

# The Stabilization of Bisphenol-A Based Polycarbonate by Phosphine Oxide

S. Ozden,<sup>1</sup> A. K. Shaov,<sup>2</sup> A. M. Charaev<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering, Erciyes University, Kayseri, Turkey

<sup>2</sup>Kabardino-Balkar State University, Faculty of Chemistry, 360004 Nalchik, KBR, Russia

Received 31 August 2008; accepted 22 October 2009

DOI 10.1002/app.31688

Published online 4 January 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A Bisphenol-A based polycarbonate was stabilized by a new polymer stabilizer named di(*p*-butoxyphenyl)cyclohexylphosphine oxide. The stabilizer was mixed with the polymer in methylene chloride solution. Later, the solution was vaporized and the stabilized polymer was dried. Specimens were cut and heat treated at different temperature and durations. Small amounts of stabilizer enhanced the breaking strength and elongation at break properties of as

molded and heat treated polycarbonate. The modulus of elasticity reduced with stabilization. The stabilizer had a plasticizing effect too. At high stabilizer rates ( $c > 1\%$ ) both thermal and mechanical properties were deteriorated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1475–1482, 2010

**Key words:** stabilization; polycarbonates; mechanical properties; aging

## INTRODUCTION

The derivatives of phosphinic compounds with five covalent bonds are commonly used types of polymer stabilizers.<sup>1,2</sup> As the stabilizers are frequently employed in polymers, their effects on the mechanical and thermal properties need further investigation to enhance the positive effects of these stabilizers. In the literature, there have been works in which different stabilizers were employed for different purposes such as plasticization, stabilization, modification, increasing fire resistance, etc.

Jeong et al.<sup>3</sup> showed that poly(arylene ether phosphine oxide) (PEPO) improved the adhesive behavior and flame resistance of epoxy resins. Morgan and Tour<sup>4</sup> synthesized several alkyne-and phosphorus-containing materials (including phosphine oxides, phosphates, diphosphates, and oligophosphates) and showed that the new materials had good-to-excellent thermal stability with high-onset decomposition temperatures. The flame retardancy of the epoxy resin was significantly increased with the inclusion of cyclic phosphine oxide and tetraoxirane rings in the main chain.<sup>5</sup>

Chang et al.<sup>6</sup> reported that a new fire retardant containing phenylphosphonic dichloride increased the flame retardancy of poly(ethylene terephthalate) epoxy resin and unsaturated polyester.

Shau et al.<sup>7</sup> obtained phosphorylated epoxy polymers by reacting cyclic phosphine oxide epoxy and 10-phenylphenoxaphosphine-3,8-diglycidylester-10-oxide with different curing agents and reported that the new polymers demonstrated excellent thermal properties and high char yield. Poly(arylene phosphine oxide) materials synthesized from fluorinated PEPO by post polymerization have shown high solubility and film-forming ability.<sup>8</sup> Miyatake and Hay<sup>9</sup> obtained new polymers by preparing three arylene difluoride monomers containing phosphine oxide, phosphinic acid, and polymerizing them with bisphenol. The molecular weight and the glass-transition temperature of the new polymers were affected by the presence of the phosphine groups in the main chain.

Shau et al.<sup>10</sup> synthesized a new bismaleimide, which contained epoxy units and cyclic phosphine oxide. The product showed a slower thermal degradation rate and better flame retardancy than the conventional bismaleimide resin cure with the same diamine agents. These were attributed to the introduction of phosphorus into the polymer structure.

Jain et al.<sup>11</sup> investigated the curing behavior of diglycidyl ether of bisphenol-A (DGEBA) using three novel multifunctional aromatic amines having phosphine oxide and amide-acid linkages. A decrease in initial decomposition temperature and higher char yields were observed when phosphorus containing amide-acid amines were used as curing agents for DGEBA.

Zhang et al.<sup>12</sup> reported that phosphine oxide imparted good thermooxidative stability on the polyamides.

Correspondence to: S. Ozden (ozden@erciyes.edu.tr).

In previous works, we investigated the effects of *p*-butoxyphenyl cyclohexyl phosphinic acid on aromatic block copolyethers.<sup>13</sup> Similarly a bisphenol-A based polycarbonate (PC) was reacted with a new stabilizer (*p*-butoxyphenylcyclohexyl-phosphinic acid) obtained from tri(*p*-nonyl phenyl) phosphite. The mechanical properties were initially increased with small amount of stabilizers. The mechanical properties deteriorated at higher stabilizer rates.<sup>14</sup> In a similar work, we prepared four different metallic acids from the salt derivatives of potassium, nickel and two different grades of iron metals with phosphinic acid. The effects of these stabilizers on the mechanical and thermal behavior of aromatic block copolyethers<sup>15</sup> and PC<sup>16</sup> were investigated. The results showed that while small amounts of the stabilizers had a positive effect on the both copolyethers and PC, larger amounts of stabilizers (>0.1%) had a deteriorating effect.

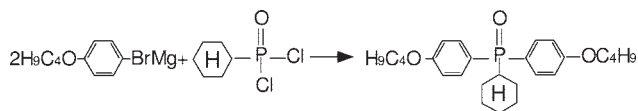
The stabilizers are wanted for physical and mechanical behaviors.<sup>17–20</sup> In polymer industry, a stabilizer, commercially known as polygrad is a widely used. It is a derivative of trivalent phosphorus—three (*p*-nonilphenyl)phosphite (polygrad) and usually added as 1.0% in mass.<sup>21</sup>

In this work, the effects of a new stabilizer named as di(*p*-butoxyphenyl)cyclohexylphosphine oxide (phosphine oxide, PhO) on the mechanical and thermal behaviors of PC was investigated. It is believed that this new field of the investigation will lead to a new understanding of the application of this stabilizer. It is hoped this new stabilizer, which can be produced more economically will be a substitute for polygrad. Therefore, the effects of polygrad on the mechanical and thermal behavior of PC were compared with PhO.

## EXPERIMENTS

### Material synthesis

The phosphorus organic compounds were synthesized by the Grignard reaction method.<sup>22</sup> The reaction process was as follows:



To confirm that di(*p*-butoxyphenyl) cyclohexyl phosphine oxide (PhO) was obtained as a result of above reaction, the calculated and measured atomic mass of the elements were compared. The atomic mass measurements were performed in a special laboratory of the Institute of Electromagnetic Compound Academy of Science. A quantitative element analyses was carried out. The specimens were burnt, and the products were separately analyzed. The results were

obtained for a molecular structure  $C_{26}H_{37}O_3P$ . The relative density  $d_{20}^4$  was 1.109 and the refraction parameter,  $n_D^{20}$  was 1.5621. The other data was found as follows: the calculated and measured content of phosphorus was 7.24 and 7.35%, respectively; similarly, the calculated and measured molecular Refraction  $MR_D$  was 124.2 and 125.4, respectively.

The PC used in our experiments had a commercial name of “Kapolaktam” and were commercially obtained from Dzerjinsk in Russia.

The PC and the stabilizer were dissolved in methylene chloride, and the solution was poured into a glass surface. Methylene chloride was vaporized, and the resultant polymeric sheet was put onto an SPT-200 oven under vacuum at 100°C for 2 hours (h). Since the vaporization temperature of methylene chloride is 36°C, the temperature was high enough for the sheets to be completely dried. The thickness of the polymer was controlled by the volume of the solution. The PC and stabilizer were in a state of molecular mixture. During the process, no chemical reaction took place. The amount of stabilizer added to the polymer changed between 0.1 and 30 wt %.

### Mechanical and thermal tests

The measurement of the mechanical properties of PC was carried out by using sheet specimens ( $100 \times 10 \times 0.1 \text{ mm}^3$ ) on a tensile test machine MRS-500 with a constant deformation rate of 40 mm/min at 20°C. Five runs were made for each type of the sample, and the average value was used for each case. Data with a scatter larger than 5% was excluded. Furthermore some of the specimens were heat treated on a SPT model oven at 200°C for 30 min and at 150°C for 250 and 500 h. After the heat treatments, the mechanical properties were measured again.

The thermomechanical analyses were conducted on a Pribor thermomechanical analyser. The temperature was increased at the rate of 4°C, and the load was kept constant to give a constant stress value of 0.05 MPa.

The main dielectric characteristic of the polymers is the dielectric loss, which represent a portion of electric field energy which is irreversibly dissipated as heat energy. The dielectric properties of pure and stabilized PC were measured by an alternating current bridge P5058 with a frequency of  $10^4$  Hz at a temperature range between 20 and 250°C.

The fire resistivity of the stabilized polymers was evaluated by the limiting oxygen index method (LOI). The LOI tests were carried out on film samples (strips) fixed vertically in the cylindrical chamber through which a laminar stream of a mixture of nitrogen with oxygen passes. The sample was set on fire from the top end with the help of a gas torch that was then withdrawn.

TABLE I  
The Mechanical Properties of Pure and Additive Added PC

No	Composition	Breaking stress $\sigma$ (MPa)	Elongation at break $\varepsilon$ (%)	Modulus of elasticity E (GPa)
1	Polycarbonate (PC)	88	17.6	1.6
2	PC + 1.0% Polygrad	82	14.7	2.3
3	PC + 1.0% PhO	94	14.7	2.1

## RESULTS AND DISCUSSION

Table I shows the results of the mechanical behavior of PC, PC + 1% polygrad and PC + 1% PhO. Stabilization by 1% polygrad had a negative effect on the breaking strength and elongation at break of PC. On the other hand, the addition of 1% PhO increased the breaking strength of PC from 88 to 94 MPa. Higher PhO stabilizer rates did not have a further positive effect on the mechanical behavior of PC.

The addition of PhO may have two opposing influences on the structure of PC. After the introduction of small amounts of PhO, it is probable that stabilizer particles containing negatively charged oxygen atoms are placed along the molecular chains of PC. These negatively charged molecules attract the positively charged polar units of neighboring PC chains. As a result, the molecular chains of PC are pulled toward each other and a more compact structure with more closely aligned molecules is obtained. On the other hand, it must be remembered that the phosphine oxide has a rather bulky size (van der Waals volume). As the rate of the PhO increased, as opposed the above statement, the PC chains are pushed away from each other by the bulky PhO particles increasing the intermolecular distance between the molecular chains of PC and thus decreasing the polar forces between the PC chains. This result may be accounted for the reduced mechanical behavior of PC at higher stabilizer rates. The mechanical behavior of PC may be affected by

these two conflicting influences depending on the amount of stabilizer.

To further assess the effects of PhO on the thermal and mechanical behavior of PC, the pure and PhO added PC were heat treated for different temperatures and times. The mechanical behavior of the pure PC and stabilizer added PC heat treated at 200°C for 30 min were presented in Figures 1–3.

Figure 1 shows that the effects of the stabilizer on the breaking strength of heat treated PC are insignificant for small concentrations and significantly negative for larger concentrations of PhO (>5%). The good mechanical properties yielded by low concentrations (0 to 1 wt %) of PhO suggests that it works relatively well as a thermal oxidative stabilizer.

The elongation at break significantly increased with the addition of 0.1 wt % PhO and then decreased with the further additions PhO (Fig. 2). Heat treatment increased the modulus of elasticity of pure PC from 1.6 to 4 GPa. (Table I and Fig. 3). This behavior is in agreement with the literature. Akay and Ozden<sup>23</sup> investigated the mechanical and thermal properties of injection molded PC. They showed that heat treatment reduced the ductility and the elongation at break dramatically. They attributed these changes to the removal of the residual stresses in the polymer during the heat treatment. According to Figure 3, the modulus of elasticity fell from 4 to 1.3 GPa at 0.1 wt % stabilizer rate and did not significantly change with further additions of PhO.

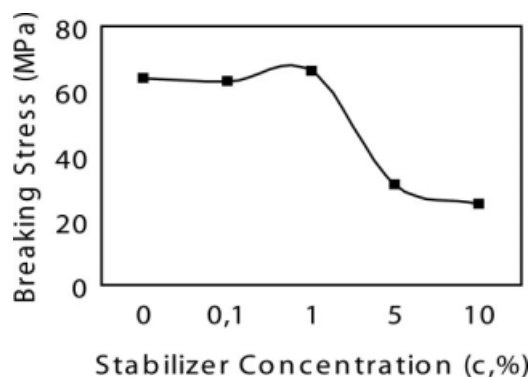


Figure 1 The relationship between breaking stress and stabilizer concentration for PC (heat treated at 200°C for 30 min).

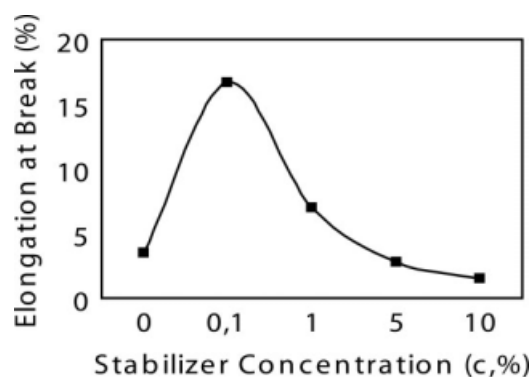
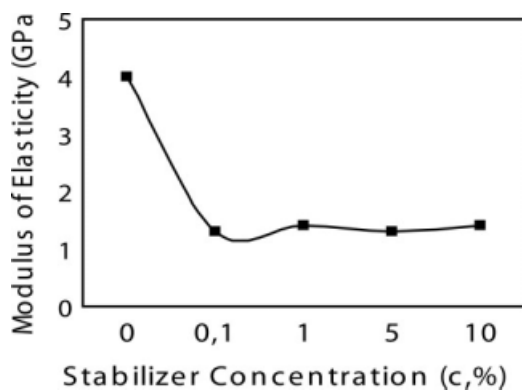


Figure 2 The relationship between the elongation at break and stabilizer concentration for PC (heat treated at 200°C for 30 min).

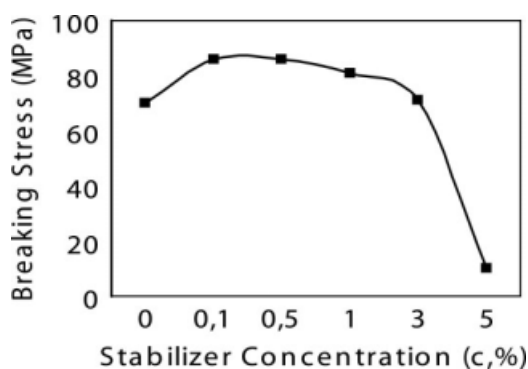


**Figure 3** The relationship between the modulus of elasticity and stabilizer concentration for PC (heat treated at 200°C for 30 min).

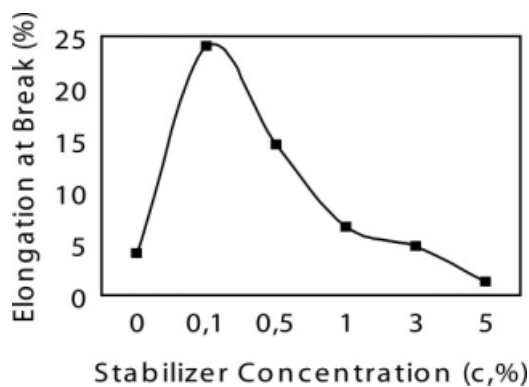
It is obvious that heat treatment introduced brittleness into the polymer. It was important to investigate whether this brittleness was a result of a crosslinking or some other effects. Actually, the lower modulus of elasticity observed for the heat treated specimens (stabilized PC) meant that the heat treatment could not have introduced crosslinking in the polymer. The crosslinked polymer could be expected to exhibit a higher modulus of elasticity and hence less elongation, because highly crosslinked polymers usually are brittle with small elongation at break.<sup>24</sup>

The most significant reductions in breaking strength and elongation at break were observed for PC stabilized with high amounts of PhO ( $c > 1\%$ ). The probable reason for the mechanical deterioration of heat treated and stabilized PC is the breakage of the phosphine oxide particles along the main molecular chain. At high temperature annealing, the acidic particles melt and active radicals were produced, which accelerated the destruction of the chains of the polymer by chain scissions which in turn deteriorated the mechanical properties.

The previous results have shown that short term thermal aging at high temperature for short times

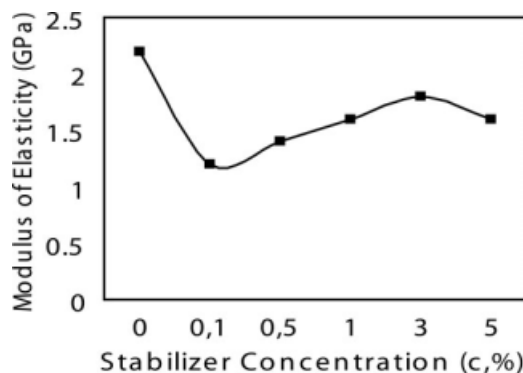


**Figure 4** The relationship between the breaking stress and stabilizer concentration for PC (heat treated at 150°C for 250 h).

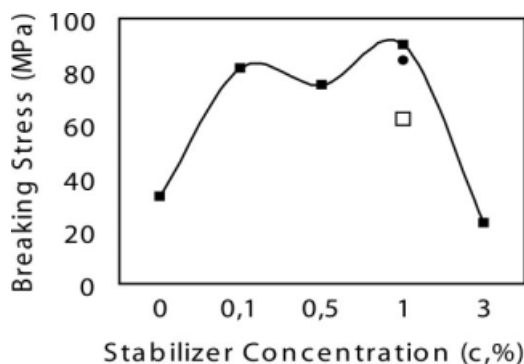


**Figure 5** The relationship between the elongation at break and stabilizer concentration for PC (heat treated at 150°C for 250 h).

mostly deteriorated the mechanical properties of the PC stabilized by high concentrations ( $c > 1\%$ ) of PhO. To enlarge the investigation field, the annealing temperature was reduced while the annealing time was increased. Pure and stabilized PCs were heat treated at 150°C for 250 and 500 h. Figure 4 shows that the phosphine oxide up to 1% has a positive influence on the breaking strength of PC. The best results were obtained for 0.1–0.5 wt % of PhO. Figure 5 shows that the ductility reached a maximum at 0.1% PhO and then decreased with further addition of PhO. The modulus of elasticity dropped to a minimum at 0.1 wt % of PhO and then gradually increased (Fig. 6). It is quite interesting that at 0.1 wt % of PhO, the breaking stress and elongation at break are maximum; whereas the modulus of elasticity is minimum. These results clearly show that the 0.1% PhO imparted ductility on PC subjected to high temperature annealing. The increase in elongation at break is apparently caused by increased mobility of molecular structures as a result of the plasticizer, which facilitated their orientation of the molecules during elongation and promoted the strengthening of the material. On the other hand,



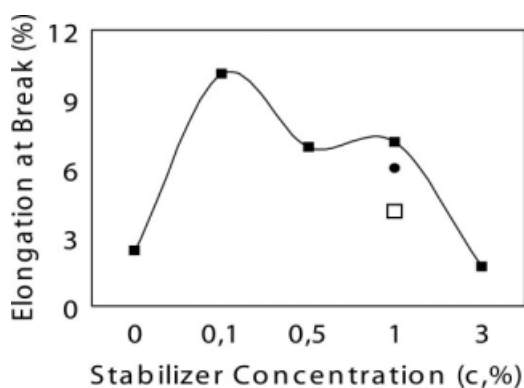
**Figure 6** The relationship between the modulus of elasticity and stabilizer concentration for PC (heat treated at 150°C for 250 h).



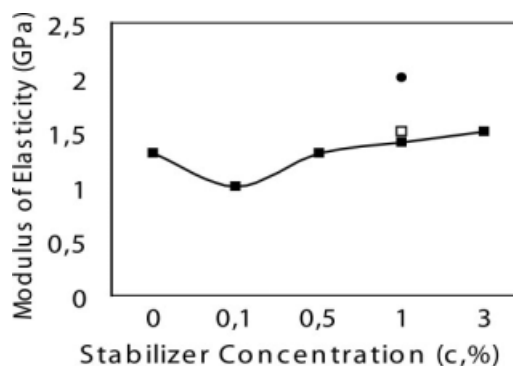
**Figure 7** The relationship between the breaking stress and stabilizer concentration for PC stabilized by: (■) PhO, (□) polygrad and (●) polygrad+PhO (heat treated at 150°C for 500 h).

the positive effect of PhO on the breaking stress was not as high as the ductility. At higher concentration rates, both strength and ductility of PC deteriorated.

Figure 7 shows that longer heat treatments (500 h at 150°C) increased the breaking strength of stabilized PC. Although pure PC had a breaking strength of 33 MPa, it was 90 MPa for 1 wt % PhO + PC. Higher concentration rates ( $c > 1\%$ ) deteriorated the breaking strength. Polygrad at 1% also had a positive influence on PC (62 MPa). When PhO and polygrad were added together to PC, its mechanical behavior further increased with heat treatment (from 33 up to 84 MPa), but the improvement was less than the one obtained by 1% PhO alone. Elongation at break also followed the same trend as the breaking stress (Fig. 8) while the modulus of elasticity first dropped to a minimum at 0.1% PhO then slowly increased (Fig. 9). This result is similar to the ones obtained for shorter annealing times. Therefore, it may be concluded that PhO (from 0.1 to 1 wt %) has a positive influence on PC under temperature conditions up to 150°C. Once again, the results obtained after prolonged aging support the effective-



**Figure 8** The relationship between the elongation at break and stabilizer concentration for PC stabilized by: (■) PhO, (□) polygrad and (●) polygrad+PhO (heat treated at 150°C for 500 h).



**Figure 9** The relationship between the modulus of elasticity and stabilizer concentration for PC stabilized by: (■) PhO, (□) polygrad and (●) polygrad+PhO (heat treated at 150°C for 500 h).

ness of PhO as an antioxidant, which is prominent over a 500-h treatment.

Although the phosphororganic including materials are important fire retardants, the chemical transformations of phosphororganic of compounds and their involvement in all stages of combustion of polymers need further investigations.

The phosphorus and its derivatives may act as inhibitors of combustion<sup>25</sup> through several factors: (1) during the combustion process, the additives influence the chemical transformations in such a way that the amount of the nonvolatile coke residue is increased and, as a result, the quantity of combustible products is decreased; (2) a viscous melted stratum of a polymetaphosphoric acid takes place at the surface of the polymer and acts a physical barrier against the conduction of the heat from the heat source (flame) to the polymer, this same stratum may also inhibit the diffusion of reagents into the polymer; (3) the gas phase is inhibited; (4) the additives may effect the heterogeneous oxidation of the carbonized products of the pyrolysed polymer.

Table II shows that the best LOI results are obtained for 20 wt % PhO. The stabilization did not significantly affect the oxygen index. It seems that during burning the phosphorous products did not

**TABLE II**  
Fire Resistance of Pure and Stabiliser Added PC

No.	Composition	LOI (%)
1	PC	26.5
2	PC + 0.1% PhO	25.0
3	PC + 0.5% PhO	24.0
4	PC + 1.0% PhO	23.5
5	PC + 3.0% PhO	23.0
6	PC + 5.0% PhO	23.0
7	PC + 10.0% PhO	24.5
8	PC + 15.0% PhO	26.5
9	PC + 20.0% PhO	28.0
10	PC + 30.0% PhO	27.5

**TABLE III**  
**The Environmental Effects of Different Acid and Bases on Pure and Stabiliser Added PC at 20°C**

No.	Composition	Time (s) × 10 <sup>4</sup>	Mass loss Δ <i>m</i> (%) in 10% NaOH	Mass loss Δ <i>m</i> (%) in 40% NaOH	Mass loss Δ <i>m</i> (%) in 10% H <sub>2</sub> SO <sub>4</sub>	Mass loss Δ <i>m</i> (%) in 96% H <sub>2</sub> SO <sub>4</sub>
1	PC	8.6	+1.19	-18.3	+0.05	+1.02
2	PC	43.2	-0.57	-87.9	-0.05	+13.5
3	PC	86.4	-0.96	-	-0.22	+31.4
4	PC	129.6	-1.77	-	-0.22	+40.0
5	PC	172.8	-2.50	-	-0.43	+42.9
6	PC	216.0	-3.16	-	-0.43	+54.4
7	PC	259.2	-3.64	-	-0.60	+59.9
8	PC + 1.0% PhO	8.6	-0.41	-12.8	0	+1.70
9	PC + 1.0% PhO	43.2	-0.72	-50.6	-0.10	+23.5
10	PC + 1.0% PhO	86.4	-0.82	-80.8	-0.10	+42.3
11	PC + 1.0% PhO	129.6	-1.74	-	-0.10	+44.2
12	PC + 1.0% PhO	172.8	-2.36	-	-0.15	+56.9

melt and decompose into acids which could generate a barrier against heat. This result is in confirmation with the literature<sup>26</sup> where it is argued that while the decomposing of the phosphorous materials constitute an effective fire retardant, generating a barrier against the heat from the flame, PhO is ineffective in fire retarding.

When the polymers are subjected to an aggressive medium, the destruction of the polymers may take place as a physicochemical process.<sup>27,28</sup> There can be different ways of decomposition as: (1) random degradation, where the main chain of macromolecules is randomly broken; (2) depolymerization, where monomer units are split from the ends of the main chain; (3) elimination of a small molecule from a substituent group and formation of a double bond; (4) weak-link degradation, where the chains break at lowest energy bonds and generation of new bonds between the main macromolecular chains.

Pure and stabilized PCs were subjected to different aggressive mediums composing of 10–40% solutions of caustic soda (NaOH) and 10–96% solutions of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). It is necessary to remember that, although the mass change in a hostile environment is used as a measure of endurance of the polymers to the aggressive medium, this method does not yield a quantitative assessment of the effects of the hostile environment on chemical resistance of

the polymers. Therefore, after the test specimens were kept at these hostile environments at 20°C for 30 days, their mass changes were measured, and their mechanical behaviors also were investigated.

PC is more enduring against sulfuric acid than sodium hydroxide (Table III). PC lost 3.64% of its mass in 10% NaOH, whereas it lost only 0.6% of its initial mass in 10% sulfuric acid after 30 days. On the other hand, PC lost 87.9% of its mass in 40% NaOH only in 5 days, whereas it swelled and its mass increased by 13.5% in 5 days in 96% H<sub>2</sub>SO<sub>4</sub>. Under the same conditions, the mass increased by 59.9% in 30 days. PhO at 1% improved the endurance of PC against dilute sulfuric acid and mass loss decreased from 0.43 to 0.15% in 20 days. Its swelling in concentrated sulfuric acid increased more significantly: It rose from 42.9 to 56.9% swelling in 20 days.

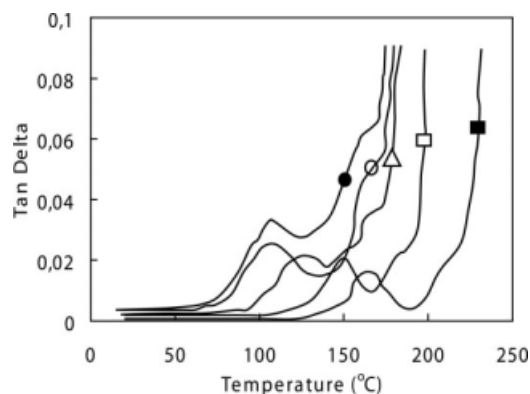
Table IV shows some interesting features due to chemical aging. The breaking stress of pure PC increased from 88 to 122 MPa and elongation at break decreased from 17.6 to 12.1% after immersion in H<sub>2</sub>SO<sub>4</sub>. Although we did not investigate thoroughly the reasons behind this change, the may be due post polymerization took caused by chemical aging. Although chemical aging in H<sub>2</sub>SO<sub>4</sub> embrittled stabilized PC, the change in breaking stress was not very significant (a decrease from 94 to 88 MPa). On the other hand, immersion in NaOH dramatically

**TABLE IV**  
**The Mechanical Properties of Pure and Stabiliser Added PC After Chemical Aging at 20°C for 30 Days (259.2 × 10<sup>4</sup>)**

No.	Composition	Breaking stress σ (MPa)	Elongation at break ε (%)	Modulus of Elasticity E (GPa)
1	PC <sup>a</sup>	77	6.3	1.4
2	PC <sup>a</sup> + 1.0% PhO	56	1.24	1.6
3	PC <sup>b</sup>	112	12.1	1.9
4	PC <sup>b</sup> + 1.0% PhO	87	4.3	2.0

<sup>a</sup> Exposed to 10% solution of caustic soda.

<sup>b</sup> Exposed to 10% a solution of sulfuric acid.



**Figure 10** The relationship between Tan delta and temperature for: (■) PC, (□) PC + 1.0% PhO, (Δ) PC + 10 wt % PhO, (○) PC + 15 wt % PhO, (●) PC + 20 wt % PhO.

decreased the breaking stress (from 94 to 56 MPa) and elongation at break (from 14.7 to 1.24%) of modified PC. It is probable that hydrolysis of modified may be the cause of this drop in tensile properties.

Figure 10 shows the dielectric analysis results where the variation of tan delta loss ( $\text{tg}\delta$ ) of pure and stabilized PC as a function of temperature is given. The diagram is characterized by two areas of relaxation: the low-temperature relaxation corresponds to the transition of polymer from glassy state to a plastic state while the high-temperature relaxation corresponds to a transition from a plastic state to a viscous state. During the second transition the crystalline parts of PC also melt. The maxima of  $\text{tg}\delta$  corresponds to the temperature at which the main chains are completely mobilized.

The tan delta peaks versus temperature results show that the pure PC has a higher glass transition temperature ( $T_g$ ) than the stabilized ones. There is about 50°C difference in the glass transition temperature for pure PC and PC + 20%PhO. As the amount of the stabilizer increased  $T_g$  decreased. The transition from glassy state to a plastic state is mainly due to the hastened molecular motion accelerated by the temperature increase. The  $T_g$  values for stabilized PC indicates that the presence of the stabilizer accelerated the molecular movement. This is an expected result. Because the presence of the high rates of stabilizer in the polymer matrix separated the main chains from each other thus increased the free volume of the polymer and caused a decrease in  $T_g$ . Probably only a small amount of PhO is truly combined with PC was adsorbed into the structure and acted as a boundary lubricant which facilitated the segmental mobility and reduced the glass transition temperature up to a particular limit.

The increase of molecular mobility at plasticization reduced not only rigidity, but also melting tem-

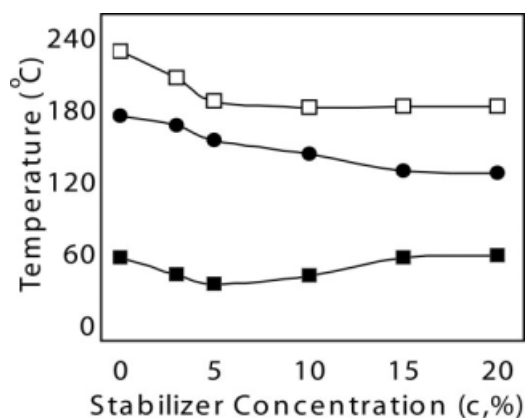
perature ( $T_m$ ) of PC. Figure 11 shows that the small amount of PhO (up to 1 wt %) significantly reduced the melt temperature. The effect of PhO on  $T_{\text{melt}}$  is stronger than on  $T_g$  and therefore the difference ( $T_m - T_g$ ) decreased. As the stabilizer content is further increased its negative effect on  $T_g$  became stronger than  $T_m$  and, as a result, the difference between the two temperatures ( $T_m - T_g$ ) increased. PhO contents higher than 5 wt % virtually had no effect on  $T_m$ .

## CONCLUSIONS

The mechanical and thermal behavior of PC was affected by the presence of a phosphinic stabilizer, *p*-butoxyphenylcyclohexyl-phosphine oxide. The mechanical properties were initially increased with small amount of stabilizers. At high stabilizer rates of ( $c > 1\%$ ), the mechanical properties deteriorated. When large amounts PhO are used, the rather bulky stabilizers pushed away the molecular chains of PC decreasing the polar forces between the PC chains which resulted in reduced tensile behavior.

The heat treatment at 200°C for 30 min had a detrimental effect on the mechanical behavior. Small amounts of stabilizer enhanced the breaking strength and elongation at break properties of heat treated PC. These effects were more significant at longer heat treatment times at lower temperatures (at 150°C for 250 and 500 h). The modulus of elasticity is usually reduced with stabilization. The melt temperature and glass transition are reduced with the stabilizer. This was probably because of the increased free volume of the polymer.

The effect of PhO on the tensile behavior of PC was similar to those obtained by different metallic phosphinic acids on the tensile behavior of PC.<sup>16</sup> On the other hand, PhO was a better thermal stabilizer for PC than the metallic phosphinic acids.



**Figure 11** The effects of stabilizer on the melt temperature and glass transition temperature of PC: (□) melt temperature ( $T_m$ ), (●) glass transition temperature ( $T_g$ ) and (■)  $T_m - T_g$ .

The stabilizer improved the resistance of PC against acidic environments. PhO was a better stabilizer than metallic phosphinic acids against basic environment.<sup>16</sup>

The work showed that stabilizer contents up to 1% may be employed as a plasticizer and stabilizer for PC used at high temperature applications up to 150°C and chemically hostile environments.

## References

1. Mark, H. F.; Gaylord, N. G. (editors). *Encyclopedia of Polymer Science and Technology*; Interscience Publishers: London, 1970; Vol. 12.
2. Allen, N. S. *Degradation and Stabilisation of Polyolefins*; Applied Science Publishers Ltd.: Essex, 1983.
3. Jeong, K. U.; Park, I. Y.; Kim, I. C.; Yoon, T. H. *J Appl Polym Sci* 2001, 80, 1198.
4. Morgan, A. B.; Tour, J. M. *J Appl Polym Sci* 1999, 73, 707.
5. Shau, M.; Wang, T. S. *J Appl Polym Sci* 1998, 68, 1397.
6. Chang, Y. L.; Wang, Y. Z.; Ban, D. M.; Yang, B.; Zhao, G. M. *Macromol Mater Eng* 2004, 289, 703.
7. Shau, M. D.; Lin, C. W.; Yang, W. H.; Lin, H. R. *J Appl Polym Sci* 2002, 84, 950.
8. Rusch-Salazar, L. A.; Sheares, V. V. *J Polym Sci A: Polym Chem* 2003, 41, 2277.
9. Miyatake, K.; Hay, A. S. *J Polym Sci Part A: Polym Chem* 2001, 39, 1854.
10. Shau, M.; Tsai, P.; Teng, W.; Hsu, W. *Eur Polym J* 2006, 42, 1899.
11. Jain, P.; Choudhary, V.; Varma, I. K. *Eur Polym J* 2003, 39, 181.
12. Zhang, Y.; Tebby, J. C.; Wheeler, J. W. *Eur Polym J* 1999, 35, 209.
13. Ozden, S.; Shaov, A. H.; Charayev, A. M.; Bidanikov, A. Y. *Polym Polym Compos* 1998, 6, 103.
14. Ozden, S.; Shaov, A. H.; Charayev, A. M.; Gurdaliyev, X. X. *J Appl Polym Sci* 2001, 80, 2113.
15. Ozden, S.; Shaov, A. H.; Charayev, A. M.; Mikitaev, A. K.; Bedanokov, A. Y. *Polym Polym Compos* 2001, 9, 213.
16. Ozden, S.; Shaov, A. H.; Charayev, A. M. *J Appl Polym Sci* 2007, 104, 3628.
17. Andreyev, A. P.; Galenko, N. V. *Plast Masses* (in Russian) 1968, 12, 63.
18. Bumistrov, E. F.; Kazaryan, K. S.; Borzenkova, A. Y. In *Organization of Researches on Synthesis and Determining the Effectivity of Polymer Stabilizers*, Chemistry Publishing House: Moscow, 1973; p 8.
19. Matveyeva, E. N.; Demidova, V. M.; Makarova, G. P. *Ways of Increasing Polyolefine Stability*, Chemistry Publishing House: Moscow, 1973; p 12.
20. Emanuel, N. M. *Vestnik AS* 1969, 7, 41.
21. *The quick reference on plastic masses*, Chemistry Publishing House: Moscow, 1969; Vol. 2, p 441.
22. Joffe, S. T.; Nesmeyanov, A. N. *Electromagnetic methods in chemistry* (in Russian), AN: Moscow 1963.
23. Akay, M.; Ozden, S. *Plast Rubber Compos Process Appl* 1996, 25, 138.
24. Powell, P. C. In *Engineering with Polymers*. Chapman and Hall: NewYork, 1983.
25. Aseyeva, R. M.; Zaikov, G. E. In *The Combustion of Polymeric Materials*. Nauka Publishing House: Moscow, 1981; p 280.
26. Silverstein, R.; Bussler, H.; Morrill, T. *Spectrometric Identification of Organic Compounds*, Mir Publishing House: Moscow, 1977.
27. Moiseyev, Y. V.; Zaikov, G. E. In *Chem Stability of Polymers in Aggressive Conditions*. Chemistry Publishing House: Moscow, 1979; p 288.
28. Fried, J. R. *Polymer Science and Technology*, Prentice Hall: New Jersey, 1995.