

Boiling Water Aging of Polycarbonate and Polycarbonate/Acrylonitrile–Butadiene–Styrene Resin and Polycarbonate/Low-Density Polyester Blends

Chaoqin Li, Yong Zhang, Yinxi Zhang

Research Institute of Polymer Materials, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT: The effects of boiling water on the mechanical and thermal properties and morphologies of polycarbonate (PC), PC/acrylonitrile–butadiene–styrene resin (PC/ABS), and PC/low-density polyester (PC/LDPE) blends (compositions of PC/ABS and PC/LDPE blends were 80/20) were studied. PC and the PC/ABS blend had a transition from ductile to brittle materials after boiling water aging. The PC/LDPE blend was more resistant to boiling water aging than PC and the PC/ABS blend. The thermal properties of glass-transition temperature (T_g) and melting temperature (T_m) in PC and the blends were measured by DSC. The T_g of PC and PC in the PC/ABS and PC/LDPE blends decreased after aging. The T_g of the ABS component in the

PC/ABS blend did not change after aging. The supersaturated water in PC clustered around impurities or air bubbles leading to the formation of microcracks, which was the primary reason for the ductile–brittle transition in PC, and the microcracks could not recover after PC was treated at 160°C for 6 h. The PC/ABS blend showed slightly higher resistance to boiling water than did PC. The highest resistance to boiling water of the PC/LDPE blend may be attributed to its special structural morphology. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 589–595, 2003

Key words: aging; polycarbonates; blends; polyethylene; mechanical properties

INTRODUCTION

Polycarbonate (PC) is a widely used engineering plastic, especially for its superior ductility and outstanding impact-resistance behavior. However, PC is apt to undergo molecular degradation after long-term exposure to warm, humid environments or in hot water. The degradation is primarily attributable to molecular weight reduction that is caused by hydrolysis at the carbonate linkage. The solubility of water in PC increases from 0.3% at room temperature to 0.6% at 100°C. However, these relatively low concentrations of water have significant and even dramatic effects on the mechanical properties and structure of the polymer.¹

With regard to structure, formation of microcracks (microvoids) in PC and the molecular degradation after aging in boiling water were previously reported by some researchers.^{2–4} The microcracks were actually disc-shape pockets filled with water. It occurred because of the creation of water supersaturation conditions by cooling water-saturated specimens from 100°C to room temperature, resulting in water phase separation, clustering, and microvoiding.

Water absorption was known to cause serious deterioration of PC's mechanical properties and was studied seriously by several researchers.^{5–7} Early publications suggested that the deterioration of mechanical properties was attributable to the observed molecular degradation. Robert and John⁵ found that PC went through a transition from ductile to brittle failure along with the reductions in molecular weight. Moreover, Gardner and Martin⁶ found that hydrolytic embrittlement might occur when the molecular weight of PC decreased by about 25%. Although hydrolysis reactions cause molecular breakdown, other factors may also play a role. Later, Petrie et al.⁷ reported that the water influence on mechanical properties should be interpreted in relation to the internal stress distribution. In addition, Narkis et al.² related the deterioration to microvoids. In general, residual stress will form in injection molding as the result of the temperature gradients that exist during solidification. Under normal molding conditions, the stresses that form in the interior of the molding are tensile and fairly weak, and those at the surface are compressive and can be quite strong. In a study by Ram et al.,⁸ the residual stresses present in the moldings were measured after various conditioning procedures, including immersion in hot water, and they deduced that the changes in residual stresses were responsible for the reduced toughness in PC after water absorption. Qayyum and White⁹ got the same results as Ram and coworkers; both studies

Correspondence to: Yong Zhang.

proved that, after hot-water conditioning, the residual stress in a molding bar reversed, which was to say, there was tensile stress at the surface. Under the tensile stress, flaws formed at the surface of the bar. The reduction of toughness may originate from fracture nucleation at the surface.

Because of researchers' desire to solve the shortcomings of PC, such as sensitivity to notch and difficulty in processing and high cost, blends of PC have been the focus of much attention. PC/acrylonitrile-butadiene-styrene resin (PC/ABS) and PC/polyethylene (PC/PE) blends are two important blends whose mechanical properties and morphology have been thoroughly studied.¹⁰⁻¹⁵ However, the effects of boiling water aging on these blends have seldom been reported.

The objective of this investigation was to explore new factors influencing the formation of microcracks in PC. The effects of microcracks on the properties were also examined. In addition, the effects of water aging on polycarbonate/low-density polyethylene (PC/LDPE) blend and PC/ABS blend were investigated.

EXPERIMENTAL

Materials and specimen preparation

PC (Makrolon 2858) was produced by Bayer Co. LDPE, Q200 [melt flow index (MFI) = 0.9 g/10 min] was obtained from Shanghai Petrochemical Co. (China). ABS was made by Chimei Plastics Co. (China). The PC/LDPE blend (weight ratio of PC/LDPE was 80/20) and the PC/ABS blend (weight ratio of PC/ABS was 80/20) were prepared by an SHL-35 corotating twin-screw extruder with $L/D = 25$. Before extrusion, the PC was dried for 12 h at 120°C, and ABS was dried for 12 h at 80°C. The extruded strands were dipped in a cool water bath and chopped into granules about 5 mm long. Before injection molding, the granules of PC and the two blends were dried for 10 h at 100°C.

Boiling water treatment

Water aging was done through a commutative process. First, the injection-molded samples were immersed in boiling deionized water for 12 h and then in cool deionized water for another 12 h. A cycle was carried out in 1 day. At the end of a cycle, mechanical properties were measured. Each sample had 20 cycles in the experiment.

Measurement of mechanical properties

Tensile properties were measured on an Instron tester at a crosshead speed of 10 mm/min according to ASTM D638. Notched Izod impact strength was tested

on a Ray-Ran Universal Pendulum Impact tester at a pendulum speed of 3.5 m/s according to ASTM D256 and the dimension of the samples was $63.5 \times 12.66 \times 3.18$ mm. Flexural properties were tested on the Instron tester using a three-point-loading rig, and the central head loaded on the specimen at the speed of 2.0 mm/min according to ASTM D790. In each of the tests, at least five samples were tested and the average results were reported.

Thermal analysis

Samples for thermal analysis were cut from the injection-molded sample bars at the same place. The glass-transition temperatures of the samples were measured by differential scanning calorimetry (DSC, Mode Pyris 1; Perkin Elmer Cetus Instruments, Norwalk, CT). The samples were dried at 120°C for 12 h before being measured and then measured in DSC from 50 to 200°C at a heating rate of 10°C/min.

Structure and morphology

The microcracks in PC were observed by an optics microscope and the fracture surface was investigated by a scanning electron microscope (Hitachi S-2150, Tokyo, Japan). Before observation, the fracture surface was sputtered with gold.

RESULTS AND DISCUSSION

Effect of boiling water aging on mechanical properties

The effects of boiling water aging on the tensile strength and elongation at break of PC, PC/ABS, and PC/LDPE blends are shown in Figure 1. The tensile strength of PC and the blends increased after the first 4-day aging. The increase in tensile strength should be ascribed to the annealing effect of PC.⁶ The annealing effect of PC on the mechanical properties was reported to reduce localized stresses and increase short-range order. After 4 days, the tensile strength of PC decreased with increased aging time; however, the tensile strength of the PC/ABS and PC/LDPE blends changed only slightly. The elongation at break of PC and the PC/ABS blend decreased rapidly in the first 2-day aging. The drop in elongation at break indicated that the PC and the PC/ABS blend had a ductile-brittle transition. The elongation at break of the PC/LDPE blend experienced little change after aging.

The effects of aging time on the notched Izod impact strength are shown in Figure 2. After the first 2-day aging, the impact strength of all the materials decreased by varying degrees. The impact strength of PC decreased by 90% (from 913 to 93 J/m), the impact strength of the PC/ABS blend decreased by 78% (from

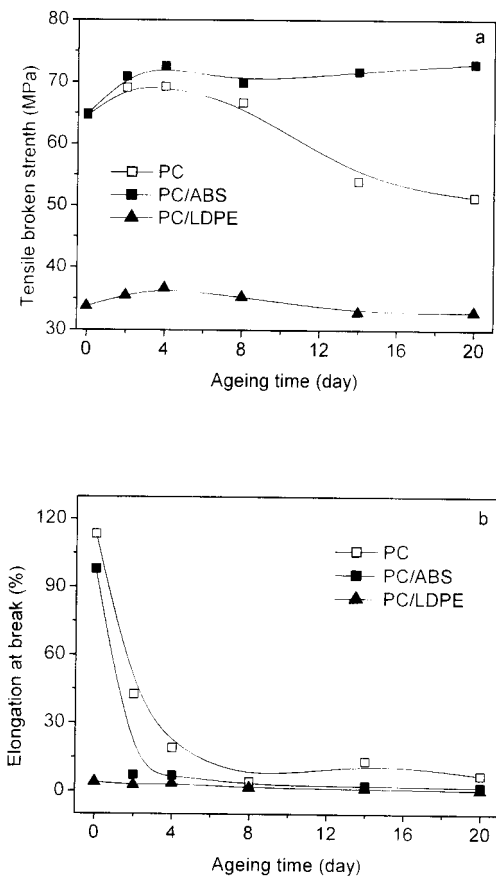


Figure 1 Effect of aging time on (a) tensile strength and (b) elongation at break.

725 to 155 J/m), and the impact strength of the PC/LDPE blend decreased by 33% (from 550 to 371 J/m). Even though the impact strength of PC and the PC/ABS blend was higher than that of PC/LDPE blend, the impact strength of PC and the PC/ABS blend nevertheless decreased sharply and was second to that of the PC/LDPE blends after the 2-day aging. By this finding, it can be said that the PC/LDPE blend has

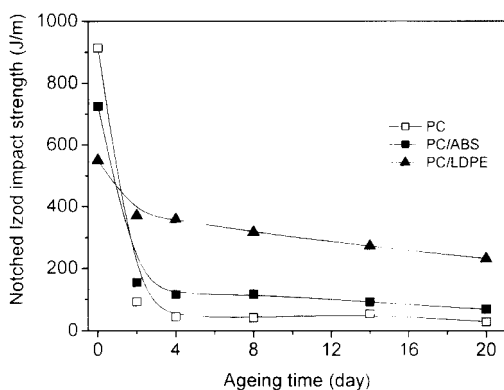


Figure 2 Effect of aging time on Izod notched impact strength.

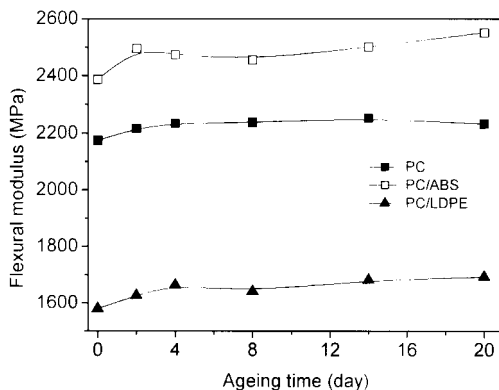


Figure 3 Effect of aging time on the flexural modulus.

much higher resistance to boiling water than either PC or the PC/ABS blend.

The effects of aging time on the flexural modulus are shown in Figure 3. The flexural modulus of all the materials increased after the first 4-day aging. After that, the aging time had only a slight effect on the flexural modulus.

Effect of boiling water aging on thermal properties

DSC thermograms for the PC, PC/ABS, and PC/LDPE blends are shown in Figure 4 and the data are listed in Table I. The glass-transition temperature (T_g) of PC was 145°C before aging. The T_g of the PC component in the PC/ABS blend was 139.7°C before aging. It was reported that PC and the styrene-acrylonitrile copolymer (SAN) in ABS had a certain compatibility,¹⁶ so the T_g of the PC component was lower than that of pure PC. The T_g of the PC component in the PC/LDPE blend was 145.3°C before aging, which was very close to the T_g of pure PC. This result implied poor compatibility of the PC/LDPE blend.

The T_g of PC and the PC component in the PC/ABS and PC/LDPE blends decreased by about 3°C after the first 2-day aging. Golovoy and Zinbo⁴ reported that the weight-average molecular weight of PC decreased with increased aging time. It is well known that the T_g of a polymer decreases with a decrease in the average molecular weight. By increasing the aging time from 2 to 20 days, the T_g of PC and the PC component in the blends remained unchanged. Narkis and Bell³ reported that during the water boiling step of PC, its molecular weight distribution was modified by hydrolytic degradative reactions and by a removal process through leaching of low molecular weight species. The observed change in T_g should reflect the change in the average molecular weight occurring by the two opposing effects.

From the thermograms shown in Figure 4, an abnormal heat peak at the temperature of glass transition of PC and the PC component in the PC/ABS and

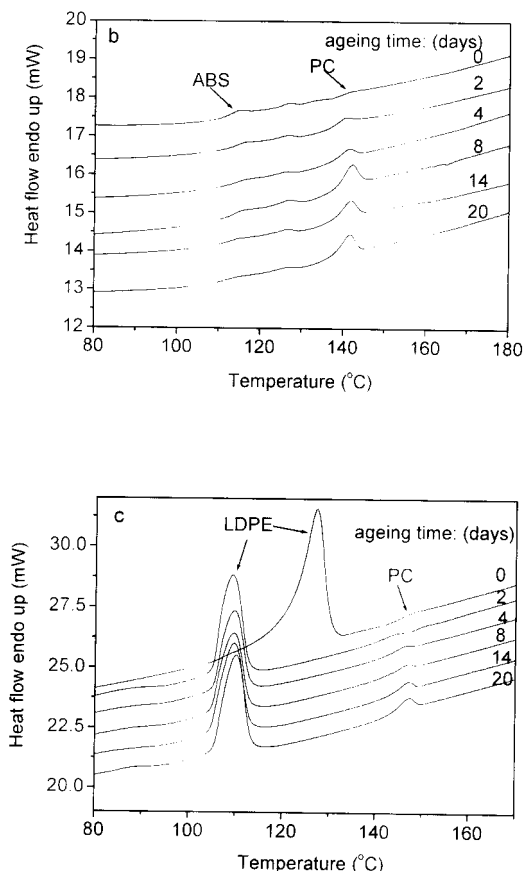


Figure 4 Effect of aging time on the thermal properties of (a) PC, (b) PC/ABS, and (c) PC/LDPE blends.

PC/LDPE blends may be observed to have grown significantly with the increasing aging time. From Table I, it may be seen that the T_g of the ABS component in the PC/ABS blend changed very little after aging. The melting temperature (T_m) of the LDPE component in PC/LDPE decreased by 18°C from 127.2 to about 109.2°C in the first 2-day aging, and changed only slightly with further increases of aging time.

Morphology of the impact-fracture surface

Morphology of the middle part of the impact-fracture surface of the samples before aging and after 20-day aging is shown in Figure 5. Typical ductile morphology may be observed on the PC fracture surface with extensive riblike lines parallel to the direction of crack propagation. After the 20-day aging of the PC specimen, an absolutely different impact-fracture morphology was observed, as shown in Figure 5. The fracture surface was very smooth and the microcracks were present on the fracture surface. For the PC/ABS blend, the difference on the fracture surface of the samples before aging and after aging was also very obvious. The ductile morphology could be seen on the fracture surface. After aging for 20 days, the fracture surface

was smooth but the microcracks could not be seen. Based on observations of the fracture surfaces of PC and the PC/ABS blend, the two materials should have experienced a ductile–brittle transition, as mentioned earlier in the analysis of mechanical properties. The fracture surfaces of the PC/LDPE blend before aging and after aging were very coarse [shown in Fig. 5(c₁), (c₂)]. The change in the fracture surface of the PC/LDPE blend was not as obvious as that in PC and the PC/ABS blend. Thus, the notched Izod impact strength of the PC/LDPE blend did not change to the same degree as did the PC and PC/ABS blend after aging.

The fracture surface of the PC sample after aging for 20 days and then treated at 160°C for 6 h is shown in Figure 5(d), where the microcracks may also clearly be seen on the fracture surface. The morphology of the sample after treatment was quite similar to the morphology of the sample before treatment [Fig. 5(a₂)].

Formation of microcracks

The morphologies of injection-molded PC samples aging for 4, 8, and 20 days are shown in Figure 6. The water-filled microcracks, usually having a disc shape and light-reflecting properties, may be seen clearly. The distribution of microcracks was irregular and not

TABLE I
 T_g Values of PC and PC/ABS and PC/LDPE Blends and T_m Values of PC/LDPE Blend after Aging

Aging time days	PC/ABS blend			PC/LDPE blend	
	PC T_g (°C)	$T_{g,PC}$ (°C)	$T_{g,ABS}$ (°C)	$T_{g,PC}$ (°C)	$T_{m,LDPE}$ (°C)
0	145.0	139.7	110.3	145.3	127.2
2	143.2	136.8	111.9	141.5	109.2
4	142.0	136.6	111.2	142.5	109.6
8	142.6	136.8	111.1	141.9	109.5
14	143.1	136.2	111.0	142.1	109.6
20	143.1	135.9	111.6	142.3	110.1

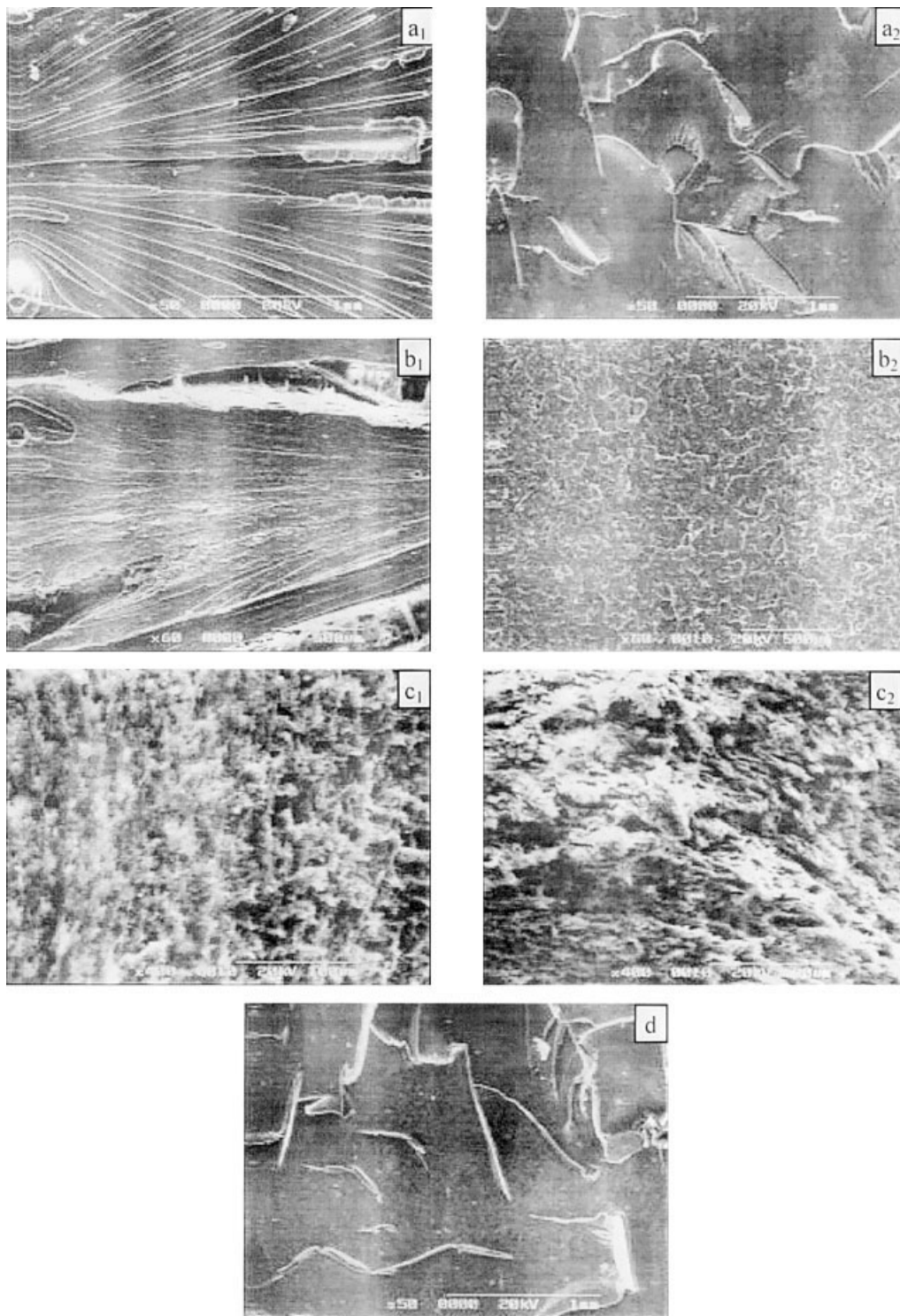


Figure 5 Notched Izod impact fracture surfaces of PC, PC/ABS, and PC/LDPE blends. Before aging: (a₁) PC; (b₁) PC/ABS; (c₁) PC/LDPE. After aging for 20 days: (a₂) PC; (b₂) PC/ABS blend; (c₂) PC/LDPE blend. (d) PC (treatment at 160°C for 6 h).

in orientation. The number of microcracks increased with aging time extension. Moreover, the maximum size of a microcrack was about 1.5 mm. From Figure 7, it may be seen that the microcracks always formed around impurities or air bubbles that were generated during the injection molding.

The PC samples became saturated with water after being exposed to boiling water for 12 h, and a balance of water absorption and desorption was reached between the samples and the surrounding boiling water. When the samples were removed to cool water, the samples became supersaturated with water and the

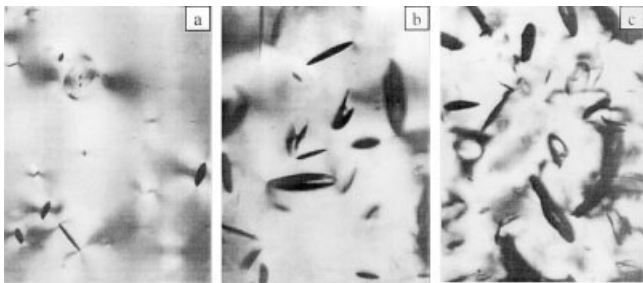


Figure 6 Microcracks in PC specimens after aging for (a) 4 days, (b) 8 days, and (c) 20 days ($\times 25$).

water tended to diffuse out from the specimens. Because of the slow diffusion of water from the thick PC specimens in the cool water in our experiment, the excess dissolved water would form small water pockets around impurities or in bubbles because there were always some flaws between the PC matrix and the impurities. By increasing the amount of water coming into the small pockets, a static pressure would act on the wall of the pocket, and then the small water pockets grew into microcracks with characteristic disc shape. By increasing the extent of aging time, the microcracks grew larger with circles like annual rings of a tree. A circle formed during one aging cycle of 1 day. Because PC is sensitive to cracking and crazing, when the microcracks formed, the notched Izod impact strength and elongation at break should both have decreased.

To test whether the microcracks could recover, a thermal treatment was done. The PC, PC/ABS, and PC/LDPE blend samples were treated in a vacuum oven without any external pressure at 160°C for 6 h. The notched Izod impact strength was measured and the morphology of PC was observed after the treatment. The impact strength of the samples is shown in Figure 8. The impact strength of the samples increased only slightly after treatment. The result indicated that some of the small microcracks might have closed. However, the impact strength was far less than that of the sample before aging. Traces of the microcracks in the PC sample may also be observed, as shown in Figure 9.



Figure 7 Formation of microcracks around impurities and bubbles in PC ($\times 25$).

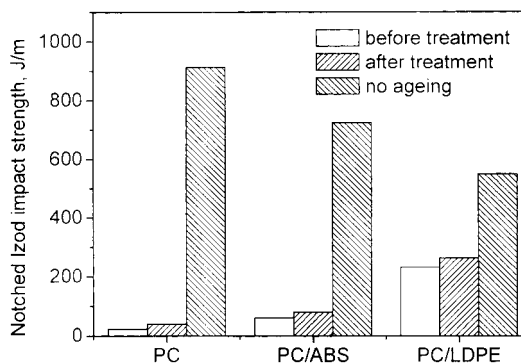


Figure 8 Effect of treatment at 160°C on the notched Izod impact strength for PC, PC/ABS blend, and PC/LDPE blend.

Kunori and Geil^{17,18} and Leclair and Favis¹⁹ reported that there was no adhesion between the PC and the high-density polyethylene (HDPE), and the HDPE inclusion was loosely sitting in the holes in the PC matrix. Leclair and Favis¹⁹ proposed an idealized diagram of HDPE in PC [shown in Fig. 10(a)]. When the PC/LDPE blend was in a supersaturated state in cool water, the excess dissolved water would diffuse to both the external environment and the void between PC and LDPE inclusions. Furthermore, the static pressure would be distributed around the wall of the void. The possibility of microcrack formation would be less than that in PC. The PC/LDPE blend would be more negatively affected than PC by the formation of microcracks.

It was previously reported that PC is only partially compatible with ABS.²⁰ The excess dissolved water might cluster at the poorly adhering interfaces between ABS and PC. For a large number of ABS domains dispersed in the PC matrix, there would be quite a number of points clustered with water. The microcrack would not grow large and ABS domains would put an end to some of the microcracks. Thus, the tiny microcracks could not be observed on the impact fracture surface [shown in Fig. 5(b)].

CONCLUSIONS

The boiling water aging had great effects on the mechanical properties of PC, PC/ABS, and PC/LDPE



Figure 9 Trace of microcracks in PC after treatment at 160°C ($\times 40$).

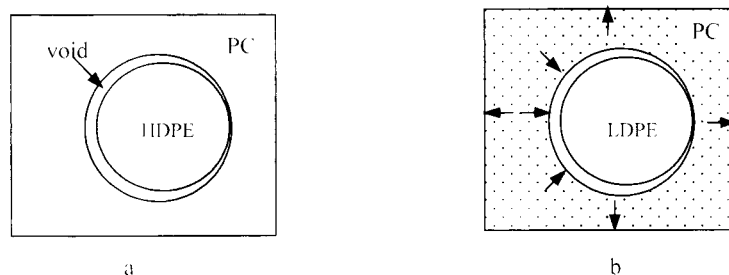


Figure 10 Idealized diagrams of HDPE in PC and water dissipation of PC/LDPE blend: (a) PC/HDPE blend; (b) PC/LDPE blend with supersaturated water.

blends. The elongation at break and notched impact strength of PC and the PC/ABS blend experienced a sharp decrease after aging. The PC/LDPE blend showed more resistance to boiling water than did either PC or the PC/ABS blend.

The T_g of PC and PC in the PC/ABS and PC/LDPE blends decreased after aging. The T_g of the ABS component in the PC/ABS blend did not change after aging. The T_m of the LDPE component in PC/LDPE decreased in the first 2 days of aging, and did not undergo much change with further increases of aging time.

The morphology of the fracture surface of PC and PC/ABS blend had a ductile–brittle transition after aging. The fracture surface of the PC/LDPE blend scarcely changed.

The water clustering around the impurities and bubbles in PC led to the formation of microcracks, which were unrecoverable. Compared with the resistance of PC and the PC/ABS blend, the higher resistance of the PC/LDPE blend was attributed to its special structural morphology.

References

1. Ito, E.; Kobayashi, Y. *J Appl Polym Sci* 1978, 22, 1143.
2. Narkis, M.; Nicolais, L.; Apicella, A. *Polym Eng Sci* 1984, 24, 211.
3. Narkis, M.; Bell, J. P. *J Appl Polym Sci* 1982, 27, 2809.
4. Golovoy, A.; Zinbo, M. *Polym Eng Sci* 1989, 29, 1733.
5. Robert, J. G.; John, R. M. *J Appl Polym Sci* 1979, 24, 1269.
6. Gardner, R. J.; Martin, J. R. *DPE ANTEC Tech Papers*, 1978, 24, 328.
7. Petrie, S. P.; Dibenedetto, A. T.; Miltz, J. *Polym Eng Sci* 1978, 18, 1200.
8. Ram, A.; Zibler, O.; Kenig, S. *Polym Eng Sci* 1985, 25, 577.
9. Qayyum, M. M.; White, J. R. *J Appl Polym Sci* 1991, 43, 129.
10. Wu, J. S.; Shen, S. C.; Chang, F. C. *Polym J* 1994, 26, 33.
11. Kim, B. K.; Yoon, L. K.; X. E. *J Appl Polym Sci* 1997, 65, 795.
12. Zhang, X. F.; Chen Y. S.; Zhang, Y. *J Appl Polym Sci* 2001, 81, 831.
13. Yang, M.; Zhang, Z. J. *Polym Eng Sci* 1998, 38, 879.
14. Mekhilef, N.; Kadi, A. A.; Aji, A. *Polym Eng Sci* 1992, 32, 894.
15. Mascia, L.; Valenza, A. *Adv Polym Technol* 1995, 14, 327.
16. Kim, W. N.; Burns, C. M. *Polym Eng Sci* 1988, 28, 1115.
17. Kunori, T.; Geil, P. H. *J Macromol Sci Phys Part B* 1980, 18, 93.
18. Kunori, T.; Geil, P. H. *J Macromol Sci Phys Part B* 1980, 18, 135.
19. Leclair, A.; Favis, B. D. *Polymer* 1996, 37, 4723.
20. Keitz, J. D.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1984, 29, 3131.