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Secondary effects of antioxidant on PS/PVME blends

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Abstract

Interactions between the antioxidant Santonox (4,4′-thiobis(6-*tert*-butyl-*m*-cresol)) and the LCST polymer blend of polystyrene (PS) and polyvinylmethylether (PVME) were examined. The presence of the antioxidant caused inhomogeneities in blend films cast from toluene solutions at antioxidant compositions greater than 0.25 wt% of the PVME. Also, the cloud-point of the blend decreased linearly with antioxidant content with a slope of 21 °C/wt%. As expected, the ability of the antioxidant to prevent degradation of the PVME within the blend was found to increase with increasing Santonox composition. Based on these results, an antioxidant composition of no more than 0.10 wt% is recommended in the studies of PS/PVME blends. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyvinylmethylether (PVME) and polystyrene (PS) are used extensively in the literature as a model LCST blend for the studies of phase behavior, dynamics, rheology, and morphology (e.g. Refs. [1–5]); several dozen papers have been published on this system in the last four years alone. However, PVME has been shown in the literature [6–8] to be thermally unstable above temperatures of ~100 °C and this lack of stability can lead to erroneous characterizations of the blend behavior. Typically, this problem is corrected by the addition of antioxidant to the PVME. However, the presence of antioxidant, in sufficient quantities, can also lead to alterations in the behavior of the blend. This brief communication seeks to quantify some of those effects.

The antioxidant Santonox (4,4′-thiobis(6-*tert*-butyl-*m*-cresol)), a commercial product from Flexsys, was chosen for study. A very similar antioxidant has been used at a concentration of 0.05 wt% by others studying the PS/PVME blend [6]. Blend samples containing between 0.05 and 0.80 wt% antioxidant (referenced to the PVME weight only) were characterized to determine the effect of antioxidant composition on cast film clarity and cloud-point temperature. In addition, the effectiveness of the antioxidant in preventing changes in the molecular weight distribution of the PS/PVME blend was examined for all the samples.

2. Experimental section

2.1. Materials

The PS/PVME blend samples that were examined in this study were identical except in the antioxidant content. The PS was used as supplied by Pressure Chemical at a weight-average molecular weight of 123,000 g/mol and a polydispersity of 1.06. The PVME was obtained from Scientific Polymer Products in a polydisperse form and fractionated using differential precipitation with toluene as the solvent and heptane as the precipitant. The molecular weight fraction of PVME that was employed in this work had a weight-average molecular weight of 138,000 g/mol and a polydispersity of 1.7. The eight blend compositions contained 48.5 wt% PVME and between 0.05 and 0.8 wt% (referenced to the PVME weight only) of the antioxidant Santonox.

2.2. Sample preparation

The blend samples were prepared by solution casting. Small (~5 mm diameter), round films of sample were cast on glass plates in the same manner as in many studies (for example, cf. Refs. [4,9,10]). As with similar procedures in the literature, casting solutions that were approximately

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10% polymer in toluene were formulated [4,6,10,11]. The Santonox was added by pipette as a dilute solution in toluene.

After mixing overnight on a wrist-action shaker, the solutions were evaporated down to 40–60% polymer. They were then dropped onto pre-cleaned glass microscope slides with pipettes. Care was taken to produce films with a thickness of at least 50 μm, a value significantly larger than that of the films for which the cloud-point temperature has been shown to be dependent upon film thickness [12,13]. Once cast, the films were dried under ambient conditions in a hood for about 24 h, then transferred to a vacuum oven at 50 °C for 3–4 days.

As PVME is both hydroscopic [7,14] and prone to oxidation [6–8], the blend samples were kept either in a room-temperature nitrogen atmosphere or under vacuum at 50 °C. This latter method was suggested by Kwei et al. [15] as the best way to prevent changes in the character of the PVME. Periodic gel permeation chomotography (GPC) checks on the molecular weight distributions of the blend samples indicated that the attempts to stabilize the PVME were successful. After the blend films with the different amounts of antioxidant had dried, the appearance of each was recorded.

2.3. Cloud-point measurement

The cloud-point temperatures were determined by visual observation. For a given composition, the temperature was slowly raised in a convection oven operating with a nitrogen atmosphere until a phase transition was detected as a precipitous decrease in the transparency of the sample. As has been reported by others [2], blends of PS and PVME first turn blue, then become white and completely opaque at temperatures 2–10 °C higher. The cloud-point temperature was defined as the temperature at which the blue color, associated with the scattering from small droplets, first appeared. At high antioxidant concentrations, samples appeared hazy at temperatures well below the expected cloud-point temperature (see later). However, for all antioxidant concentrations, a distinctive and unambiguous change in sample opacity occurred as the temperature was increased to and above the apparent cloud-point temperature.

2.4. Thermal stability measurements

Each of the films was subjected to a temperature of 105 °C in a nitrogen atmosphere, and the molecular weight distributions of the films were examined after 1.75, 4.0, 6.5, 9.5, 26, 39, and 52 h. The molecular weight distributions were determined with a Waters GPC instrument operating with tetrahydrofuran (THF) and outfitted with three different Styragel columns in series: HMW7, HT4, and HR3. The instrument was calibrated with nearly monodisperse ($M_w/M_n \sim 1.05$) PS samples from Pressure Chemical that were themselves commercially characterized using light scattering and intrinsic viscometry. The Mark–Houwink coefficients for PVME in THF are given in the literature [16] to be $K = 2.33 \times 10^{-4}$ ml/g, and $b = 0.70$, and these values were used to calculate the PVME calibration curve from the measured curve for PS. The molecular weight distributions of the blend samples were calculated in terms of the PVME molecular weight.

3. Results and discussion

3.1. Film transparency

A description of each of the compositions is given in Table 1. Two optical qualities of the blend films changed with increasing antioxidant content. First, an increasing number of surface distortions, or ripples, were seen. Secondly, the blends became increasingly hazy, becoming first slightly blue in color, then completely hazy at the highest Santonox concentration of 0.80%.

A visual survey of some of the films was also completed with an optical microscope. Samples with antioxidant compositions of 0.59 and 0.80% were examined, and the haziness was caused by micron-scale structure within the blend. The morphology was unevenly distributed through the film, seeming to be most prominent in the areas immediately adjacent to the lines of surface distortion, which were also visible under the microscope. Optical micrographs are shown in Fig. 1.

The cause of the antioxidant-induced phase separation within the PS/PVME blend is unknown, and a complete investigation of the Santonox-blend interactions was beyond the scope of the present study. The conclusion based on this phenomenological exploration is that the Santonox content must be limited to less than 0.25 wt% of the PVME in order to produce homogeneous single-phase blends.

3.2. Cloud-point depression

The results of the cloud-point measurements are shown as a function of antioxidant concentration in Fig. 2. A linear decrease in the apparent cloud-point temperature with antioxidant composition at a rate of 21 °C/wt% is seen. The

Table 1
Qualities of cast Blend 1, $\phi = 0.485$ films vs. Santonox content

Santonox content (wt% of PVME)	Surface distortion	Clarity
0.05	None	Clear
0.16	None	Clear
0.26	Slight around the edge	Clear
0.37	Fairly extensive	Very slight blue tinge
0.48	Extensive	Uniform blue tinge
0.59	Extensive	Blue, hazy in places
0.69	Extensive	Blue, mostly hazy
0.80	Extensive	Hazy

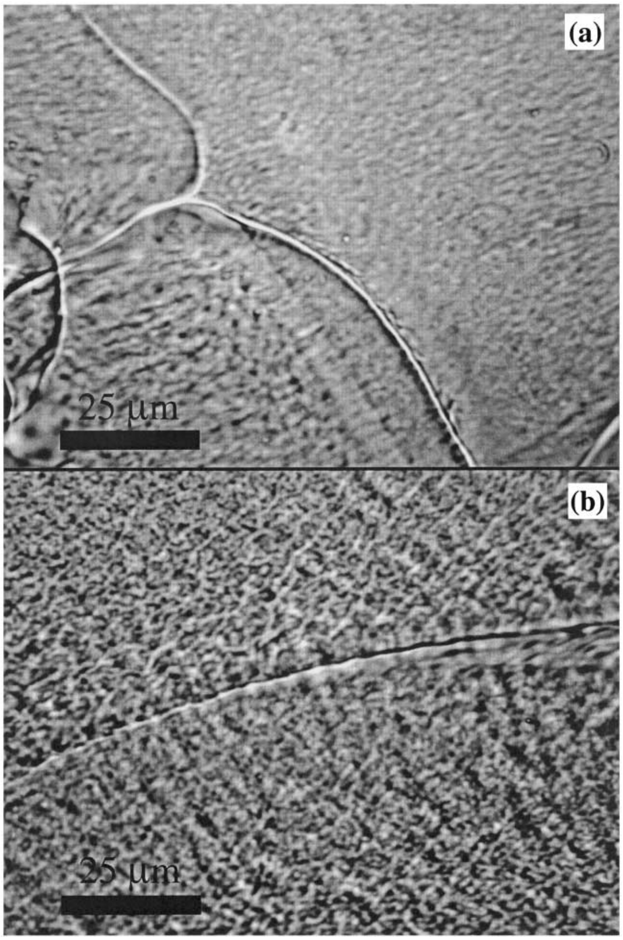

Fig. 1. Optical micrographs of room-temperature cast films containing (a) 0.59% and (b) 0.80% Santonox (based on PVME weight only).

extent of this effect of the antioxidant on the phase transition temperature, particularly at these low fractional contents, was unanticipated.

3.3. Thermal stability

Fig. 3 consists of a set of GPC traces showing the molecular weight distributions of the PS/PVME test blends after 52 h at 105 °C under nitrogen. The degree of degradation was not high for any of the samples, even after 52 h, although a slight increase in the amount of PVME at higher molecular weights was recorded. However, it was clear that the blends containing more antioxidant experienced less of a change in molecular weight distribution.

As Fig. 3 clearly indicates, the GPC differential refractive index detector is more sensitive to PS than PVME, and as a result, the PS peak at 100,000 g/mol (PVME basis) dominates the traces and obscures much of the PVME peak. Although the PS peak did complicate the data analysis, thermal degradation tests were performed with the blends rather than with pure PVME since in the latter degradation occurred on a much shorter time scale. A crude quantification of the degree of PVME degradation was derived from the integrated area under the GPC curve in the same high molecular weight region shown in the inset of Fig. 3. The PS peaks were normalized to a height of unity, and the area under that portion of the curve, from 170,000 to 600,000 g/mol was determined as a function of time for all the antioxidant compositions. The data reveal a monotonic increase in degradation with time for all antioxidant concentrations, and a decrease in degradation with increasing antioxidant concentration as expected. The changes in molecular weight slow considerably after the first 10 h of the experiment.

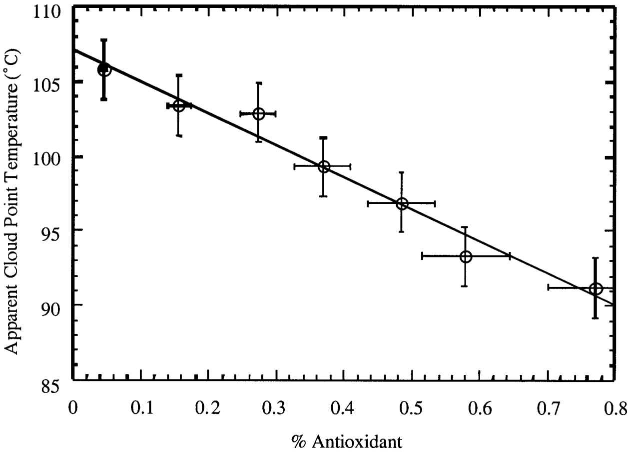

Fig. 2. The effect of Santonox content on apparent cloud-point temperature.

4. Conclusions

Based on the results of this study, it would seem that the most desirable Santonox concentration is between 0.07 and 0.10 wt% of the PVME in the blends. This is a good compromise between preventing degradation in the PVME and avoiding difficulties with the secondary effects of film haziness and cloud-point depression. The haziness of the

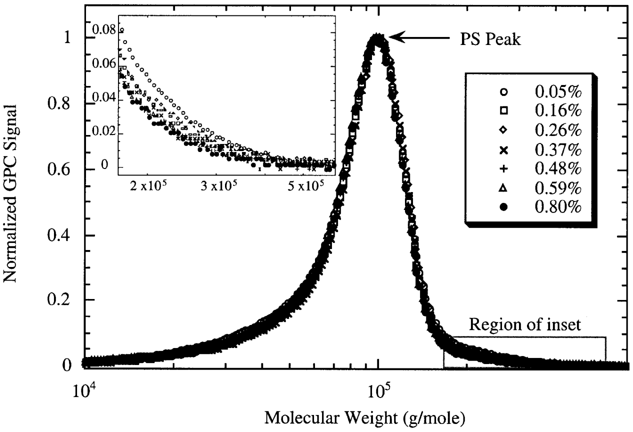

Fig. 3. Molecular weight distributions after 52 h at 105 °C. The inset is a close-up of the high molecular weight end of the curve, shown boxed, that indicates that less degradation occurred when more antioxidant was present.

cast films containing higher concentrations of antioxidant, evident even well below the apparent cloud-point temperature, suggests that the PS/PVME/Santonox system may be far more complex than is commonly accepted.

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