Photo-degradability of ketone modified PS/HIPS blends

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Abstract

The present work studies the degradability of PS/HIPS blends (50/50%, w/w) modified with different amounts of acetophenone and benzophenone (2.5 and 5%), aiming at the improvement of its decomposition when exposed to natural environment. Suitable characterization techniques, such as infrared and UV-Vis spectroscopy, viscosimetry and tensile tests were used to monitor the extent of the degradation. Evidence for the formation of hydroperoxides and carbonyl groups, occurrence of chain scission and loss of mechanical properties was achieved, being higher for samples with benzophenone. Further, it was also observed that for the same ketone level, benzophenone caused higher changes of mechanical properties, which is in agreement with the decrease of molecular weight observed. Thus, the photo-degradability of PS/HIPS blends could be enhanced by adding this type of chemical compound.

The results obtained are presented and discussed aiming at the optimization of the degradation of PS/HIPS when exposed to the natural environment.

Keywords: Photo-degradation; Polystyrene; High-impact polystyrene; Benzophenone; Acetophenone

Introduction

Polystyrene (PS) is a well-known, brittle, commodity polymer with good processing characteristics. Its brittle nature can be much improved by grafting small amounts of rubber during its polymerisation [1]. The resulting multiphase material, which exhibits dispersed rubber domains in a PS matrix, is known as high-impact polystyrene (HIPS). As the higher impact resistance is achieved at the expense of reductions in other properties, like tensile strength or hardness, selecting one PS grade for a specific application requires finding a compromise for the final part properties. Although

HIPS can be produced with different rubber levels, blending PS and HIPS is a common low cost procedure to yield systems with a wide range of intermediate properties relative to the base materials.

Parts made from PS/HIPS blends (like other commodity plastics) used in the packaging industry make up a considerable share of the waste disposed on dumping grounds. Due to the increasing volume of municipal solid waste and the decreasing landfill capacity for disposing of it, plastic waste disposal has been recognized as a worldwide environmental problem. Therefore, to make degradable plastics by accelerating their decomposition is particularly desirable.

One approach to making common plastics degradable is to introduce sensitizers or initiators, which accelerate chain scission and, consequently, decrease molecular weight when exposed to environmental conditions. The photochemical reactions that occur from absorption of ultraviolet radiation induce the formation of ketone groups on the polymer backbone, which induces brittleness and biodegradation may occur by microbial attack [2].

The photo-degradation of PS has been extensively studied [2 – 4] and a mechanism accounting for the photoproducts has been established. Recently, some studies have been published [5,6] concerning the modification of this polymer in order to improve its degradability.

The development of methods permitting acceleration of the measurements of the chemical and physical properties of the films was, and still is, considered very important [7-9]. In many cases, accelerated weathering is used to predict the lifetime of polymers under service conditions. Most accelerated weathering devices (Weather-Ometer, Xenontester, Suntester, etc.) show a lack of correlation between the stabilities measured with them and those measured outdoors. However, it was demonstrated [10] that filtered Xenon lamps have a UV spectrum which is comparable to the UV spectrum of the sun and, if operated at not too high temperatures, are expected to represent better outdoor ageing. Thus, under these experimental conditions the results obtained can be correlated with the results of natural exposure.

The objective of this work was to investigate the influence of the addition of acetophenone (Ac) and benzophenone (B) on the degradability of PS/HIPS blends, aiming at the improvement of the decomposition of this material when exposed to natural environment. The oxidative photo-degradation was carried out using an artificial source of UV radiation.

Experimental

Materials

A general purpose polystyrene (PS, Lacqrene 1540, MFI = 12 g/10 min at 200°C/5 kg) and a high-impact rubber-modified PS (HIPS, Lacqrene 7240, MFI = 4.5 g/10 min at 200°C/5 kg) were supplied by Atofina. Acetophenone and benzophenone were purchased from Sigma-Aldrich, and used as received. The samples were dried and stored under vacuum, without influence of light.

Compounding

PS and HIPS (50/50%, w/w) were tumble mixed and processed in a laboratory modular Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder, with a coupled flat sheet line (Fig. 1). The screw contains a series of transport elements separated by three mixing zones, consisting of staggered kneading disks and a left-hand element, respectively. They produce intensive mixing, together with the development of local pressure gradients.

Acetophenone and benzophenone, previously dissolved in ketone, were added during extrusion-when the polymer was molten-in order to improve mixing. An ISMATEC MS-REGLO peristaltic pump was used to add both chemical compounds in the required proportions to ensure sheet samples with 2.5 and 5% (w/w). For all experiments, the barrel temperature and the die were set at 210°C, the screw speed at 120 rpm and the flow rate at 5 $kg\ h^{-1}$. The calendar roll temperature was set at 70°C. The sheet produced was 200 mm wide and 0.8 mm thick.

Degradation and characterization

The degradation experiments were performed in a Xenotest 150S from Heraeus (Original Hanau) using a filtered Xenon lamp with an intensity of 60 $W\ m^{-2}$, according to reference [11]. The specimens used in degradation experiments, dimensions 135 × 45 mm, were cut from thin films (about 150μm thick) previously prepared by compression moulding at 200°C. Samples were taken after various exposure times and characterized by the techniques indicated below.

The characterization of the degradation products was carried out by FTIR (Bomen spectrophotometer, 10 scans, 4 cm^{-1} resolution) and UV spectroscopy (Shimadzu UV-2501 PC, using a solid film support).

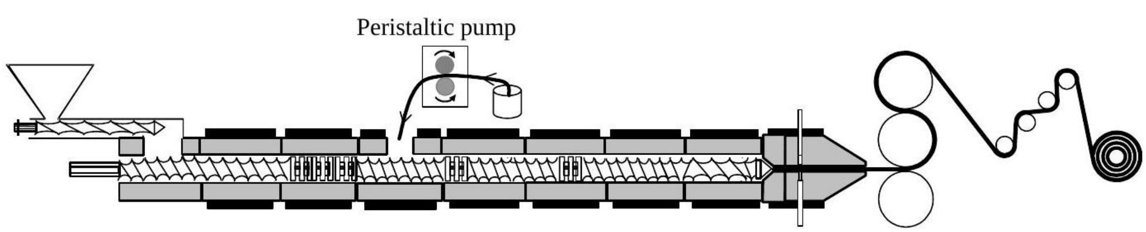


Fig. 1. Laboratory modular Leistritz LSM 30.34 with a coupled flat sheet line.

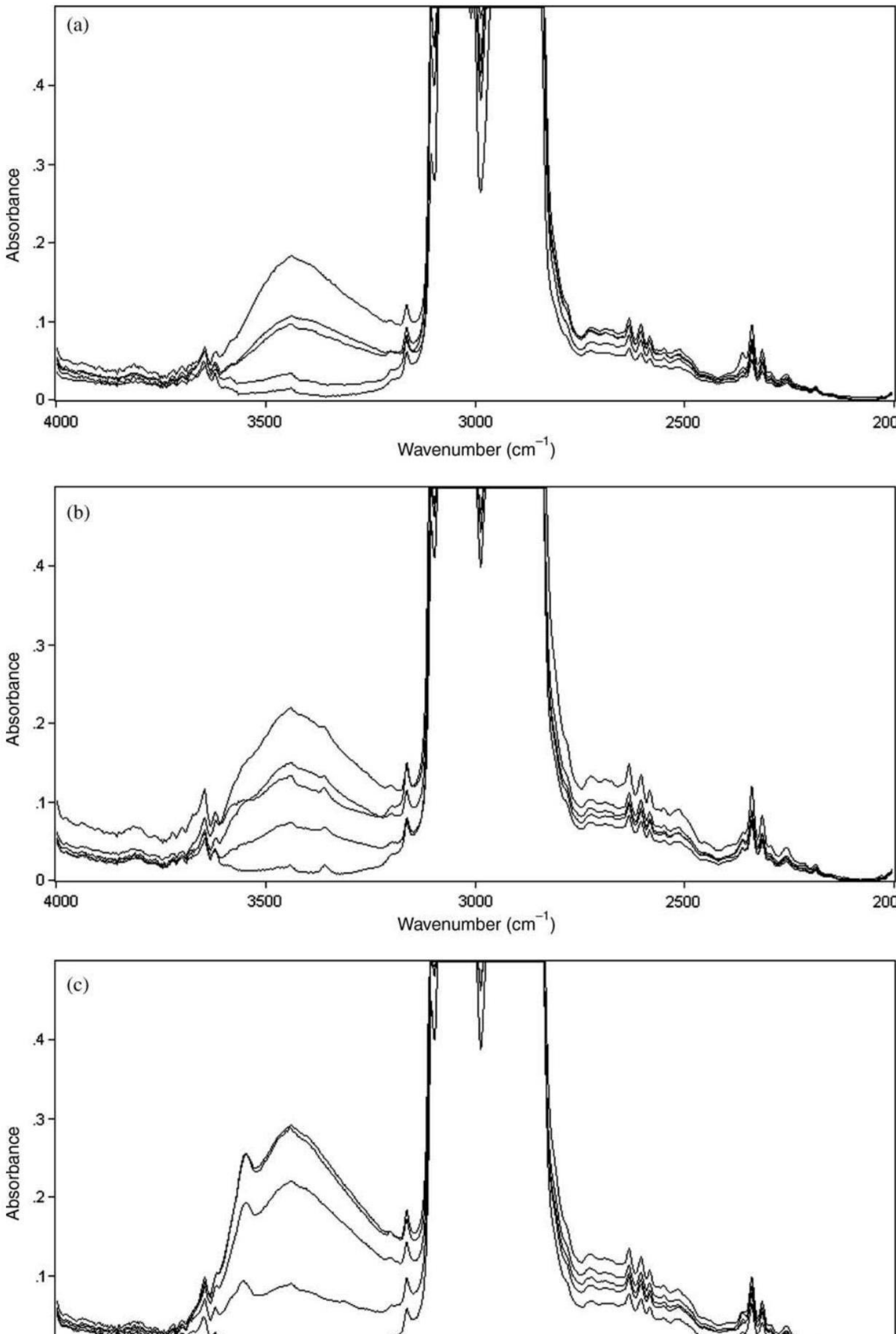
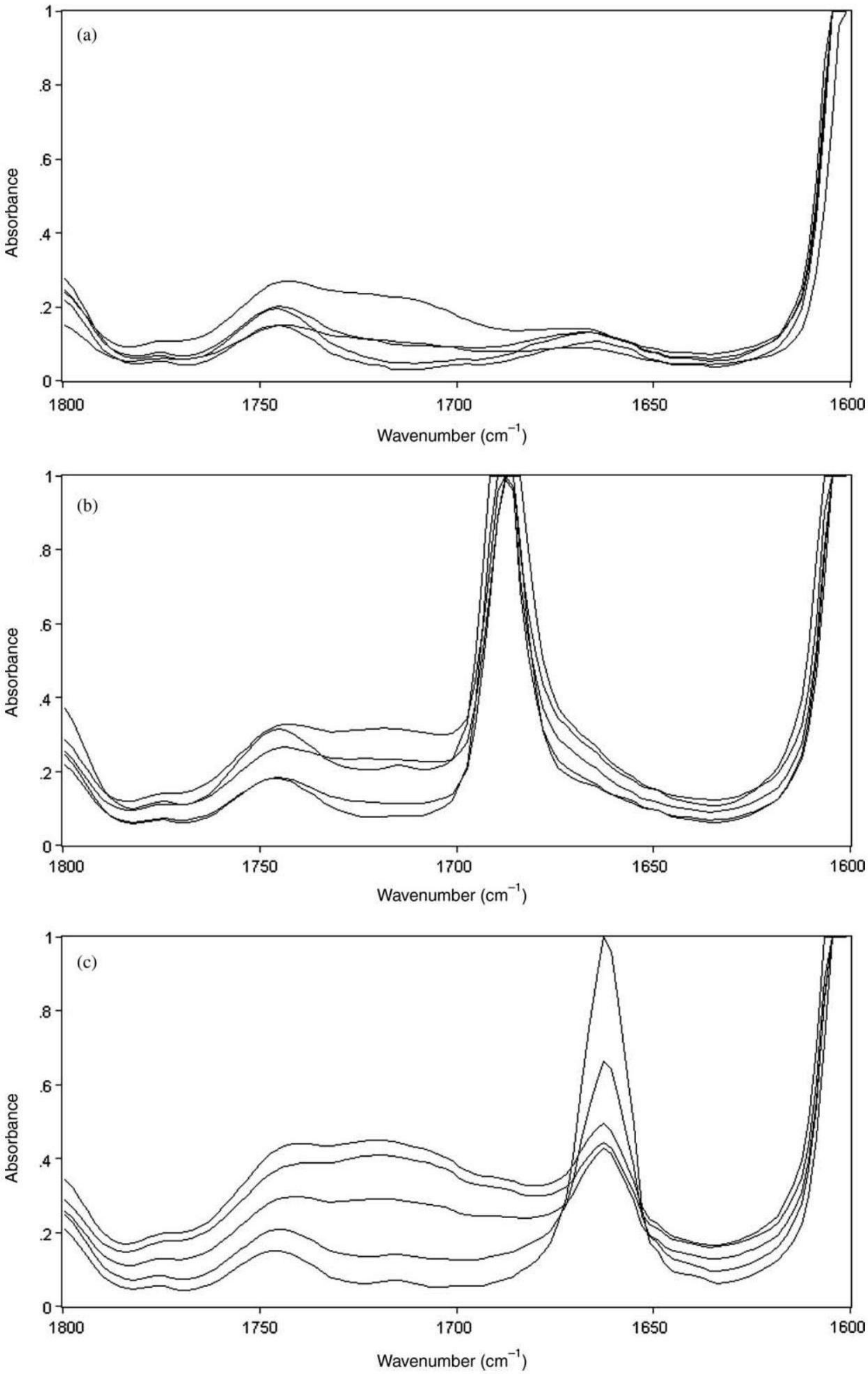

(a)
(b)
(c)
Absorbance
Wavenumber (cm^{-1})
0
.1
.2
.3
.4
4000
3500
3000
2500
2000

Fig. 2. Evolution of the FTIR spectra in the hydroxyl region for (a) PS/HIPS, (b) PS/HIPS +5% A and (c) PS/HIPS +5% B before and after 4,8,12 and 20 h of UV-radiation.


(a)
(b)
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Absorbance
Wavenumber (cm^{-1})
0
.2
.4
.6
.8
1
1800
1750
1700
1650
1600

Fig. 3. Evolution of the FTIR spectra in the carbonyl region for (a) PS/HIPS, (b) PS/HIPS +5% A and (c) PS/HIPS +5% B before and after 4,8,12 and 20 h of UV-radiation.

The inherent viscosity, η_{inh}, was determined from $0.002\ \text{g mL}^{-1}$ solutions in toluene using a Ubbelohde capillary viscometer at $25 \pm 1\ ^{\circ}\text{C}$. The uniaxial tensile properties of the material were determined using a ZWICK/ROELL tensile test machine. Rectangular samples with 5 mm width were cut from exposed and unexposed UV films. A micrometer with an accuracy of 0.01 mm was used for measuring the thickness of each specimen. The tensile tests were conducted at room temperature at a crosshead speed of $50\ \text{mm min}^{-1}$. At least 10 specimens for each condition were tested. Since the samples with high ketone content (5% B and Ac) and high degradation times, spontaneously break in the course of cutting or installing in the grips of the tensile machine, it was impossible to perform these measurements.

Results and discussion

FTIR spectroscopy

As expected, the FTIR spectra of all degraded samples showed significant changes in the hydroxyl ($3700-3200\ \text{cm}^{-1}$) and carbonyl ($1800-1600\ \text{cm}^{-1}$) regions. As an example, Fig. 2a-c show the FTIR spectra in the hydroxyl region for PS/HIPS, PS/HIPS +5% of acetophenone and PS/HIPS +5% benzophenone, respectively.

It can be observed that degraded PS/HIPS samples showed two bands at 3540 and $3450\ \text{cm}^{-1}$. These bands were also present in photodegraded PS and, according to Gardette [3,4], are due to alcohols and hydroperoxides, respectively. The formation of these compounds increase in the presence of acetophenone or benzophenone, indicating that these compounds accelerate the chemical reactions that occur in the presence of UV-radiation. Moreover, in samples containing benzophenone the formation of new chemical compounds associated with the degradation was much higher in comparison with the samples containing acetophenone. This has been explained by the lifetime of the triplet excited state of benzophenone, which is over 60 times longer than acetophenone, and by the occurrence of termination reactions occurring in higher proportions in the presence of acetophenone [12,13].

The shapes of the FTIR bands appearing in the carbonyl-stretching domain are shown in Fig. 3. The bands at 1687 and $1662\ \text{cm}^{-1}$ in Fig. 3b and c correspond to carbonyl groups of Ac and B , respectively [3]. The spectra of PS/HIPS (Fig. 3a) showed a slightly increase in the carbonyl region (17801700 cm^{-1}). However, changes in this region are

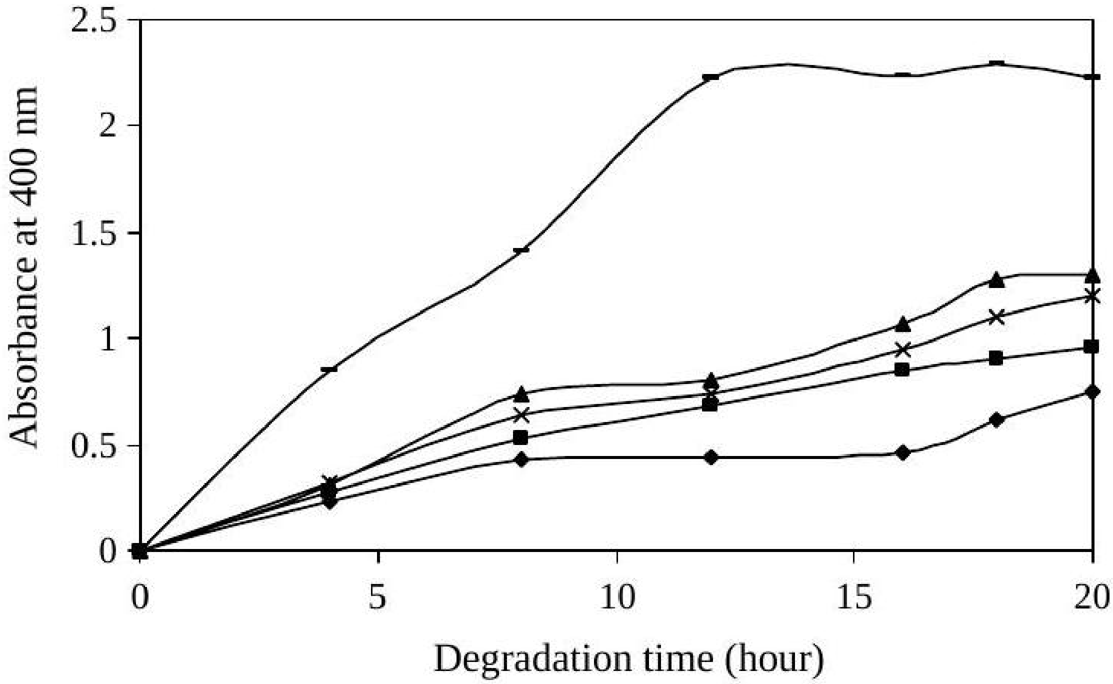

Fig. 4. Absorbance at 400 nm during degradation time for the polymer samples: (∨) PS/HIPS, (■) PS/HIPS +2.5%Ac, (Δ) PS/HIPS +5%Ac, (×)PS/HIPS + 2.5% B and (−)PS/HIPS + 5% B.

much more pronounced in PS/HIPS samples with 5% of Ac and 5% B, being higher for the latter.

UV-Vis spectroscopy

Concerning the UV-Vis results, it is known that conjugated double bonds are formed during the photo-degradation of PS [12]. Usually, a suitable number of conjugated double bonds can be attributed to different bands in the spectra [14]. However, in this case, a general increase in absorption was detected, without showing any defined maximum from the nearUV domain to the visible region that is responsible for the observed yellowing [15]. It could be observed that yellowing was enhanced in all modified samples (Fig. 4), which can be attributed to the formation of chromophore groups. Although an increase in yellowing can be observed for all samples, a more pronounced effect can be perceived for the samples with 5%

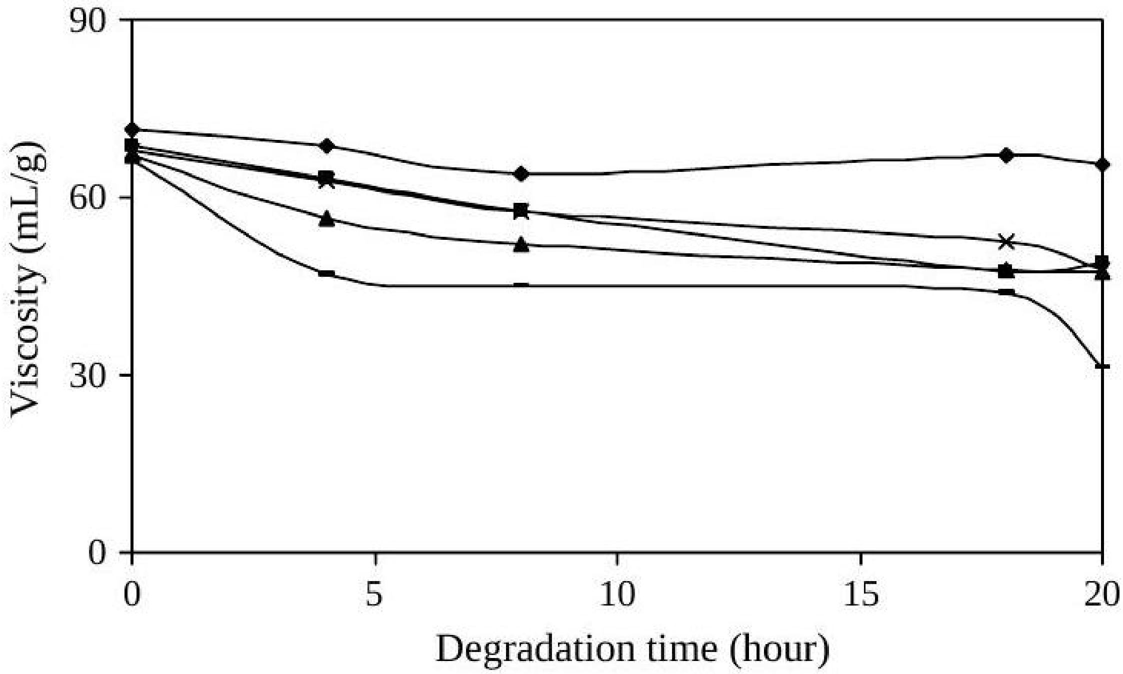

Fig. 5. Viscosity during degradation time for the polymer samples: (↓) PS/HIPS, (■) PS/HIPS +2.5%Ac, (Δ) PS/HIPS + 5%Ac, (×) PS/HIPS +2.5% B and (–) PS/HIPS +5% B.

benzophenone, which is in agreement with the results observed using FTIR spectroscopy.

Viscosity measurements

Fig. 5 shows the evolution of the intrinsic viscosity during degradation for PS/HIPS and PS/HIPS with different amounts of acetophenone and benzophenone. The slight decrease of viscosity observed for PS/HIPS blends indicates that, under the same experimental conditions, the variation of molecular weight was very small. On the other hand, the decrease observed for all other samples is due to the formation of low molecular weight products after chain scission [16].

It could also be noted that, while the extension of bond scission in samples with 2.5% is very similar for both chemicals, a higher chain scission could be observed for samples with 5% B. Thus, the results indicate that photodegradation of PS/HIPS induces scission of C-C bonds, which is strongly increased by the presence of benzophenone. This increase can be explained by the degradation products detected by FTIR and UV spectroscopy.

Mechanical properties

The effects of photo-degradation on mechanical properties are of major importance in most product applications. It is generally believed that chain scission reactions occurring during photo-degradation are directly related to mechanical failure. As expected, the mechanical properties are sensitive to degradation time and deteriorate with the introduction of ketones. This can be seen in Fig. 6, which depicts the evolution of the maximum strength for all tested samples. Due to the ductile behaviour of PS/HIPS blends, the registered values can be the

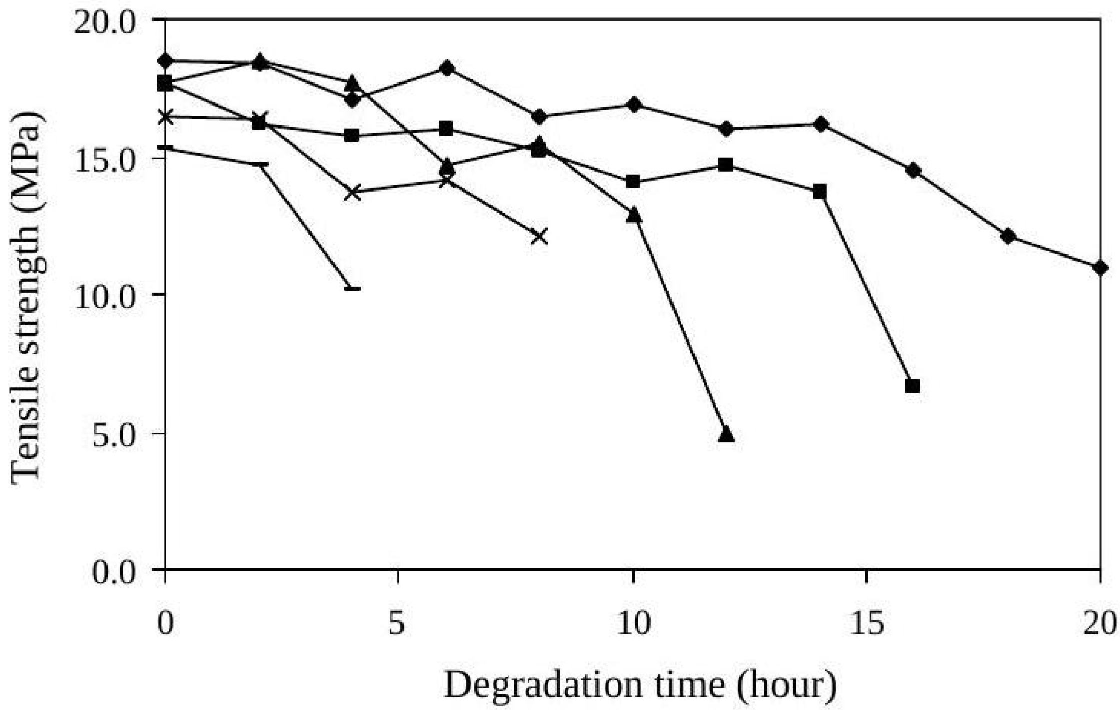

Fig. 6. Maximum tensile strength evolution during degradation time: ( ) PS/HIPS, ( ) PS/HIPS +2.5%Ac, (Δ) PS/HIPS + 5%Ac, (×) PS/HIPS +2.5% B and (–) PS/HIPS +5% B.

yield strength, for shorter irradiation times, or the stress at breaking point, when brittleness occurs at longer times.

Once again, and in accordance with the results observed above, the minor decrease in the maximum strength registered for PS/HIPS blends corroborates that the variation of molecular weight was small. Additionally, the material only becomes brittle after 8 h of exposure to the UV radiation.

The mechanical properties of the samples containing acetophenone present an evolution like PS/HIPS blends, indicating that the variation of the molecular weight is similar (which is in agreement with the viscosity variation). This can also be confirmed by comparing the time to brittleness, which was 6 h for samples with 2.5 and 5% of ketone (in contrast with 8 h registered for the material without additives). The smaller values observed are related with the lower molecular weight induced by the ketone activity.

For PS/HIPS blends containing benzophenone, the mechanical properties show a strong decrease with the exposure time (Fig. 6), attesting a significant molecular weight decrease that has been shown before. Samples with 2.5% of ketone become fragile after 4 h and break spontaneously after 8 h of irradiation, which is half of the time needed when acetophenone is used. From the results previously presented, samples with 5% of benzophenone are highly photo sensitive and, consequently, the stress at break decreases significantly.

Conclusions

In this work, the degradability of PS/HIPS blends and PS/HIPS blends containing different amounts of acetophenone and benzophenone were studied. For the same ketone level, benzophenone causes higher changes in chemical structure, molecular weight and consequently in mechanical properties. For all undegraded samples, the ductile behaviour of PS/HIPS blends was not influenced, indicating that the production of these modified polymers can be achieved.

The results obtained clearly show that the photodegradability of PS/HIPS blends could be enhanced by adding these type of chemical compounds, suggesting the possibility of using different compositions for the production of degradable plastics in the natural environment.

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