Thermal Aging of Impact-Modified Polycarbonate

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SYNOPSIS

Glassy polymers undergo relatively rapid physical aging just below their glass transition temperatures that can lead to embrittlement of normally tough materials like polycarbonate (PC). One approach for solving the embrittlement problem is to incorporate an impact modifier that can cause toughening when the matrix loses its inherent ductility due to physical aging. The effects of thermal aging below the glass transition temperature of polycarbonate on selected properties of blends of PC with various core-shell impact modifiers have been studied. Observed changes in mechanical properties are related to rubber content, free volume, fracture morphology, discoloration, enthalpy relaxation, glass transition temperature, intrinsic viscosity, and dynamic mechanical behavior. Blend mechanical properties are affected by chemical changes in the impact modifier that occur simultaneous with the physical aging of the PC matrix. The degradation mechanisms involved reduce the effectiveness of the modifier for toughening and also lead to a loss of molecular weight of the PC matrix. Blends containing 10% methacrylated butadiene-styrene (MBS) core-shell impact modifiers give the maximum extension of time to embrittlement at 135°C in air. More thermally stable modifiers are required for further extending the ductile mode of failure for physically aged PC blends.

INTRODUCTION

Physical aging of amorphous polymers is a consequence of the nonequilibrium nature of the glassy state.[1,2] There is a driving force for such materials to proceed toward a more dense equilibrium state. This process is extremely slow at ambient conditions for engineering polymers, but is accelerated by annealing just below the glass transition temperature, T_g.[1-4] During the last three decades, a number of studies demonstrated the effect physical aging can have on properties,[3-8] while others have offered theories or models for understanding the mechanism[9-12] and for quantitatively predicting this behavior.[13-20]

Polycarbonate (PC) is an important, amorphous, engineering material because of its outstanding properties, and consequently the effects of physical aging on the properties of PC have been studied extensively.[7-11,17-35] Polycarbonate rapidly loses its toughness during physical aging at temperatures just below T_g. To expand the usefulness of PC in a variety of applications, it is important to explore ways to prevent or minimize this loss in toughness that accompanies such thermal history. Polymers that are inherently brittle can often be toughened by addition of suitable impact modifiers. Thus, one approach to the physical aging problem is to blend such materials with PC to provide toughening of this matrix after it loses its inherent toughness through physical aging.[36-40] The purpose of this study is to examine in detail the effectiveness of this strategy using a series of blends containing various amounts of several core-shell impact modifiers. In addition to monitoring the impact strength as a function of aging time, changes in enthalpy, density, molecular weight, thermal reversibility, dynamic mechanical behavior, and fracture morphology were also examined. It is shown that chemical degradation of the impact modifier is a major concurrent mechanism that must be considered in addition to physical aging. An important fundamental question is whether an ideally stable modifier could completely circumvent embrittlement by physical aging or only delay its occurrence.[36-39]

EXPERIMENTAL

The bisphenol-A PC used is a commercial product of the Dow Chemical Co. designated as Calibre 300 having $M_w = 36,000$. It has a glass transition at approximately 151°C by thermal analysis using the onset method and does not crystallize when melt processed by conventional methods. The impact modifiers used are commercial products of the Rohm and Haas Co. with the designation of Acryloid KM 680, EXL 3607, EXL 3300, and EXL 3330. KM 680 is a methacrylated butadiene-styrene (MBS) material typically used for impact modification of poly(vinyl chloride). Details of this grafted emulsion rubber have been described.[41,42] The particles are about 0.18 μm in diameter and contain about 80% butadiene-based rubber as a core that is grafted with 20% methylmethacrylate (MMA)-based chains to produce a shell. Three other modifiers of the core-shell type with a poly(methylmethacrylate) (PMMA)-based shell but reported to be thermally more stable than KM 680 were also used. They are available in pelletized form, rather than as powders. EXL 3607 is an MBS modifier similar to KM 680. EXL 3300 (previously designated KM 330) is similar to these MBS modifiers except the core is an n-butyl acrylate-based elastomer. EXL 3330 has roughly twice the particle diameter of EXL 3300. The majority of blends in this study were based on KM 680, with the three additional modifiers used for comparison.

Prior to mixing, the PC pellets were dried for a minimum of 24 h in an air-circulating oven at 105°C, while the modifiers were dried at 75°C. Each batch was melt blended by two passes through a Killion single-screw laboratory extruder (D = 1.0 in, L/D = 30) to ensure uniform mixing. The extruded strand was pelletized in-line and dried at 100°C overnight prior to injection molding into tensile (ASTM D-638) and Izod (ASTM D-256) bars using an Arburg Allrounder 305 molding machine. Samples were aged at various temperatures (controlled within ± 1°C) in either a vacuum or an air oven. In some cases, a heat treatment of molded bars at 165°C (above the T_g of PC) was used to reverse the effects of physical aging and to examine chemical degradation at this temperature. For this treatment, the samples were wrapped with aluminum foil and placed into a mold held closed by a compression press. Thus, exposure to air was somewhat limited.

Tensile specimens were tested using an Instron 1137 with a computerized data acquisition system at a crosshead speed of 0.2 in/min. Notched Izod impact strengths were measured using a pendulum type tester. For some specimens, a new razor blade was pressed into the standard machine-made notch to give a sharp notch. A Dynatup GRC 703-I instrumented impact testing system was used for investigating the load and the energy dissipation process during impact at room temperature. The tup weight was 21 lb and the testing velocity was fixed at 6 ft/s. At least five bars were tested to give each data point reported. After thermal aging, specimens were kept at room temperature for 24 h before testing.

The enthalpy relaxation during aging for PC and its blends was monitored by a Perkin-Elmer Differential Scanning Calorimetry DSC-7 System at a heating rate of 20°C/min. Unless stated otherwise, the samples used for DSC analysis were cut from molded bars and included the entire cross-section. In some cases, the samples were cut from the molded bar so that only the core region or the surface (skin) region was included.

The densities of small samples cut from the entire cross-section of as-molded and aged impact bars were measured at 27°C using a calcium nitrate-based aqueous density gradient column (DC-1 single column, Techne Inc.) according to ASTM D-1505-60T. The typical density gradient employed was 0.035 g/mL per 700 mm of column length.

Intrinsic viscosity was measured at 25°C using an Ostwald-Fenske capillary viscometer. Solutions were prepared by dissolving 0.1 g sample in 10 mL methylene chloride. Other concentrations were obtained by dilution with additional solvent.

Dynamic mechanical properties at 3 Hz were measured in the single cantilever bending mode by a Polymer Laboratories DMTA at a heating rate of 2°C/min. The specimen cross-section was 12 × 3 mm^2 with a span of 8 mm.

A JSM-35C scanning electron microscope (SEM) was used to examine sample fracture surfaces. Samples were coated with gold/palladium (60/40) using a Pelco Model 3 Sputter Coater prior to viewing.

MECHANICAL PROPERTIES

Notched Izod Impact Strength

The choice of physical aging temperature is important to achieve the maximum effect in a practical time frame. Typically, 10 to 25°C below T_g provides a convenient aging temperature to observe major mechanical property changes in PC.[1-4,23,32] Figure 1 shows the effect of aging temperature on the time to reach the ductile-brittle transition of injection-
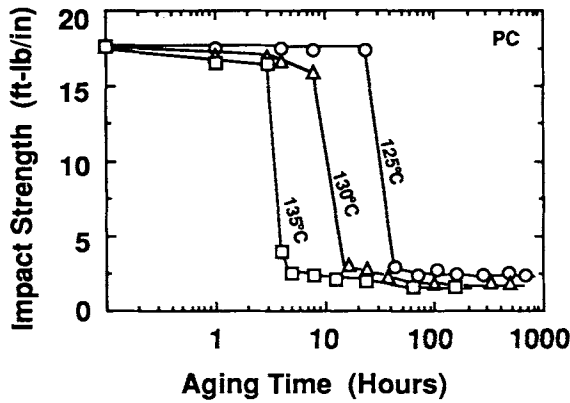
Figure 1   Effect of aging time in air at various temperatures on Izod impact strength (standard notch) of injection-molded PC.

Figure 2   Effect of KM 680 content on Izod impact strength of as-molded PC/KM 680 blends with standard and sharp notches.

molded PC. In this and subsequent plots with a logarithmic time scale, the points located directly on the abscissa represent the properties for as-molded samples. The Izod impact values for PC near the transition region fluctuated between two extremes, either above 15 ft-lb/in or below 4 ft-lb/in. The time to embrittlement was selected as the point where 80% of the tested bars were embrittled. This transition was complete after 45, 16, and 5 h of aging at 125, 130, and 135°C, respectively. Similar results have been reported in previous studies.[4,23-27] Since molecular weight, specimen thickness, and other factors influence the mechanical property response to the aging process,[4,21-27] there is considerable variation in the reported times to embrittlement.

The notched Izod impact strength of most polymers is a function of notch radius.[29,43,44] The standard notch, with radius of 0.01 ± 0.002 in, can be sharpened with a razor blade to increase the stress concentration. Impact strengths of as-molded PC/KM 680 blends with standard and sharp notches are shown in Figure 2. Impact data for as-molded PC/EXL blends are similar. The sharp notch causes a catastrophic reduction of impact strength for PC and the blends containing 2% modifier. PC blends with 5% or more of these modifiers failed in a tough mode, although the impact values were reduced with increasing modifier content. Thus, with a sufficient amount of modifier to enhance local shear yielding,[45] the increased stress concentration effect caused by a sharpened notch can be effectively depressed. The effect of specimen thickness on impact strength is summarized in Table I. Neat PC fails in a tough mode when sample thickness is within the range from 0.065 to 0.125 in (1.6 to 3.2 mm), but fails in a brittle mode when the thickness is 0.25 in (6.4
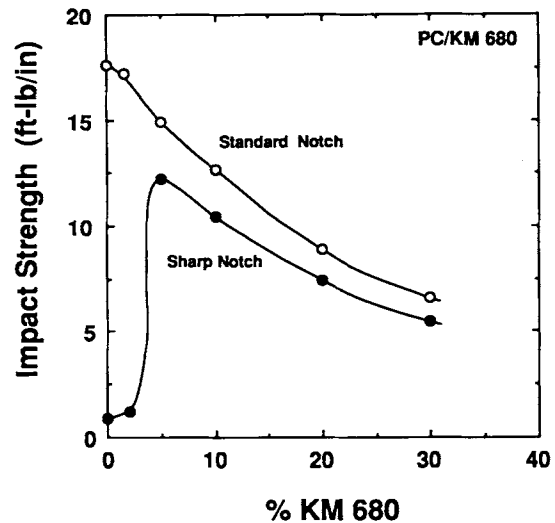
mm) or greater owing to a transition from plane stress to plane strain conditions as thickness increases.[26-30] Blends containing 5 to 20% KM 680 fail in a tough mode over the whole sample thickness range.

Typical force-energy-time curves for as-molded PC and a PC/KM 680 (95/5) blend obtained by instrumented impact testing[38,46] are shown in Figure 3. It is apparent that the modified PC retains the characteristic ductile deformation features of PC, although failure occurs at a somewhat lower load due to the softening effect of the modifier. The effect of modifier content on the maximum loading force is shown in Figure 4. The load level gradually decreases as the KM 680 content is increased for specimens with standard notches. This lower load, rather

Table I   Effect of Specimen Thickness on Izod Impact Strength[a] of PC and Selected PC/MBS Blends

Material	Thickness (in)				
	0.065	0.075	0.105	0.125	0.250[b]
PC	12.60	13.45	13.81	17.60	1.92
PC/KM 680					
(95/5)	—	13.39	—	14.95	13.40
(90/10)	—	11.13	—	12.70	11.42
(80/20)	—	7.80	—	8.87	8.84

[a] Units = ft-lb/in; standard notch.
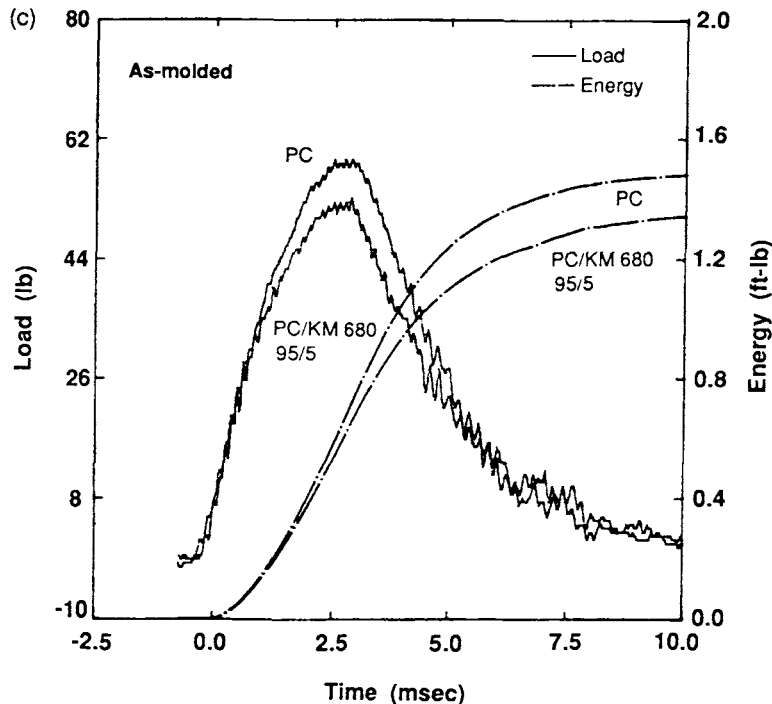[b] Compression-molded specimen.

Figure 3 Typical load-time plots from instrumented impact test of as-molded PC and PC/KM 680 (95/5) blend. (Oscillations are caused by ringing in force transducer.)

than reduced deformation, accounts for the diminution of impact strength when modifier is added to PC. For PC specimens with sharp notches, the maximum impact load is dramatically reduced. As impact modifier is added, the impact load increases and goes through a maximum at about 10% MBS.
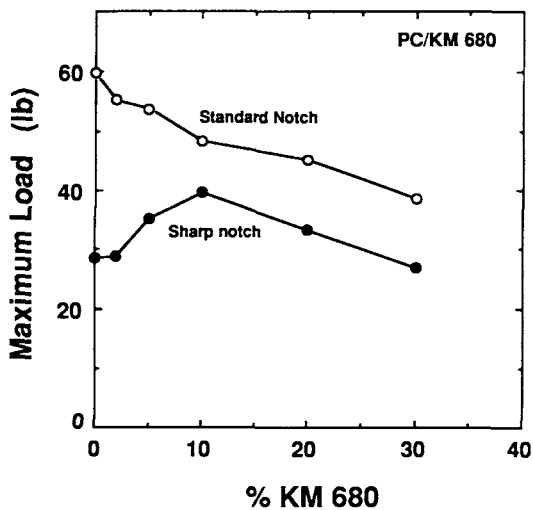

Figure 4 Effect of KM 680 content on maximum load during impact of as-molded PC/KM 680 blends with standard and sharp notches.

These trends roughly parallel the results for the Izod impact strength shown in Figure 2.

Tensile Properties

Tensile properties of as-molded PC and its blends with KM 680 and EXL 3300 are summarized in Table II. Typically, there is a decrease in tensile strength and modulus on addition of the core-shell modifier. Blends of PC with all of the EXL modifiers have somewhat higher moduli and tensile strengths at yield compared to the PC/KM 680 blends. The moduli of PC blends with 2% EXL 3300 is slightly higher than that of PC, but on the whole the properties are lower as the modifier content is increased. The elongation at break data have a higher average standard deviation, up to 40%, for PC and blends containing 2% modifier; however, the standard deviation is gradually reduced to lower than 15% for blends containing 20% modifier.

Effect of Aging on Impact Strength

Izod impact strength of PC/KM 680 blends was monitored as a function of time at 125°C in a vacuum oven, and the results are shown in Figures 5 and 6. For injection-molded specimens with the standard notch, only PC and the PC/KM 680 (98/

Table II   Tensile Properties of As-Molded Blends

Material	Modulus[a] (10³ psi)	Yield Stress[a] (10³ psi)	Elongation[b] (%)
PC	295	8.10	129
PC/KM 680			
(98/2)	295	7.77	> 130
(95/5)	275	7.34	> 130
(90/10)	259	6.76	> 130
(80/20)	217	5.62	> 130
(70/30)	173	4.56	125
PC/EXL 3300			
(98/2)	312	8.11	> 130
(95/5)	282	7.65	> 130
(90/10)	264	7.15	> 130
(80/20)	220	6.00	> 130

[a] Standard deviation is under 5%.
[b] Standard deviation is under 30% of values shown and even lower for blends with higher modifier levels.

2) blend embrittled (after 40 and 900 h, respectively) while all compositions with higher KM 680 content remained ductile over the aging time scale used as seen in Figure 5. Figure 6 shows the impact strength of injection-molded specimens having a sharp notch. The impact strengths of PC and the PC/KM 680 (98/2) blend were reduced dramatically by the sharp notch, and all the specimens failed in a brittle fashion. Modified PC containing 5% or more KM 680 remained ductile during aging at 125°C up to 800 h; however, the sharp notch reduced the impact strength by about 15 to 20% relative to specimens with the standard notch. Compression-molded samples were also examined and showed similar results.
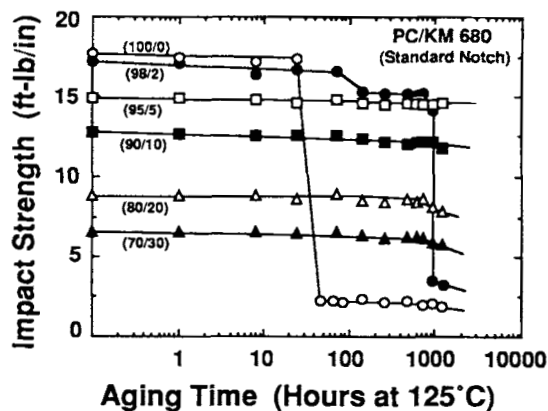

Figure 5   Izod impact strength (standard notch) of injection-molded PC and PC/KM 680 blends after aging in a vacuum oven at 125°C for various lengths of time.
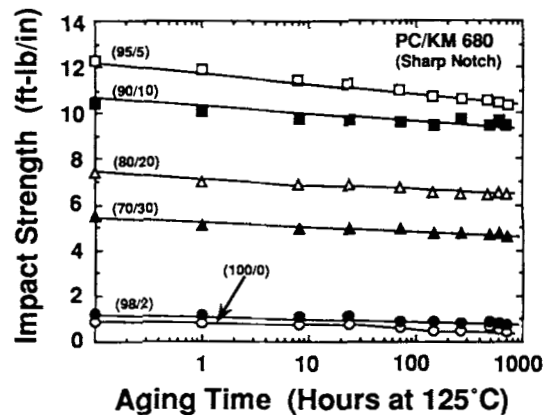

Figure 6   Izod impact strength (sharp notch) of injection-molded PC and PC/KM 680 blends after aging in a vacuum oven at 125°C for various lengths of time.

It is not clear whether the blends containing more than 2% KM 680 shown in Figures 5 and 6 would eventually embrittle at the aging temperature of 125°C or not. To gain insight into this question, it was decided to increase the aging temperature to 135°C since this should considerably accelerate the time scale of the experiments. It was further decided to conduct the aging in an air convection oven rather than in a vacuum oven for two reasons. First, this greatly expanded our capacity to age samples. Second, most practical uses of such materials will involve an air environment so this method of aging better simulates high-temperature applications. Thus, all subsequent results are for samples aged at 135°C in air. As will become clear later, it would be useful to compare air vs vacuum aging in more detail to better understand the possible separate effects of temperature and environment (O_2 and H_2O) on chemical aging.

As shown in Figure 7, embrittlement occurs much more rapidly when samples are aged in air at 135°C. Limited experiments shown in Figure 8 demonstrate that aging PC/KM 680 blends in air gives somewhat different results than aging in vacuum (where moisture and oxygen concentrations are much lower). The PC/KM 680 (80/20) blend became embrittled after 360 h of aging in air at 135°C, but it had a similar Izod value as the as-molded sample after 480 h of aging in vacuum at 135°C. In addition, the extent of surface discoloration of blend specimens is clearly greater when aged in an air environment. As shown in Figure 7, embrittlement occurred for all PC/KM 680 blends after a certain aging time at 135°C in air that depends on the blend composition. Table III summarizes the time to embrittlement for blends of PC with all of the core-shell modifiers when
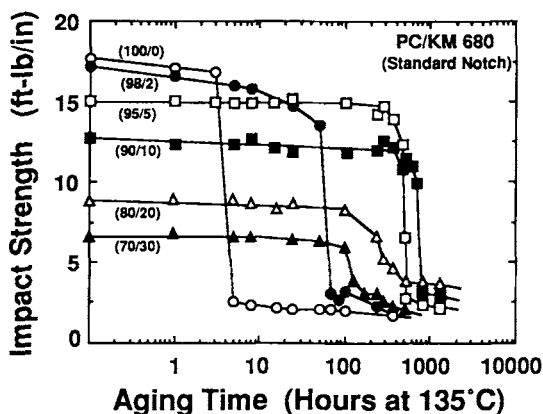
Figure 7   Izod impact strength (standard notch) of PC and PC/KM 680 blends aged in an air oven at 135°C for various lengths of time.

aged in air at 135°C. The data demonstrate that the time for embrittlement of PC under these conditions is extended by the addition of the impact modifier, but the phenomenon is not eliminated altogether. After embrittlement, the Izod values are similar for all samples except blends containing 20% or more modifier, which tend to exhibit somewhat higher levels of toughness.

Figure 9 illustrates typical load–energy–time curves during an impact test for as-molded PC and the PC/KM 680 (95/5) blend after aging for 7 h at 135°C in air. Comparison with Figure 3 shows that heat aging depresses the maximum load achieved for PC while for the PC/KM 680 (95/5) blend the change is not appreciable within this aging time frame. Aging dramatically reduced the extent of deformation and, thus, energy dissipation for PC, but
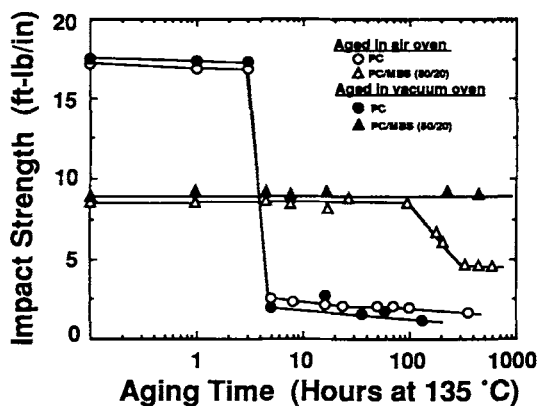

Figure 8   Comparison of Izod impact strength (standard notch) of injection-molded PC and PC/KM 680 (80/20) aged in a vacuum oven and an air oven at 135°C.

the ductile failure mode was maintained after aging for the blend containing 5% KM 680.

Figure 10 shows the time to embrittlement at 135°C in air as a function of the content of KM 680 and EXL 3607. PC containing 10% of either modifier exhibits the maximum extension of the embrittlement time. Discoloration of blend specimens accompanied aging, especially in air, in all cases. This yellowing of the specimen clearly indicates some chemical changes take place at 135°C, as will be discussed more fully later.

Thermal Reversibility

Physical aging effects can be erased by heating the aged material above its T_g and rapidly cooling to ambient conditions.[1] In this study, some of the aged samples were subsequently heated at 165°C (T_g = 151°C) for 15 min and then immediately quenched to room temperature. Izod impact strengths (standard notch) of samples with different heat histories are compared in Table IV. The Izod impact strength of PC and its blends that embrittled by aging in air

Table III   Time to Embrittlement of Blends Aged at 135°C in Air

Material	Time to Embrittlement (h)	Impact Strength[a] (ft-lb/in)
PC	5	2.5
PC/KM 680		
(98/2)	70	3.0
(95/5)	520	2.8
(90/10)	800	3.0
(80/20)	360	4.6
(70/30)	125	3.9
PC/EXL 3607		
(98/2)	120	2.7
(95/5)	960	2.5
(90/10)	2280	1.7
(80/20)	1800	4.3
PC/EXL 3330		
(98/2)	910	3.1
(95/5)	> 4500	—
(90/10)	> 4500	—
(80/20)	2980	4.0
PC/EXL 3300		
(98/2)	120	2.9
(95/5)	> 4500	—
(90/10)	> 4500	—
(80/20)	2590	3.8

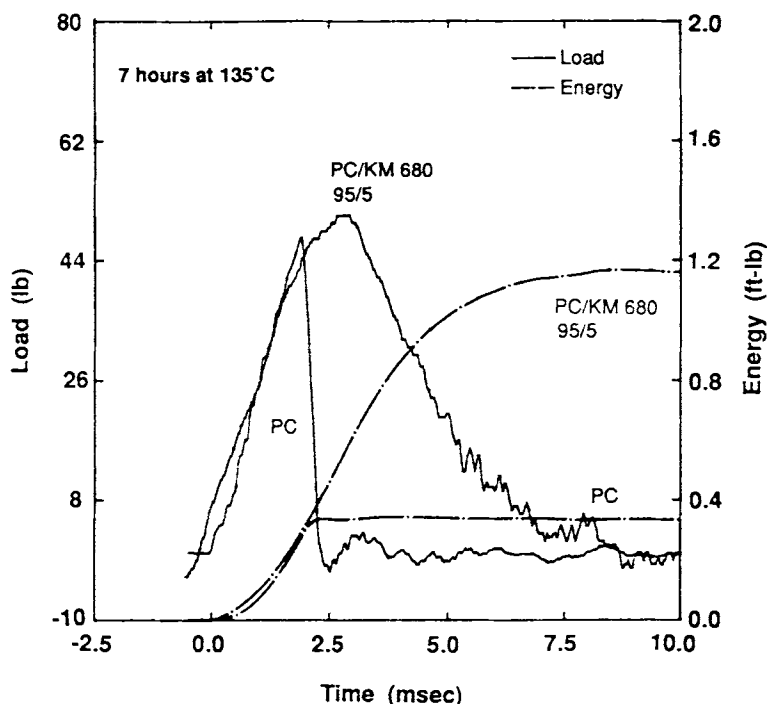[a] Notched Izod impact values after ductile to brittle transition.

Figure 9 Dynatup traces of load and impact energy of PC and PC/KM 680 (95/5) after aging in air at 135°C for 7 h.

could be restored by this heat treatment provided the modifier level was 10% or less. However, the impact strength of PC blends containing 20% or more modifier was not improved by this treatment but actually became worse. The extent of impact strength recovery depends on the aging history as shown by selected data for PC/MBS blends given in Table V. The data suggest that chemical deterioration accompanies the thermal aging process. The aging temperatures used in this study are sufficiently high to thermally crosslink and/or degrade butadiene-based rubber.[47-49] It has also been reported that PMMA may depolymerize at this temperature under certain circumstances.[50] We believe that the yellowing observed is caused by chemical changes in the rubber phase. Samples aged in air have a more intensely yellowed surface than those aged in vacuum. This difference is due to the extra thermooxidative change that occurs on the sample surface because of exposure to oxygen.[49] The discoloration of PC/EXL 3300 blend is much less than observed for PC/MBS blends due to the difference in the composition of the modifier core. n-Butyl acrylate rubbers are more stable toward thermal/oxidative changes than butadiene-based ones. The extent of discoloration caused by rubber degradation is a function of rubber content. While both chain scis-

sion and crosslinking can occur for butadiene-based elastomers, crosslinking is reported to be the predominant reaction.[47,48] Such a change in the rubber phase can lead to a reduced effectiveness of the impact modifier. Furthermore, free radicals formed in
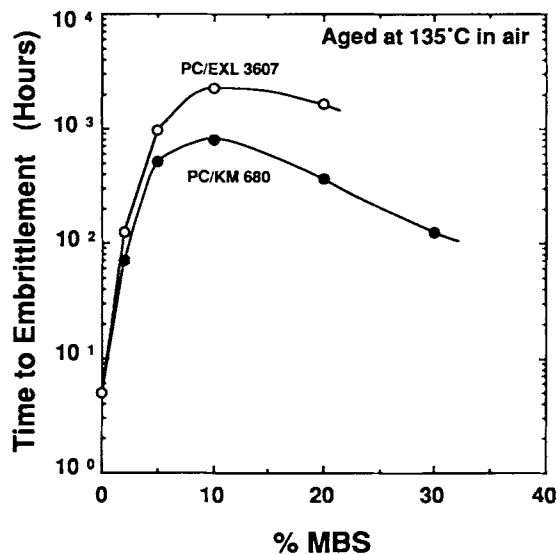

Figure 10 Effect of MBS modifier content on time to embrittlement in air at 135°C.

Table IV   Recovery of Notched Izod Impact Strength of Blends after Heating Above T_g

Material	Impact Strength (ft-lb/in)			Aging Time at 135°C[b] (h)
	As-Molded	Aged	Recovered[a]	
PC	17.6	2.5	17.5	5
PC/KM 680				
(98/2)	17.2	3.0	17.6	70
(95/5)	15.0	2.8	15.8	520
(90/10)	12.7	3.0	10.9	800
(80/20)	8.9	4.6	3.5	360
(70/30)	6.6	3.9	2.8	125
PC/EXL 3607				
(98/2)	16.6	2.8	17.1	120
(95/5)	15.5	2.5	15.0	960
(90/10)	13.0	1.7	6.7	2280
(80/20)	9.8	4.3	2.1	1800

[a] After thermal treatment at 165°C for 15 min (done in a closed but not evacuated mold) to reverse the physical aging of the PC matrix.
[b] Aging time to embrittlement in air.

Table V   Effect of Aging Time on Reversibility of PC/MBS Blends

Material	Time to Embrittlement at 135°C (h)	Aging Time in Air at 135°C (h)	Recovered[a] Impact Strength (ft-lb/in)
PC	5	5	17.5
		240	17.7
		480	17.5
PC/KM 680			
(98/2)	70	70	17.6
		240	16.7
(95/5)	520	520	15.8
		660	15.3
		850	14.5
(90/10)	800	800	10.9
		870	10.8
		950	9.8
(80/20)	360	360	3.5
		480	3.2
(70/30)	125	125	2.9
		480	2.0
PC/EXL 3607			
(98/2)	70	70	17.5
		600	16.3
(95/5)	960	960	15.0
		2590	13.6
		2760	3.0
(90/10)	2280	2280	6.7
		2760	4.4
(80/20)	1800	1800	2.1
		2760	1.8

[a] After thermal treatment at 165°C for 15 min (done in closed but not evacuated mold) to reverse the physical aging of the PC matrix.

Table VI   Growth of Yellowed Skin Layer of Blends during Aging in Air Oven[a]

PC/KM 680 Composition	10 d at 135°C		20 d at 135°C	
	Comp. Molded	Inj. Molded	Comp. Molded	Inj. Molded
(98/2)	30	33	43	45
(95/5)	22	30	35	37
(90/10)	19	20	27	28
(80/20)	18	19	24	26
(70/30)	18	18	22	24

[a] Values shown denote the thickness of yellowed layer in mil.

the particle shell may attack the polycarbonate chain, causing chain scission in the matix at lower temperatures than required for homolysis of neat PC.[51] These combined effects could render a thermally aged blend irreversibly brittle.

Closer examination of the discoloration that accompanies aging in air reveals that it begins at the surface and apparently progresses inward with aging time. This observation was made for both injection- and compression-molded specimens as summarized in Table VI. The rate of growth of the yellowed region tends to decrease with increased modifier content; however, blends with higher contents of mod-

ifier have sharper boundaries and darker color. Specimens aged in air have thicker and darker skin layers than those aged in a vacuum oven. As mentioned earlier, this is believed to be due to additional thermooxidative changes that can occur in an oxygen-rich environment.[49] To explore the effect of this chemically changed surface layer, the yellowed portion of the specimen surface was removed mechanically using a milling machine. Impact strengths of injection-molded specimens with and without removal of this layer are compared in Table VII. Milling reduced the average thickness from 125 to 57 mil for the blend containing 5% EXL 3607 and to

Table VII   Effect of Skin Layer on Notched Izod Impact Strength

Material	Thickness (mil)	Izod Impact Strength (ft-lb/in)		
		As-Molded	Aged[a]	Recovered[b]
Skin layer not removed				
PC	125	17.6	2.1	17.5
PC/EXL 3607				
(95/5)	125	15.5	2.5	15.0
(90/10)	125	13.0	1.7	6.8
(80/20)	125	9.8	4.3	2.1
PC/KM 680				
(80/20)	125	8.9	3.5	3.3
(70/30)	125	6.6	3.0	2.4
Skin layer removed by milling				
PC	75	13.5	1.7	13.7
PC/EXL 3607				
(95/5)	57	8.5	7.4	8.6
(90/10)	61	7.9	7.2	7.9
(80/20)	65	7.4	5.1	6.8
PC/KM 680				
(80/20)	75	7.8	7.0	7.3
(70/30)	77	6.3	5.0	5.8

[a] Izod impact strength of aged samples at the time of embrittlement for unmilled sample.
[b] Izod impact strength of aged samples after heating in a closed but not evacuated mold for 15 min at 165°C.

Table VIII Notched Izod Impact Strength[a] of Blends Due to Heating in Air at 135 and 165°C

Material	As-Molded	Hours at 135°C		Hours at 165°C[b]	
		100	200	100	200
PC	17.6	2.0	1.7	17.5	17.7
PC/KM 680					
(98/2)	17.2	3.1	2.2	16.5	15.7
(80/20)	8.9	8.2	6.9	4.9	4.3
PC/EXL 3607					
(98/2)	16.6	7.9	2.8	16.5	16.1
(80/20)	9.8	9.2	8.1	6.7	4.5
PC/EXL 3300					
(98/2)	17.1	7.6	2.9	17.5	16.2
(80/20)	12.3	12.1	11.0	9.4	1.0

[a] Units = ft-lb/in.
[b] Heating was done in a closed but not evacuated mold in an air oven.

77 mil for the blend containing 30% KM 680. The impact strength of as-molded but milled specimens were reduced somewhat, probably due to the thickness difference or the loss of an oriented skin; however, the tough failure mode was retained. As can be seen in Table VII, milling an aged PC sample did not improve its toughness. However, milling away the surface layer for aged PC blends did restore toughness to nearly the as-molded values. Heating at 165°C for 15 min prior to milling fully restored the toughness of aged PC and also increased the impact strength for aged blends, especially those with lower rubber content. This experiment demonstrates that the thermally irreversible embrittlement noted earlier is associated with a process that progresses inward from the external surface (controlled by oxygen diffusion) since removal of this discolored layer effectively restores toughness. Evidently, it is associated with the deterioration of the modifier since milling of aged, neat PC does not restore its toughness. Bucknall and Street showed that a brittle skin layer can cause brittle failure of a ductile specimen by lamination of a brittle SAN skin onto ABS to simulate the effects of outdoor aging of ABS.[52]

The effects of extended thermal aging above T_g (165°C) and below T_g (135°C) on impact strength are compared in Table VIII. Blends containing 2% of the various modifiers embrittled at 135°C but remained ductile at 165°C, similar to unmodified PC. In contrast, blends containing 20% of the various modifiers showed a larger decrease in impact strength at 165°C than at 135°C, especially those based on EXL 3300. This is undoubtedly due to

thermally induced changes in the modifier. As will be seen later, such chemical changes in the modifier itself can also cause molecular weight degradation of the PC matrix.

Effect of Aging on Tensile Properties

Figure 11 shows that the yield stress of PC increases with aging time at 125 and at 135°C in air. In both cases, there is a transition in the rate of change in the yield stress at about 9600 psi (66 Mpa). Similar results have been reported before.[4,37] The time to this yield stress transition is quite close to the ductile–brittle transition time as measured by impact testing. Thus, the yield stress at this transition has been identified with the craze stress.[4] When the yield stress exceeds the craze stress, the material tends
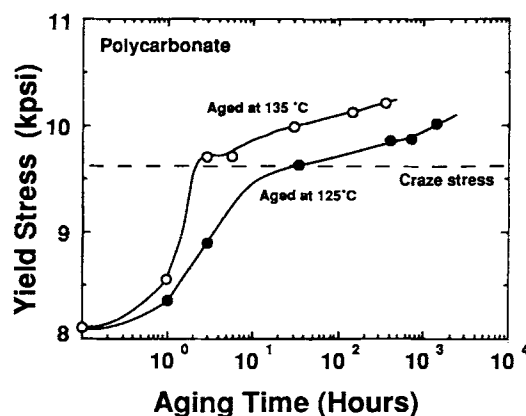

Figure 11 Effect of aging in air on yield stress of PC. Dotted line indicates the craze initiation stress for PC.[4,37]
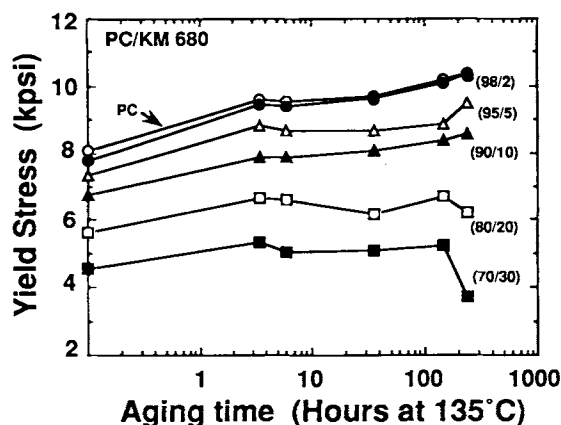
Figure 12 Effect of aging on yield stress of PC/KM 680 blends in air at 135°C.

Figure 14 Effect of aging on elongation at break of PC/KM 680 blends in air at 135°C.

to undergo a brittle deformation. Figure 12 shows the effect of aging in air on the yield stress of PC/KM 680 blends. Only the yield stress for the 2% blend reaches the craze stress level, while the yield stress for blends with higher KM 680 content remain well below this level. These results are consistent with the impact results and might be considered as a reason why the 2% blend is brittle with a sharp notch and the embrittlement time is extended to only 70 h for samples with the standard notch. As seen in Figure 12, the yield stress for the (95/5) and (90/10) blends continue to increase with increasing aging time and may approach the craze stress level. The fact that the yield stress eventually decreases for the (80/20) and (70/30) blends after aging for about 150 h might be an indication that
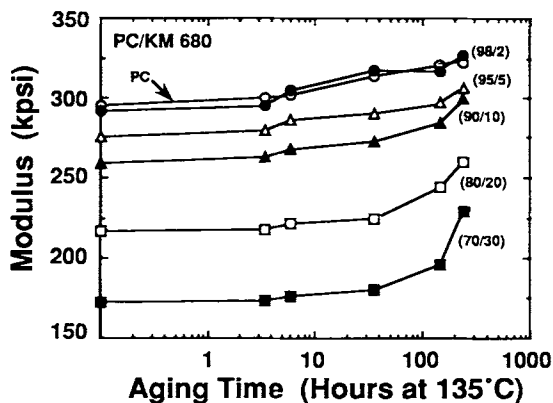
chemical degradation of the rubber phase is the cause for embrittlement of these blends.

The modulus of PC and its blends increases slowly in the early stages of the aging process as shown in Figure 13; however, after approximately 150 h the rate accelerates. Physical aging of PC can cause an increase in modulus,[21] whereas degradation processes may cause the modulus of the modifier to increase. Figure 14 shows that the elongation at break remains over 100% for blends containing more than 5% KM 680 up to 36 h at 135°C in air. After 240 h, all samples show relatively brittle behavior as indicated by a significantly reduced elongation at break. The blends containing 20% and more modifier are particularly brittle, showing less than 5% elongation. It is apparent that blends with a modifier content between 5 and 20% would be most useful for maintaining ductility over extended periods of time.

CHARACTERIZATION

Differential Scanning Calorimetry

A glassy polymer aged below T_g has lower segmental mobility than an unaged glass. Thus, during heating from the glassy state the aged sample is not able to reorganize at a rate commensurate with the rate of heating and consequently shows a T_g overshoot.[3,32,53] During thermal analysis, this leads to an apparent endotherm in the T_g region that is related to the extent of enthalpy relaxation that occurred during aging. The changes in thermal properties that occur

Figure 13 Effect of aging on modulus of PC/KM 680 blends in air at 135°C.

on sub-T_g aging of PC were documented previously in this laboratory by differential thermal analysis.[32] Similar results were obtained as a part of this study using differential scanning calorimetry (DSC). Here, samples were cut from specific locations within the cross-section of molded bars as mentioned in the experimental section. Typical thermograms at 20°C/min are shown in Figure 15 for injection-molded PC where a comparison is made between an as-molded sample and samples aged at 135°C in air for 3 h or 14 d. The samples were cut from molded bars including the entire cross-section. It is clear that the extent of enthalpy relaxation increases significantly with aging time. Figure 16 shows thermograms for small samples taken from the skin and core regions of the injection-molded PC after aging at 135°C in air for 20 d. The sample from the skin region shows a somewhat larger excess enthalpy peak than that of the core sample. This may be due to residual stresses in the skin developed during injection molding.[25,54] The difference between the areas A and B (as shown in Fig. 15), computed using the Perkin-Elmer DSC-7 system, gives the enthalpy changes caused by aging. A similar method was described by Richardson and Savill.[53] The change in

Figure 16 DSC scans (heating rate of 20°C/min) of skin and core materials taken from injection-molded PC bar aged in air at 135°C for 20 d compared to as-molded sample.

the endotherm area and the apparent T_g (defined as the onset of the base line shift) increase with aging time as shown in Figure 17 for PC. It is important to note that PC can experience chemical change (yellowing, molecular weight loss, etc.) after
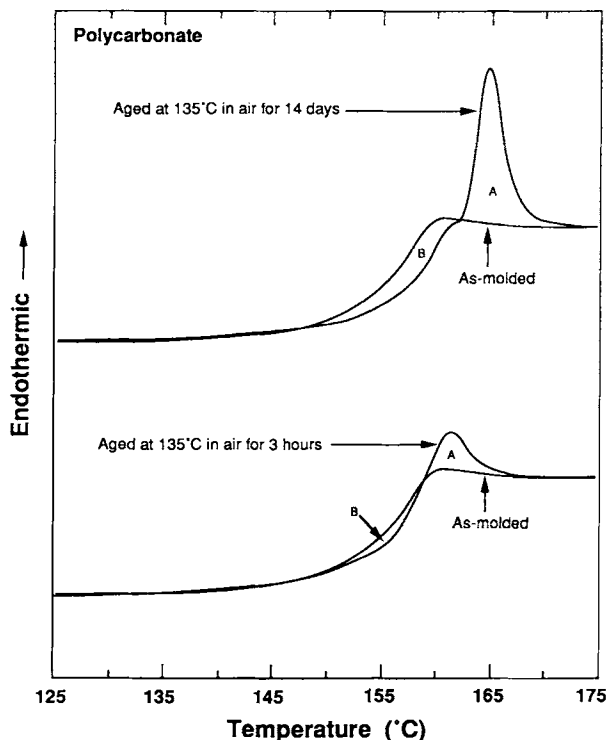

Figure 15 DSC scans (heating rate of 20°C/min) of injection-molded PC with various thermal histories. Samples aged in air at 135°C for 3 h and 14 d compared to as-molded sample.
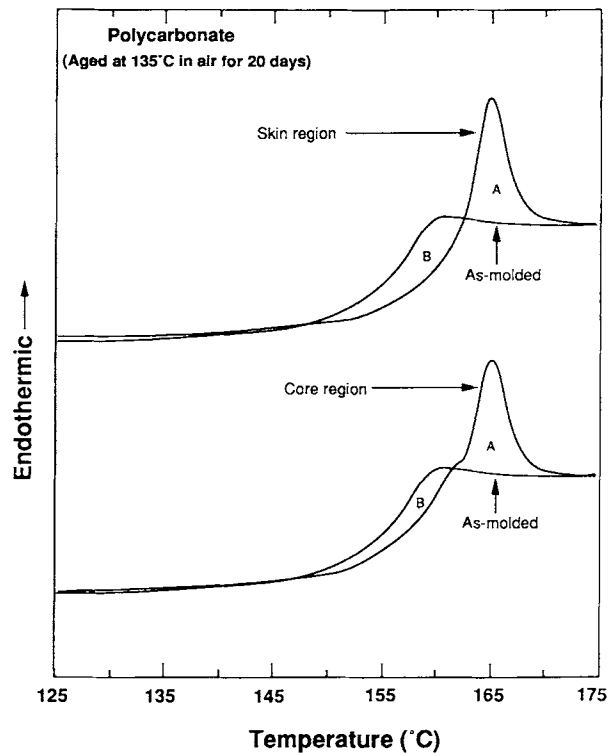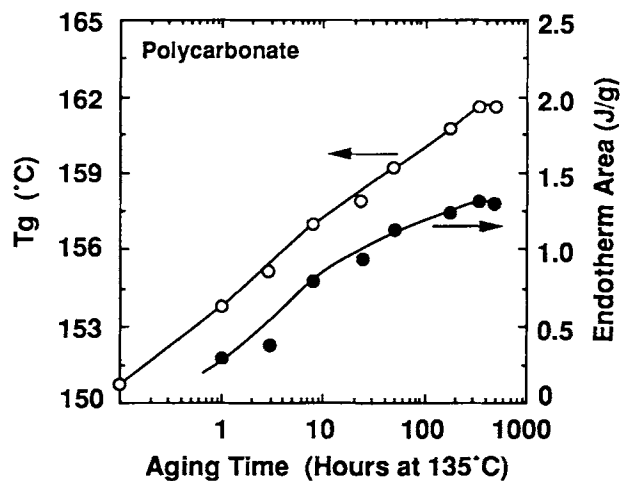

Figure 17 Effect of aging time on the excess enthalpy peak area and T_g (onset) of neat PC in air at 135°C.

several months at these conditions in addition to simple physical aging.

Typical thermograms for injection-molded PC/ KM 680 (80/20) blends as-molded and after aging in air for various times are shown in Figure 18. When the sample consists of the entire cross-section of the molded bar, the DSC scan after aging for 50 h is similar to those for polycarbonate shown in Figure 15. After further aging (25 d), however, the thermograms have distinctly different shapes as shown in Figure 18. There is a shift to lower temperature such that the overlap area B is missing and the peak temperature is significantly depressed. Thermograms of aged material (25 d) taken from the core and from the yellowed skin are also shown in Figure 18. The core material shows behavior somewhat similar to that of aged PC; although for the blend, area B is essentially eliminated and the onset of the T_g occurs at a lower temperature. For the yellowed surface material, the response is even more dramatic, with no indication of a typical sub-T_g aging response. The glass transition region is much broader and the T_g defined by the onset method is about 133°C,

Figure 19 Effect of aging time on the excess enthalpy peak area and T_g (onset) of PC/KM 680 (80/20) blend in air at 135°C.
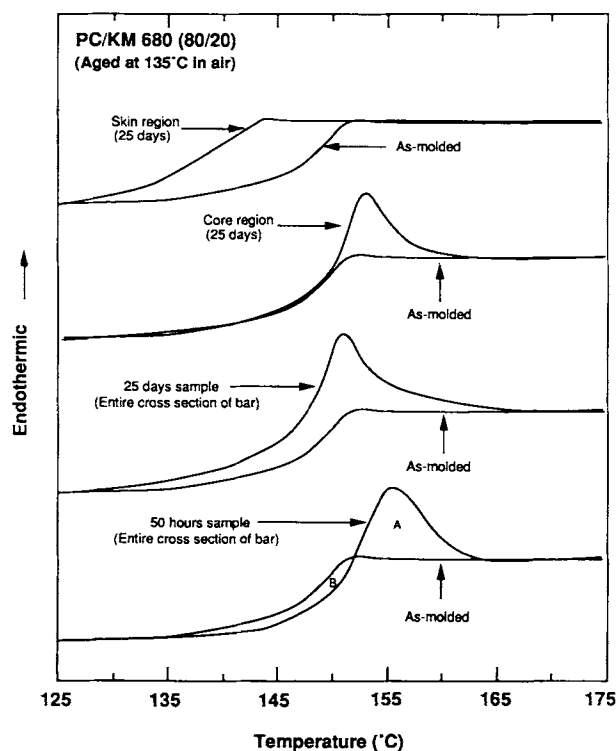

Figure 18 DSC scans (heating rate of 20°C/min) of injection-molded PC/KM 680 (80/20) blends after aging at 135°C in air for 50 h and 25 d compared to as-molded sample. Skin and core regions of aged sample (25 d) are also compared to as-molded sample.
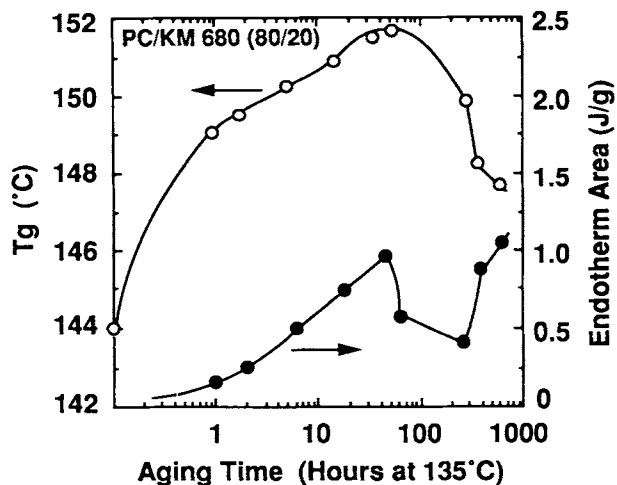
which is below the aging temperature. Thus, this heat treatment causes some changes other than physical aging especially in the skin region. Figure 19 shows the apparent T_g and endotherm peak area for samples from the core of molded bars made from a PC/KM 680 (80/20) blend at various stages of aging at 135°C in air. After 30 h, both T_g and the excess enthalpy area begin to decrease. This suggests a reduction in PC molecular weight by chemical reaction. There is a subsequent increase of the endotherm peak area after about 300 h that probably reflects further complex chemical changes rather than resumed enthalpy relaxation. Evidence for multiple chemical processes that can occur during thermal aging will be presented.

Dynamic Mechanical Behavior

Dynamic mechanical behavior of the neat modifier materials has proven to be a useful means of documenting the changes that occur during heat aging. The dynamic mechanical properties of as-molded and heat-treated KM 680 and EXL 3330 at 3Hz are shown in Figures 20(a) and 20(b). EXL 3330 is similar to EXL 3300, except for its larger particle size. In blends with PC, it showed comparable changes in properties due to aging at 135°C. Aging in air at 135°C for 20 d substantially depresses the rubber-phase T_g peak for KM 680 while the diminution of the peak for EXL 3330 is somewhat less. The peak maximum shifts from −63 to −52°C for KM 680 and from −32 to −12°C for EXL 3330. Above the rubber-phase T_g, the modulus of KM 680

is substantially elevated by the aging process, which most likely reflects extensive crosslinking of its butadiene-based rubber core.[56] For EXL 3330, there is no corresponding hardening during aging (only an increase in the rubber phase T_g), which is consistent with the greater chemical stability of its acrylate-based rubber core.

These results give further strong evidence that degradation of the core-shell modifiers occurs in these blends during heat aging and no doubt contributes to the loss in blend toughness observed.

Density

Densification occurs as a glassy polymer approaches its equilibrium state at the aging temperature, and LeGrand[4] showed that this process occurred on the same time scale as mechanical embrittlement of PC. Similar results from this investigation are shown in Figure 21. Thus, density is, in principle, a useful way of following the fundamental changes in the glassy state that occur during physical aging. It was thought that this might be a way to monitor the
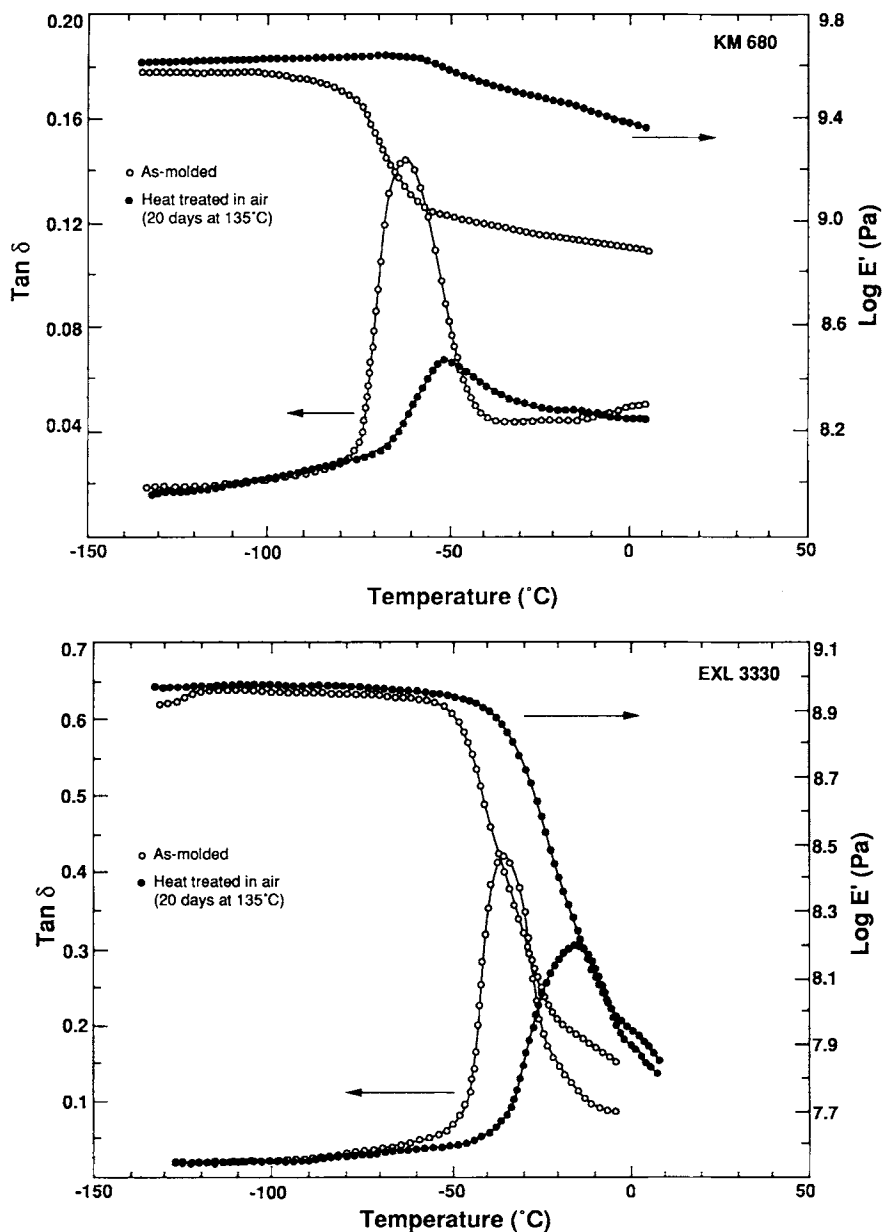

Figure 20 Effect of heat treatment in air at 135°C on dynamic mechanical properties of core-shell modifiers. (a), KM 680; (b), EXL 3330.
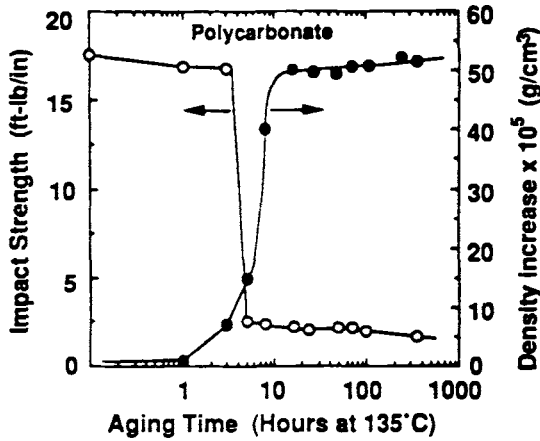
Figure 21 Comparison of density and Izod impact strength changes due to aging PC in air at 135°C.

Figure 22 Density increase of PC/KM 680 blends in air at 135°C as function of aging time.

state of the PC matrix of blends during aging. This did not prove to be the case because of more massive changes in the density of modifier that occur on aging in air at 135°C as listed in Table IX. The density increase at 135°C for PC is about 0.04% after aging for 1 d and any further change by continued aging is not evident. The density changes for the modifiers used in this study are quite substantial, particularly for MBS. Figure 22 shows the density changes for PC, KM 680, and their blends with aging time at 135°C in air. On this scale, the densification of PC is imperceptible, whereas that of KM 680 is 5.75%. The blends show intermediate levels of change. It is interesting to compare the change in toughness and density during aging for PC (Fig. 21) and a selected blend, PC/KM 680 (80/20), in Figure 23. It should be noted that the scales of density change in Figures 21 and 23 differ by two orders of magnitude. There seems to be some correlation between the processes associated with density increase and

the loss in toughness. However, in the blend the density change is simply an indicator of the chemical changes in the modifier and not the subtle change in the matrix that accompanies its physical aging.

Dilute Solution Viscosity

The evidence presented already strongly supports the notion that there is chemical change in these modifiers during the heat aging process. The reduction in apparent T_g of the skin region of an aged specimen noted by DSC (Fig. 18) suggests that the molecular weight of the PC phase may also be re-

Table IX   Increase in Density Caused by Aging in Air

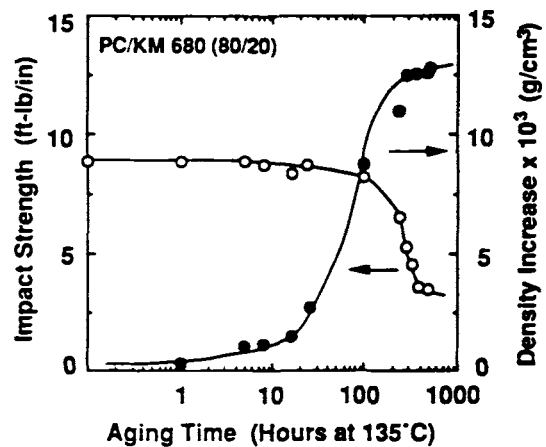| Material	Density of As-Molded Sample (g/cc)	Density Increase Caused by Aging in Air at 135°C (%)		
		5 d	10 d	20 d
PC	1.194	0.04	0.04	0.04
KM 680	0.995	0.97	3.86	4.15
EXL 3607	0.975	0.77	3.10	3.86
EXL 3330	1.090	0.19	0.65	2.20
EXL 3300	1.088	0.51	1.20	1.96

Figure 23 Comparison of density and Izod impact strength changes due to aging PC/KM 680 (80/20) in air at 135°C.

duced. To test this possibility, a convenient means of monitoring the molecular weight of the PC component in blends was needed. Unfortunately, there is no convenient way to remove the modifier so this test must be done with this material present. For this purpose, the intrinsic viscosity of the blend sample was measured in methylene chloride. Assuming the PC molecular weight does not change, one should not expect the intrinsic viscosity of the blend to be the same as that of the neat PC. One possibility is that the modifier particles do not contribute to the solution viscosity at all; however, because their mass (mass fraction in blend = w) is included in the concentration of polymer, the observed intrinsic viscosity, $[\eta]$, will be lower than that of the PC, $[\eta]_{PC}$, by the amount given by

$$[\eta] = [\eta]_{PC}(1 - w) \tag{1}$$

because of this dilution effect. To interpret $[\eta]$ measurements on aged blends, we first determined $[\eta]$ for as-molded blends where the molecular weight of the PC presumably has not changed because of molding. These results are shown in Figure 24. One point is shown for a solution-prepared blend of PC plus KM 680, which agrees well with that for the melt blend of the same composition. The broken line was calculated from eq. (1). Obviously, the simple dilution notion does not fully describe the dilute solution behavior of these mixture; however, the data shown can serve as a calibration for any actual molecular weight change.

Intrinsic viscosity measurements for blends containing 20% of the various modifiers that had been aged in air for 20 d at 135°C are shown in Table X along with appropriate controls. The as-molded values for blends (and not for pure PC) are the ones
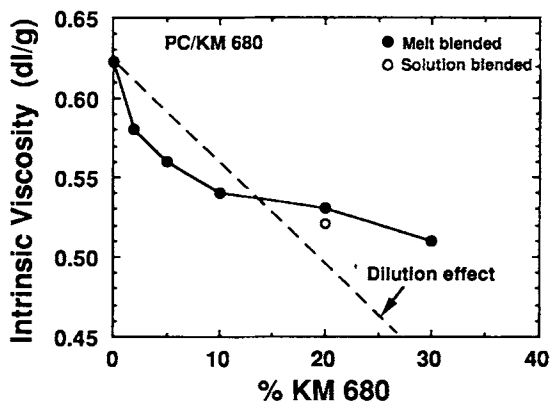
Table X   Effect of Aging on Intrinsic Viscosity of PC and Various Blends

| | Intrinsic Viscosity (dL/g) | | |
| | | 20 d at 135°C in Air | |
Material	As-Molded	Core	Skin
PC	0.62	0.61	0.60
PC/KM 680 (80/20)	0.53	0.49	0.33
PC/EXL 3607 (80/20)	0.50	0.48	0.40
PC/EXL 3300 (80/20)	0.54	0.51	0.46

that the aged blends should be compared with since these account for the effect shown in Figure 24. Heat aging of pure PC causes only a relatively minor decrease in its intrinsic viscosity. Likewise, the core portion of aged blend specimens are only slightly reduced relative to the as-molded control. However, there is a more serious decline noted for material excised from the "skin" region of aged blends. This decline is most serious for blends of KM 680 and less so for EXL 3607, both of which are of the MBS type. The relative reduction of the intrinsic viscosity of the skin material is considerably less for the all-acrylic modifier EXL 3300.

Thus, there is clear evidence for reduction of the molecular weight of the PC in the skin region of aged specimens that contain modifiers and especially those based on butadiene rubber. This explains the reduced T_g shown in Figure 18. The loss of the heat capacity overshoot peak is probably due to the approach of the sample T_g to the temperature of aging. Since there is no comparable loss in molecular weight for pure PC, one must conclude that the degradation of the modifier triggers the degradation of the matrix PC.

The role of oxygen in the degradation of the elastomer phase in KM 680 and in the concurrent reduction of PC molecular weight is shown in Table XI by comparing intrinsic viscosities of blends that were aged in vacuum and in air. The data clearly indicate that there is no appreciable viscosity difference in the core and the skin of blends due to aging in vacuum for 20 d at 135°C. DSC data also showed that the T_g of the specimen obtained from the skin region had not changed due to aging in vacuum. However, the intrinsic viscosity of the skin layer is significantly reduced for both injection- and compression-molded specimens when the heat aging was carried out in air. We will examine possible chemical mechanisms later.

Figure 24   Intrinsic viscosity of PC/KM 680 blends as a function of KM 680 content.

Table XI Effect of Aging on Intrinsic Viscosity for PC/KM 680 (80/20) Blends Prepared and Aged by Different Techniques

Material	Intrinsic Viscosity (dL/g)		
		20 d at 135°C	
	As-Molded	Core	Skin
Aged in air oven			
Injection molded	0.53	0.49	0.33
Compression molded	0.51	0.45	0.36
Aged in vacuum oven			
Injection molded	0.53	0.48	0.49
Compression molded	0.51	0.46	0.47

Fracture Morphology

SEM photomicrographs of Izod fracture surfaces for PC and the PC/KM 680 (80/20) blend are shown in Figure 25. The features of as-molded samples are compared with those of the same composition after aging at 135°C for 20 d. The interpretation of these photomicrographs is facilitated by the schematic representations shown in Figure 26. The fracture surface of as-molded PC is similar to those described in earlier reports.[4,21,22,25,28] It is characterized by a ductile fracture that shows necking and drawing, i.e., pulling in of specimen sides due to the prevailing plane-stress conditions [Fig. 25(a)]. The fracture surface shows markings emanating from the crack initiation region that first converge and then fan out into a "feathery" area near the ultimate failure point. A schematic representation, similar to that suggested by Mallick and Jennings,[28] further shows the presence of the plane-stress zone near the surface of the tough as-molded samples [Fig. 26(a)].

A fracture surface for PC that has embrittled by physical aging is shown in Figure 25(b). There is no indication of pulling in of the side surfaces due to necking. A slow crack growth zone[25] is observed
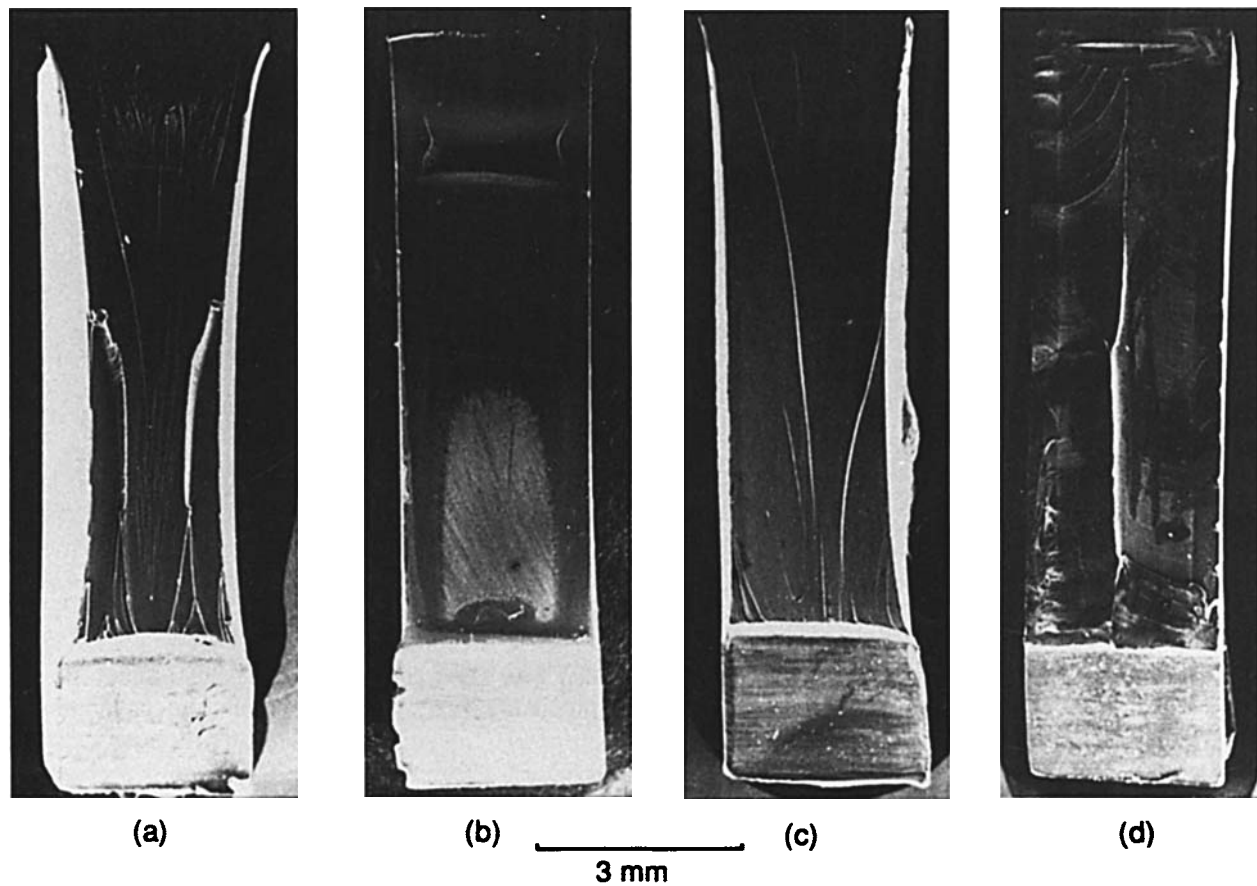

(a)   (b)   (c)   (d)

3 mm

Figure 25 SEM photomicrographs of fracture surfaces of notched Izod impact specimens. (a), as-molded PC; (b), aged PC (20 d in air at 135°C); (c), as-molded PC/KM 680 (80/20); (d), aged PC/KM 680 (80/20) (20 d in air at 135°C).
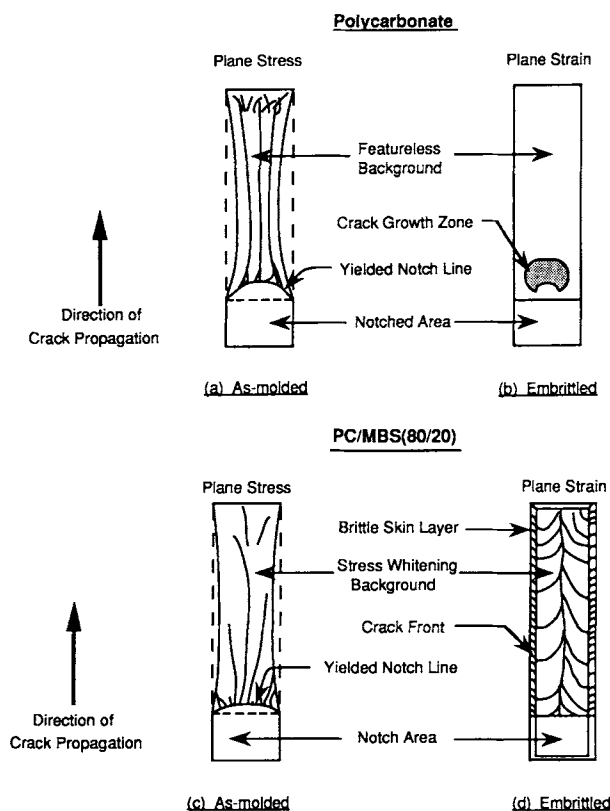
Polycarbonate

(a) As-molded   (b) Embrittled

PC/MBS(80/20)

(c) As-molded   (d) Embrittled

Figure 26 Schematic representation of fracture surfaces. (a), as-molded PC; (b), PC embrittled by aging; (c), as-molded PC/KM 680 (80/20); (d), PC/KM 680 (80/20) embrittled by aging.

beyond the initiation region that is characterized by some mildly featured area, often referred to as a "misty" area.[21] The featureless area beyond this reflects fast crack growth typical of brittle fracture [Fig. 26(b)].

Figures 25(c) and 25(d) show the fracture surfaces of PC/KM 680 (80/20) blends. The as-molded sample fractures in a ductile fashion. As seen from Figure 25(c), there is an inward movement of the side walls, typical of a ductile failure. In addition, there are long markings, eminating from the fracture initiation zone, present in the fracture surface, similar to those in PC. Furthermore, the entire fracture surface seems to involve deformed polymer, visible to the naked eye as a whitened surface. The aged blend has a more complex fracture surface as seen in Figures 25(d) and 26(d). To the naked eye, it is clear that the surfaces of the bar are distinctly yellowed, but the discoloration in the core area is only slight compared with the skin. The thickness of skin layer for blends depends on both the KM 680 content

and aging time as discussed before (Table VI). The yellowed skin layer is apparently brittle since no stress whitening is observed, which results in a detrimental contribution to the overall toughness of the specimen.[52] The brittle surface layer is capable of initiating failure from the sides as well as constraining the center portion so that a plane-strain failure mechanism prevails. Since stress whitening is still observed in the center portion, the core region of the air-aged sample is apparently still capable of ductile deformation. On careful examination of the multiple elliptical markings in the brittle layer, it is apparent that they may initiate similar markings that have the opposite curvature and propagate toward the center of the specimen. While the causes for the formation of these lines and their nature are not clear, Siegmann and Ben-Tzur[57] reported similar features in the fracture of a three-layered composite sheet involving PVC. As seen earlier in Table VII, the removal of this brittle skin allows the remaining core to resume its tough failure mode and to a certain extent allows recovery of ductility by heating at 165°C for 15 min. It seems that if the degraded PC in the core area retains its molecular weight above a critical value[22,38,40] then it is still capable of being modified by the presence of elastomer particles. The constraint imposed by the brittle outer layers of the aged PC blend causes the overall failure to proceed predominantly by a plane-strain mechanism that results in brittle fracture.

DEGRADATION MECHANISM

The results described above make it clear that chemical degradation of the modifier has a detrimental effect on toughness of heat-aged PC. Blends with the relatively stable, all-acrylic modifiers, EXL 3300 and EXL 3330, fail in a tough mode for longer periods of aging than blends with the less stable MBS modifiers. Heat aging causes the T_g of the rubber phase of the modifier to shift to a higher temperature and the shear modulus above the rubber phase T_g to increase, especially for KM 680 (Fig. 20). This chemically induced hardening of the modifier will render it less effective for toughening of the blend. In addition, chemical processes that occur because of the presence of the modifier apparently cause degradation of PC, especially near the outer surface of the specimen. Both of these chemical changes, in addition to any physical aging of the PC matrix, contribute to specimen embrittlement. Figure 27 accounts in a schematic way for the obser-

Figure 27 Schematic representation of degradation mechanism of PC/MBS blends.

vations made here. Thermal and oxidative processes can occur simultaneously to cause chemical degradation of MBS modifiers during prolonged exposure in air at 135°C. The PMMA shell and the rubber core may be affected simultaneously. Free radicals generated either thermally or oxidatively are responsible for the crosslinking reaction that renders the rubber phase less effective as an impact modifier.[47-49] PMMA degradation in the shell can lead to free radicals that may attack the PC chain and cause it to undergo scission.[50,51] The work of Adam et al.[49] has shown that thermooxidation of 1,2-polybutadiene at 60°C leads to formation of hydroperoxides and evolution of H_2O, CO_2, and CO. Thus, the formation of water and acidic impurities are expected when butadiene-based rubber is exposed to air at 135°C. This can also lead to molecular weight reduction of PC by hydrolysis. The extensive yellowing of blend samples is primarily caused by degradation processes in the modifier phase that progress from the exterior surface inward presumably because of the role of oxygen transport. Degradation processes in the modifier phase trigger either hydrolytic or free radical processes that reduce the molecular weight of the PC phase in the skin region that progresses toward the interior of the molded bar with aging time.

CONCLUSIONS

Changes in physical and mechanical properties of PC and its blends with various commercial core-shell impact modifiers caused by heat treatment near the PC glass temperature have been investigated. Based on the experimental results, the following conclusions are reached.

The embrittlement of PC that occurs by physical aging at temperatures below its glass transition can be significantly mitigated by adding core-shell impact modifiers. However, these blends do eventually embrittle, at least in practical aging environments that include air. The extent to which the time to embrittlement is prolonged is influenced by the amount of impact modifier added, aging temperature, aging environment, and thermal stability of

the modifier, etc. Blends of PC containing 10% of a butadiene-based MBS modifier remain ductile for the longest periods of time during aging at 135°C in air. Blends containing n-butyl acrylate-based rubber in the impact modifier retain toughness for much longer periods than those containing butadiene-based rubber or MBS modifiers.

Blends of PC with MBS modifiers discolor extensively and become embrittled faster when aged in air compared with samples aged in vacuum. Air aging leads to a more extensively yellowed skin on the samples. This skin layer can lead to embrittlement of the entire sample before degradation penetrates deeply into the interior. This was demonstrated by machining away the skin layer, leaving only the core region, which remained tough.

Dynamic mechanical properties show that the butadiene-based rubber core of MBS modifier undergoes extensive changes during air aging at 135°C that lead to increased rubber-phase T_g and modulus. Results from DSC and intrinsic viscosity measurements also suggest that the molecular weight of PC matrix is reduced, especially in the skin region. Thus, chemical reactions that take place during thermal treatment at 135°C substantially contribute to the deterioration of mechanical properties of these blends in addition to physical aging of the PC matrix. The impact modifier becomes less effective for toughening and its degradation is responsible for the formation of active radical species that cause reduction in molecular weight of the polycarbonate. These concurrent chemical changes limit the effectiveness of these modifiers for solving the problem of PC embrittlement by physical aging. Therefore, the thermooxidative stability of the elastomer phase is a major concern for choosing impact modifiers designed for applications that require prolonged use at elevated temperatures.

An important question is whether an ideally chemically stable impact modifier would be able to totally circumvent embrittlement due to physical aging of the PC matrix or whether such a modifier could only further prolong the occurrence of embrittlement when all chemical mechanisms are eliminated. An unambiguous answer to this question cannot be reached even from the extensive study conducted here. However, there is no fully convincing evidence given here that this goal is not achievable. While additional studies on aging in the absence of oxygen or water would be interesting, this is unlikely to lead to complete removal of chemical changes that cause embrittlement since purely thermal mechanisms do exist for many of these modi-

fiers. A more promising and practical answer lies in development of more stable modifiers. However, a practical issue is the length of the experiments required to know whether eventual embrittlement caused by a purely physical mechanism will occur or not.

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