Effect of Antioxidants on Properties and Morphology of Poly(Acrylonitrile–Butadiene–Styrene)/Polycarbonate Blends

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SYNOPSIS

Poly(acrylonitrile–butadiene–styrene), polycarbonate (PC), and two types of antioxidants have been blended by an extruder twin screw. Notched Izod impact strength, tensile property, and melting flow index (MFI) were measured for the blends including different amounts of antioxidants, and morphology of the blends was investigated by scanning electron microscopy (SEM). The antioxidant action, especially on mechanical properties and the phase structure of the blends, has been studied for the undegraded samples. It was found that the phenolic antioxidant, tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyloxymethyl)methane, $C_{73}H_{108}O_{12}$, whose commercial name is KY-7910, and phosphite antioxidant, triphenyl phosphite (TPP), $(C_6H_5O)_3P$, all decrease the Izod impact strength and tensile modulus of the blends and increase the elongation at break if a small amount of the antioxidants (such as less than 0.7%) was mixed into the blends. When the content of the antioxidants is increased, surpassing 0.7%, KY-7910 has little effect on impact property of the blends, but TPP made the Izod impact strength decrease and the MFI increase to a great degree. SEM results show that the two phases of ABS/PC with a weight ratio of 30/70 is cocontinuous; this structure is destroyed by addition of the two antioxidants, and in ABS/PC/antioxidants blends, the size of the ABS phase, as dispersion, does not change not much with increasing KY-7910 content, but becomes more scattered and greater with increasing content of TPP. These results are consistent with the mechanical tests.

INTRODUCTION

Polymer alloys are more and more widely used with the development of the plastic industry. When polymer alloys are made into articles and used in practice, not only must they have a high level of mechanical properties but also good resistance to aging, so that the original properties of the articles can remain. For example, antioxidants are often added in polymers to inhibit or delay color change and brittleness, of the formed articles, induced by oxygen and peroxide. This is an effective method to prevent aging of polymer articles.

The acrylonitrile–butadiene–styrene (ABS) polymer and polycarbonate (PC) can be blended to form into a plastic alloy with excellent properties,[1,2] and many research articles dealing with this blend system have been published.[3–11] Some researchers studied the effect of compositions of ABS and PC on the properties and structure of the blends.[3–7] Some investigated the effect of processing on the properties of the blends.[8,9] The weathering of several commercial ABS/PC alloys was also studied by Cooney.[10]

Much attention has been given to the role of antioxidants on the aging property of polymer materials, but less on the properties and morphology of polymer materials, especially polymer alloys. In this article, we studied the mechanical properties and observed the morphology for ABS/PC blends containing two types of antioxidants and found that the types and content of antioxidants obviously affect the mechanical properties and morphology of the ABS/PC blends.

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EXPERIMENTAL

Materials

The ABS resin used was ABS 301 made by Lanzhou Chemical Industry Co., China. Composition: 22.2% butadiene and 55.0% styrene; melting flow index (MFI) = 1.5 at 200°C/5 kg. The PC used was PG-2y made by Changzhou Organic Chemical Plant, China, and was of a standard grade of medium melt viscosity with M_w = 30,000, MFI = 1.07 at 260°C/2.16 kg. The antioxidants, tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyloxymethyl)methane, $C_{73}H_{108}O_{12}$, with the commercial name KY-7910, was made by the Beijing Third Chemical Plant. The antioxidant, triphenyl phosphite (TPP), $(C_6H_5O)_3P$, was made by the Beijing Branch of Chinese Medicine Co.

Melt Blending

ABS/PC with a weight ratio of 30/70, after being dried *in vacuo* at 80°C for 24 h, was compounded with various weight percentages of the two kinds of antioxidants, 0.1, 0.4, 0.7, 1.0, and 2.0, and then blended in an extruder twin screw Model SHJ-30 at 215–230°C. The real temperature of the melting blends, indicated in the extruder, was higher than 250°C. The pieces for mechanical testing were prepared by injection molding at 230–240°C. The samples for SEM testing were prepared by compression molding in a 1 mm-thick frame. Each compounding was first preheated at 220°C for 7 min before it was compressed at 100 kg/cm^2 for 5 min and was then taken in another hydraulic press and cooled to room temperature.

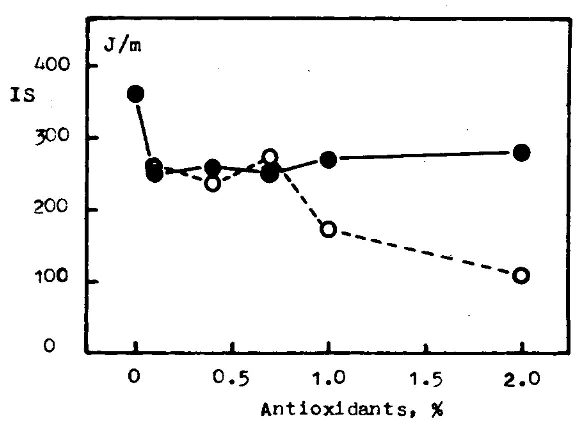

Figure 1 Dependence of notched Izod impact strength (IS) on percentage of antioxidants, (●) KY-7910 and (○) TPP, for the blends of ABS/PC/antioxidants.

Mechanical Properties

Tensile properties were measured by the ASTM D638 test method using an Instron universal testing machine Model 1121. The speed was 50 mm/min; the data were recorded and treated by the computer. Notched Izod impact strength was measured by the ASTM D256 test method using the Izod type. The thickness was $\frac{1}{4}$ in.

Melting Flow Index (MFI)

The MFI of each blend was measured by the HG2-1171-77 test method at 260°C with a 2160 g load using an MFI tester model XRZ-400.

Scanning Electron Microscopy (SEM)

The morphology of the cross section of compression-molded sheets was examined by SEM in a Joel Model JXA-840 microscope after sputter coating. The fracture surfaces of the sheets were prepared by crogenic fracturing at liquid nitrogen temperature.

RESULTS AND DISCUSSION

Mechanical Properties

The notched Izod impact strength of the blends of ABS/PC/antioxidants is shown in Figure 1. It is directly seen that the phenolic (KY-7910) and the phosphite (TPP) antioxidants affect the notched impact strength in different manners. When the percentage of the antioxidants added in the blends is between 0.1 and 0.7%, the impact strength of the blends containing KY-7910 and TPP is close and much lower than that of pure ABS/PC blend, and it changes very little. As the percentage of the antioxidants in the blends is higher than 0.7% and increased, the impact strength changes to a very limited degree for the blends containing KY-7910, but decreases to a great magnitude for the blends containing TPP. Notched impact strength equals 284 J/m for the KY-7910 system, but only 111 J/m as 2.0% antioxidants were added to the blends.

Stress–strain curves for the ABS/PC/antioxidants blends are presented in Figure 2. For the sake of the figure's clearness, the figure does not show all the stress–strain curves for the tested samples. It is directly seen that yield stress and yield strain vary very little with varying antioxidant concentration, whereas modulus shows a notable decrease for the blends containing 0.4% KY-7910 and 0.1% TPP.

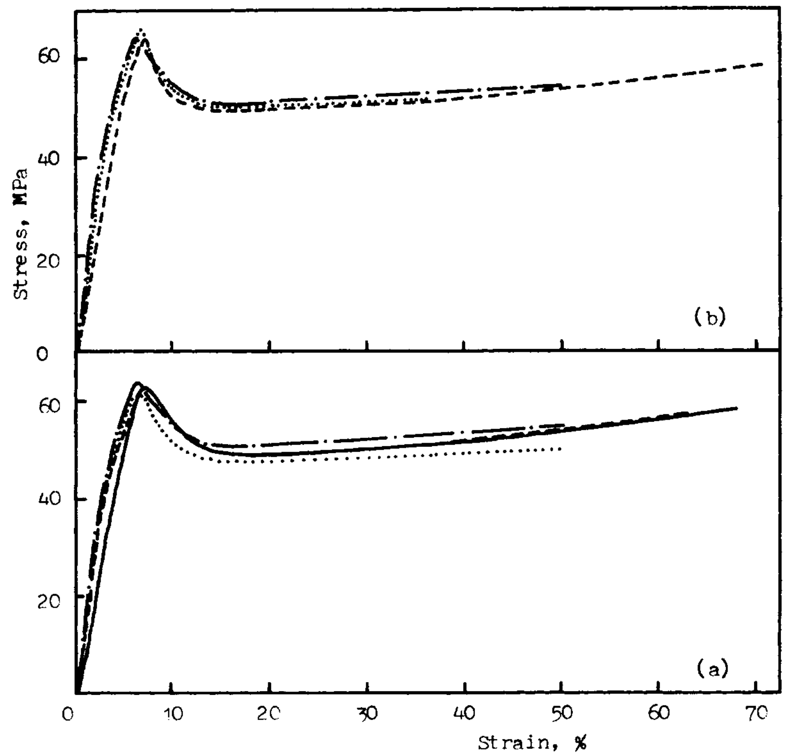

Figure 2 Stress–strain curves for ABS/PC/antioxidants blends containing (a) KY-7910 and (b) TPP. Antioxidants content: (– · –) 0; (– – – –) 0.1%; (——) 0.4%; (· · · · ·) 2.0%.

Dependence of modulus and tensile yield strength of ABS/PC/antioxidants blends on percentage of the antioxidants is presented in Figure 3. The modulus of elasticity changes in a similar manner for both of the two blend systems, i.e., it decreases at first and increases later with increasing the antioxidant content, showing a minimum for the blends containing 0.1% TPP and 0.4% KY-7910, respectively. It seems that the tensile strength of the blends containing TPP increases, but that of the blends containing KY-7910 decreases somewhat as the amount of the antioxidants is increased.

Variation of elongation (ϵ_b) at break and (ϵ_y) at yield with percentage of the antioxidants is shown in Figure 4. The elongation at break increases at first, appearing at a maximum for the blends containing 0.1% TPP and 0.4% KY-7910, respectively, and decreases later with increasing the content of the antioxidants. As the content of the antioxidants added in the blends amounts to 2.0%, ϵ_b of the ABS/PC/TPP blend, with a value of 36%, is lower than that of ABS/PC/KY-7910 blend, with a value of 49%. It is also seen that the two blend systems have the same elongation ϵ_y at yield, which does not change with the content of the antioxidants.

Melting Flow Property

Dependence of MFI of the blends on percentage of the antioxidants is presented in Figure 5. The MFI of the blends containing TPP increases monotonously with increasing content of TPP, but that of the blends containing KY-7910 does not increase with increasing content of KY-7910 up to 1.0%, and it shows a little increase as the content of KY-7910 equals 2.0%. Almost all the MFI values of the blends containing TPP are higher than that of the blends containing KY-7910, and the difference of the MFI values between the two blend systems increases with increasing content of the antioxidants, indicating that the triphenyl phosphite (TPP) is very effective in improving the fluidity of the ABS/PC blends.

Morphology

To study the phase structure, SEM micrographs of fracture surfaces for the blends were obtained, as shown in Figure 6. All the blends show a multiple-phase structure. A structure with ribbon-shaped co-continuous phases is observed in micrograph (a) for the ABS/PC (30/70) blend. In the two micrographs of the blends containing 0.7% (b) and 2.0% KY-

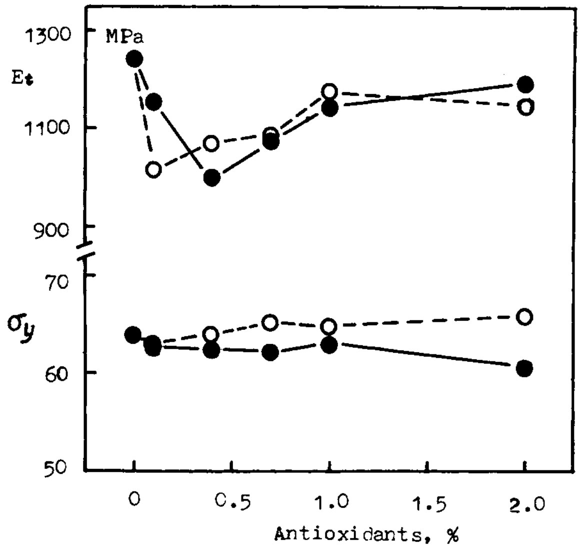

Figure 3 Dependence of modulus, E_t, tensile yield strength, σ_t, on percentage of the antioxidants, (●) KY-7910 and (○) TPP, for the blends of ABS/PC/antioxidants.

7910 (c), the morphology of one being a continuous phase, and the other, dispersion, has no real difference. According to our unpublished work, the phases with many small holes are ABS; therefore, the continuous phase is PC. It seems that the ABS phase size of the blend containing 0.7% KY-7910 [Fig. 6(b)] is a little greater than that of the blend containing 2.0% KY-7910 [Fig. 6(c)], and some ABS phases in Figure 6(b) tend to be but are not continuous. The SEM micrograph (d) of the blend containing 0.7% TPP shows a phase structure similar to (b) and (c). However, the phase structure of the blend containing 2.0% TPP [Fig. 6(e)] is obviously different from micrograph (c). The dispersed phases are more scattered, and some of the biggest phases, with a size more than ca. 10 μm, are much greater than these in Figure 6(d), with a size less than ca. 3 μm. There are many small particles in micrograph (e) that we do not know if are the phases of TPP itself, but they are not in micrograph (c) for the blend containing 2.0% KY-7910.

The morphology of various compositions of ABS/PC blends, extruded twice by a single-screw extruder, has been studied by us.[11] We found that blends of ABS 301/PC PG-2y with compositions of 20/80 and 30/70 have the "network" structure of two continuous phases; the blends with other compositions present one dispersed PC phase and another continuous ABS phase. Results of Figure 6(a) are consistent with that observation. However, we see that in Figure 6 one phase is dispersed and another continuous for all the four blends containing antioxidants, indicating that the two antioxidants, KY-7910 and TPP, have destroyed the structure of cocontinuous phases of ABS/PC (30/70) blends. Although the morphology of the blends containing 0.1 and 0.4% antioxidants was not observed in Figure 6, we believe that they would be similar to the phase structure in Figure 6(b) and (d). This can explain why the impact strength (Fig. 1), the modulus (Fig. 3), and the elongation at break (Fig. 4) are obviously affected even if an amount of antioxidants as small

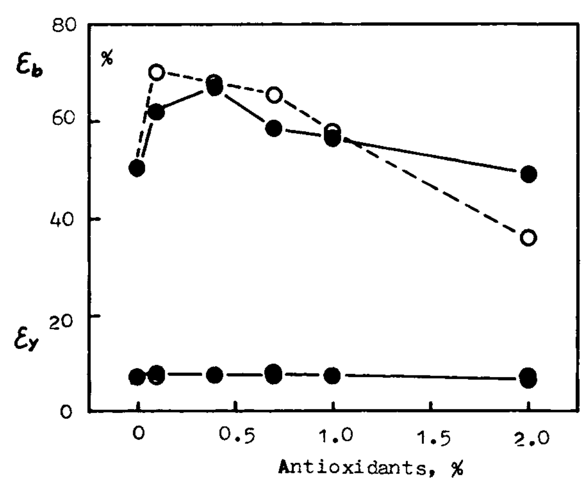

Figure 4 Dependence of elongation ϵ_b at break and ϵ_y at yield on percentage of the antioxidants, (●) KY-7910 and (○) TPP, for the blends of ABS/PC/antioxidants.

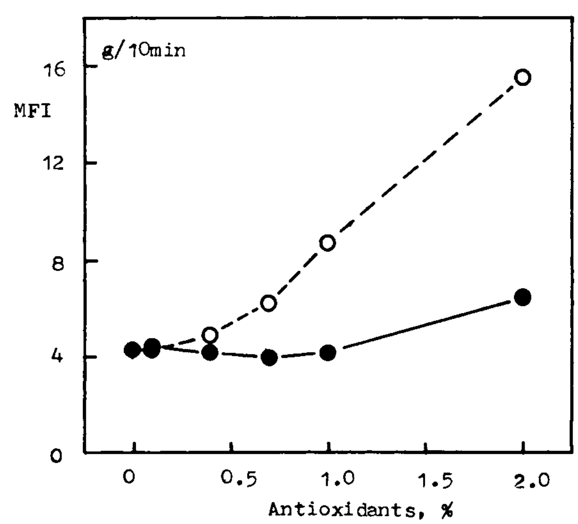

Figure 5 Dependence of MFI on percentage of antioxidants, (●) KY-7910 and (○) TPP, for the blends of ABS/PC/antioxidants.

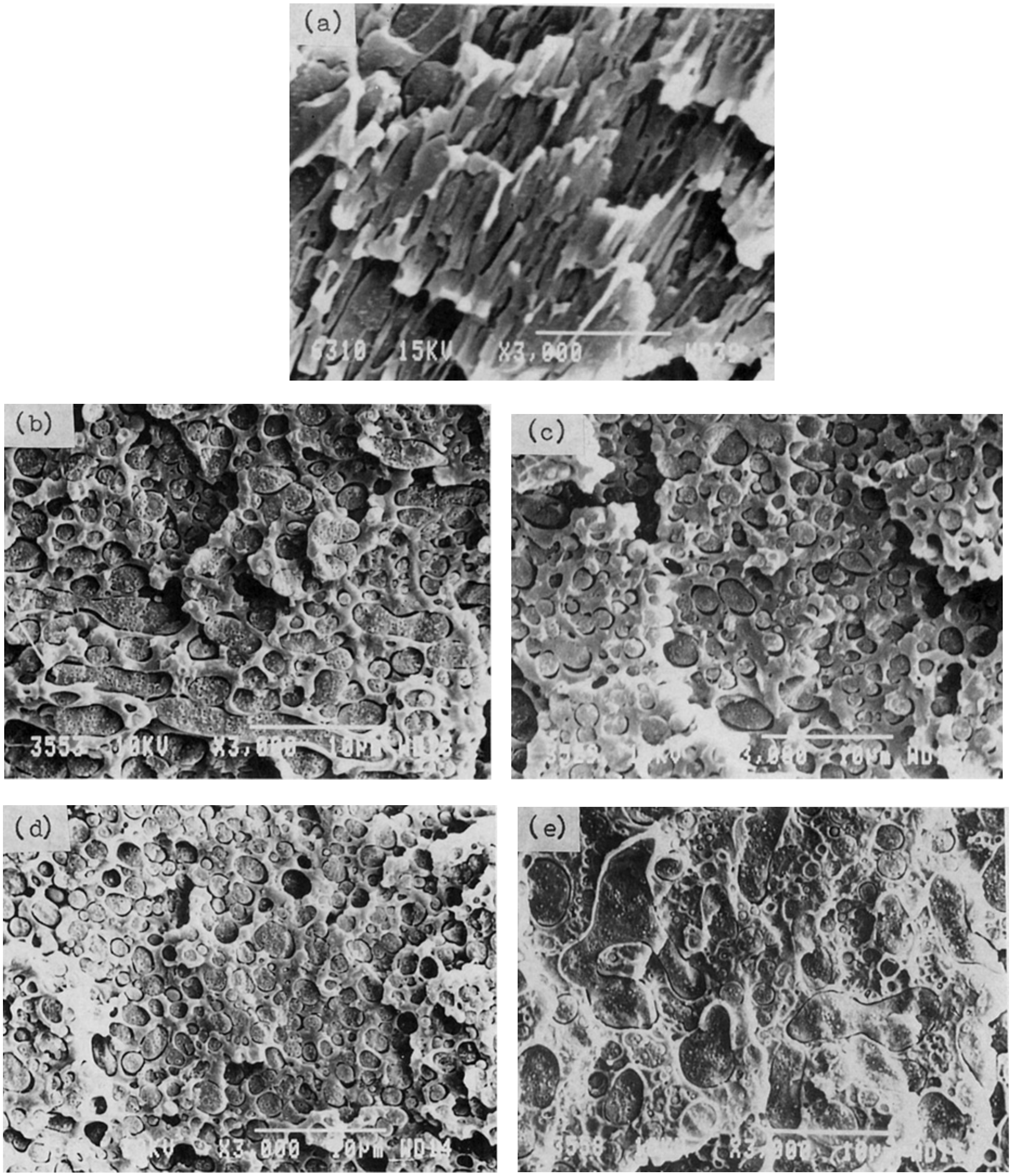

Figure 6 SEM micrographs obtained from cryogenically fractured cross-section surfaces of compression-molded sheets for ABS/PC/antioxidants blends containing (a) 0% antioxidants, (b) 0.7% KY-7910, (c) 2.0% KY-7910, (d) 0.7% TPP, and (e) 2.0% TPP.

as 0.1% or 0.4% is mixed into these blends. As expected, volume fraction and viscosity dominate among the factors determining the dual-phase continuity. But the capillarity number (which includes interfacial tension) might play an important role as well.[12] Because for our blend system the volume fraction and viscosity of the two polymers, ABS and PC, do not change, it is possible that addition of a small amount antioxidants has decreased the capillarity number and increased the interfacial tension due to lack of the miscibility between the antioxidants and the polymers. Therefore, the antioxidants have a dramatic effect on the morphology and properties even at very low concentration.

If the content of antioxidants added in ABS/PC blends is continuously increased to 0.2%, the phosphite antioxidant, TPP, makes the size of the dispersed phases more scattered and greater, which may result from the decrease of capillarity number in the melt, but the phenolic antioxidant, KY-7910, changes the phase morphology very little (Fig. 6). Therefore, the Izod impact strength of the blends containing TPP greatly decreases, but that of the blends containing KY-7910 is nearly constant (Fig. 1). On the other hand, how the tensile properties of the blends are affected by their phase morphology is related to many factors of detailed structure, such as the miscibility of each component in the blends, which we cannot explain clearly here due to its complexity.

CONCLUSION

In ABS/PC/antioxidants blends, both of the antioxidants, KY-7910 and TPP, affect the properties and morphology of the blends. A small amount of the antioxidants, when added to ABS/PC blends, will decrease the Izod impact strength and the Young's modulus of the blends and increase the elongation at break. This is explained by destroying of the antioxidants to the structure of cocontinuous phases of ABS/PC blend itself. When the content of antioxidants is increased, surpassing 0.7%, the Izod impact strength decreases and the MFI increases in great magnitude for blends containing the TPP antioxidant, but both the impact strength and the MFI show little increase for blends containing the phenolic antioxidant, KY-7910. A large decrease of the impact strength of the blends induced by adding TPP to the blends results from that the TPP makes the size of the ABS phase, as dispersion, more scattered and much greater, as revealed in the SEM micrographs of the blends. The tensile strength of ABS/PC/antioxidants blends increases with increase of TPP content and decreases with increase of KY-7910 content; both of the changes are very limited.

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