Effect of Ionic Additives on Deformation Behavior of Bisphenol A Polycarbonate

SANG-SOO LEE,[1,2] KILWON CHO,[1] JOONKYUNG KIM[2]

[1]Department of Chemical Engineering/Polymer Research Institute, Division of Electrical and Computer Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

[2]Polymer Hybrids Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

ABSTRACT: The deformation behavior of bisphenol A polycarbonate containing only a small amount of oligoionomeric additives in the range of a few parts per hundred parts of resin was examined. The impact strength of polycarbonate markedly decreased as the content of additive increased, and brittle fracture of polycarbonate was observed in tensile tests when the concentration of additive was above 2.5 phr. The ductile-to-brittle transition that was determined using a comparison of the critical shear yield stress and the critical craze stress appeared to exist in the range of 2.5–3.5 phr of additive. The measured entanglement density was also found to decrease significantly with the addition of a few parts per hundred parts of resin of additives, and the change of the dominant deformation mechanism from ductile to brittle failure was recognized as a result of the change of the entanglement density of polycarbonate. Therefore, it was concluded that the presence of a small amount of ionomeric additives caused the loss of entanglement density that induced transition of the deformation mechanism of polycarbonate from ductile to brittle failure and led to the corresponding deterioration of impact strength. © 2001 John Wiley & Sons, Inc. J Polym Sci Part B: Polym Phys 39: 2635–2643, 2001

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INTRODUCTION

The physical properties of polymer mixtures containing low molecular weight molecules have been investigated extensively because of the importance of additives in industrial applications. From these studies it is well known that additives significantly affect relaxation processes in glassy polymers, as evidenced by phenomena such as plasticization[1,2] and antiplasticization.[3] In the liquid range, the plasticization effect whereby the glass-transition temperature (T_g) of the polymer is reduced when additives are added is defined as an acceleration of the cooperative α-relaxation processes of the polymer, and the effect has been satisfactorily explained on the basis of conventional free-volume theories.[4,5] In the glassy state well below T_g of the polymer mixture, the situation is entirely different. The glassy mixtures are not at all plasticized but rather found to be hardened and more brittle than the neat polymers. This antiplasticization effect is possibly related to the phenomenon that in many polymeric mixtures the secondary mechanical relaxation processes are suppressed.[3,6–8] In this regard, Fisher et al.[9] have derived strong evidence from small-

angle X-ray scattering experiments that the suppression of the secondary relaxation process is associated with a reduction not of the average free volume but of free-volume fluctuations. On the other hand, there are few reports on the antiplasticization that results from a decrease in free volume upon the addition of the diluent.[10,11] According to Fisher et al.[9] either the polymer chains have some small degree of mobility that allows them to align themselves in a more ordered densely packed state or the additives fill the excess volume of the polymer glass. Anderson et al.[12] examined the mechanical properties of the mixture of polystyrene with mineral oils and found that antiplasticization in polymers is molecular weight dependent and additive concentration dependent. On the basis of these results, they made a hypothesis that the phenomenon can be attributed to a chain-end effect, that is, the additive may initially fill the smaller holes at the chain ends. Mobility of the chain ends is restricted and results in embrittlement of the polymer.

Most previous works[3,6–16] have relied solely on either a mechanical or an analytical test to verify antiplasticization and speculated on a mechanism for antiplasticization. Few attempts have been devoted to relating the microscopic behavior of the additive to the molecular motion of the polymer. Moreover, it is rare to have information dealing with antiplasticization of engineering plastics such as bisphenol A polycarbonate (PC), although they are becoming central materials in every field of high technology industry. To fill out this lack of information, PC/additives were studied as a model system.

PC is widely used as an optical data-storage medium such as a compact disc. However, the PC-based materials tend to become electrostatically charged, and this property is a serious obstacle not only in the production process of such a material but also in using products made from PC. Therefore, during melt processing, low molecular weight ionic molecules such as dodecylbenzene sulfonic acid tetra-n-butyl phosphonium salt (DSP, see Structure 1 of DSP) are usually added as an antistatic agent. However, there has been a significant reduction of impact strength even when PC is mixed with only a small amount of

antistatic agent in the range of a few parts per hundred parts of resin. Because DSP is one of the permanent antistatic agents used commonly in the polymer industry, it is worthwhile to scrutinize the effect of DSP on the mechanical properties of polymer materials containing it. In this article, to elucidate the reduction of impact strength of PC by the addition of DSP, several experiments were conducted and the results are reported.

EXPERIMENTAL

Materials and Preparation of Samples

PC was a commercial molding grade [number-average molecular weight (M_n): 30,000 g/mol, polydispersity (M_w/M_n): 1.75, and $T_g = 147$ °C] and supplied by Sam Yang Petrochemical Co., Korea. DSP ($M_w = 508$ g/mol) was purchased from Takemoto Co., Japan (Elecut S-418). DSP, in the form of a highly viscous liquid, and PC received as pellets were used without any purification except drying at 100 °C for 24 h in a vacuum oven.

To mix PC and DSP, a Brabender internal mixer equipped with a computerized viscosity monitoring system was used. The mixing temperature was 240 °C, and the rotor speed was 120 rpm. Mixing time was controlled by the viscosity, that is, when no fluctuation of viscosity was noted, the mixing was stopped. The mixtures of PC and DSP were slightly colored regardless of the amount of DSP incorporated. After vacuum-drying at 110 °C for 24 h, the mixtures were compression molded into sheets of 1 and 6 mm thickness, respectively. From a sheet of 6-mm thickness, rectangular specimens 60 mm long and 12.5 mm wide were prepared for Izod impact tests. A notch was introduced by using a notch cutter with a 0.25-mm radius, chilled by liquid N_2 to prevent plastic deformation around the notch tip. In addition, dumbbell-shaped specimens with a gauge length of 10 mm and a width of 3 mm for uniaxial tensile tests were machined from the sheet of 1-mm thickness.

Mechanical Tests and Microscopy

The Izod impact tests were performed at room temperature. The tests were carried out for at least 10 specimens. The uniaxial tensile tests for dumbbell-shaped specimens were conducted on
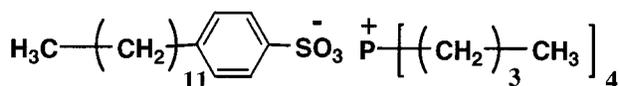
an Instron 4201 universal testing machine. A crosshead speed of 5 mm/min and ambient temperature were used.

The fracture surfaces of impact-tested specimens were examined using scanning electron microscopy (SEM, Hitachi S-2500C). Specimens were sputter-coated with a thin layer of gold and examined at 10 keV accelerating voltage.

Thermal and Physical Characterization

Investigation of thermal behaviors was accomplished with a PerkinElmer differential scanning calorimeter, DSC-7. PC/DSP mixtures were heated at a rate of 10 °C/min to find T_g. The temperature at the half-height of the heat-capacity change was taken as T_g.

To ascertain the effect of DSP on the γ-relaxation behavior of PC, dynamic mechanical thermal analysis (DMTA) was conducted using a Polymer Laboratory DMTA MK II instrument. A dual cantilever beam testing mode was used. A heating rate of 3 °C/min, strain-cycle frequency of 1 Hz, strain amplitude of 64 mm, and temperature range from −150 to 50 °C were used.

Entanglement density ν_e was determined by the equation

$$\nu_e = \rho/M_e \qquad (1)$$

where ρ and M_e are the density and entanglement molecular weight, respectively. Entanglement molecular weight was acquired from the equation

$$M_e = \rho_T RT/G_N^0 \qquad (2)$$

where ρ_T is the melt density at temperature T, R is the gas constant, and G_N^0 is the rubbery plateau modulus. To determine entanglement density, the rubbery plateau modulus was measured on a Rheometrics RDS II using a specimen of 25 mm diameter and 2 mm thickness. The measurement was carried out by frequency sweep measurements from 180 to 240 °C in 10 °C intervals under the N_2 atmosphere.

Determination of Crazing and Shear Yield Stresses

The critical stress for initiation of craze was determined using three-point bending tests. Specimens ($70 \times 10 \times 6.0$ mm) were prepared by machining for three-point bending tests. A notch with a radius of 0.5 and 2.0 mm long was intro-

duced by making a saw cut at the center of the specimen edge. An internal craze was produced ahead of the crack tip by pressing the specimen using a universal testing machine. The experiment was conducted with a crosshead speed of 2 mm/min at room temperature. After the test, a thin section was sliced from the crack-tip region of the test piece using a low-speed diamond saw, and the distance between the notch tip and the nucleation point of the craze was measured using transmission optical microscopy.[19] The stress distribution around a notch was obtained using slip-line field theory,[17–19] and crazing stress was calculated from the equation

$$\sigma_c = \tau_y \left[1 + 2 \ln\left(1 + \frac{x}{r} \right) \right] \qquad (3)$$

where τ_y is the critical shear yield stress, x is the distance between the notch tip and the nucleation point of the craze, and r is the notch radius.

Shear yield stress was determined from a uniaxial tensile test using the following von Mises yield criterion:[19]

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6\tau_y^2 \qquad (4)$$

where σ_1, σ_2, and σ_3 are principal stresses. In this case, σ_1 is the maximum stress, and σ_2 and σ_3 are equal to zero. Therefore, shear yield stress is the product of $1/\sqrt{3}$ and the uniaxial yield stress obtained from the stress-strain curve.

RESULTS AND DISCUSSION

Phase Morphology

Because the intrinsic properties of multicomponent materials are critically dependent on their phase behavior and corresponding morphology, it is very necessary to determine their miscibility before assessing mechanical properties. Conventionally, miscibility of polymer blends is monitored using the criterion that a miscible blend exhibits a single T_g, whereas a phase-separated blend shows two separate T_g's. In cases of oligomer-containing polymer blends, however, it is hard to define the T_g of oligomers. Thus, it is not effective to determine the miscibility for such cases by T_g measurements. Instead, a method using a refractive-index difference was used in this experiment because a large difference in the

refractive index between PC ($n_D^{25} = 1.585$)[20] and DSP ($n_D^{25} = 1.492$)[21] makes it possible to assess the miscibility of PC and DSP. It was observed that the transparency of the molded PC/DSP mixtures was retained up to 5 phr of DSP. Moreover, when the cryogenically fractured surfaces were examined by SEM, no heterogeneous phase morphology was detected. In fact, because of large differences in the chemical structure and molecular weight, it was reasonable to expect the deficiency of miscibility between PC and DSP. However, because the DSP content introduced was too small to form its own independent phases, on the basis of the evidence of the transparency test, it seemed that PC/DSP mixtures exhibit a homogeneous single phase up to around 4 phr of DSP.

Impact Strength

Figure 1 shows the change of impact strength of the PC/DSP mixture as a function of DSP concentration. The impact strength decreased rapidly as the DSP content increased and appeared to become stable over 4 phr of DSP. Although pure PC is distinguished for its high thermal stability, additives may facilitate thermal breakdown or chemical modification under severe conditions of high temperature, high shear, and so forth. Thus, it is not unusual to experience the deterioration of mechanical properties corresponding to the drop of molecular weight in processing. In our study, it was imperative to exclude the effect of molecular weight change, and thus the molecular weights before and after compounding were measured.

As shown in Figure 2, a slight and gradual decrease of molecular weight was found. This result, however, resulted not from PC degradation during compounding but from the presence of DSP of low molecular weight. In fact, the molecular weight normalized by the content of PC did not show a considerable change irrespective of DSP concentration. Therefore, the rapid drop of
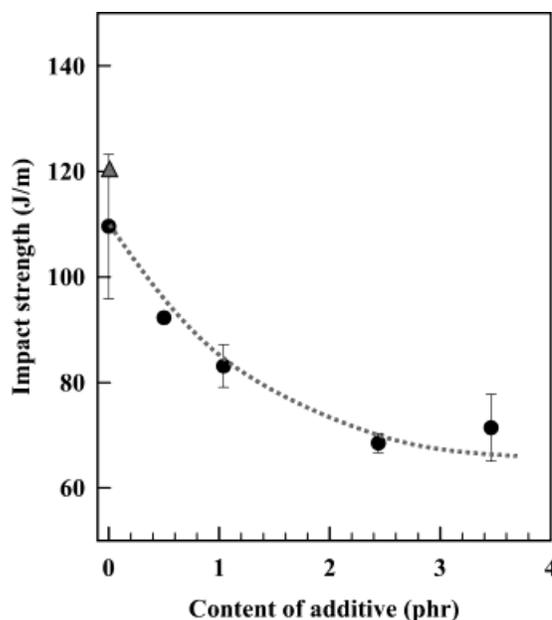

Figure 1. Impact strength of PC/DSP mixture as a funcion of DSP content. The experiments were conducted under ASTM D256 with specimens of 6.0-mm thickness at room temperature. For comparison, a solid triangle is given to show the reported value of PC impact strength that was measured with specimens of 6.4-mm thickness.[22]

impact strength by the addition of a very small amount of DSP was attributed to the enhanced chain mobility as a result of the plasticization effect of low molar mass molecules. The enhanced chain mobility affected the flow stress or charging stress during the molding process, which changed the microdeformation mechanism. This is discussed subsequently in more detail after examination of the fracture surface and evaluation of the critical stress for crazing or shear yielding. The enhanced chain mobility by the addition of DSP was evidenced by the drop of the T_g. As shown in Figure 3, only a small amount of DSP significantly reduced the T_g of the PC mixture,

Table I. Characteristics of the Materials Used

Designation	Molecular Weight	Remarks
Bisphenol-A polycarbonate (PC)	M_n = 30,000 g/mol[a] PD = 1.75[b]	T_g=147°C
Dodecylbenzene sulfonic acid tetra-n-butyl phosphonium salt (DSP)	584 g/mol	—

[a,b] The number-average molecular weight and polydispersity index were obtained on GPC calibrated with PS standards.
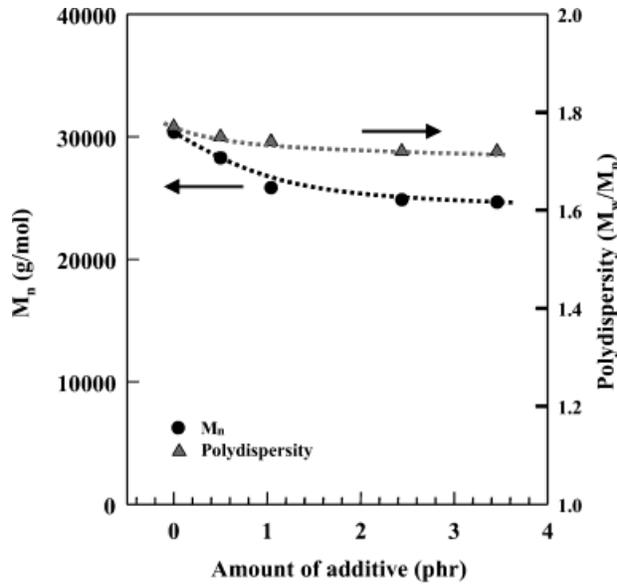
Figure 2. Molecular weight measurement of the PC/DSP mixture as a function of DSP content.

which is a typical phenomenon when polymer contains low molar mass molecules.

However, in the glassy state well below the T_g of the mixture, the mixtures are not at all plasticized but sometimes found to be rather hardened. This antiplasticization effect was reported to be re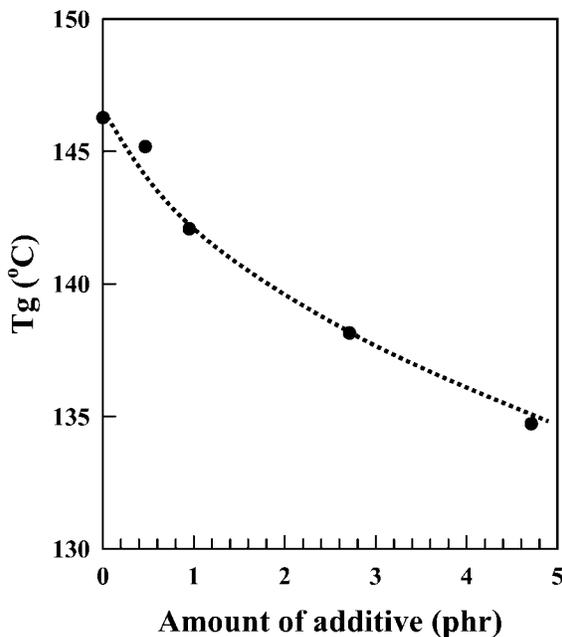lated to the suppression of secondary relaxation of the polymer mixture.[8] Thus, to check the antiplasticization effect in this particular system, the secondary relaxation process of the PC/DSP mixture was characterized, and the loss moduli variation with temperature is reported in Figure 4. In Figure 4, there was no significant change in the values of the secondary relaxation peak maximum nor was peak position changed for all compositions tested. This result implies that secondary relaxation of the PC/DSP mixture is not suppressed by the addition of DSP. Consequently, the previously reported model of antiplasticization effect cannot be applied to this particular system.

In Figure 1, the scattering of data of the impact strength was reduced when DSP was incorporated. In the case of pure PC, because of the high melt viscosity of PC, inhomogeneous stress distribution is frequently obtained in the compression-molded specimens that causes the large fluctuation in impact strength, as seen in Figure 1. The reduction of the data scattering with DSP incorporation is also attributed to the enhanced chain mobility by the lubricating role of DSP, that is, the mobile DSP molecules would facilitate the chain motion of PC molecules, causing easier flow
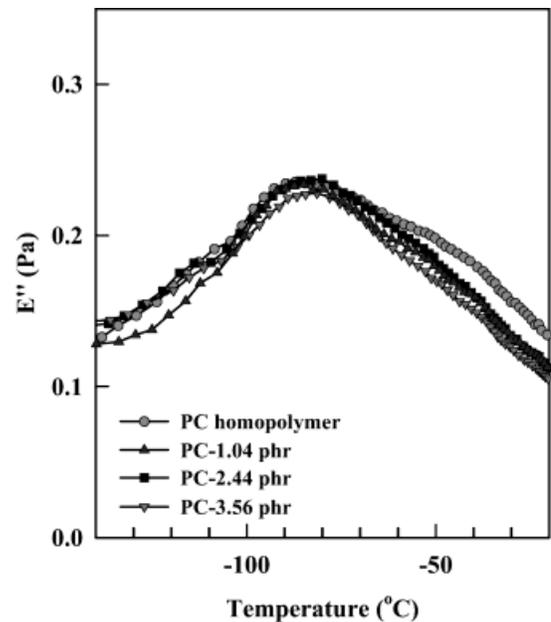

Figure 3. Glass-transition temperature of PC/DSP mixture as a function of DSP content.

Figure 4. DMTA spectra showing γ-relaxation behavior of PC. The measurements were conducted in a bending mode, and conditions of 1.0-Hz frequency and 3 °C/min heating rate were applied. As seen, spectra were displayed with loss modulus rather than tan δ to show that there is no significant change in either the absolute value of γ-relaxation behavior or its position.

of the PC melt and the corresponding reduction, as well as much more homogeneous distribution of residual stress after molding.

Fractography

In addition to the impact-strength results, the fracture surfaces reveal that DSP significantly affects the deformation behavior of PC. It has been well known that fracture behavior of a notched PC specimen is sensitive to thickness. PC specimens of about 6 mm thickness have been reported to appear to be somewhat brittle.[23] Figure 5(a) shows the fracture surface of pure PC. As expected, only a few river lines can be seen, and a large area of the fracture surface is relatively smooth and featureless. On the other hand, the fracture surface of PC-1.04 phr [the mixture of PC and DSP 1.04 phr, in Fig. 5(b)] shows that crazing occurred as well as a large number of arrest bands that implies the dominant deformation mechanism is still yielding. When the amount of DSP increased more, as shown in Figure 5(c) of PC-3.56 phr, the size of the plastic deformation zone that is proportional to the distance from the notch tip to the nucleation point of craze appeared to substantially decrease, and it was observed that crazing is dominant all over the fracture surface.

Tensile Deformation Behavior

Figure 6 depicts the stress-strain curves of the uniaxially tensioned specimens whose mixing compositions are the same as those for impact tests. As expected, pure PC showed typical yielding and successive strain-hardening behavior before fracture. For PC-0.67 and PC-1.04 phr, yield behavior was also observed, and the yield stresses taken at load maximum were very similar to that of pure PC. However, the strain at break showed a distinct difference, that is, as DSP content increased, the extension of specimens after yielding reduced. Moreover, when the DSP content increased to 3.56 phr, yielding did not take place and brittle failure occurred. This result is very consistent with the impact-test result, that is, crazing appeared as the dominant failure mechanism at higher DSP concentration for impact tests. It has been well known that for PC a ductile-brittle transition is observed as the test temperature or strain rate is varied. The results of tensile tests conducted on pure PC and the mixture of PC and DSP imply that PC is also capable of undergoing a ductile-brittle transition as the

DSP content is varied. The appearances of tensile-tested specimens clearly show that as the DSP content increased, the tendency of necking and elongation after yielding gradually diminished, and at last brittle fracture took place.

Ductile-Brittle Transition

A simple explanation of the ductile-brittle transition in tensile tests can be given in terms of two competing stresses, the brittle stress and the yield stress.[24] Because any stress system can be described by two components, a deviatoric (shear) component and a hydrostatic (triaxial) component, both contribute until the failure of the specimen. It is the relative contributions of each that determine whether a specimen undergoes brittle failure or ductile failure. Brittle failure is associated with a *brittle stress*, defined as the stress at break, and ductile failure with a *yield stress*, defined as the stress at the peak load of the yield point. It is assumed that brittle failure and yielding are independent from one another and give rise to separate curves for brittle stress and yield stress. If the conditions of the experiment are such that two stresses are equal, then the conditions at which this equality occurs defines the ductile-brittle transition.

On a microscopic level, brittle failure is often associated with crazing whereas ductile failure is associated with shear yielding. The ultimate mode of failure is then the result of a competition between yielding and crazing. If the craze stress is higher than the yield stress, then yielding will be the readily occuring form of deformation, and the material will fail in a ductile manner. However, if the craze stress is lower than the yield stress, then brittle failure by crazing will ensue.

The shear yield stress and craze stress for pure PC and the mixture of PC and DSP are given in Figure 7. The ductile-to-brittle transition seems to exist in the range of 1.5–3.0 phr of DSP. The results tell us that as the DSP content increased, it became increasingly easier to induce crazing and brittle failure of the specimens.

The question arises as to why and how the incorporation of DSP in PC induces crazing. Among many studies conducted on the crazing phenomenon, Kramer and coworker[25,26] proposed that the entanglement density is one of the key factors deciding whether the material fails by shear yielding or crazing. Typically a polymer with a higher entanglement density will have a high crazing stress; such a polymer may deform
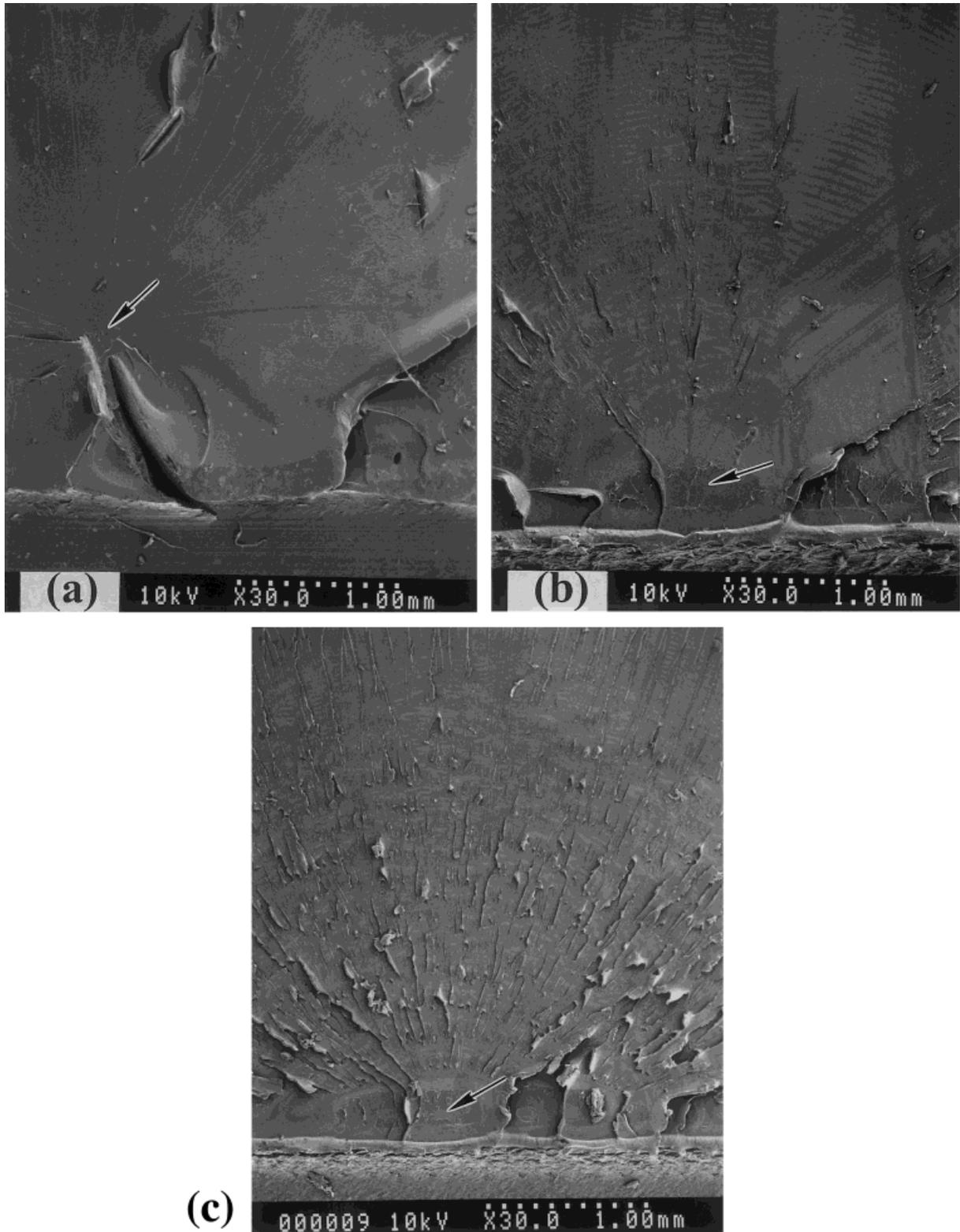
Figure 5. Fracture surfaces of the specimens impact-tested at room temperature: (a) pure PC, (b) PC-1.04 phr, (c) PC-3.56 phr. The arrow end represents the nucleation point of craze.
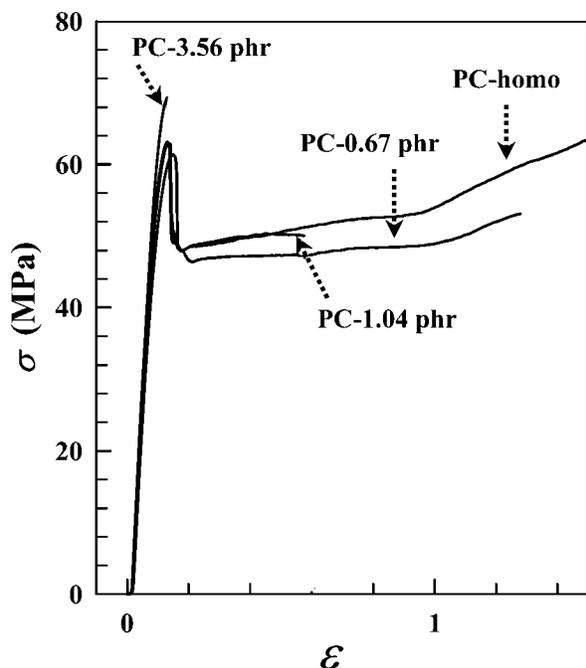
Figure 6. Stress-strain curves of PC as a function of DSP content.

more easily by shear yielding. The yield-craze transition (ductile-brittle transition) can be understood in terms of the relative ease of shear yielding versus crazing as the entanglement density is changed.
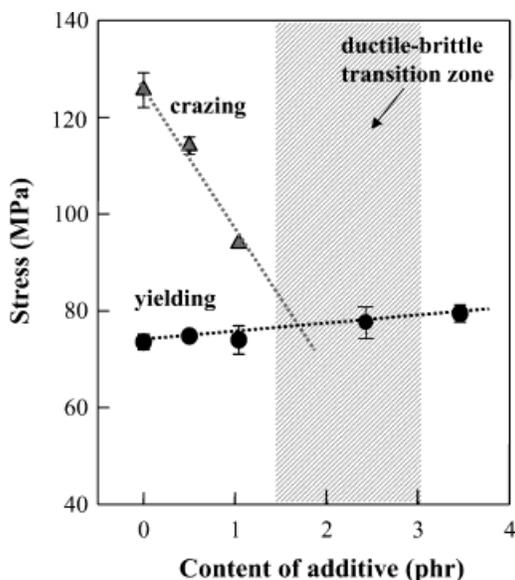

Figure 7. Yield and craze stresses as a function of DSP content. The shadowed area is assumed to be the ductile-brittle transition zone.
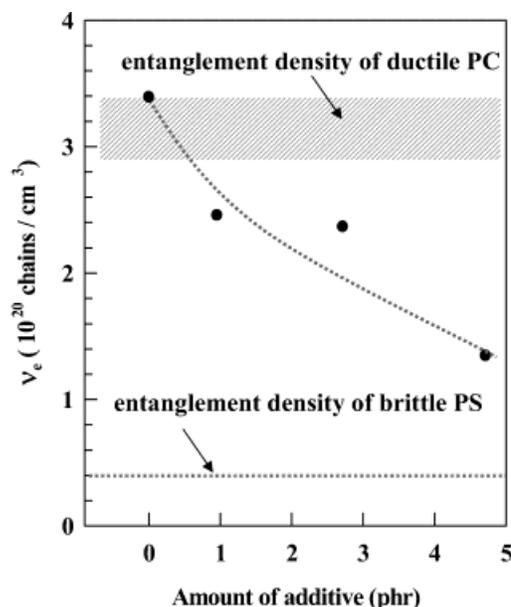

Figure 8. The change of entanglement density of PC as a function of DSP content. The shadowed area and dotted line are the entanglement densities of pure PC[26] and polystyrene[27,28] reported elsewhere, respectively.

Figure 8 illustrates the result of the entanglement-density measurement. The entanglement density was significantly reduced even to a value comparable to those of brittle polymers such as polystyrene,[27,28] as the DSP content increased, which corresponds well to the expectation arising from the comparison of the craze stress and yield stress. Therefore, the presence of DSP induces the loss of entanglement density that causes the transition of the dominant deformation mechanism of PC from yielding to crazing, and the corresponding deterioration of impact strength, and facilitates the macroscopic α-relaxation, that is, the drop of the T_g of PC.

CONCLUSION

The deformation behavior of PC containing oligo-ionomeric additives has been examined. The impact strength of PC markedly decreased as the content of additive increased, and a brittle fracture of PC was observed on tensile tests when the concentration of additive was beyond 2.5 phr. The ductile-to-brittle transition seems to exist in the range of 1.5–3.0 phr of additive. The change of the dominant deformation mechanism was recognized as a result of the significant decrease of the

entanglement density of PC. Therefore, the presence of ionomeric additives caused the loss of entanglement density that induced the transition of the deformation mechanism of ductile PC to crazing and led to the corresponding deterioration of impact strength.

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