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Natural Weathering Evaluation of LDPE-Mango Starch Blends by Mechanical Properties and High Field NMR

Tathiane Cordeiro Rodrigues, Maria Inês Bruno Tavares, Victor Jayme Roget Rodriguez Pita*

Summary: The low-density polyethylene/mango starch blends were obtained and submitted a natural degradation. Their mechanical properties and structures changes were determined by tensile, low and high field nuclear magnetic resonance characterization after different weathering times. The exposition time and starch content could be correlated to the polymer matrix changes from void formation theories. The blend deformations were affected by the starch degradation time. The starch degradation, confirmed by nuclear magnetic resonance, could be able to form voids and improve the blends fragmentability at relative low weathering times.

Keywords: LDPE; mechanical properties; natural degradation; NMR; starch

Introduction

Greats environmental problems were created with the large-scale polymers consume and one-trip packaging disposal.[1] The adverse polymer environmental effects have been the objective of many studies. The natural/synthetic polymer blends are an important aspect of these studies. Synthetic polymers natural degradation take long times, but the natural polymers present relative lowest degradation time. Whereas, the addition of natural polymer at the synthetic polymer matrix could be improve the environmental degradation and minimize the environmental impacts.[2] The polyolefin/starch blends productions involve advances, how: special properties, low prices when used in blends and environmental friendly from the degradability.[3] The starch natural degradation induces the void formation; increase the porosity and causes loss of the integrity of the blends.[4] The voids and the defect formation can induce the fragmentability of the polymer matrix with mechanical properties loose.[5,6] When large amounts of starch (>5%) are applied some works observed the stress and elongation at break decrease and the resulting materials have poor film forming properties.[7] This deterioration arises from the different polar characteristics of starch.[7] The purpose of this work was to characterize the low-density polyethylene/starch blends (LDPE/starch) natural weathering. A peculiar mango starch was applied to obtain the blend. Mechanical properties and carbon-13 nuclear magnetic resonance (^{13}C NMR) were used to characterize the blends at different degradation times and starch blends contents.

Materials and Methods

The LDPE sample was supplied by Polibrasil Company (Brazil), with melt flow index 2.7 g/10 min. The mango starch was purchased by University of Cuiabá (MT, Brazil). A series of polyethylene/starch blends were prepared with different starch proportions, using roller rotors in a mixing chamber, Rheomix 600, Rheocord 9000, Haake. Mixing was performed at 170 °C and 60 rpm for 10 min. Before the natural

Instituto de Macromoléculas Prof[a] Eloisa Mano, Universidade Federal do Rio de Janeiro, Cidade Universitária, Centro de Tecnologia, Bl. J, CP68525, CEP21945-970, Rio de Janeiro, Brasil
E-mail: tathiquimcr@uol.com.br

weathering, the blends were molded by pressing. For the LDPE/starch blends, two different levels of mango starch were used namely, 0.5 and 2 wt%. The tensile tests and NMR characterization were applied to the samples at different weathering times.

The natural weathering was carried out during four months at Rio de Janeiro city, Brazil, from July to November, according to ASTM D1435.[8] The mechanical properties were conducted by means of a universal testing machine, model 4204, Instron, at 100 mm/min according to ASTM D638.[9] The values of stress and elongation at break were determinate. The high-resolution NMR analyses were performed at 75.4 MHz Varian Mercury 300, for ^{13}C nucleus. The standard condition pulse sequence was used for signal acquisition. All samples were dissolved at tetrachloroethane (TCE) in a 10 mm NMR tube at 95 °C.

Results and Discussions

The sample degradation was monitored by NMR signals and mechanical properties. When the NMR spectra were compared from 0 days with 30 days of exposition, a small signal variation could be observed for the LDPE containing 2 wt% starch. The 30 days sample showed signals at 18.6 ppm (CH_3), 52.0 ppm (CH_3) and 100.4 ppm (C–O) from anomeric carbons derived from starch degradation. These signals were not observed at 0 days. Some NMR signal differences were detected after 60 days exposition time for LDPE-mango starch blends with 0.5 and 2 wt% of starch contents. The resins with 0.5 wt% starch contents showed signals at 18.9 ppm (CH_3), 58.7 ppm (CH_3–O, CH_2–O) and 100.3 ppm (C–O) from anomeric carbons. At the same way, these signals also indicate the starch degradation. For the LDPE blends with 2 wt% starch content was observed only one small signal derived from the anomeric carbons at 100 ppm. This result pointed to the starch disappears at 60 days from 2 wt% starch blends. After 90 and 120 days of exposition time, the starch NMR signals were not observed for all compositions. These results probably indicate the natural starch degradation and/or the lixiviation of starch degradation products. From these results could be observed that the starch degradation probably start between 30 and 60 days weathering times. These results could be correlated with changes in the polymer matrix. After the long natural weathering, the blend morphology could be changed by the starch degradation and induce fragmental effects on the LDPE matrix.

The stress-strain curves in tension of not exposed natural weather sample are typical from soft and tough materials. Figure 1 exhibits the results when the time exposition was changed to 2 months. The mechanical test profiles show basically a same behavior from 0 days and for all contents of starch. The 4 months stress-strain curves are shown in Figure 2. When the LDPE/mango starch systems achieve 4 months of natural exposition, a material profile characteristic becomes more brittle and quickly harder. These behaviors suggest a potential time degradation effect on this kind of materials.

The Table 1 shows the stress and elongation at break values from LDPE/starch blends compositions and degradation times. The different elongations values were obtained from starch contents. The relative strains at break were decreased by the starch presence. This effect was noted from 0 to 60 days exposition times. Apparently, the voids could be formed by the starch degradation and, consequently, the material fragility was induced from the inherent porosity. After the long natural weathering, the polymer and blend morphology could be changed at different ways, but with the similar final degradation and fragmental effects. However, if the stress at break values are analyzed an energetic barrier could be identified. An ultimate stress decrease was induced by the starch presence at low degradation times. If the stress at break is lower, it could be suggested that the fragmentabilty was more easily obtained.

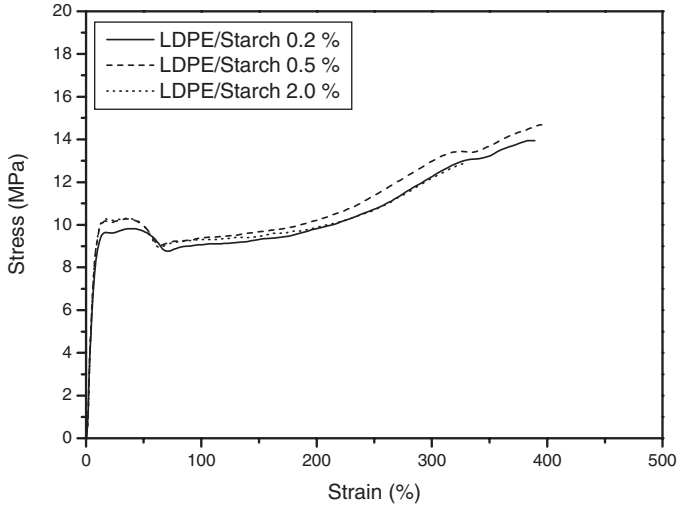

Figure 1.
LDPE/starch blends mechanical properties after 60 days of exposition time.

The stress and elongation at break dependence was showed with the starch presence. After weather degradation, the LDPE/mango starch blends showed a potential capability to induce the material broken. The degradation of starch component could change the integrity and morphology of the blends.

Conclusions

The results suggested that the low starch contents and weathering times would be responsible to the polymer matrix changes and, consequently, by the material degradation profile. The starch weathering degradation could be detected by the

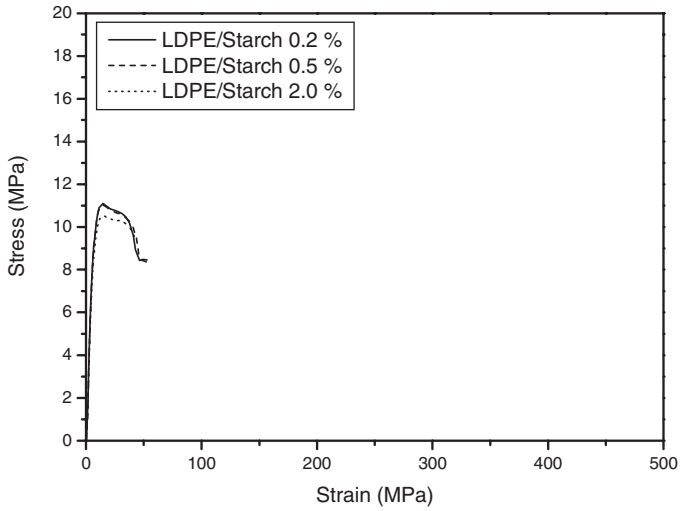

Figure 2.
LDPE/starch blends mechanical properties after 120 days of exposition time.

Table 1.
Mechanical Properties of LDPE-mango starch blends after weathering.

Starch Content (%)	Exposition time (days)	Stress at break (MPa)	Elongation at break (%)
0	0	16.7 (±2.0)	448 (±78)
	30	16.2 (±1.2)	460 (±42)
	60	13.2 (±1.1)	363 (±43)
	90	11.6 (±0.6)	283 (±47)
	120	8.4 (±0.4)	75 (±23)
0.5	0	13.8 (±0.8)	377 (±32)
	30	13.4 (±0.5)	363 (±22)
	60	12.9 (±0.8)	328 (±28)
	90	9.4 (±0.6)	98 (±53)
	120	8.3 (±0.3)	57 (±15)
2.0	0	12.9 (±0.4)	324 (±18)
	30	13.3 (±0.3)	329 (±19)
	60	13.2 (±0.5)	322 (±23)
	90	10.9 (±0.1)	241 (±42)
	120	8.7 (±0.8)	51 (±11)

NMR signals, which pointed the void formation and the polymer matrix changed probability. The LDPE/starch blends fragmentability potential was demonstrated by the stress and elongation properties losses. Apparently, the starch degradation would be able to affect the LDPE systems decomposition.

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