POLYMER TESTING

ROGER BROWN

Material Characterisation

Mechanical, thermal and morphological characterization of polypropylene/biodegradable polyester blends with additives

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A R T I C L E   I N F O

A B S T R A C T

The (bio)degradation of polyolefins can be accelerated by modifying the level of crystallinity or by incorporation of carbonyl groups by adding pro-oxidants to masterbatches or through exposure to ultraviolet irradiation. In this work, we sought to improve the degradation of PP by adding cobalt, calcium or magnesium stearate to Ecoflex®, PP or Ecoflex®/PP blends. The effect of the pro-oxidants on biodegradability was assessed by examining the mechanical properties and fluidity of the polymers. PP had higher values for tensile strength at break and Young's modulus than Ecoflex®, and the latter had little influence on the properties of PP in Ecoflex®/PP blends. However, the presence of pro-oxidants (except for calcium) reduced these properties. All of the pro-oxidants enhanced the fluidity of PP, a phenomenon that facilitated polymer degradation at high temperatures.

1. Introduction

Plastics are used in the manufacture of a large range of short-life products [1,2], primarily because of the ease with which these polymers can be processed [3–6]. The widespread use of plastics has resulted in their extensive accumulation as residues of domestic garbage [6,7]. The accumulation of plastic waste is harmful to life [8,9] since the degradation of conventional synthetic plastics such as polypropylene (PP), polyethylene (PE) and polystyrene (PS) is extremely slow and requires abiotic factors and the action of microorganisms [6–8].

The biodegradation of polyolefins such as PP and PE can be facilitated by incorporating carbonyl groups and pro-oxidants in masterbatches [4,10–12] or through exposure to ultraviolet (UV) irradiation [12,13]. The thermal degradation of plastics can be enhanced by stearate (St)

complexes of transition metals such as zinc (ZnSt), copper (CuSt), silver (AgSt), cobalt (CoSt), nickel (NiSt), manganese (MnSt), chromium (CrSt) and vanadium (VSt), or alkaline earth metals such as magnesium (MgSt) and calcium (CaSt) [14–23]. At high temperature, polymers containing these pro-oxidants start to release free radicals that are very unstable and quickly attack the polymeric chains, resulting in bond scission and polymer degradation [15,20,21,24]. Pro-oxidants have been included in blends of starch, cellulose or polylactic acid used to produce shopping bags, organic garbage bags, food packing and plastic sheets used to cover soil [7].

Wang et al. [5] compared the biodegradability of films of poly(3-hydroxybutyrate-co-3-hydroxyhexanoatohydroxy-hexanoate), (PHBHH$_x$), poly(β-hydroxybutyrate) (PHB) and Ecoflex® (a synthetic, aliphatic–aromatic, biodegradable copolyester containing the monomers 1,4-butanediol, adipic acid and terephthalic acid) [25] exposed to activated mud. After 18 days, the films containing PHB-co-12%-HHx or 20% PHB were completely degraded, whereas films made with

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Ecoflex® showed only a 5% mass loss. Scanning electron microscopy showed that the surface of Ecoflex® was smoother than that of PHB-*co*-12%-HHx and PHB. Surface morphology was an important factor in the degradation of PHBHHx since the low crystallinity and rough surface of PHB-*co*-12%-HHx enhanced its degradation. Witt et al. [7] examined the biological degradation of Ecoflex® and the products formed during this process. The thermophylic fungus *Thermomonospora fusca* isolated from compost material was used to assess the susceptibility of Ecoflex® to degradation at 55 °C. After incubation for 22 days, most (>99.9%) of the copolyester had been degraded into its diacid and diol constituents, with gas chromatography (GC) and mass spectroscopy (MS) being used to detect the monomers (1,4-butanediol, adipic acid and terephthalic acid) and their monoesters. None of the products of degradation (intermediate monoesters, monomer or oligomers) were toxic to *Daphnia magna* or *Photobacterium phosphoreum*. This lack of toxicity indicates that Ecoflex® could be useful in studies of polymer degradation in compost [11]. The greater susceptibility of Ecoflex® to degradation makes this material excellent for use in short-life products such as protective packing and film for foods and agricultural applications.

In this work, we examined the effect of different concentrations of CoSt, CaSt or MgSt on the biodegradation of PP in the absence and presence of Ecoflex®, based on changes in the mechanical and thermal properties and morphology of the blends compared to pure PP.

2. Experimental

2.1. Materials

Polypropylene (PP) – Prolen®, supplied as pellets (lot no. D00617) by Polibrasil S.A. (Suzano, São Paulo, Brazil).

Ecoflex® *(ECO)* – type FBX7011, supplied as pellets (lot no. 97021947G0) by BASF S.A. (São Paulo, São Paulo, Brazil).

Polyethylene-graft-glycidyl methacrylate – (PE-g-GMA) – supplied as pellets in *pellets* (quality AX-8840, lot B205 R013) by Atofina DPT Cours Michelet (Usine de Carling, Paris, France).

Calcium stearate (CaSt) – supplied as powder, by Dacarto Benvic S.A. (Diadema, São Paulo, Brazil).

Cobalt stearate (CoSt) – supplied as flakes (lot no. H08M23) by Alfa Aesar S.A. (São Paulo, São Paulo, Brazil).

Magnesium stearate (MgSt) – supplied as powder (lot no. 200604295) by AMC do Brasil Ltda.

2.2. Modification of polypropylene

Masterbatches of PP containing a pro-oxidant were obtained by adding stearates of cobalt (CoSt), calcium (CaSt) or magnesium (MgSt) to yield PP + CoSt, PP + CaSt and PP + MgSt in which the final concentration of metal stearate was 20% relative to the mass of PP. Modified PP was produced by the drawing process using pure PP and the desired masterbatch in an LGEX 25/26 extruder with a length/diameter (L/D) ratio of 25 (LGMT Equipamentos Industriais Ltda., Piracicaba, SP, Brazil). The temperatures used for zones 1 and 2, were 210 °C and 190 °C, respectively.

Table 1
Denominations of compositions developed.

Composition denomination	Proportions of components in the blends (%, in mass)					
	PP	Calcium Stearate	Magnesium Stearate	Cobalt Stearate	Ecoflex®	PE-g-GMA
100PP	100	–	–	–	–	–
100ECO	–	–	–	–	100	–
100/0/CaSt	100	0.2	–	–	–	–
100/0/MgSt	100	–	0.2	–	–	–
100/0/CoSt	100	–	–	0.2	–	–
95/5/CaSt	95	0.2	–	–	5	2
90/10/CaSt	90	0.2	–	–	10	2
80/20/CaSt	80	0.2	–	–	20	2
70/30/CaSt	70	0.2	–	–	30	2
95/5/MgSt	95	–	0.2	–	5	2
90/10/MgSt	90	–	0.2	–	10	2
80/20/MgSt	80	–	0.2	–	20	2
70/30/MgSt	70	–	0.2	–	30	2
95/5/CoSt	95	–	–	0.2	5	2
90/10/CoSt	90	–	–	0.2	10	2
80/20/CoSt	80	–	–	0.2	20	2
70/30/CoSt	70	–	–	0.2	30	2

2.3. Incorporation of Ecoflex®

Ecoflex® was incorporated into PP containing stearates by extrusion, and the temperatures used for zones 1 and 2 were 210 °C and 190 °C, respectively. The PP$_{St}$/Ecoflex® mass ratios used were 95/5, 90/10, 80/20 and 70/30. A compatibilizer (PE-g-GMA) was also incorporated (2% by mass relative to the modified PP). Films approximately 50 mm wide and 0.4 mm thick were obtained using a metal mold. Table 1 shows the obtained formulations.

2.4. Mechanical properties

Plates (200 mm × 200 mm × 1.0 mm) were prepared by solvent casting and type IV specimens (ASTM-D-638/08)
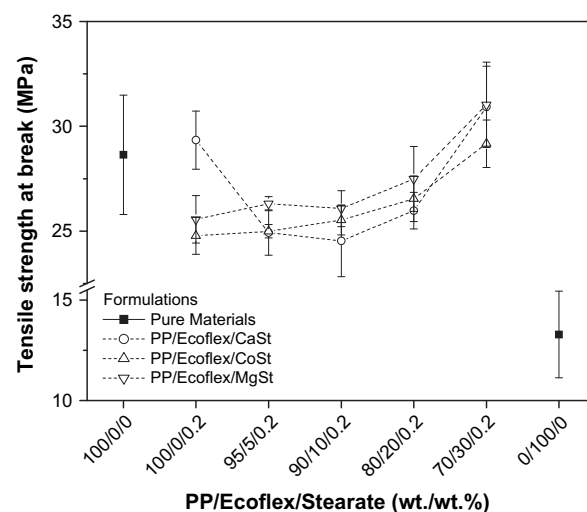

Fig. 1. Tensile strength at break for pure PP, *Ecoflex®* and their blends.
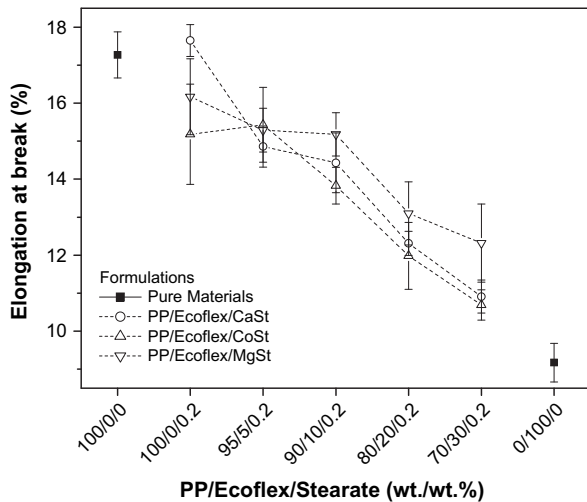
Fig. 2. Elongation at break for pure PP, *Ecoflex*® and their blends.

[26] were stamped with a cutting tool. The tests were done using a model DL 2000 NS 5921 universal testing machine (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil). The control program used was Tesc version 3.01, the load cell had a capacity of 20 kgf and the speed of stretching was 50 mm min⁻¹.

2.5. Melting flow index (MFI)

The melt flow index of PP and its blends was determined using a model MI-1 plastometer (DSM Instrumentação Cientifica Ltda., São Paulo, SP, Brazil), according to ASTM-D-1238/04c (190 °C/2.160 kg) [27].

2.6. Thermal analysis

Thermal analysis was done with a DSC 50 differential scanning calorimeter (Shimadzu, Tokyo, Japan) in an atmosphere of nitrogen (flow rate: 50 ml min⁻¹) at a heating
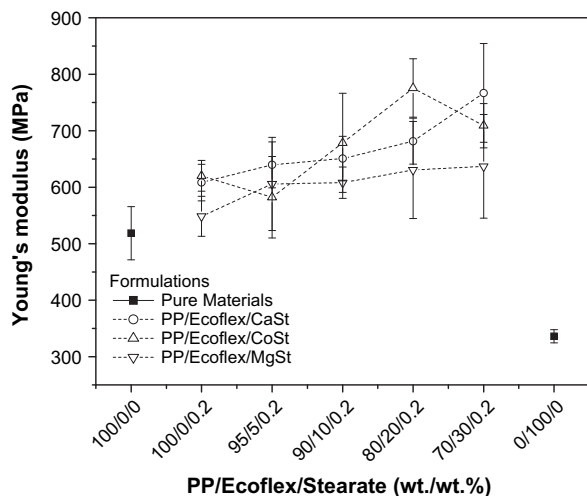

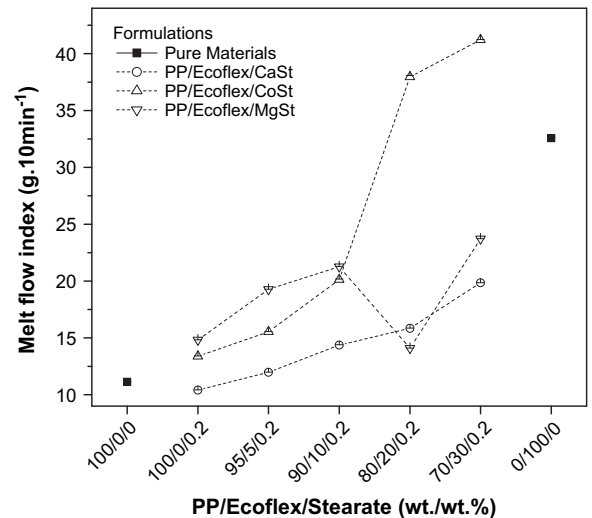Fig. 3. Young's modulus for pure PP, *Ecoflex*® and their blends.

Fig. 4. Melt flow index for pure PP, *Ecoflex*® and their blends.

rate of 10 °C/min. The materials (average mass: 5 mg) were heated to 200 °C. All of the DSC experiments were done in duplicate. The crystallinity of PP was determined using a heat of fusion value (ΔHo) of 209 J/kg [28] for 100% crystalline PP.

2.7. Scanning electron microscopy (SEM)

Cross-sections of PP, Ecoflex® and their blends with stearates were cryofractured, coated with gold in a Baltec SCD 050 sputter coater (40 mA for 60 s) and then examined with a JEOL JSM-5900LV scanning electron microscope (JEOL Ltd., Akishima, Japan) operated at 10 kV.

3. Results and discussion

3.1. Mechanical properties

The tensile strength at break, elongation at break and Young's modulus for the pure polymers and their blends are shown in Figs. 1–3.

Pure Ecoflex® was two-fold less resistant (tensile strength at break) than pure PP (Figs. 1 and 2) and Young's modulus for Ecoflex® was 40% lower than that of PP (Fig. 3), in agreement with Pollet et al. [4].

In Ecoflex®/PP blends containing pro-oxidants, the incorporation of CoSt resulted in a tensile strength lower than that of pure PP, which suggested a reduction in the interaction between Ecoflex® and PP. In agreement with Roy

Table 2
Melting temperature for PP in formulations.

PP/Ecoflex®/Stearate Formulations	Melting temperature (°C)		
	CaSt	CoSt	MgSt
100/0/0.2	163.5	162.8	163.6
95/5/0.2	163.1	163.0	163.7
90/10/0.2	162.6	161.8	162.3
80/20/0.2	162.3	157.7	163.3
70/30/0.2	162.0	159.0	161.9

Table 3
Crystallinity for PP in formulations.

PP/Ecoflex®/Stearate Formulations	Crystallinity for PP		
	CaSt	CoSt	MgSt
100/0/0.2	31.3	29.4	29.8
95/5/0.2	30.4	28.2	29.9
90/10/0.2	27.8	28.8	25.8
80/20/0.2	26.6	25.3	28.7
70/30/0.2	21.1	21.8	23.6

et al. [22], who examined the effect of CoSt in low-density polyethylene (LDPE), our results indicate that this stearate complex did not degrade during processing of the materials. There was a gradual reduction in the elongation at break with increasing content of Ecoflex® when compared to pure PP (Fig. 2). This effect was particularly marked in the 70/30/ CoSt (app. 30%) blend in which the presence of Ecoflex® reduced the polymer elasticity two-fold.

Fig. 3 shows that the rigidity of blends containing CoSt increased with the content of Ecoflex®, with the values for all blends being greater than the maximum value for pure PP. This increase in rigidity reflected the presence of two rigid materials (PP and Ecoflex®) and the degree of compatibility between them. Figs. 1 and 2 show that the incorporation of Ecoflex® reduced the tensile strength and elongation at break of PP in the presence of CaSt, i.e., increased the rigidity of this blend (Fig. 3). This reduction in elongation suggested greater interaction between PP and Ecoflex® in the presence of PE-g-GMA.
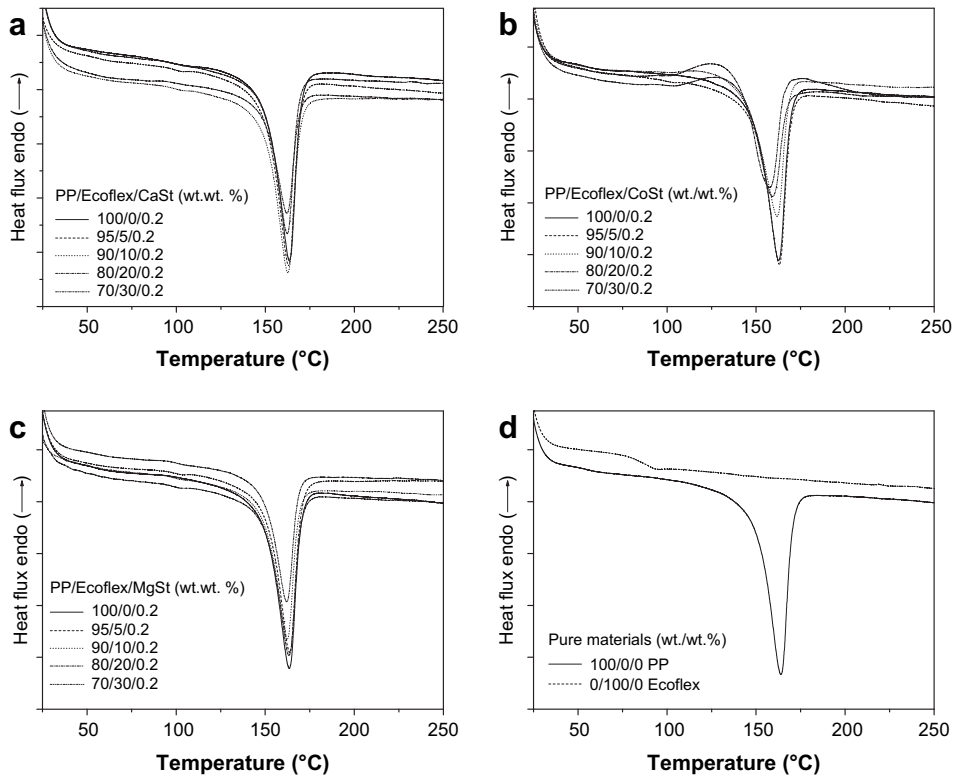

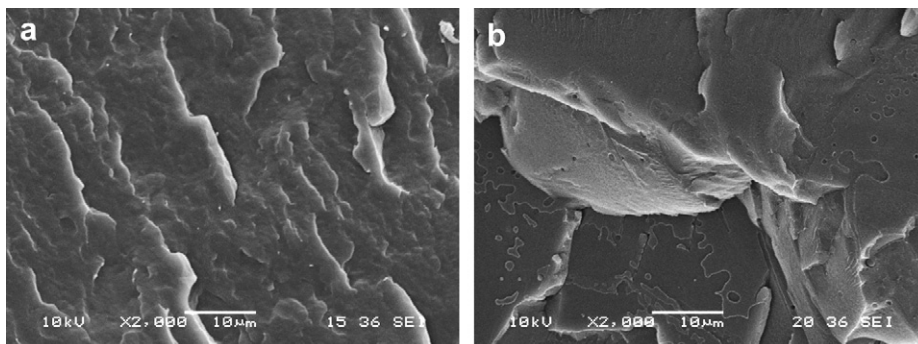**Fig. 5.** Termograms for pure PP, *Ecoflex*® and their blends.

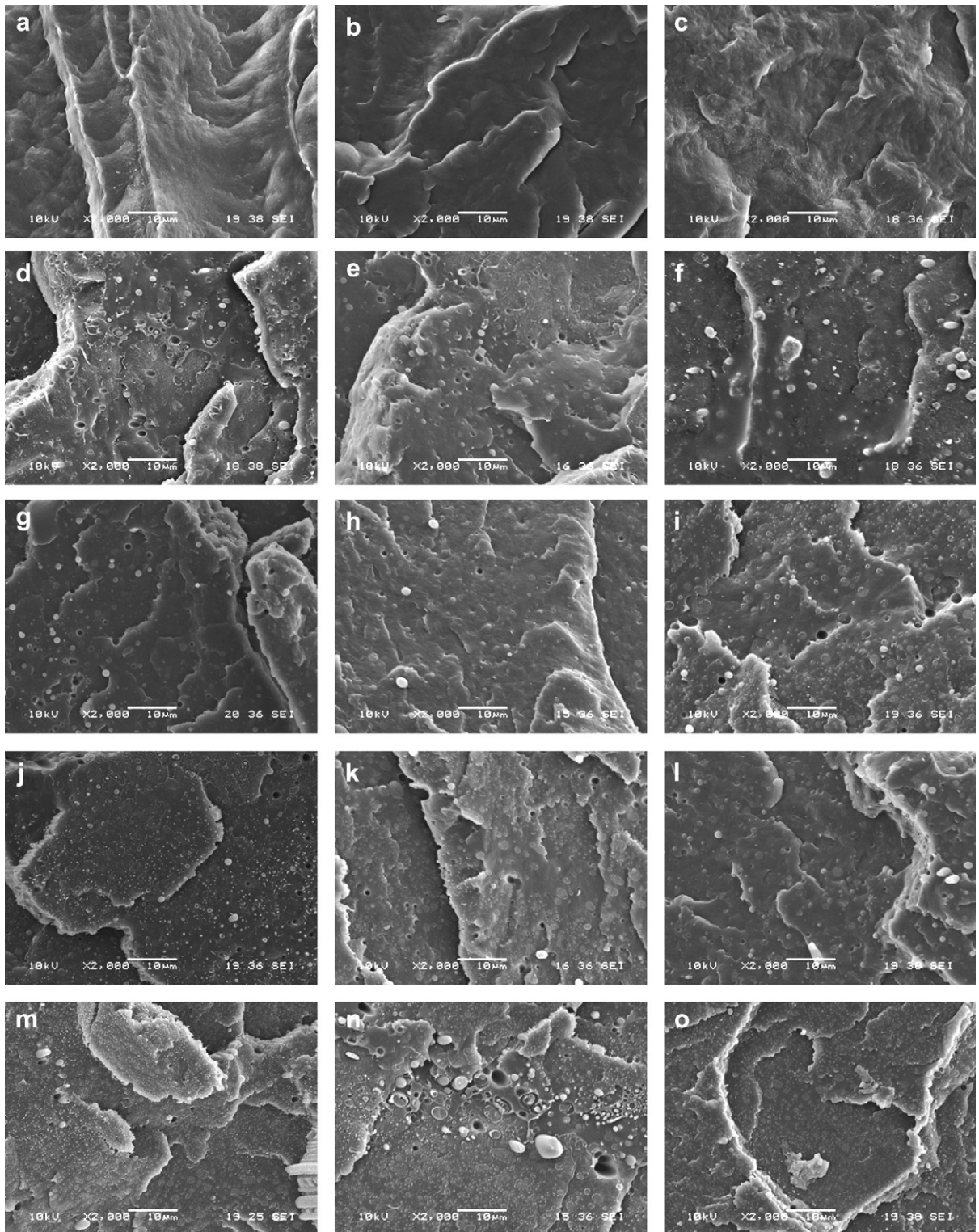**Fig. 6.** SEM micrographs for pure both PP (a) and *Ecoflex*® (b).

Fig. 7. SEM micrographs for blends PP/*Ecoflex*®/Stearates: a) 100/0/CaSt; b) 100/0/CoSt; c) 100/0/MgSt; d) 95/5/CaSt; e) 95/5/CoSt; f) 95/5/MgSt; g) 90/10/CaSt; h) 90/10/CoSt; i) 90/10/MgSt; j) 80/20/CaSt; k) 80/20/CoSt; l) 80/20/MgSt; m) 70/30/CaSt; n) 70/30/CoSt; o) 70/30/MgSt.

3.2. Melting flow index (MFI)

Fig. 4 shows the MFI of pure PP and its blends. PP had a lower MFI than pure Ecoflex® (about 300% less), indicating that the latter was probably more susceptible to degradation than PP, possibly because of its lower content of crystalline regions.

All of the pro-oxidants enhanced the fluidity of PP, indicating an enhancement of polymer thermal degradation of PP during the exposure time in the barrel. In these experiments, MgSt gave the best results, with a 33% increase in fluidity when compared with pure PP (blend 100/0/0.2 in Fig. 4). The inclusion of Ecoflex® in the blends also increased the general fluidity of the system when compared with pure PP. In general, the polymer fluidity increased proportionally to the content of Ecoflex®, except for the blend containing MgSt.

3.3. Thermal analysis

Tables 2 and 3 and Fig. 5 show the thermal behavior of pure PP, Ecoflex® and their blends in the absence and presence of pro-oxidants. Table 2 and Fig. 5 show that the incorporation of Ecoflex® did not significantly alter the melting temperature (T_m) of PP although there was a slight reduction in T_m at high concentrations of Ecoflex®.

CoSt and MgSt reduced the T_m when compared with CaSt, which suggested that these two complexes made the polymers more susceptible to thermal degradation than CaSt. This increased susceptibility was possibly associated with alterations in the crystalline regions, e.g., molecular weight variations resulting from chain breakage and secondary recrystallization [11,22].

Table 3 shows that the crystallinity of PP in PP/Ecoflex®/stearate blends was strongly influenced by the presence of Ecoflex®, i.e., an increase in the proportion of Ecoflex® in the blend reduced the crystallinity of PP, probably because the initial changes associated with degradation occurred in the amorphous phase of the polymer, with a consequent reduction in the crystalline regions [29]. This reduction may have enhanced the biodegradation of the samples through the presence of an amorphous phase.

The greatest reductions in crystallinity were seen with CaSt and CoSt, and this would probably make the blends more susceptible to attack by microorganisms. This conclusion was supported by the reduction in mechanical properties shown in Figs. 1–3. Feng et al. [30] suggested that CaSt acts as a nucleating agent for PP and induces the formation of a β-phase in this polymer, in addition to reducing the crystalline phase (as indicated by DSC curves). Together, these results indicate that pro-oxidants can modulate polymer composition, either by defining a given structure or by producing secondary structural effects [22,29].

3.4. Scanning electron microscopy (SEM)

Fig. 6 shows cross-sections of pure PP and Ecoflex®. PP had a uniform morphology, with no evidence of phase separation (Fig. 6a). In contrast, Ecoflex® had an irregular morphology and contained different phases indicative of the various monomers (1,4-butanediol, adipic acid and terephthalic acid) used to produce the polymer (Fig. 6b).

Fig. 7 shows the morphology of PP, Ecoflex® and their blends in the presence of CaSt. The addition of stearates did not significantly change the morphology of PP (Fig. 7a–c). However, in Ecoflex®/PP blends the incorporation of stearates resulted in phase separation that was not influenced by the type of stearate. The blends contained voids and tubular shapes characteristic of phase separation, particularly blends with CaSt and CoSt. The presence of CaSt resulted in poor interaction between the polymers, as shown by spaces at the PP/Ecoflex® interface. These findings agreed with the observation that CoSt and MgSt reduced the tensile strength in blends containing 5, 10 and 20% Ecoflex®. Blends containing MgSt (such as 5% Ecoflex®) had fewer spaces and a more homogeneous morphology.

4. Conclusion

The incorporation of pro-oxidants increased the fluidity of PP and probably enhanced polymer degradation at high temperature. CoSt and MgSt reduced the T_m compared to CaSt, indicating that the former two stearates made the blends more susceptible to thermal degradation. However, the addition of stearates did not significantly alter the morphology of PP.

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