humidity, respectively).

3.4. Thermal analysis

The DSC thermal traces for the thermoplasticized starch and for the composites are shown in Fig. 3. The thermograms obtained permitted the experimental determination of the glass transition temperature (T_g) only for the thermoplasticized starch ($T_g = 2$°C). and for the composites containing 10, 40 and 60 phr, respectively −0.5, −4.5 and −6.7°C. The ΔC_p was in the range of 0.02–0.03 W g^{-1}. The

Table 2
Sorption of moisture for the samples conditioned in 43 and 100% relative humidity determined at 25 ± 2°C

Kaolin content (phr)	Moisture Sorption (%)	
	43% Relative humidity	100% Relative humidity
0	5.0	27.0
10	2.9	20.0
20	2.5	17.0
30	1.8	14.6
40	1.8	14.4
50	1.6	13.4
60	1.6	14.1

observed decrease is proportional to the amount of kaolin present in the composites. Considering the heterogeneity of the composite system, the small decrease in the glass transition temperature could be explained assuming a slight modification in the matrix composition.

The results obtained from the TG experiments showed almost the same behavior for all samples. Thermoplasticized starch showed a weight loss of 26% from ambient temperature to 320°C. In the same temperature range, the weight losses showed a decrease proportional to the amount of kaolin in the composites (13–19%). The decomposition loss occurs at 315–320°C for all composites, which corresponds to the temperature obtained for the thermoplasticized starch employed in this work. The residual weight were in the range of 10–40% relative to the original weight samples, which correspond to the kaolin content in the composites.

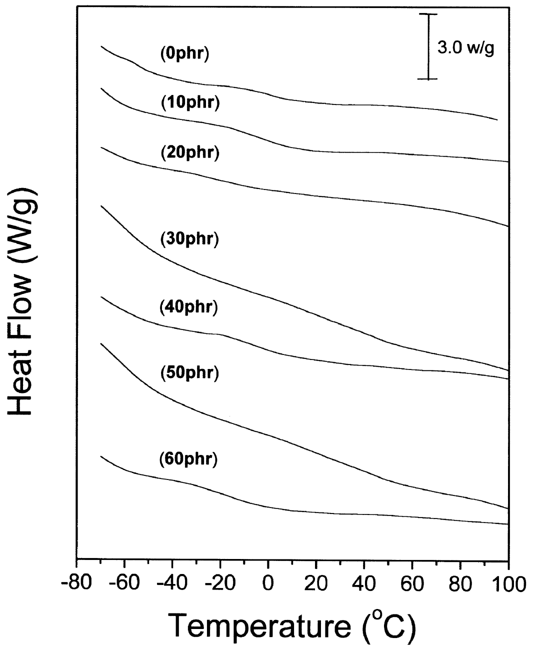

Fig. 3. DSC scans for the thermoplastic starch and its kaolin composites.

4. Conclusions

This study provided a first insight in the preparation and characterization of thermoplasticized starch–kaolin composites.

Thermoplasticized starch showed a very good compatibility with kaolin in the concentration range of 10–60 phr. The SEM micrographs showed a very good dispersion of kaolin in the matrix. The adhesion between the matrix and kaolin was also very good even after the fracture of the sample.

The modulus and tensile strength presented a maximum for the composition with 50 phr. Tensile strength and the correspondent modulus for this composite exhibited an increase of 135 and 50%, respectively, relative to the sample prepared without kaolin. The presence of kaolin decreases the water uptake of the composites, this decrease being more pronounced until 20 phr.

The glass transition temperatures of the composites were slightly lower when compared with the value registered for thermoplasticized starch. The observed decrease was proportional to the amount of kaolin present in the composites.

All samples exhibited the same behavior when submitted to the TG analysis. The decomposition loss occurred at same temperature and the residual weight was proportional to the kaolin content in the samples.

Acknowledgements

The authors acknowledge FAPESP and Mixcim.

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