Photochemical Aging and Processability of Life-Time-Controlled Polystyrene/High-Impact Polystyrene Blends

A. V. Machado,[1] F. M. Duarte,[1] G. Botelho,[2] I. Moura[1]

[1]Institute for Polymers and Composites, Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[2]Centro de Química, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

ABSTRACT: This work investigated the influence of the addition of acetophenone and benzophenone (2.5 and 5%) on the photodegradability of polystyrene/high-impact polystyrene blends (50/50 w/w) prepared by sheet extrusion, aiming to improve their decomposition during exposure to a natural environment. The modified materials were submitted to photodegradation under controlled conditions, and the extent of degradation was monitored by suitable characterization techniques, such as infrared and ultraviolet–visible spectroscopy, viscosimetry, and measurements of the mechanical properties. The processability of the modified blends was also studied by capillary and oscillatory rheometry. Evidence for the formation of hydroperoxides and carbonyl groups, the occurrence of chain scission, and the loss of mechanical properties was achieved, being greater for samples with benzophenone. It was also observed that for the same ketone level, benzophenone caused greater changes in the mechanical properties, and this was in agreement with the decrease in the molecular weight observed. Thus, the addition of this type of chemical compound could enhance the photodegradability of polystyrene/high-impact polystyrene blends without a significant effect on their processability and mechanical performance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2930–2938, 2007

Key words: blends; mechanical properties; polystyrene; processing; rheology

INTRODUCTION

One of the main areas of application for polystyrene (PS)/high-impact polystyrene (HIPS) is products obtained by thermoforming, in which a previously extruded plastic sheet is heated above its softening temperature and stretched into a female or male mold by the application of a pressure difference across the sheet surface, which is eventually assisted by direct mechanical loading. Once the polymer is cooled, it retains the mold details and becomes ready to be removed.[1]

During the heating cycle of a thermoforming process, the polymer sheet is clamped and heated to the thermoforming temperature. As the sheet heats up, it softens and undergoes sag under its own weight. Through the deformation stage, the hot sheet is progressively stretched against the cold surface of the mold, and this prevents it from undertaking any further deformation, inducing parts with thickness variations.[2,3] The deformation behavior of the polymer sheet, which governs the stretching sequence, controls the final thickness distribution and the draw ratio. A good thermoforming material should therefore yield the least amount of sag during heating but flow well during the forming stage.[2,4]

Different tests and techniques have been used to characterize the material properties to predict processability behavior in thermoforming, such as tensile testing at elevated temperatures,[5–9] bubble inflation,[10–12] and isothermal oven sagging testing.[13–16] However, as thermoforming is always carried out in a semifluid/semisolid state, the viscoelastic properties, such as the extensional viscosity and dynamical shear viscosity, are frequently used to evaluate some relevant material characteristics, such as resistance to sag, ease of flow, and deep draw capability.[13,17–20]

Because there is no shear deformation involved during the sagging of a polymer sheet, measuring the storage and loss modulus of the polymers as a function of temperature in the low frequency (low shear rate) region can also be used to quantify the sagging propensity.[13] Therefore, tan δ, which is the ratio of the loss modulus (measure of the viscous response) to the storage modulus (measure of the elastic response), should be close to 1 in the thermoforming temperature and frequency range, that is, from 0.1 to 10 s^{-1},[2,13,20] corresponding to a frequency range of 0.1–10 rad/s in dynamics viscoelastic measurements, provided that the Cox–Merz rule is valid.[4] Amorphous polymers

such as PS and PS/HIPS blends have been widely used for thermoforming because their rubbery elastic state is exhibited over a wide temperature range; that is, they have a large processing window. The processability of polymers during sheet extrusion and thermoforming depends on the material characteristics under the processing conditions.

In the last years, the use of polymers such as PS and PS/HIPS has been growing in a wide range of application fields: packaging, household accessories, toys, medical articles, garden furniture, and so forth. Consequently, large amounts of PS and PS/HIPS waste are generated annually. Therefore, to decrease the amount of these materials in landfills, it is particularly desirable to make degradable plastics through the acceleration of their decomposition. It is generally known that organic ketones, because of the presence of C=O groups absorbing ultraviolet (UV) radiation at about 270–280 nm, are one of the more important groups of compounds accelerating photochemical reactions in polymers.[21–23] The photochemical reactions that occur from the absorption of UV radiation induce the formation of ketone groups on the polymer backbone and chain scission, which induces brittleness, and biodegradation may occur by microbial attack.[24] The photodegradation of PS has been extensively studied,[25,26] and a mechanism accounting for the photoproducts has been established. Recently, some studies have been published[23,27] concerning the modification of this polymer to improve its degradability.

Until now, studies on the photodegradability of polymers using photoinitiators have been performed with cast films and powder mixtures. However, to match future demands and reproduce simultaneously the real processing conditions used in the packaging industry, another production methodology, such as sheet extrusion, must be used and evaluated. Furthermore, because the addition of ketones to PS/HIPS in molten polymers may introduce changes in the material properties, the photodegradability behavior, the mechanical performance, and the processability must also be assessed. Thus, the aim of this work was to investigate the influence of the addition of acetophenone and benzophenone on the photodegradability of PS/HIPS blends prepared by sheet extrusion, aiming to improve the decomposition of this material when it is exposed to a natural environment. Furthermore, the effect of the ketone addition as well as the ketone content on the rheological and mechanical properties was also evaluated.

EXPERIMENTAL

Materials

Blended PS sheets 0.8 mm thick, made from equal parts (w/w) of general-purpose PS (Lacqrene 1540; melt flow index = 12 g/10 min at 200°C/5 kg) and
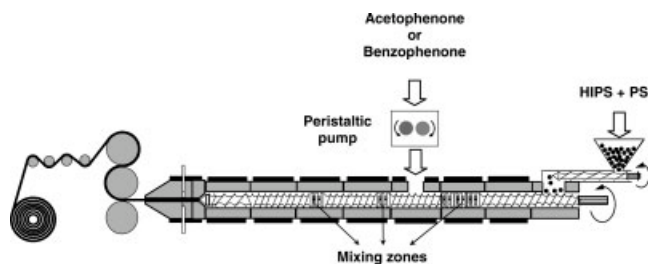
Figure 1 Layout of the Leistritz LSM 30.34 laboratory modular intermeshing corotating twin-screw extruder with a coupled flat sheet line used for the sample preparation.

HIPS (Lacqrene 7240; melt flow index = 4.5 g/10 min at 200°C/5 kg), both from Atofina, were used. The sheets, 200 mm wide, were processed in a Leistritz LSM 30.34 laboratory modular intermeshing corotating twin-screw extruder (Nuremberg, Germany) coupled to a flat sheet line (Fig. 1). The extruder screw contained a series of transport elements separated by three mixing zones, consisting of staggered kneading disks and a left-hand element, to produce the required intensive mixing, together with the development of local pressure gradients.

The barrel and die temperatures were set at 210°C, whereas the calendar roll temperature was set at 70°C. Acetophenone (weight-average molecular weight = 120.15 g/mol) and benzophenone (weight-average molecular weight = 182.22 g/mol), purchased from Sigma–Aldrich, were previously dissolved in acetone and injected at the end of the first kneading zone, when the polymer was molten, by means of an Ismatec MS-Reglo peristaltic pump (Wertheim-Mondfeld, Germany) ensuring the addition of 2.5 and 5% (w/w) concentrations of the chemicals.

Degradation

The degradation experiments were performed in a Xenotest 150S from Heraeus (Original Hanau, Germany) with a filtered xenon lamp with an intensity of 60 W/m^2 according to ref. 28.

Samples used in photodegradation experiences (100 mm × 45 mm × 150 μm) were cut from films previously prepared by compression molding in a manual press at 200°C. The samples were collected after various exposure times, ranging from 0 to 12 h, and characterized by the techniques described next.

Characterization

Fourier transform infrared (FTIR) and UV spectroscopy

The degradation was followed by FTIR with a Bomen spectrophotometer (10 scans, 4 cm^{-1} resolution) (Quebec, Canada) and by UV spectroscopy with a Shimadzu UV-2501 PC (Kyoto, Japan). Because the

samples were thin films, they were analyzed directly with a solid film support.

Viscosity measurements

Chain scission (inherent viscosity) was measured by viscometry with an Ubbelohde capillary viscometer (IllkirchCedex, France). The measurements were performed in 0.002 g/mL polymer solutions in toluene at $25 \pm 1°C$.

Melt flow index

The melt flow index of the PS/HIPS blends produced under the aforementioned conditions was measured according to ASTM Standard D 1238 at 200°C/5 kg. The samples to be tested were cut into small pieces from the previously extruded sheets.

Rheological measurements

The samples were characterized in steady and oscillatory shear flow in a Rosand/Bohlin Instruments RH10 advanced capillary rheometer (North Birmingham, UK) and in a Reologica StressTech HR stress-controlled rotational rheometer fitted with plate–plate geometry, respectively.

The steady shear experiments were performed around the recommended extrusion temperatures, 180 and 210°C, and in a range of shear rates from 40 to nearly 3000 s^{-1}, which easily covered the sheet extrusion shear rates (from 100 to 1000 s^{-1}). The tests were performed two times for each condition, an experimental error being found of less than 5%. To perform the oscillatory shear tests, circular discs 25 mm in diameter and 0.8 mm thick were cut from the previously extruded sheets samples. The frequency sweep tests were performed at 140 and 160°C, which are the usual thermoforming upper and lower temperature limits,[2] over a frequency range of 0.025–250 rad/s, covering thermoforming strain rates, both in the oven and during part formation.[20] The validity of the empirical Cox–Merz rule of the linear range of deformations was previously confirmed. The frequency sweep tests were performed three times for samples without ketones, at 140 and 160°C, and for samples with 2.5 or 5% benzophenone at 160°C to assess the reproducibility of the experiment, a maximum experimental error of 12% being found.

Mechanical properties

The uniaxial tensile properties were measured with an Instron tensile test machine (Darmstadt, Germany). Type M-II standard dumbbell samples according to ASTM D 638M-97 were cut from a previously extruded sheet (unexposed UV material). The thickness of each specimen was measured with a digital micrometer with an accuracy of 0.01 mm. The tensile tests were conducted at room temperature at a crosshead velocity of 50 mm/min. At least 10 specimens for each composition were tested.
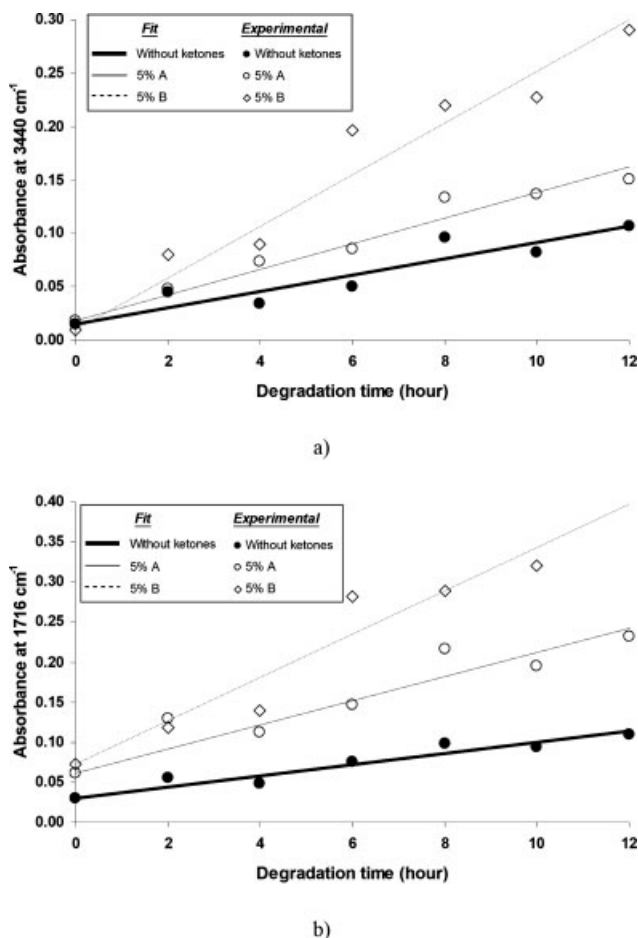
RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 2 shows the FTIR spectra for PS/HIPS, PS/HIPS + 5% acetophenone, and PS/HIPS + 5% benzophenone with the degradation time. The main changes
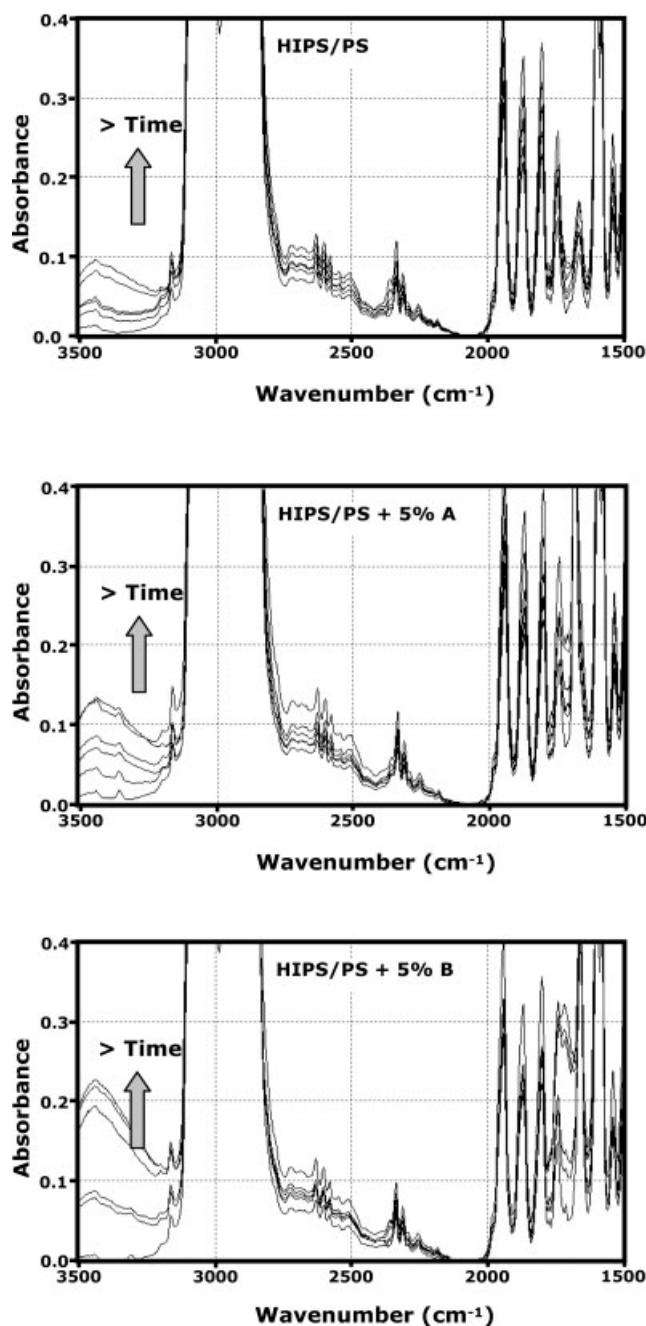
Figure 2 Evolution of the FTIR spectra with the degradation time for PS/HIPS, PS/HIPS + 5% acetophenone (A), and PS/HIPS + 5% benzophenone (B).

a)

b)

Figure 3 Absorbance evolution with the degradation time for PS/HIPS, PS/HIPS + 5% acetophenone (A), and PS/HIPS + 5% benzophenone (B) in the (a) hydroxyl and (b) carbonyl regions.

occur in the hydroxyl (3700–3200 cm^{-1}) and carbonyl (1800–1600 cm^{-1}) regions. However, the changes in these regions are much more pronounced in PS/HIPS samples with 5% acetophenone or benzophenone, being higher for the latter, indicating that the ketones accelerate the chemical reactions that occur in the presence of UV radiation. The data of these spectra are plotted in Figure 3(a,b) (showing the absorbances at 3440 and 1716 cm^{-1}, respectively) to show in more detail the degradation evolution during exposure to UV radiation with the time. The points are the experimental values, whereas the lines represent the corresponding fits.

The absorbance evolution with the time depends on the ketone used, following, in a general way, a linear behavior. The formation rate of the new species is approximately 2 times higher for samples with acetophenone and 4 times higher for samples with benzophenone (vs unmodified PS/HIPS samples).

Ultraviolet–visible (UV–vis) spectroscopy

It is well known that conjugated double bonds appear in PS during its exposure to UV.[29] Usually, a suitable
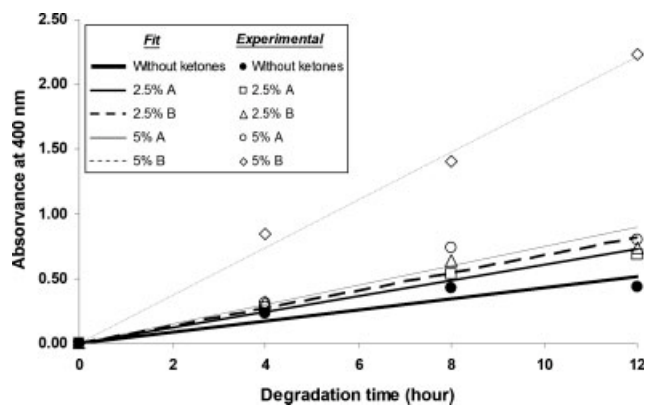
Figure 4 Absorbance evolution with the degradation time for all the materials at 400 nm (A = acetophenone; B = benzophenone).

number of conjugated double bonds can be attributed to different bands in the spectra.[30] However, there are no clear maxima in the absorption spectrum, but there is a systematic increase in the absorbance, which is responsible for the observed yellowing, in the whole UV–vis region. The yellowing was enhanced in all the modified samples (Fig. 4), and this can be attributed to the formation of chromophore groups. Although an increase in yellowing was observed for all the samples, a more pronounced effect could be perceived for the samples with 5% benzophenone, and this is in agreement with the results observed with FTIR spectroscopy.

Intrinsic viscosity measurements

Table I shows the intrinsic viscosity for 0 h of exposure to assess the influence of the ketone addition on the material properties. The intrinsic viscosity of the ketone-modified materials is slightly lower than that of the PS/HIPS blends, this difference, however, being less than 5% for all tested samples. This decrease in the intrinsic viscosity could be explained by the degradation that may have occurred during the sample preparation. Because the samples were prepared by extrusion at 210°C, reactions between the polymer and the organic ketones could take place, inducing the scission of the carbon–carbon bonds of the polymer chain.[29]

The evolution of the intrinsic viscosity with the degradation time for PS/HIPS and PS/HIPS with different amounts of acetophenone and benzophenone is depicted in Figure 5. As anticipated from the FTIR and UV–vis spectroscopy results, the viscosity of the unmodified PS/HIPS blends decreases slightly, indicating that for the experimental conditions used, the variation of the molecular weight is insignificant. In opposition, the decrease observed for all the other samples is related to the formation of low-molecular-weight products after chain scission.[31] Although the

Intrinsic Viscosities (mL/g) of PS/HIPS Samples With and Without Ketones

PS/HIPS	PS/HIPS + 2.5% acetophenone	PS/HIPS + 5% acetophenone	PS/HIPS + 2.5% benzophenone	PS/HIPS + 5% benzophenone
71.4	68.6	67.1	67.9	66.2

extension of bond scission for both samples with 2.5% ketone is very similar, higher chain scission could be observed for samples prepared with 5% concentrations of the chemicals, that is, when benzophenone was used. After 12 h of degradation, the intrinsic viscosity of the PS/HIPS blends with 5% benzophenone was 53% lower than that of the unexposed UV samples and 51% lower than that of the PS/HIPS blends without ketone addition. These results indicate that the photodegradation of PS/HIPS induces the scission of C—C bonds, which is strongly increased by the presence of benzophenone, this being explained by the degradation products detected by FTIR and UV spectroscopy.

Melt flow index measurements

The melt flow index results for all the prepared materials are shown in Table II. In accordance with the intrinsic viscosity, the melt flow index increases with the ketone addition, being higher for a higher level of ketone.

As mentioned previously, these results could be explained by the degradation that may have occurred during the sample preparation and during the experiments because the samples had to remain at 200°C for 10 min before the test was started. Furthermore, the role of the diffusion of low-molecular-weight ketones may also have contributed to the observed increase in the melt flow index.
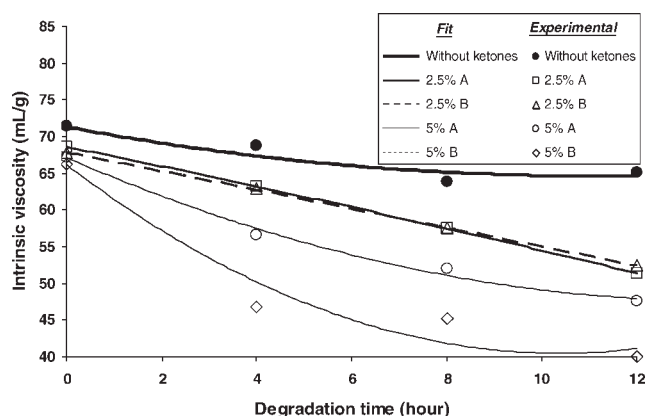

Figure 5 Intrinsic viscosity evolution with the degradation time for all the materials (A = acetophenone; B = benzophenone).

Dynamic shear test analysis

Figures 6 and 7 depict the storage modulus and loss modulus of all tested samples as a function of frequency at 140 and 160°C, respectively. In the low frequency region, because of the sufficient time that the polymer chains have to flow and respond to the applied stress, the viscous component dominates, the loss modulus therefore being higher than the storage modulus. As the frequency increases, both the loss modulus and the storage modulus increase too (albeit at different rates) because they are less dependent on the molecular weight.[20]

Concerning the effect of the ketone on the rheological properties, it can be seen that modified PS/HIPS blends show lower storage and loss moduli than the PS/HIPS blend without ketones, the moduli decreasing with higher ketone contents. This effect is related to the decrease in the molecular weight induced during the sample preparation (see Table I), being more pronounced in the lower frequency region in which the differences in the molecular structure are more suitable to be observed. Because of the highest effect induced by benzophenone, blends with the same ketone level show lower storage and loss moduli when this type of ketone is added. As expected, these differences are temperature-dependent, increasing for the experiments performed at higher temperatures.

Figure 8 shows the variation of tan δ, within the characteristic frequencies of thermoforming, at 140 [Fig. 8(a)] and 160°C [Fig. 8(b)] for all the PS/HIPS blends. In general, modified PS/HIPS blends show a higher value of tan δ than PS/HIPS blends without ketone; this shows, as previously mentioned, the presence of polymer chains with a lower molecular weight. This behavior is temperature-independent, being more significant at 160°C. Nevertheless, the difference between modified and unmodified PS/HIPS blends is small for lower ketone concentrations, being almost negligible for the tests performed at 140°C. As previously observed, blends with 5% ketone or, with the same amount, modified with benzophenone have higher values of tan δ. As expected, as the frequency increases, the time that the polymer chains have to respond to the applied stress diminishes, like tan δ.

As previously mentioned, a better thermoforming material should provide a good balance of sag resistance during the heating cycle and flow during the forming cycle. Because of higher tan δ values, the

PS/ HIPS	PS/HIPS + 2.5% acetophenone	PS/HIPS + 5% acetophenone	PS/HIPS + 2.5% benzophenone	PS/HIPS + 5% benzophenone
5.0	6.5	12.9	8.6	13.8

ketone-modified blends sag more than the unmodified PS/HIPS blend. At the same time, the higher viscosity component should provide a better flow for ketone-modified PS/HIPS blends, leading to thermoformed parts with the highest mold replication. However, the observed differences and effects are small (or even negligible for the lowest forming temperature) in comparison with those values of tan δ observed for typical materials with a lack of thermoformability, such as polypropylene, whose tan δ value is around 3 in the thermoforming region.[20,27] These results show that modifying PS/HIPS blends with ketones to improve their photodegradability leads to a moderate effect on the sag resistance and flow during forming; that is, the thermoformability is not significantly influenced.

Capillary test analysis

Figure 9 shows the shear steady viscosity for all tested samples at 180 [Fig. 9(a)] and 210°C [Fig. 9(b)]. As already mentioned, because of the lower molecular weight that characterizes the blends modified with ketones, the viscosity is lower than that observed for the samples without additives. The effect of the ketone content and type is also in accordance with the results obtained from the intrinsic viscosity measurements, that is, lower for blends with benzophenone and for higher ketone contents. This behavior can be observed at 180 and 210°C, the lower values of the viscosity being measured for the higher testing temperature.
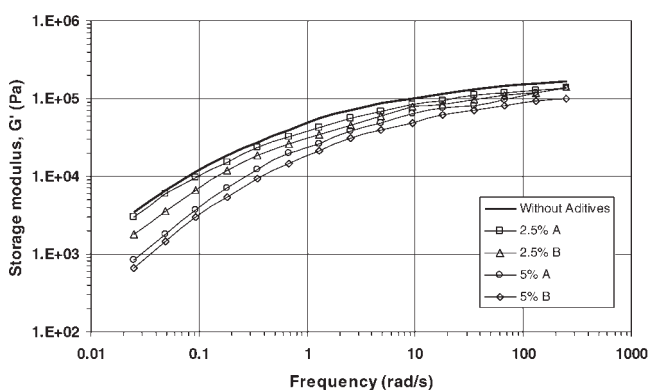
These effects can be seen in more detail in Figure 10, in which the viscosity at 180 and 210°C for typical
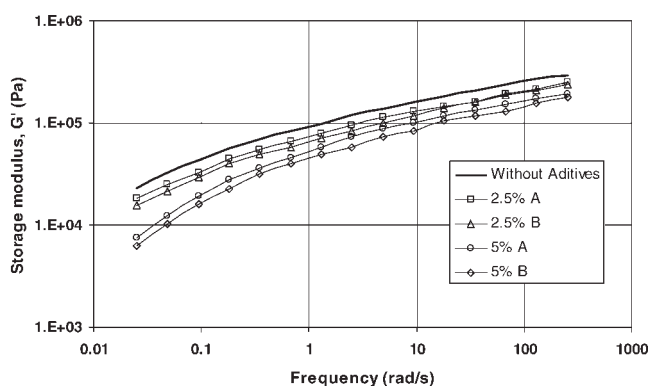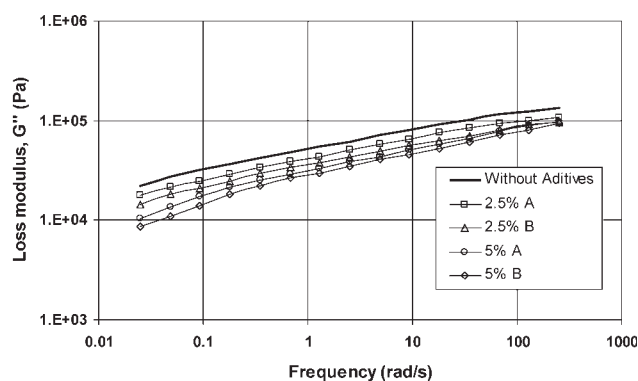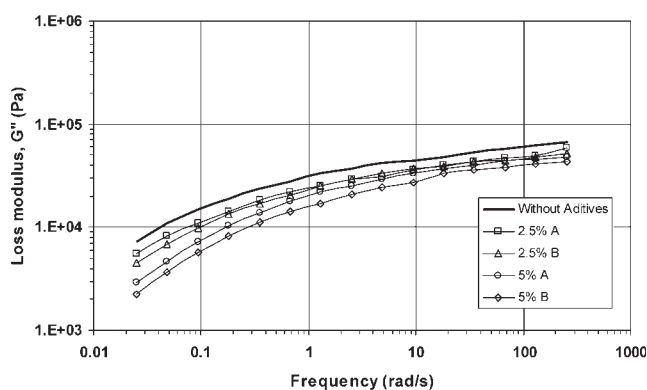
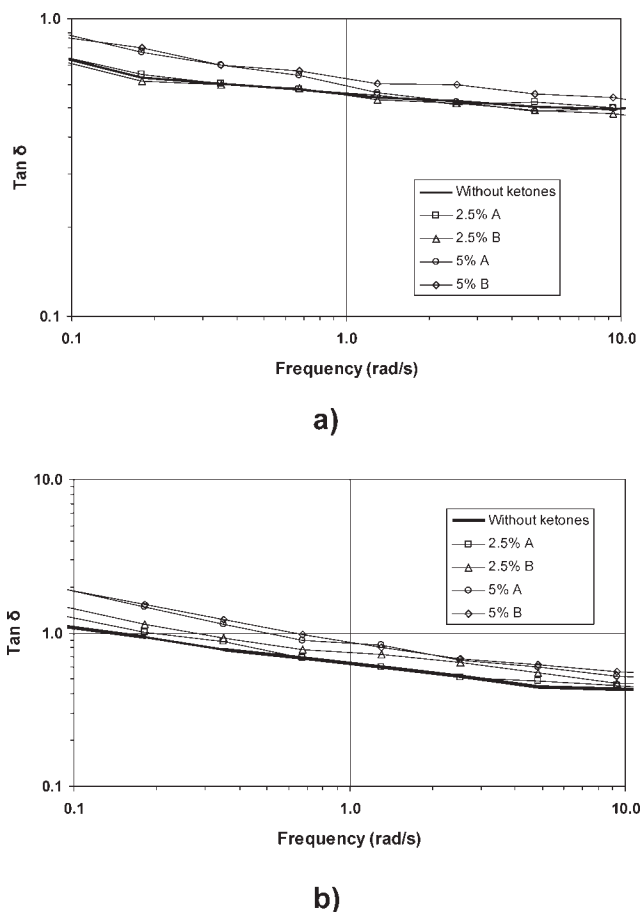**Figure 6** Storage modulus of all PS/HIPS blends: (a) 140 and (b) 160°C (A = acetophenone; B = benzophenone).

Figure 7 Loss modulus of all PS/HIPS blends: (a) 140 and (b) 160°C (A = acetophenone; B = benzophenone).

Figure 8 Variation of tan δ for all PS/HIPS blends: (a) 140 and (b) 160°C (A = acetophenone; B = benzophenone).

shear rate range limits that occur during sheet extrusion (100 and 1000 s^{-1}) is depicted. For these shear rate limits, the shear viscosity difference in relation to PS/HIPS blends ranged between 6.7% for blends with 2.5% acetophenone at 180°C and 1000 s^{-1} and 34% for blends with 5% benzophenone at 210°C and 100 s^{-1}.

These results show that the addition of acetophenone and benzophenone can induce a moderate effect on the shear viscosity. To overcome potential processing difficulties, some care must be taken when the extrusion temperature of these PS/HIPS blends is set. Considering the results obtained at 180 and 210°C for the PS/HIPS blends without ketones and the blends with 5% benzophenone, we think that an extrusion temperature reduction between 5 and 10°C will be enough to increase the viscosity for the required values.

Mechanical properties

The mechanical properties of the PS/HIPS blends, such as the deformation at break, tensile strength, and Young's modulus, are shown in Figure 11(a–c), respectively. As expected, the mechanical properties are sensitive to the introduction of ketones, the tensile

strength being the mechanical property less susceptible to the action of acetophenone and benzophenone.

For all tested samples, the tensile strength average and standard deviation values of the modified PS/HIPS blends are very similar to those observed for the PS/HIPS blends without any ketone. The highest registered difference is 10% (2.7 MPa), the average values, however, being within the limits defined by the standard deviation of PS/HIPS blends without any ketone.

As for the deformation at break, it can be seen that the introduction of ketones leads to materials with less deformation capability. In agreement with the molecular weight reduction observed and shown in Table I, the deformation at break decreases as the ketone content increases, and for the same level of ketone, blends with benzophenone have lower deformation capability. The reduction of the deformation capacity generates brittleness materials, increasing therefore the Young's modulus [Fig. 11(c)]. However, because of the higher values of the standard deviation, namely for the deformation at break, these results must be understood as a general tendency.

Despite the observed changes in the mechanical properties of the modified PS/HIPS blends, the ductile behavior characteristics of the PS/HIPS blends are
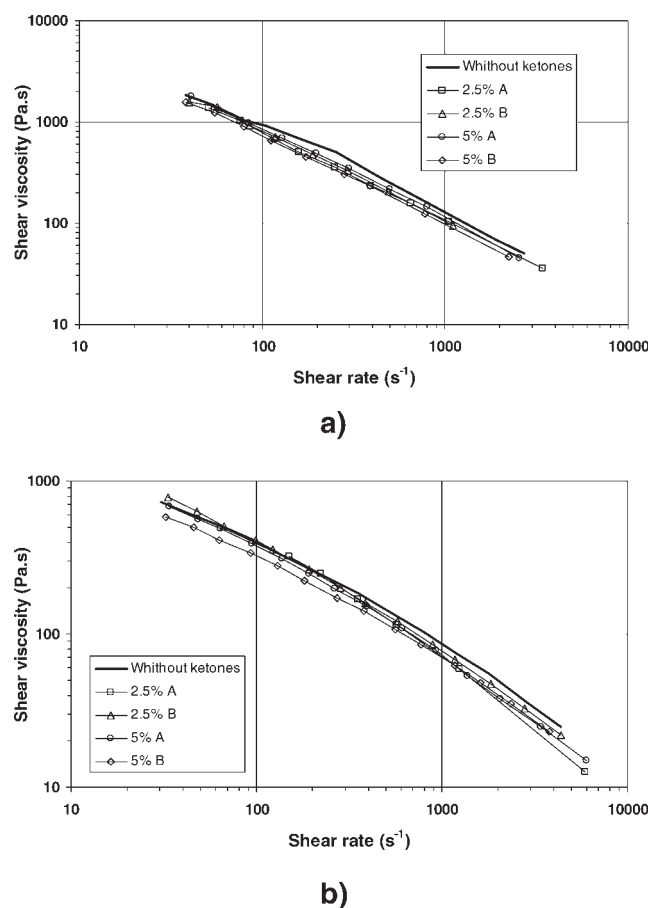
Figure 9 Shear viscosity for all PS/HIPS blends: (a) 180 and (b) 210°C (A = acetophenone; B = benzophenone).
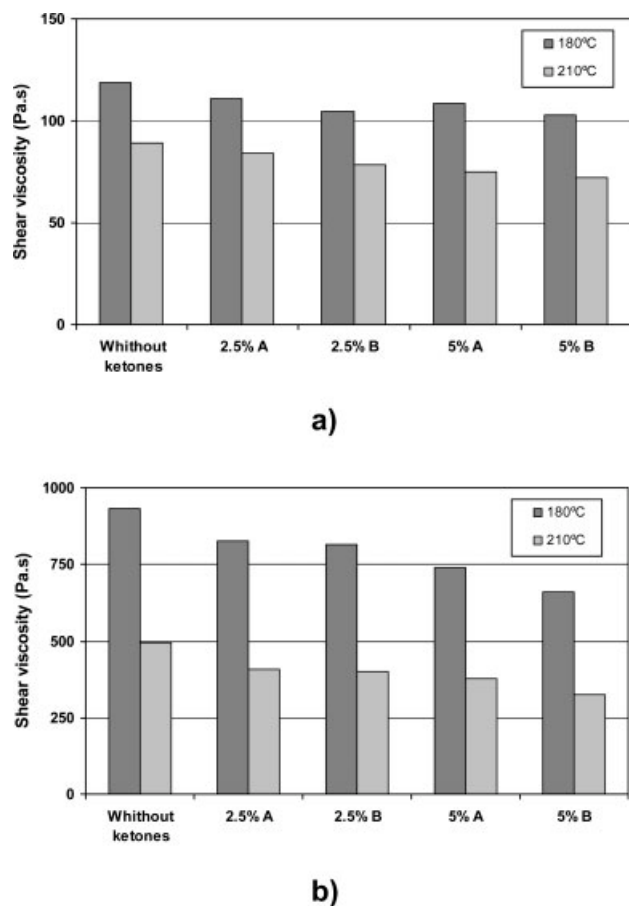
Figure 10 Shear viscosity difference with respect to PS/HIPS blends: (a) 1000 and (b) 100 s^{-1} (A = acetophenone; B = benzophenone).

not affected, and this attests to fact that the molecular weight changes induced by the ketone activity are not significant. The results show that the ketone-modified PS/HIPS blends preserve, in a general way, their own characteristic mechanical properties, not jeopardizing significantly the mechanical performance of the parts made from these types of materials.

CONCLUSIONS

In this work, the photodegradability and processability of PS/HIPS blends and PS/HIPS blends containing different amounts of acetophenone and benzophenone prepared by extrusion were studied.

The photodegradability results showed that the absorbance in the hydroxyl and carbonyl regions, related to the PS degradability, increases with the addition of these organic ketones. The UV–vis and intrinsic viscosity results are in agreement, showing higher conjugated double bonds and a decrease in the molecular weight occurring with the photodegradation time when acetophenone or benzophenone is added, respectively. Furthermore, the photodegradability is

proportional to the added ketone amount, and for the same ketone quantity, benzophenone induces higher changes in the chemical structure and molecular weight.

Concerning the processability, it has been found that the addition and subsequent sheet extrusion of ketone-modified PS/HIPS blends lead to materials with a slightly lower molecular weight in comparison with unmodified PS/HIPS blends and consequently changes in the rheological behavior and in the me-
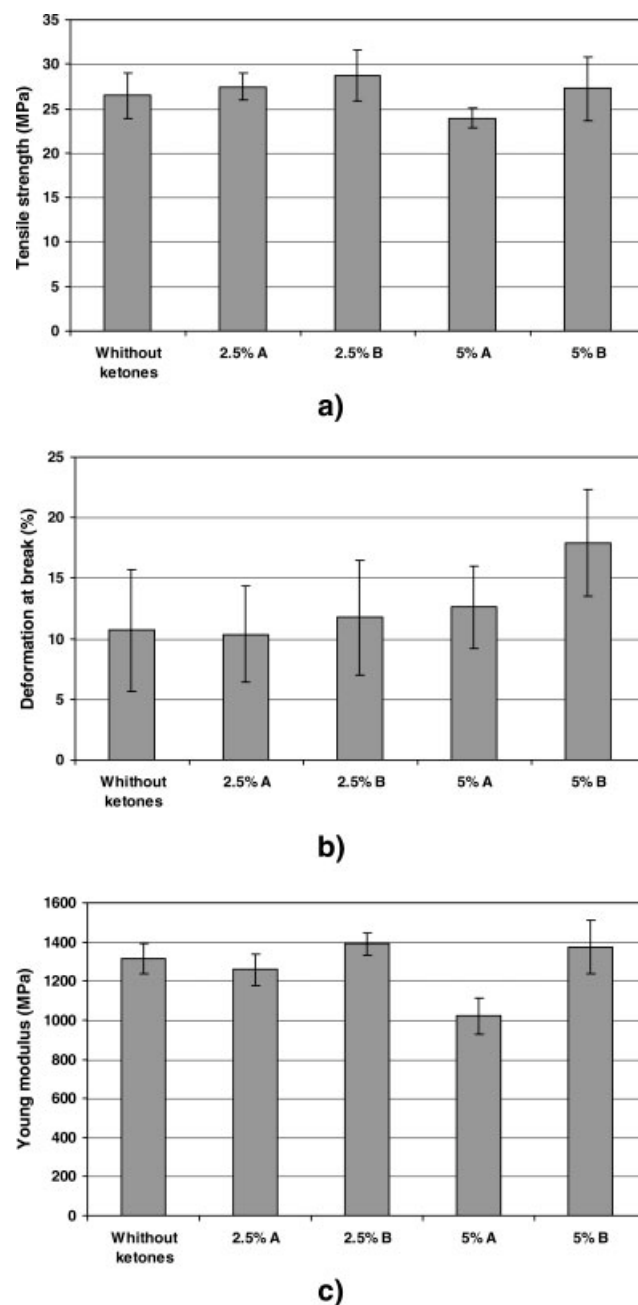
Figure 11 Mechanical properties of PS/HIPS specimens with and without ketones: (a) the tensile strength, (b) the deformation at break, and (c) the Young's modulus (A = acetophenone; B = benzophenone).

chanical properties. In general, modified PS/HIPS blends show a higher value of tan δ, having therefore a greater propensity to sag during the heating stage and to thermoform parts with the highest mold replication. The observed differences and effects are, however, small or even negligible, specifically for the lower thermoforming temperature limit (140°C).

The capillary test analysis results show some differences in the shear viscosity, namely for the lower shear rate limit that typically occurs during sheet extrusion (100 s^{-1}) and for the higher tested temperature (210°C). A reduction of a few degrees centigrade in the sheet extrusion temperature must be therefore considered to overcome some potential processing difficulties.

As for the mechanical properties, the results demonstrate that the addition of ketones leads to slightly brittle materials (a high Young's modulus and tensile strength) with less deformation capability. However, the ductile behavior characteristics of the PS/HIPS blends are preserved. Despite the registered changes in the chemical and molecular structure, the processability of the modified PS/HIPS materials is not significantly affected, and this suggests that the addition of organic compounds between 2.5 and 5% concentrations guarantees good-quality sheets, yielding thermoformed parts whose mechanical performance is, in a general way, kept. As anticipated from the photodegradability results, all the aforementioned effects are proportional to the added ketone amount and more visible for blends with benzophenone.

The aforementioned results clearly show that ketone-modified PS/HIPS materials can be prepared by extrusion, which ensures that the materials keep their photodegradability capabilities and, in a general way, their processability and mechanical characteristics.

References

1. Duarte, F. M.; Covas, J. A.; Barroso, V. C.; Maia, J. M. J. Polym Eng 2005, 25, 115.
2. Throne, J. L. Technology of Thermoforming; Hanser: Munich, 1996.
3. DeLorenzi, H. G.; Nied, H. F. In Modelling of Polymer Processing; Isayev, A. I., Ed.; Hanser: Munich, 1991.
4. Morye, S. S. Polym Eng Sci 2005, 45, 1369.
5. Lai, M. O.; Holt, D. L. J Appl Polym Sci 1975, 19, 1209.
6. Gauvin, R. J. Plast Film Sheeting 1987, 3, 312.
7. Prosser, W.; Hine, P. J.; Ward, I. S. Plast Rubber Compos 2000, 29, 401.
8. Giménez, E.; Lagarón, J. M.; Cabedo, L.; Gavara, R.; Saura, J. J. Polym Eng Sci 2004, 44, 598.
9. Morye, S. S. Polym Eng Sci 2005, 45, 1377.
10. DeVries, A. J.; Bonnebat, C. Polym Eng Sci 1976, 16, 93.
11. Denson, C. D.; Hylton, D. C. Polym Eng Sci 1980, 20, 535.
12. Martin, P. J.; Tan, C. W.; Tshai, K. Y.; McCool, R.; Menary, G.; Armstrong, C. G.; Harkin-Jones, E. M. A. Plast Rubber Compos 2005, 34, 276.
13. Hylton, D. Soc Plast Eng Tech Pap 1991, 51, 580.
14. Macaulay, N.; Harkin-Jones, E. M. A.; Murphy, W. R. Polym Eng Sci 1998, 38, 516.
15. Johnson, R. W.; Ilenda, S. C. Soc Plast Eng Tech Pap 1992, 38, 501.
16. Keith, A. A.; Cruz, C. C.; Palm, J. P. J. Plast Film Sheeting 1993, 9, 293.
17. Yoo, H. J.; Done, D. Soc Plast Eng Tech Pap 1992, 50, 569.
18. Lau, H. C.; Bhattacharya, S. N.; Field, G. J. Polym Eng Sci 1998, 40, 1915.
19. Olovyov, S. E.; Virkler, T. L.; Scott, C. E. Proceedings of the PPS Meeting, Yokoama, Japan, 1998.
20. Spence, T.; Hylton, D. Soc Plast Eng Tech Pap 1998, 56, 681.
21. Rabek, J. F. Photodegradation of Polymers: Physical Characteristics and Applications; Springer-Verlag: Berlin, 1996.
22. Guillet, J. Polymer Photophysics and Photochemistry; Cambridge University Press: Cambridge, England, 1987.
23. Kaczmarek, H.; Swiatek, M.; Kaminska, A. Polym Degrad Stab 2004, 83, 35.
24. Bottino, F. A.; Cinquegrani, A. R.; Pasquale, G.; Leonardi, L.; Pollicino, A. Polym Test 2004, 23, 405.
25. Mailhot, B.; Gardette, J. L. Macromolecules 1992, 25, 4119.
26. Mailhot, B.; Gardette, J. L. Macromolecules 1992, 25, 4127.
27. Botelho, G.; Queirós, A.; Ferreira, J. C.; Frangiosa, P.; Machado, A. V. Polym Degrad Stab 2004, 86, 493.
28. Plastics—Methods of Exposure to Laboratory Light Sources; ISO 4892; Geneve, Switzerland, 1994.
29. Kaczmarek, H.; Kaminska, A.; Swiatek, M.; Sanyal, S. Eur Polym J 2000, 36, 1167.
30. Geuskens, G.; Baeyens-Volant, D.; Delaunois, G.; Lu-Vinh, Q.; Piret, W.; David, C. Eur Polym J 1978, 14, 291.
31. Torikai, A.; Takeuchi, T.; Fucky, K. Polym Photochem 1983, 3, 307.