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Characterization of polymer soil burial degradation by thermal analysis and mechanical spectroscopy

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SUMMARY: Polypropylene (PP) and High density polyethylene (HDPE) / Polypropylene (PP) blend with different biodegradable additives (Granular starch/iron oxide mixture, Bioefect 72000 and Mater-Bi AF05H) were selected for degradation experiments. All the samples, processed by injection as seedboxes, have been subjected to an outdoor soil burial test and removed at different periods of time between 0 and 21 months. Their chemical structure and morphology have been analysed. Studies of dynamic-mechanical relaxation spectra of the samples before and after each exposure time have been carried out. The three characteristic relaxation zones α, β and γ, in order of decreasing temperature, have been obtained. It has been observed that due to the degradation process both, the HDPE/PP blend and the PP matrix, become more brittle than the undegraded ones regardless of the additive used. Degradation seems to start from the molecular chains of the amorphous phase or interfacial region. However the analysis of the mechanical behaviour manifested that the crystalline zone is also been affected by the exposure time.

Introduction

Interest in degradable plastics has resulted from the growing and uncontrolled increasing volume of solid wastes. A satisfactory solution might be to convert materials into degradable versions of themselves by the simple addition of a biodegradable masterbatch additive. Biodegradable polyolefins have found a niche in agricultural uses being processed as seedboxes. These seedboxes allow a proper plant growth in seedbeds and their later biodegradation in the fields, avoiding thereby their removal cost.

In order to predetermine the service-life of these materials it is necessary to know the degradation mechanism of such polyolefins. Since a variety of environmental factors as

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well as properties of the material itself may affect the degradation rate, the polymer degradation is manifested with changes in its chemical and physical properties. An extensive knowledge on the chemical structure of polyolefins as well as on their morphological and mechanical characterisation, may be a useful tool to analyse their degradation process.

The objective of this work was to analyse the degradation of polyolefins filled with some biodegradable additives subjected to an outdoor soil burial test, by means of the study of their mechanical behaviour and its morphological changes.

Experimental

Polypropylene 1148-TC (PP) supplied by BASF (Germany) and a High density polyethylene 5218 (HDPE) supplied by British Petroleum (Spain) were used. Four types of samples, labelled A, B, C and D have been prepared. They all contain 10% by weight of biodegradable additive incorporated in the form of a masterbatch into the polymeric matrix. Samples A, B and C have the same polymeric matrix made up of a 40/60% by weight HDPE / PP blend, but have been filled with a different additive. Sample A contains a 92/8% (by weight) granular starch / iron oxide mixture, sample B Bioefect 72000 supplied by Proquimaq Color, S.L. (Spain) and sample C Mater-Bi AF05H obtained from Novamont North America. Sample D is formed by a PP matrix into which Bioefect 72000 has been incorporated. All the samples have been processed by injection as seedboxes.

Samples have been subjected to an outdoor soil burial test in Ayora (Valencia, Spain) and have been removed after 0, 3, 6, 9, 12, 15, 21 months. The soil has a pH (measured in water) of 6.75. After removal, samples were carefully washed with a soap solution and in order to stop the biodegradation process, they were dried with a piece of paper before being analysed.

The chemical structure was studied by Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet 510 spectrophotometer. Special interest was focused on the following absorption peaks: 1740 cm^{-1} ester carbonyl, 1713 cm^{-1} ketone carbonyl, 1640 cm^{-1} double bonds and 915-905 cm^{-1} vinyl bonds. In order to compensate the differences in the polymer films thickness, all the absorbances were measured relative to the CH_2 scissoring peak at 1463 cm^{-1} and the obtained values were called functional group index.

The samples morphology was analysed by Differential Scanning Calorimetry (DSC) with a PERKIN-ELMER DSC-4 calorimeter. The sealed pans, with one hole in each pan cover, were scanned at a heating rate of 10 °C/min from 0 to 200°C

The viscoelastic properties were determined by means of a Polymer Laboratories Ltd Dynamic Mechanical Thermal Analyzer, MARK II DMTA. The E' and tan δ values have been measured from -140 to 200°C at the frequencies of 0.3, 1, 3, 10 and 30 Hz with a heating rate of 1 °C/min.

Results and Discussion.

The changes in the chemical structure of the samples can be followed by measuring the functional group indexes. The carbonyl and double bonds indexes decrease with the degradation time. Ester groups were present in all the samples.

Figure 1 shows the d.s.c. thermograms of samples A and D. Sample A displays two separate peaks. The first endothermic peak has been assigned to HDPE and the second one to PP. Similar figures were obtained with samples B and C. Sample D exhibits the endothermic peak of PP. It is noted that in all cases both, HDPE and PP, show a wide main peak which melting temperature is about 129 and 166°C respectively, regardless the type of additive used. The observed peak width indicates a broad distribution of lamellar sizes. As the degradation time increases, the peaks shape changes revealing a transformation in the lamellar sizes distribution.

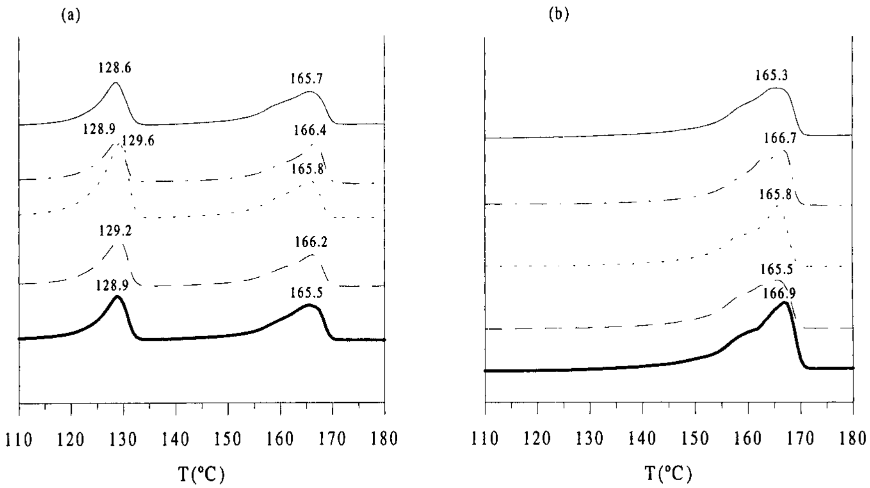

Fig. 1: DSC thermograms of (a) sample A and (b) sample D after different exposures times: —— 0,········ 6, — — 12, ——15 and —— 21 months.

The crystalline content (X) values shown in table 1 were calculated according to the equation: $X = (H_a - H_c) / H_m$, were H_a and H_c are the enthalpies in the melt state and the crystalline state respectively. Their difference is directly obtained from the thermogram. H_m is the change of the melting enthalpy of a perfect crystal of infinite size. Wunderlich[1] proposed the value of H_m of 70 cal/g ≈ 293 J/g for the PE and H_m = 50 cal/g ≈ 209 J/g for the PP. The crystalline content of the samples subjected to different exposure soil burial times tend to change slightly although no regular evolution appears. These differences are however quite significant, since they are greater than the deviation between parallel runs within the same series. Thus, in a first stage the crystalline content increases but after a time of about 9 or 15 months (depending on each sample) a second stage begins in which the crystalline content decreases more quickly than it increased during the first one.

Tab.1. Total crystalline content, X of samples A and D. 1 and 2 indicates the values assigned to HDPE and PP respectively.

Months of exposure	Sample A		Sample D	
	X_1	X_2	X_1	X_2
0	0.19	0.26	-	0.47
6	0.27	0.22	-	0.48
12	0.28	0.21	-	0.51
15	0.22	0.26	-	0.50
21	0.18	0.26	-	0.48

In order to follow the analysis of the degradation process, the complete mechanical relaxation spectrum of all the samples has been obtained.

Figures 2 and 3 give as example the relaxation spectrum of sample A in terms of the storage modulus (E') and loss tangent (tan δ) respectively as a function of temperature and for different exposure times. Similar spectra have been obtained for samples B and C. It is noted from these figures, and from the ones of all the other samples, that both E' and tan δ have the same behaviour that the one observed in the previous thermograms. In a first stage, the E' and tan δ values increase gradually as the exposure time increases regardless the additive used. However, afterwards these values decrease in a second stage. This fact is more obvious in terms of the loss modulus E'' (E''= E' x tan δ).

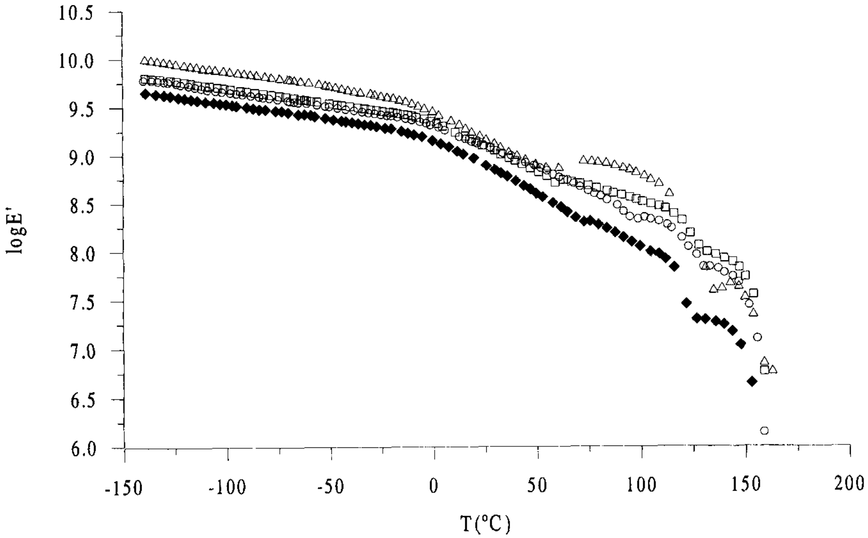

Fig. 2: Values of log E' versus temperature at 1 Hz frequency for sample A: ◆, undegraded; Δ, 6 months; , 15 months; o, 21 months subjected to soil burial test.

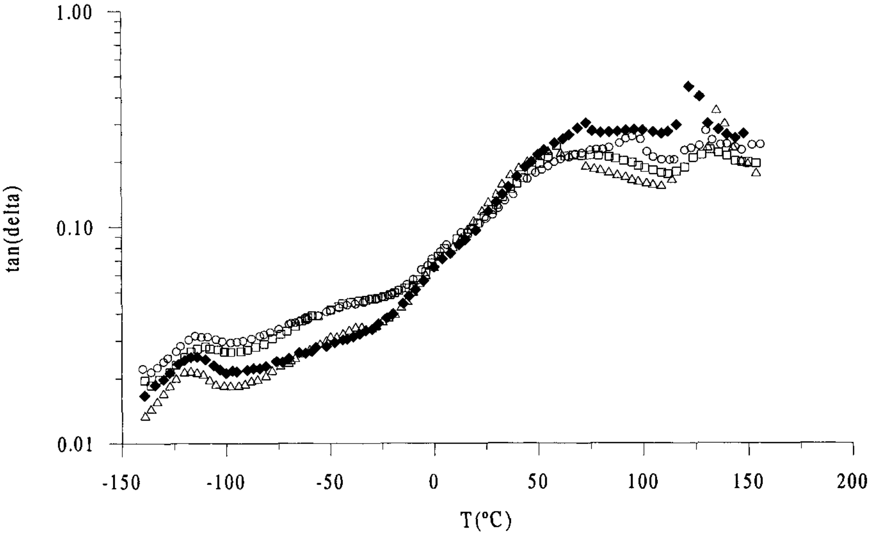

Fig. 3: Values of tan δ versus temperature at 1 Hz frequency for sample A: ◆, undegraded; Δ, 6 months; , 15 months and o, 21 months subjected to soil burial test.

Figure 4 gives the loss modulus (E'') as a function of temperature for sample A. Similar spectra have been obtained for samples B, C and D. These spectra exhibit three clearly distinguished relaxation zones, α, β and γ, in order of decreasing temperature in agreement with those obtained by other authors. Boyd[2], Polpy[3] and ourselves[4-5] have established that the α relaxation is attributed to the molecular chain movements that occur in the crystalline zone. The β relaxation may result from motions taking place at the crystalline-amorphous interface. The γ relaxation can be associated to movements of molecular chains that take place in the amorphous phase of the polyethylene. The PP only presents the α and β relaxation zones, the γ relaxation appears as a weak shoulder.

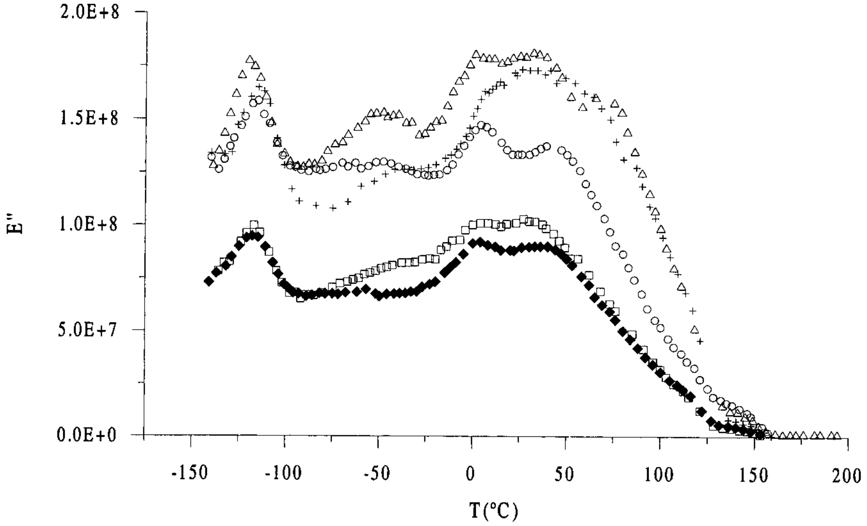

Fig. 4: Plot of E'' versus temperature at 1 Hz frequency for sample A: ◆, undegraded; □, 3 months; Δ, 6 months; +, 12 months and o, 21 months subjected to soil burial test.

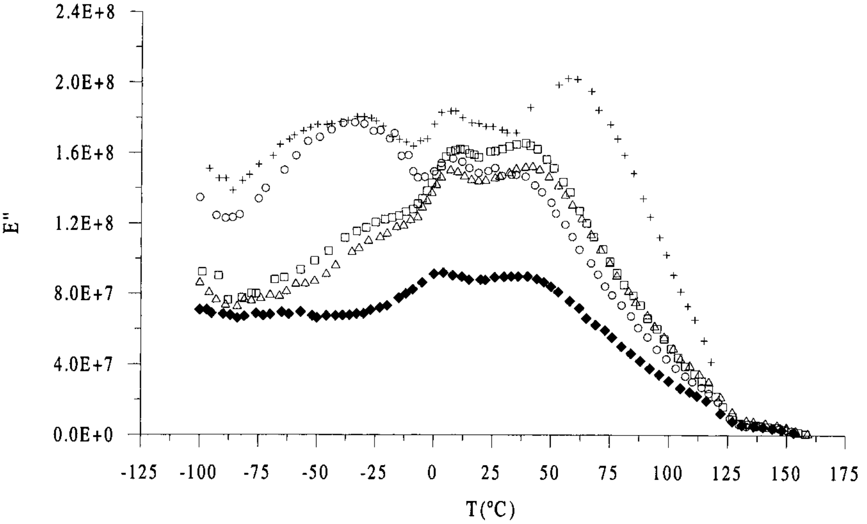

Fig. 5: Plot of E'' versus temperature in the β– and α–mechanical relaxation zone at 1 Hz frequency for sample C: ◆, undegraded; □, 3 months; Δ, 6 months; +, 12 months and o, 21 months subjected to soil burial test.

In order to analyse each one of these relaxation zones and to characterize this mechanical behaviour, the dependence of the mean relaxation times on temperature has been adjusted to the Arrhenius equation: $\ln f = \ln f_0 + \exp(E_a/RT)$ (1)

where E_a is the apparent activation energy.

T_m and f_m are respectively the temperature and the frequency of the maximum of the loss modulus.

Figure 4 shows the γ relaxation from -140 to -100°C. It can be observed that the maximum values of E" also gradually increase as the degradation time increases. The activation energies estimated for the γ relaxation are about 20-26 Kcal/mol. These values are similar to the ones found by these authors[6]. It is noted that depending on the additive used the apparent activation energy has a different tendency as the exposure time increases. The β zone is located from -80 to -20°C as shown figures 4 and 5. This zone is the most sensitive to the exposure time, increasing its height with this factor. The estimated values of the activation energy for this relaxation are about 60 Kcal/mol as found these authors[6] for high density polyethylenes irradiated at low doses (2 and 20 Mrad). This suggests that the origin of the β relaxation is the same in both cases. These results are in agreement with the idea that oxygen is usually insoluble in the crystalline regions of polyolefins[7-8]. Oxidation, and consequently the biodegradation process, will therefore be confined in the first stages to the chains between the crystallites that form the crystalline-amorphous interface. This effect is more significant in sample C suggesting that Mater-Bi is the additive that faster accelerates the biodegradation of the inert polymeric matrix.

On the other hand, the values obtained for the α relaxation zone are in agreement with the thermograms, but in the relaxation spectra (figures 4 and 5) the changes of the E'' values are more apparent. In the first stage, when the crystalline content increases and basically when the lamellar sizes distribution changes, the E'' values increase. However the E'' values drop after 9-15 months (depending on each sample). This is in good agreement with the beginning of the second stage of the degradation process when the crystalline content decreases, the lamellar sizes display a broad distribution and a weakening of the polymeric matrix is produced.

Conclusions

Due to the degradation process, the PP inert matrix and the HDPE / PP blend become more brittle than the undegraded ones in a first step, but after a certain exposure time the storage modulus decreases regardless of the additive used. The observed changes have a different time scale for each additive as the biodegradation begins and develops.

Degradation seems to start from the molecular chains of the amorphous phase or interfacial region since carbonyl groups are not formed in the crystalline regions of polyolefins. However this attack leaves a weakened crystalline structure and enhances the polymer matrix disintegration.

The analysis of dynamic-mechanical relaxation spectra may be a useful and efficient tool to evaluate the degradation process, and together with chemical and morphological characterisations it may clarify some of the many factors that influence the degradation mechanism of polymers.

Mater-Bi is the most suitable additive when introduced into an inert matrix as prodegradant because it needs the least induction period to trigger the degradation mechanisms upon environmental exposure.

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