

The Effects of *p*-Butoxyphenylcyclohexyl-phosphinic Acid on the Properties of PC Based on Bisphenol A

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ABSTRACT: A polymer stabilizer, *p*-butoxyphenylcyclohexyl-phosphinic acid, was introduced into an industrial polymer, a Bisphenol A-based polycarbonate, and the effects of this stabilizer on the mechanical and thermal properties were investigated. The mechanical properties were improved with small amount of stabilizers, while thermal properties were not effected significantly. For higher contents of stabilizer, both thermal and mechanical properties were deteriorated. This deterioration was caused by the increase of molecular distance between the chains, which lead to the reduction of polar forces and an increase in the free volume of the polymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2113–2119, 2001

Key words: stabilizer; polycarbonate; *p*-butoxyphenylcyclohexyl; phosphinic acid; polar forces

INTRODUCTION

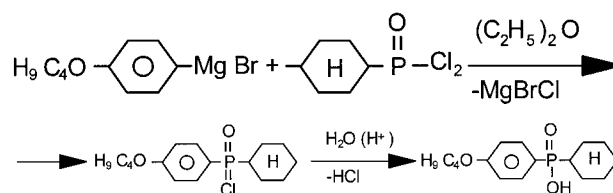
Phosphinic compounds with five covalent bonds are one of the most commonly used types of polymer stabilizers.¹ One of these stabilizers is tri-(*p*-nonyl phenyl) phosphite. Although the stabilizers are frequently employed in polymers, their effects on the mechanical and thermal properties have been neglected. Therefore, it is important to investigate the effects of this stabilizer on polymers. In the polymer industry, a stabilizer, commercially known as polygrad, is widely used. The current work is aimed to introduce a new stabilizer that can be produced more economically and may be a substitute for polygrad. It is believed that this new field of the investigation will lead to a new understanding of the application of this stabilizer. In the present work, a polycarbonate

(PC) obtained from Bisphenol A was reacted with a new stabilizer (*p*-butoxyphenylcyclohexyl-phosphinic acid) obtained from tri-(*p*-nonyl phenyl) phosphite. The mechanical behavior and the thermal stability of the pure and stabilizer added polymers were compared.

EXPERIMENTS

Material Synthesis

The phosphorus compounds were synthesized by the Grignard³ reaction method. The reaction process was as follows:



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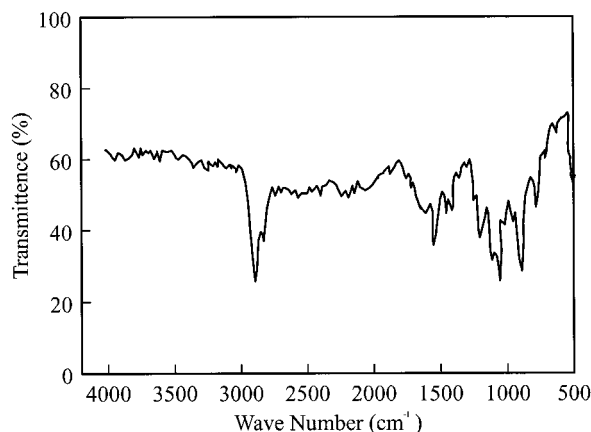


Figure 1 The IR spectrum of cyclohexyl phosphinic acid.

To confirm that the resultant product on the right-hand side of the equation was *p*-butoxyphenylcyclohexyl-phosphinic acid, the calculated and measured atomic masses of the elements were compared, and the following results were obtained for a molecular structure $C_{16}H_{25}O_3P$: Calculated, %: P 10.47, C 64.86, H 8.45; measured, %: P 10.52, C 64.43, H 8.57.

The IR-spectrometric results of phosphinic acid revealed (see Fig. 1) absorption bands at 1350–1175, 1600, and 820–750 (wave number, cm^{-1}). These absorption band peaks correspond to $P=O$, $C=C$ (aromatic links) and $P-C$ groups, respectively.⁴ Both IR-spectrometry and molecular mass calculation confirmed that the end product was *p*-butoxyphenylcyclohexyl-phosphinic acid.

The polycarbonate and the stabilizer were dissolved in methylenchloride (CH_2Cl_2), and the solution was poured into a glass surface. Methylenchloride was vaporised and the resultant polymeric sheet was put into an SPT-200 oven under vacuum at 100°C for 2 h. Because the vaporization temperature of methylenchloride 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. To obtain a chemical reaction between the polymer and stabilizer, high temperatures were necessary. For our experiments, the high temperatures that could lead to chemical reactions were avoided.

The usual fabrication methods give a PC with an amorphous molecular structure. In our work, a semicrystalline PC was employed. To obtain a

semicrystalline structure, the polymer and the stabilizer were dissolved in methylenchloride inside a plate. The fast vaporization of the methylenchloride was prevented by covering the plate, and the speed of the process was significantly reduced. The mixture was kept for 1 day and night and, therefore, the polymer had enough time to crystallize.

The semicrystalline polymers have a more ordered structure, and it was thought that the application of the stabilizer to a crystallized polymer would be more prominent and easy to investigate its end effects. This is because the stabilizer particles will be placed between the crystalline surfaces and thus influence the behavior of the polymer more significantly. The PC used in our experiments had a commercial name of “Kaprolaktam” and were commercially obtained from Dzerjinsk in Russia.

The amount of stabilizer added to the polymer changed between 0.1–30% by weight.

Mechanical and Thermal Tests

The measurement of the mechanical properties of PC was carried out by using sheet specimens ($100 \times 10 \times 0.1$ mm) 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. Specimens were heat treated on a SPT model oven at 200°C for 30 min and at 150°C for 250 h. Following the heat treatments, the mechanical properties were measured.

The thermomechanical analyses were conducted on a Pribor thermomechanical analyzer. 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.

Thermogravimetric analyses of the polymers were carried out by means of a MOM derivatography (made in Hungary). The temperature was increased at the rate of 10°C/min in air. The amount of the polymer tested was 50 mg.

The crystallinity of pure PC and stabilizer-added PC were measured by means of X-ray diffraction analyses on a DRON-3 instrument. The diffraction graphs were obtained by a CUPRUM analyzer using $Cu K\alpha_1$ radiation with a wave length of $\lambda = 1.5405 \text{ \AA}$.

The fire resistivity of the polymers was evaluated by the oxygen index method.

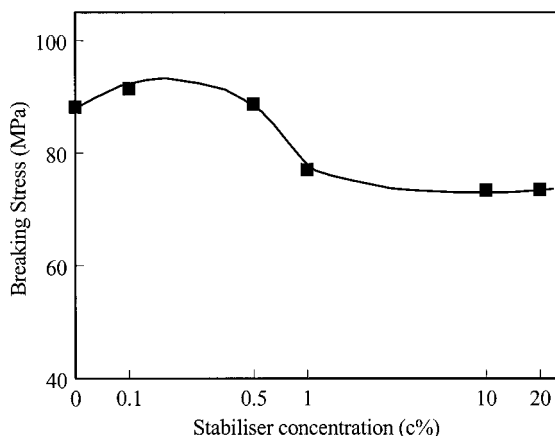


Figure 2 The relationship between the breaking tensile stress and stabilizer concentration for PC.

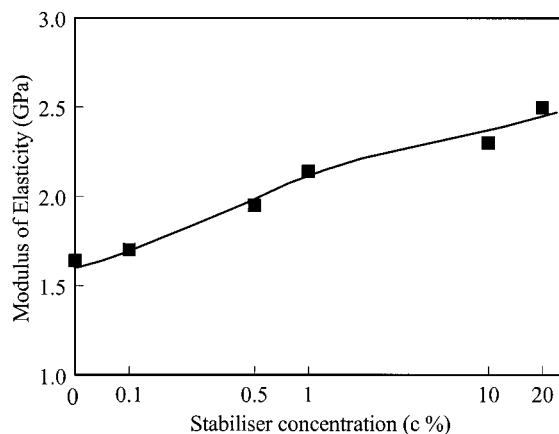


Figure 4 The relationship between the modulus of elasticity and stabilizer concentration for PC.

RESULTS AND DISCUSSION

Mechanical Properties

The effects of the stabilizer concentration on the mechanical behavior of the PC are presented in Figures 2–4. Figure 2 shows the relationship between the breaking strength and concentration rate of stabilizer. Only a slight increase (from 80 to 94 MPa) in breaking strength of PC was obtained with the increase of the stabilizer. After the concentration rate exceeded 0.5% the stress fell and flattened out at about 75 Mpa.

The relationship between the elongation at break and the stabilizer concentration is presented in Figure 3. It is interesting to observe that the elongation at break has shown a very similar behavior to the behavior of the breaking strength. The elongation

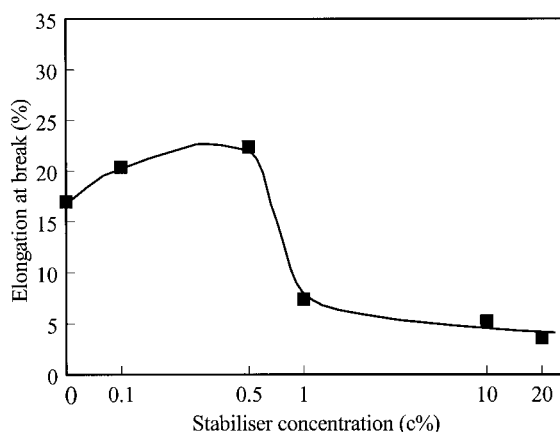


Figure 3 The relationship between the elongation at break and stabilizer concentration for PC.

at break increased steadily with the stabilizer rate, and after the phosphinic acid rate exceeded 0.5%, it fell sharply. The decrease (from 22 to 5%) was more significant than the decrease in breaking strength.

On the other hand, the modulus of elasticity, E , showed a continuous increase with the amount of the stabilizer (see Fig. 4). The change in modulus of elasticity is opposite to the behavior of the elongation at break. This is an expected behavior. As the modulus of elasticity is increased, the material becomes more rigid and consequently the elongation at break (ductility) decreases. This behavior is confirmed in Figures 2 and 3.

Although all mechanical properties were influenced by the addition of the stabilizer, the most dramatic effect was observed in elongation at break, where the reduction after 0.5% stabilizer, was about 500%.

To investigate the causes of these changes in mechanical behavior, the change in crystallinity of the polymer was also analyzed and presented in Figure 5. The crystallinity was slightly increased until 0.5% stabilizer and then fell sharply (from 41 to 33%). The change in the crystallinity with the stabilizer content was very similar to the behaviors of breaking in strength and elongation at break. Therefore, it can be concluded that, the same mechanism was responsible for all these mechanical behaviors.

After the mixing, it is probable that stabilizer particles are placed along the molecular chains of PC. It is important to remember that the oxygen atoms in the phosphinic acid are negatively charged. These negatively charged molecules attract the positively charged polar units of neighboring polymer (PC) chains. As a result, the mo-

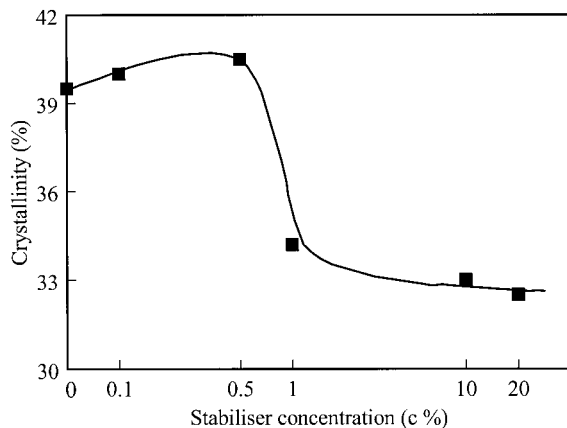


Figure 5 The relationship between the crystallinity and stabilizer concentration for PC.

lecular chains of the polymer are pulled towards each other by the negatively charged acid units and a more compact structure with more closely aligned molecules is obtained. This suggestion was supported with the crystallinity data that shows an increase in crystallinity at smaller acid ratios.

On the other hand, as the amount of stabilizer is increased, the bushy nature of the acidic compound gains prominence and the main chains of the molecules are pushed further away. As a result, the polar forces become less effective because of the increased distance between the molecule chains, and thus the density decreases. This conclusion is supported with the crystallinity data that show a decrease after the addition of 0.5% and more stabilizer.

It is probable that the stabilizer particles in the polymer matrix may have accelerated the yielding of the molecule chains and caused an initial increase in elongation at break. As the amount of the stabilizer was increased, the acidic particles that were dispersed in the polymeric matrix were agglomerated and started to behave like Griffith flaws, which caused a decrease in breaking strength and elongation at break.

To support the above argument, diffraction graph of the polymer with different stabilizer concentrations were presented in Figure 6. The diffraction graphs for pure PC and stabilizer added PC were similar, and the peak for both cases was at 17° . This meant that the distance between the molecular chains were 5.21 Armstrong (A°).⁶ It is widely known that the distance between the chains depend on their polarity. As the distance between the molecule chains decreases, the polar-

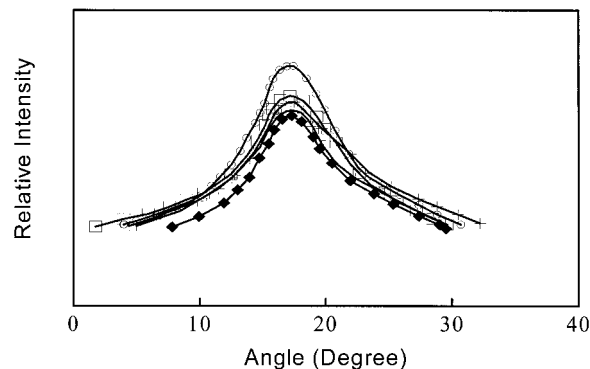


Figure 6 The relationship between the diffraction and angle for: (\square) PC, (\circ) PC+5% PHOS, (\blacklozenge) PC+10% PHOS, (\times) PC+15% PHOS, and ($+$) PC+20% PHOS.

ity increases or vice versa. The polar forces become predominant when the distance between the main molecular chains are 3–4 A° . It can be argued that, because in our research the distance between the chains were 5.21 A° , the strength of the polar forces were reduced and the polymer lost its compact and dense structure after the introducing of the high concentration ratios. Consequently, the density is reduced and the mechanical and thermal properties were deteriorated.

The IR measurements did not reveal any molecular change or branching. If the specimens were kept at high temperatures, a branching of the polymer could be expected. But the processing conditions used in our work were not high enough to enable branching.

Thermal Properties

The thermal stability of the pure PC and stabilizer added PC were presented in Table I. The

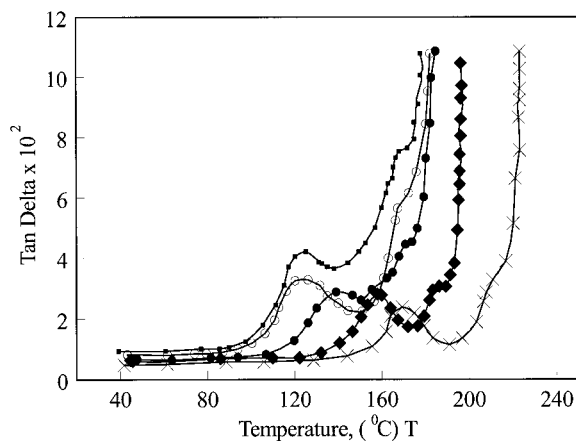


Figure 7 The relationship between the Tan δ and temperature for: (\times) PC, (\blacklozenge) PC+1% PHOS, (\bullet) PC+10% PHOS, (\circ) PC+15% PHOS, and (\blacksquare) PC+20% PHOS.

Table I The Thermal Stability of Pure and Stabilizer-Added PC

No.	Composition	Temperature (°C)			
		Beginning of Mass Loss	2% Mass Loss	10% Mass Loss	50% Mass Loss
1	PC	360	410	433	476
2	PC + 0.1% PHOS	360	400	430	468
3	PC + 0.5% PHOS	360	405	430	469
4	PC + 1% PHOS	350	375	418	469
5	PC + 3% PHOS	320	350	410	480
6	PC + 15% PHOS	310	332	375	445

effects of the stabilizer on the thermal stability of the polymers were insignificant for small concentrations and significantly negative for larger concentrations.

The heat treatment of pure PC and stabilizer (PHOS) added PC for 30 min at 200°C resulted in a dramatic reduction of the mechanical properties (see Table II). While the reduction in the breaking strength was 28% for PC, it was 135% for PC + 0.5% PHOS. On the other hand, the reduction in the elongation at break was about 400 and 900% for PC and PC + 0.5% PHOS, respectively. While the modulus of elasticity for the heat-treated pure PC showed an increase, it fell for the different rates of stabilizer. This behavior is in agreement with the literature. Akay and Ozden⁷ 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 this changes to the removal of the residual stresses in the polymer during the heat treatment.

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 (stabilizer added 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.⁵ Therefore, the reason for the mechanical deterioration of the polymer after the heat treatment is probably different. The probable reason for the mechanical deterioration is the breakage of the molecular chains caused by heat treatment. It is seen that the most significant reductions in breaking strength and elongation at break were observed for stabilizer added polymer. It is thought that the phosphinic acid particles along the main molecular chain were broken after heat treatment, and this phenomenon led to the poor mechanical and thermal performance.

To investigate the effects of heat treatment on the molecular structure of the polycarbonate, paramagnetic resonance analysis was employed. A Se/x2543 Rayopan spectrometer was used. The

Table II The Mechanical Properties of Heat-Treated Pure and Stabilizer-Added PC

No.	Composition	$T = 200^{\circ}\text{C } t = 30 \text{ min}$			$T = 150^{\circ}\text{C } t = 250 \text{ h}$		
		σ_b (MPa)	ϵ %	E (GPa)	σ_b (MPa)	ϵ %	E (GPa)
6	PC	64	3.5	4	70	4	2.2
2	PC + 0.1% PHOS	45	6.9	1.4 ^b	54	2.9	1.8
3	PC + 0.5% PHOS	46	3.4	1.5 ^b	a	a	a
4	PC + 1% PHOS	25	2.2	1.4 ^b	a	a	a
5	PC + 1% Polygrad	62	4.1	1.5 ^b	62	4.1	1.5

^a Failed without significant resistance to the forces applied.

^b Plasticized.

Table III The Oxygen Index of the Pure and Stabilizer-Added PC

No.	Composition	Oxygen Index, % (OI)
1	PC	26.5
2	PC + 0.1% PHOS	26.5
3	PC + 0.5% PHOS	27
4	PC + 1% PHOS	27.5
5	PC + 3% PHOS	27.5
6	PC + 5% PHOS	33
7	PC + 10% PHOS	34
8	PC + 15% PHOS	40
9	PC + 20% PHOS	42

specimens were heat treated at 250, 275, and 300°C for 30 min, before testing. During the spectrometer measurements, sometimes the signals showed double peaks, which indicated chain breakage along the molecular chain and initiation of new radicals. As the annealing temperature increased, the breakage also increased.

The melting temperature of PHOS is 96°C. Therefore, it is probable that at higher temperature annealing the acidic particles melt and active radicals are produced which accelerated the destruction of the chains of the polymer.

The shapes of the spectrometric results were similar for pure and heat-treated specimens. This means that the structures of the molecules were the same, and no crosslinking took place during heat treatment. The only difference was observed

in the intensity of the signal outputs. As the amount of stabilizer was reduced, the signals became smaller. When the concentration was 1%, the absorption intensity was 15% less than the pure material. On the other hand, when the stabilizer content was 20%, the intensity was too high to obtain reasonable results.

Therefore, it was concluded that chain scission is the probable cause of reduction in the mechanical properties of the phosphinic acid-added PC and after heat treatment. Probably the presence of the acidic structures encouraged this outcome.

The $\tan \delta$ peaks versus temperature results show that (see Fig. 7) the pure PC has a higher glass transition temperature (T_g). There is about 50°C difference in the glass transition temperature for pure PC and PC+20%PHOS. As the amount of the stabilizer increased the, 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 stabilizer-added PC indicates that the presence of the stabilizer accelerated the molecular movement. This is an expected result. The presence of the high rates of stabilizer in the polymer matrix separated the main chains from each other, thus increasing the free volume of the polymer and causing a decrease in T_g . These findings are in agreement with the literature.⁹

The pure and stabilizer-added PC are resistant fire. The oxygen index significantly increased

Table IV The Environmental Effects of Different Acid and Bases on the Polycarbonate at 20°C

No.	Compositions	Time (s) $\times 10^4$	Mass Loss Δm (%) in NaOH 10%	Mass Loss Δm (%) in NaOH 40%	Mass Loss Δm (%) in H ₂ SO ₄ 10%	Mass Loss Δm (%) in H ₂ SO ₄ 96%
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	-2.5	—	-0.53	+42.9
6	PC	216	-3.16	—	-0.43	+54.4
7	PC	259.2	-3.64	—	-0.6	+59.9
8	PC + 1% PHOS	8.6	-0.05	-15.5	+0.35	+2.42
9	PC + 1% PHOS	43.2	-0.98	-48.2	+0.35	+32.9
10	PC + 1% PHOS	86.4	-1.54	-85.2	+0.25	+69.1
11	PC + 1% PHOS	129.6	-2.98	—	+0.25	+70.2
12	PC + 1% PHOS	172.8	-4.14	—	+0.15	+82.5
13	PC + 1% PHOS	216	-5.29	—	-0.15	+87
14	PC + 1% PHOS	259.2	-6.31	—	-0.15	+90.3

— The polymers completely dissolved.

with higher stabilizer concentrations (see Table III). Table IV shows that the introduction of the stabilizer has a beneficial effect on the resistance of the polymer to the environmental effects.

CONCLUSION

The mechanical and thermal behavior of polycarbonate was effected by the presence of a phosphinic stabilizer, *p*-butoxyphenylcyclohexyl-phosphinic acid. The mechanical properties were initially increased with small amount of stabilizers. At high concentration rates of the stabilizer (>1%) the mechanical properties decreased. This reduction was caused by the increased distance between molecules caused by the presence of the large amounts of the acidic components between the molecules of PC. The heat treatment at 200°C for 30 min caused the chain scissions, and this heat treatment had a detrimental effect on the mechanical behavior. After heat treatment, breaking strength, modulus of elasticity, and elongation at break decreased for stabilizer-added PC. The thermal stability was also negatively effected at higher stabilizer concentrations. This

was probably because of the increased free volume of the polymer.

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