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Influence of Organophilic Ammonium-Free Nanoclay Incorporation on Mechanical Properties and Biodegradability of Biodegradable Polyester

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Summary: Disposal of petroleum-derived polymers is a growing global environmental problem of alarming proportions, which has increased interest in the use and production of biodegradable materials. In addition to biodegradation, investment in research and development in the nanotechnology area is also significant. This study evaluated the effect of incorporation of an organophilic nanoclay ammonium-free salt (Novaclay™) on the mechanical properties and biodegradation of a biodegradable polyester (Ecoflex®), according to ASTM G 160. Ecoflex with and without incorporated Novaclay was characterized before and after biodegradation in organically enriched soil for up to 180 days, by visual analysis, optical microscopy, weight loss, differential scanning calorimetry, dynamic mechanical analysis, mechanical testing, and scanning electron microscopy. The pure Ecoflex and the Ecoflex/Novaclay nanocomposite were partially biodegraded by the method used, and showed changes in their morphological and mechanical properties.

Keywords: biodegradable polyester; biodegradation; ecoflex; nanoclay; novaclay

Introduction

Biodegradable polymers were developed as a means of reducing environmental pollution, because the majority of products made from oil-based polymers are used only once and then promptly discarded.[1–3]

Recently, many biodegradable polyesters have been synthesized and their parameters investigated and discussed, but only some of these polymers have been developed on an industrial scale. One of the commercial materials available is Ecoflex®, an aliphatic-aromatic copolyester obtained by polycondensation between 1,4-butanediol and a mixture of terephthalic and adipic acids. The combination (copolymer containing aliphatic and aromatic monomers) offers novel features of biodegradability, mechanical and thermal properties, and good processability.[4–7]

This polymer is compatible with products from renewable sources (starch, wood flour, paper, etc.), is thermally stable to 230 °C, contains no heavy metals, and meets all requirements of biodegradation and compostability.[8–11]

In addition to biodegradation, nanocomposites based on biodegradable polyesters are of great interest.[12,13] Of the nanoscale materials used in the preparation of these nanocomposites, 70% of the volume is organophilic clays also known as nanoclays, which are obtained from bentonite, a very fine-grained clay composed essentially of montmorillonite.[11–14]

Chemical modification and subsequent dispersion of montmorillonite within bio-

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degradable polyester matrices can provide improvements in several properties, including increased tensile strength, chemical resistance and biodegradability, and decreased permeability and flammability, which extends their application in many fields and makes them more competitive with common thermoplastics.[15–17]

Nanocomposites can be prepared by various methods, including *in situ* polymerization, melt intercalation, or chemical modification on the polymer surface. The melt intercalation method is very attractive due to its versatility, compatibility with current polymer-processing techniques, and absence of organic solvents.[18–22]

In this study, an organophilic nanoclay ammonium-free salt was incorporated into Ecoflex by melt intercalation, and the mechanical and thermal properties and the influence of nanoparticles on the material degradation of Ecoflex and the resulting nanocomposites were evaluated, according to ASTM G 160.[23]

Experimental Part

Materials

The materials used in preparation of nanocomposites of the biodegradable polyester/Nanoclay (2.5% w/w) were: Ecoflex F-BX 7011 (supplied by Basf); Antioxidant agent Hostanox^{TM} (Clariant); Novaclay, an organophilic ammonium-free nanoclay (Ioto International; patent application for Novaclay: INPI/BR: 015100000646).

Methods

The Ecoflex/Novaclay nanocomposite was mixed in a MH 50H intensive mixer and processed in a single-screw laboratory extruder at 3600 rpm. The materials were subjected to the injection-molding process using a Romi Primax 65R injection molding machine. The injection pressure was 300 bar, and the materials were compressed at 150 bar and for 2 s. Temperatures in the heating zones were between 210 and 220 °C, with a cooling time of 45 s.

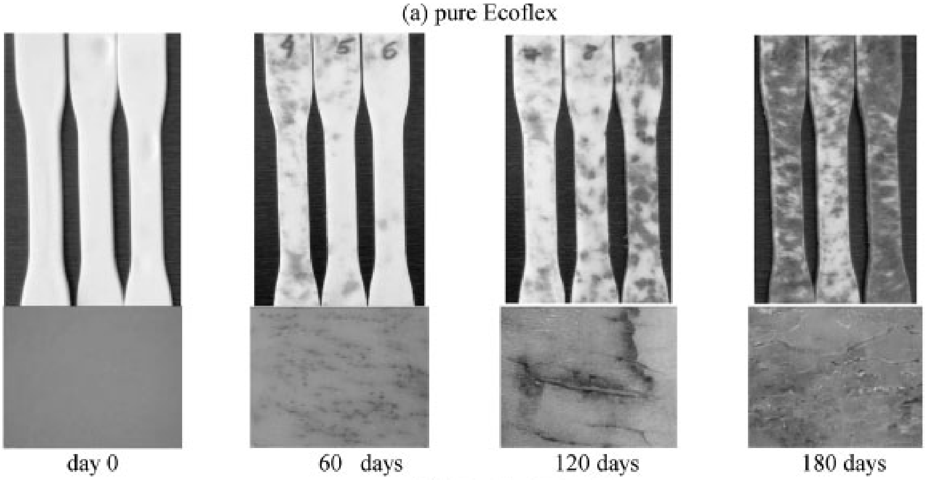
The biodegradation test was performed according to ASTM G 160, in soil composed of equal parts of fertile topsoil, horse manure and coarse sand. The pH was maintained between 6.5 and 7.5, and the soil moisture at 20 to 30%. This test was carried out in triplicate for each sample.

The characterization of the samples before and after biodegradation was performed by visual inspection, complemented by optical microscopy with the aid of a Dino-Lite digital microscope with magnification of 50 and 220 ×, weight loss (statistically tested), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), mechanical properties, and scanning electron microscopy (SEM).

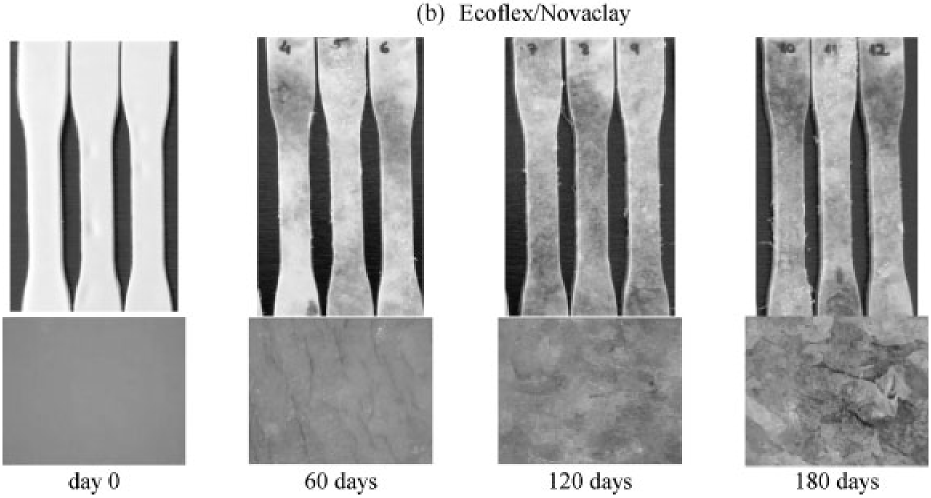
Differential scanning calorimetry (DSC) was performed on a Netzsch 200 F3 Maia differential scanning calorimeter. The weight of the samples was about 10 mg. The samples were placed in an aluminum pan and all the tests were carried out under nitrogen atmosphere ($10\,\mathrm{mL \cdot min^{-1}}$). The samples were heated from room temperature to 200 °C and maintained there for 2 min, cooled to −70 °C and maintained there for 2 min, and then reheated to 200 °C at $10\,^{\circ}\mathrm{C \cdot min^{-1}}$. The last step was recorded. The degree of crystallinity was estimated using $X_c = \Delta H_m / \Delta H^{\circ}_m$ where ΔH°_m represents the theoretical heat of fusion for 100% crystalline Ecoflex, 115 J/g.

Tensile tests by dynamic mechanical analysis (DMA) were carried out on a Thermal Instruments Dynamic Mechanical analyzer, Netzsch model 242, over a temperature range from −60 to 80 °C, single frequency (1 Hz), atmosphere of N_2 at $50\,\mathrm{mL \cdot min^{-1}}$ and heating rate of $3\,^{\circ}\mathrm{C \cdot min^{-1}}$.

In the final stress measurements, five specimens of each sample were tested, according to ASTM D 638,[24] in an Instron 4467 universal testing instrument, using a 5 kN load cell, at speed of $500\,\mathrm{mm.min^{-1}}$ and initial length (L_0) of 50 mm. The tests were performed at room temperature (23 °C) and 50% relative humidity. Values



(a) pure Ecoflex



(b) Ecoflex/Novaclay

Figure 1.
(a) Pure Ecoflex and (b) Ecoflex/Novaclay before and after biodegradation, observed - visually and by optical microscopy.

for the mechanical properties were obtained from a typical stress-strain curve.

Morphological changes in the sample surfaces before and after biodegradation were evaluated through scanning electron microscopy (SEM) with a Philips XL30 electron microscope operated at 20 kV. The samples were mounted on a copper support and sputter-coated with gold (Balzers SCD-030 sputtering system).

Results and Discussion

Visual analysis of specimens after the biodegradation test (Figure 1) showed for the pure Ecoflex, dark-brown and red dots or areas, and rugosity on the surface. These changes resulted from biodegradation, as described by Frank (1984).[25]

Ecoflex/Novaclay specimens also showed changes, but more visibly than in the pure polymer. The optical microscopy analyses confirmed these observations.

The percentage of weight loss (Table 1) was more pronounced in nanocomposite, and also after longer periods in the soil. These results also demonstrated the influence of biodegradation on the presence of nanoclay, as discussed by Ray and Okamoto (2003).[27] To verify the reliability of

Table 1.
Percent weight loss of pure Ecoflex and Ecoflex/Novaclay after biodegradation.

Materials	% weight loss			
	30 days	60 days	120 days	180 days
Pure Ecoflex	0.40 ± 0.25	0.50 ± 0.02	1.26 ± 0.09	1.95 ± 0.03
Ecoflex/Novaclay	0.87 ± 0.01	1.28 ± 0.02	1.83 ± 0.03	2.91 ± 0.03

Table 2.
Thermal properties of materials as measured by differential scanning calorimetry, at the beginning of the experiment and after 180 days in soil.

Materials	Melting temperature T_m (°C)	Heat of fusion ΔH_m (J/g)	Crystallinity degree X_c (%)
Pure Ecoflex	117	14.50	12.60
Ecoflex - 180 days	118	13.14	11.43
Ecoflex/Novaclay	120	10.84	9.43
Ecoflex/Novaclay - 180 days	120	10.59	9.20

these results, after biodegradation testing, the data were tested by single-factor analysis of variance (ANOVA), and the variability was evaluated at a significance level of 5% ($p < 0.05$).

Table 2 shows the thermal properties of the pure polymer and the polymer with added Novaclay, evaluated by DSC. The Ecoflex nanocomposite showed a low degree of crystallinity (X_c) compared to the pure Ecoflex.

Figure 2 shows the DMA results for the samples. The glass transition temperature (T_g) was defined as a transition in *tan δ* curve.

The DSC analysis comparing pure Ecoflex with Ecoflex/Novaclay revealed a slight change in the melting temperature (T_m), and a decrease in enthalpy of fusion (ΔH_m) and consequently in crystallinity (X_c). In this case, in the presence of the nanofiller, larger crystals may have formed, with larger

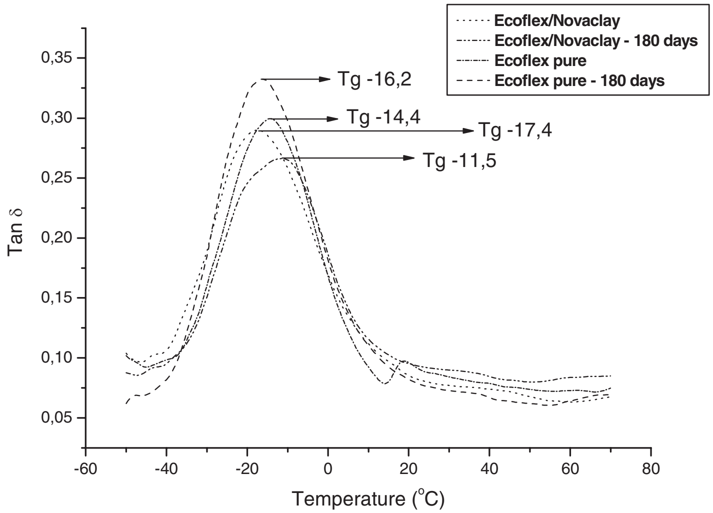


Figure 2.
Dynamic mechanical analysis of pure Ecoflex and Ecoflex/Novaclay.

amorphous regions, which facilitates movement of the chains and decreases the T_g value.

Comparing pure Ecoflex before and after biodegradation revealed a smaller change in T_m, with a decrease in ΔH_m and the degree of crystallinity. Some investigators have suggested that this change can be explained mainly by a lack of the amorphous portion, which tends to degrade before the crystalline portion,[26] or also fragments of rearrangements of the amorphous region of molecules and tie molecules in the crystallites, causing microorganisms to attack the most organized region of the nanocomposite.

These results are consistent with the values obtained in the DMA, which indicated a decrease in T_g; as to the division of the chains, after the biodegradation, the movement increased and the folding of the amorphous regions decreased.

In the nanocomposite, the behavior of T_m, enthalpy of fusion and degree of crystallinity were similar; however, the difference in values before and after the biodegradation was less marked. These results can be explained by the nature of the polymer/filler interface, which hinders movement of the polymer molecular chains, as shown by the increase in T_g of the material after biodegradation.

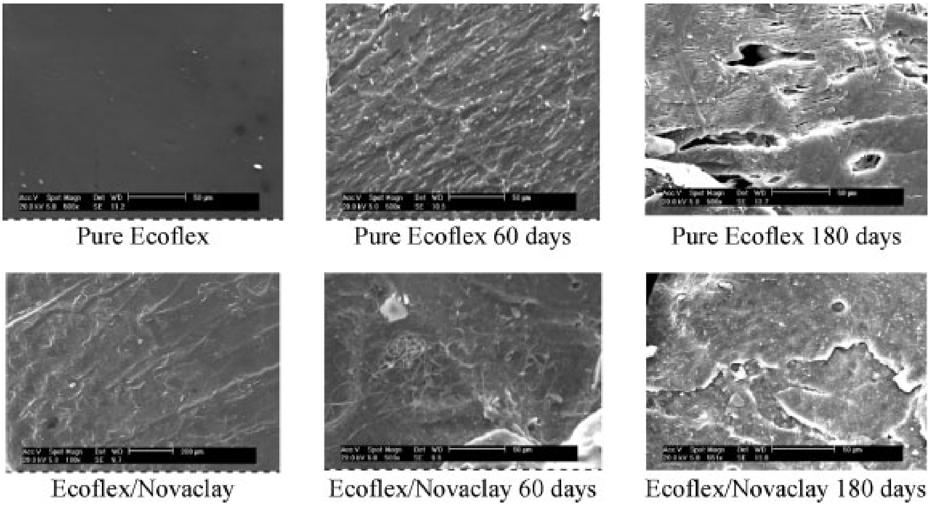
Table 3.
Mechanical Properties of pure Ecoflex and Ecoflex/Novaclay.

Materials	ε_{uts} (%)	σ_{uts} (MPa)	E (MPa)
Pure Ecoflex	961 ± 2.00	8.77 ± 0.19	71.83 ± 1.09
Ecoflex/Novaclay	978 ± 2.00	9.29 ± 0.12	83.99 ± 1.86

Table 3 shows the changes in tensile properties, including Young's modulus (E), ultimate tensile strength (σ_{uts}), and the strain at ultimate tensile strength (ε_{uts}) for the polymer and nanocomposite.

All tensile properties increased significantly with the addition of Novaclay. In the case of nanocomposite, the extent of improvement was due to the synergic effect of the polymer/filler. As expected, the stiffness and σ_{uts} both increased; however, the strain at the highest tensile strength demonstrated that the material was more resistant to tensile stress.[27]

Figure 3 shows the surfaces of specimens of pure Ecoflex and Ecoflex/Novaclay before and after biodegradation. After 180 days, both materials had an irregular morphology and contained grooves, small holes and lighter regions indicative of the



Pure Ecoflex
Pure Ecoflex 60 days
Pure Ecoflex 180 days
Ecoflex/Novaclay
Ecoflex/Novaclay 60 days
Ecoflex/Novaclay 180 days

Figure 3.
Scanning electron micrographs of pure Ecoflex and Ecoflex/Novaclay before and after biodegradation.

action of microorganisms in the biodegradation process, according to descriptions in the literature. [15,16]

The presence of nanoclay resulted in a more-biodegraded material. This enhanced degradation is explained by the presence of the Lewis acid aluminum in the inorganic layers, which catalyzes the hydrolysis of the ester linkages. Also, the addition of highly miscible clay leads to low spherulite nucleation and low bulk crystallization, and as a result, a much lower extent of crystallinity compared to the pure polymer, which facilitates access of microorganisms. Other investigators have evaluated this behavior.[11,26,28]

Conclusion

The study showed that the incorporation of an organophilic nanoclay ammonium-free salt (Novaclay) into a biodegradable polyester (Ecoflex) is possible, and that the tensile properties increased significantly with nanoclay addition.

All the samples prepared were partially biodegraded by the method used, because they showed weight loss and considerable surface changes. The sample that showed the best biodegradation results was Ecoflex/Novaclay, after 180 days in soil, which showed the greatest weight loss and most-pronounced surface changes.

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[1] K. Kasuya, N. Ishii, Y. Inoue, K. Yazawa, T. Tagaya, T. Yotsumoto, J. Kazahaya, D. Nagai, *Polym. Degrad. Stab.*, **2009**, *94*, 1190–1196.

[2] M. Pellicano, W. Pachekoski, J. A. M. Agnelli, *Polim.: Ciênc. Tecnol.*, **2009**, *19*(3), 212–217.

[3] T. F. L. Matos, V. Schalch, *Polim.: Ciênc. Tecnol.*, **2007**, *17*(4), 346–351.

[4] Z. Gan, K. Kuwabara, M. Yamamoto, H. Abe, Y. Doi, *Polym. Degrad. Stab.*, **2004**, *83*(2), 289–300.

[5] I. Vroman, L. Tighzert, *Mater.*, **2009**, *2*, 307–344.

[6] U. Witt, R.-J. Müller, W. D. Deckwer, *J. Polym. Environ.*, **1997**, *5*(2), 81–89.

[7] U. Witt, T. Einiq, M. Yamamoto, I. Kleeberg, W. D. Deckwer, R. J. Müller, *Chemosphere*, **2001**, *44*(2), 289–299.

[8] F. Kondratowicz, R. Ukielski, *Polym. Degrad. Stab.*, **2009**, *94*(3), 375–382.

[9] Ecoflex Biodegradable Plastic: Applications, Range, Properties, Processing **2011**, Retrieved March 23, 2012 from http://www.basf.com.br/default.asp?id=1216

[10] E. Sykacek, M. Hrabalova, H. Frech, N. Mundigler, *Compos. Part A.*, **2009**, *40*(8), 1272–1282.

[11] P. Bordes, E. Pollet, L. Avérous, *Prog. Polym. Sci.*, **2009**, *34*, 125–155.

[12] N. Pantoustier, B. Lepoittevin, M. Alexandre, P. Dubois, D. Kubies, C. Calberg, R. Jérôme, *Polym. Eng. Sci.*, **2002**, *42*(9), 1928–1937.

[13] X. Zhang, G. Lin, R. Abou-Hussein, W. M. Allen, I. Noda, J. E. Mark, *J. Macromol. Sci. A*, **2008**, *45*(6), 431–439.

[14] E. Pollet, C. Delcourt, M. Alexandre, P. Dubois, *Eur. Polym. J.*, **2006**, *42*, 1330–1341.

[15] L. B. de Paiva, A. R. Morales, F. R. V. Díaz, *Appl. Clay Sci.*, **2008**, *42*, 8–24.

[16] S. Ray, M. Bousmina, *Prog. Polym. Sci.*, **2005**, *50*, 962–1079.

[17] Y. Someya, N. Kondo, M. Shibata, *J. Appl. Polym. Sci.*, **2007**, *106*(2), 730–736.

[18] P. H. C. Camargo, K. G. Satyanarayana, F. Wypych, *Mater. Res.*, **2009**, *12*, 1–39.

[19] M. Alexandre, P. Dubois, *Mater. Sci. Eng.*, **2000**, *28*, 1–63.

[20] S. K. Lee, D. G. Seong, J. R. Youn, *Fibers Polym.*, **2005**, *6*(4), 289–296.

[21] Y. Di, S. Iannace, E. Di Maio, L. Nicolais, *Polym. Phys.*, **2003**, *41*(7), 670–678.

[22] Y. Someya, Y. Sugahara, M. Shibata, *J. Appl. Polym. Sci.*, **2005**, *95*(2), 386–392.

[23] ASTM – American Society for Testing and Material – Annual Book of ASTM Standard, ASTM G 160 **2003**.

[24] ASTM – American Society for Testing and Material – Annual Book of ASTM Standard, ASTM D 638-08 **2008**.

[25] H. K. Frank, in *Anais do 8° Fórum de Microbiologia*, Leipizig – DE, **1984**, 339.

[26] D. N. Bikiaris, G. Z. Papageorgiou, D. S. Achilias, *Polym. Degrad. Stab.*, **2006**, *91*, 31–43.

[27] S. S. Ray, M. Okamoto, *Prog. Polym. Sci.*, **2003**, *28*, 1539–1641.

[28] A. Marcos-Fernández, G. A. Abraham, J. S. Román, *Polymer.*, **2006**, *47*, 785–798.