Compositions Based on Aromatic Polycarbonate and Metallic Phosphinic Acids

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ABSTRACT: Four different polymer stabilizers were synthesized from the salt derivatives of phosphinic acids (*p*-butoxyphenylcyclohexyl-phosphinic acid) and potassium, nickel, and two different grades of iron metals. The synthesized stabilizers were introduced into an industrial polycarbonate (PC) and their effects on the mechanical and thermal behavior of PC were investigated. The experiments were carried on following the introduction of the stabilizer into the polymer. The mechanical properties were sensitive to the amount of the stabilizer. Small amounts of potassium increased the breaking stress, the modulus of elasticity, and elongation at break of PC. On the other hand, nickel and iron increased the modulus of elasticity and decreased the breaking stress and elongation at break. The additives negatively affected the thermal properties. This deterioration was caused by the increase of molecular distance between the chains that led to the reduction of polar forces and increased the free volume of the polymer. Heat treatment increased the brittleness and reduced the breaking strength, ductility, and modulus of elasticity of modified PC. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3628–3636, 2007

Key words: thermal properties; mechanical properties; metal–organic catalysts/organometallic; stabilization

INTRODUCTION

The derivatives of phosphinic compounds are one of the most commonly used types of polymer stabilizers.[1,2] Bai et al.[3] showed that the addition of triphenyl Phosphite into the PBT/PC blends suppressed the trans-esterfication, increased the Vicat temperature, and reduced the impact strength. Mukhamedgaliev[4] increased the oxygen index of the ED-20 epoxy resin, ABS, and polymethyl methacrylate by adding a small amount (up to 3%) of *para*-trisphosphate allyltriphenylphosphonium halide.

Jeong et al.[5] showed that poly(arylene ether phosphine oxide) improved the adhesive behavior and flame resistance of epoxy resins. Morgan and Tour[6] 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 tetra-oxirane rings in the main chain.[7]

Shu et al.[8] synthesized two kinds of phosphonate-containing bismaleimide monomers and blended them with two epoxy systems. They reported that the new materials exhibited good thermal stability and flame resistance while the mechanical strength was reduced. Wang et al.[9] reported that potassium diphenyl sulfonate, poly(sulfonyl phenylene phosphonate), and their mixtures are effective flame-retardants for polycarbonate.

A new phosphorus-containing polymeric retardant, synthesized from phenylphosphonic dichloride and 2-(6-oxido-6*H*-dibenz ⟨*c*,*e*⟩,⟨1,2⟩ oxaphosphorin-6-yl)1, 4-benzenediol increased the flame retardancy of poly (ethylene terephthalate) epoxy resin and unsaturated polyester.[10]

Other examples of phosphinic stabilizers are phosphinic acids that are between strong and weak acids.[11] Miyatake and Hay[12] obtained new polymers based on bisphenol and three arylene difluoride monomers containing phosphine oxide, phosphinic. The molecular weight and glass-transition temperature of the new polymers were affected by the phosphine group in the main chain.

Yang and Yang[13] increased the flame retardance performance of 50/50 cotton/nylon fabric and obtained excellent laundering durability with the application of hydroxyl-functional flame retardant organophosphorus oligomer to the fabric.

Lánská et al.[14] investigated the thermo-oxidative behavior of hexano-6-lactam in the presence of alkali salts of metals such as Li, Na, K, and Rb. They showed that while KCl and KBr are significant initiators of hexano-6-lactam oxidation, the other metallic salts inhibited oxidation.

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Yee and Ishida[15] showed that the incorporation of various transition metal salts increased the char formation of polybenzoxazines. Price et al.[16] studied the effects of phosphorus-containing species on polystyrene (PS). They concluded that the addition of 3.5% phosphorous to PS resulted in flame retardation. The phosphonates were more efficient flame retardants than were the phosphates for PS.

Davies et al.[17] showed that different series of metal ion–ammonium polyphosphate (APP) (particularly Mn^{2+} and Zn^{2+}) promoted thermal degradation of APP at lower temperatures enabling the flame retardant activity to commence at lower temperatures in the polymer matrix and thereby enhancing flame retardant efficiency.

Ribera et al.[18] obtained phosphorous-containing epoxy resins by crosslinking 2,4-diaminotoluene with diglycidyl ether of isobutyl bis(hydroxypropyl)phosphine oxide and diglycidyl ether of bisphenol A. They showed that the weight loss rate of phosphorous-containing resins was lower than that of the phosphorous-free resins for the thermoxidative degradation and the presence of phosphorous increased the limiting oxygen index (LOI) values.

Shau et al.[19] 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. Polyphosphazene elastomers were shown to have good fire resistance.[20] Poly(arylene phosphine oxide) materials synthesized from fluorinated poly(arylene phosphine oxide) by post polymerization have shown high solubility and film-forming ability.[21]

Although these phosphone containing stabilizers are frequently used, their effects on the mechanical and thermal properties of the polymers need further investigation. Therefore, the investigation of these effects is considered to be important. In the polymer industry a polymer stabilizer commercially known as polygrad is widely used. The current work aims to introduce a new stabilizer and investigate its effects so that it may be employed as a substitute for polygrad.

It is believed that this new field of investigation will lead to a new understanding of the applications of these stabilizers. In our previous works, the effects of the phosphinic metallic acids on the mechanical and thermal properties of copolyethers based on bisphenol-A and phenolphthalein,[22] the effects of *p*-butoxyphenylcyclohexyl-phosphinic acid on the mechanical and thermal properties of the copolyethers based on bisphenol-A and phenolphthalein,[23] and the effects of *p*-butoxyphenylcyclohexyl-phosphinic acid on the mechanical and thermal properties of PC were investigated.[24]

The present work was performed at the same laboratory as a continuation of the previous works and aimed at the introduction of novel stabilizers. Four different phosphinic metallic acidic salts, based on potassium (K), nickel (Ni), and two different grades of iron denoted as Fe(II) and F(III), were processed and mixed with polycarbonate. The mechanical behavior and thermal stability of the pure and stabilized polymers were compared.

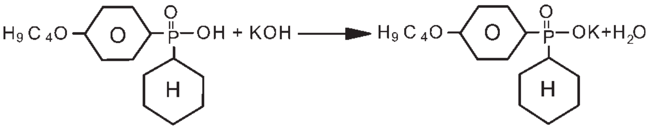
EXPERIMENTAL

Material synthesis

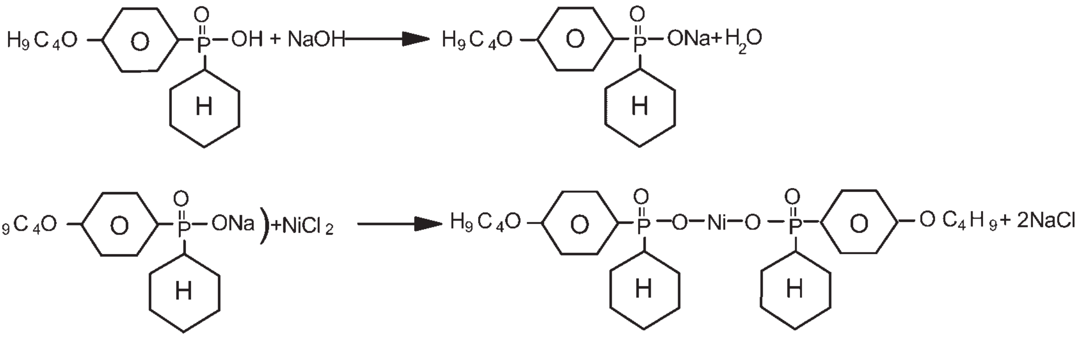
The phosphorus compounds were synthesized by the Grignard reaction method and this process was described in detail in literature.[25]

The metallic phosphinic acids were synthesized by the following reaction:

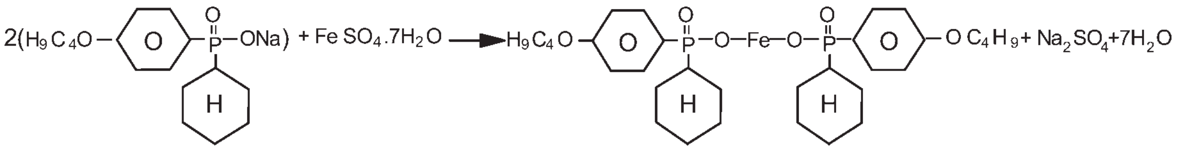
1. the synthesis of phosphinic potassium acid (denoted as K):



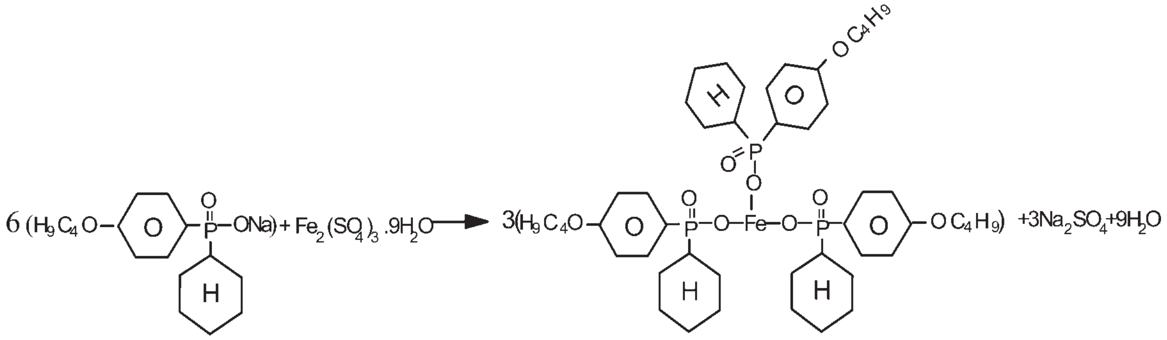
2. the synthesis of phosphinic nickel acid (denoted as Ni):



3. the synthesis of phosphinic ferrium sulfate acid (denoted as F(II)):



4. the synthesis of phosphinic ferrium sulfate acid (denoted as F(III)):



To confirm the structure of the metallic phosphinic acids, the calculated and measured atomic masses of the phosphorous element were compared (see Table I). The atomic mass measurements were performed using a quantitative element analyzer. The percentage mass of the stabilizer obtained after the chemical reactions, the melting temperatures, and colors of the resultant stabilizers are also presented in Table I.

The usual fabrication methods give a PC with an amorphous molecular structure. In our work, a semicrystalline PC was employed. 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 is placed between the crystalline surfaces and thus influence the behavior of the polymer more significantly.

The polycarbonate and the stabilizers were dissolved in methylenchloride (CH_2Cl_2) and the solution was poured into a glass surface. Both the polymer and additives are dissolved completely in the solution. To obtain a semicrystalline structure, 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 one day and night at room temperature to allow the polymer enough time to crystallize. The thickness of the polymer was controlled by the volume of the solution.

After methylenchloride was vaporized, the resultant polymeric sheet was put into an SPT-200 oven under vacuum at 100°C for 2 h. Since the vaporization temperature of methylenchloride is 36°C, the temperature was high enough for the sheets to be completely dried.

During the process no chemical reaction took place. While the PC and additives were dissolved in the sol-

TABLE I
Some Properties of the Phosphinic Metallic Salts

Composition	Percentage mass of the stabilizer (%)	Melt temperature (°C)	Color	Measured mass of P (%)	Calculated mass of P (%)
$H_9C_4OC_6H_4P(O)(c\text{-}C_6H_{11})OK$	98	285–286	White	9.51	9.28
$[H_9C_4OC_6H_4P(O)(c\text{-}C_6H_{11})O]_2Ni$	81	125–126	Grey	10.04	9.55
$[H_9C_4OC_6H_4P(O)(c\text{-}C_6H_{11})O]_2Fe$	97	205–206	Light brown	9.74	9.59
$[H_9C_4OC_6H_4P(O)(c\text{-}C_6H_{11})O]_3Fe$	96	250[a]	Yellow	10.15	9.88

[a] Degraded during melting.

vent and dried, high temperatures that could lead to chemical reactions were avoided. As the degrading temperature of PC is around 360°C, the working temperature of 100°C had no degradation effect on PC

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 and 30% by weight.

Tensile and thermal tests

The measurement of the mechanical properties of pure and stabilizer added PC was carried out according to GOST (Russian State Standards) 17-316-71 by using film specimens ($100 \times 10 \times 0.1$ 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 sample and the average values were used. To investigate the effect of heat treatment on the pure and stabilizer added PC, specimens were heat-treated in a SPT model oven at 200°C for 30 min and their mechanical properties were measured again.

Thermogravimetric analyses of the polymers were carried out by means of an electric ''Seteram'' type thermobalance. The temperature was increased at 10°C/min in Argon. The amount of the polymer tested was 50 mg.

The fire resistivity of the polymers was evaluated by the oxygen index method. The oxygen index test carried out on film samples (strips) fixed vertically in the cylindrical chamber through which passes a laminar stream of a mixture of nitrogen with oxygen. Tests are carried out at various ratios of a gas mixture until the optimum burning of the sample is reached. The sample is set on fire from the top end with the help of a gas torch that is then withdrawn.

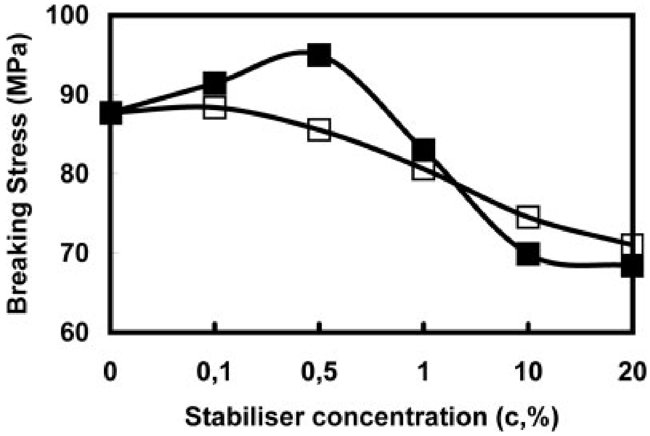


Figure 1 The relationship between the tensile breaking stress of PC and stabilizer concentration for (■) K and (□) Ni.

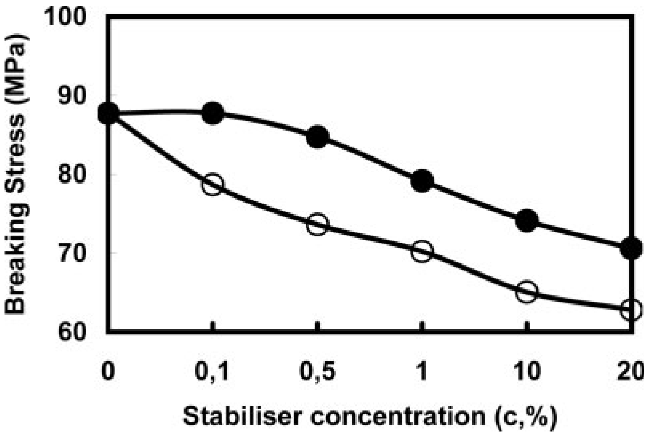


Figure 2 The relationship between the tensile breaking stress of PC stabilizer concentration for (●) Fe(II) and (○) Fe(III).

Pure and additive added PC were inserted into diluted and concentrated acids of H_2SO (10% H_2SO_4 and 96% H_2SO_4) and alkalis (10% NaOH and 40% NaOH) and kept in those environments for 1, 5, 10, 15, 20, and 30 days.

RESULTS AND DISCUSSION

Mechanical properties

The effects of phosphinic metallic stabilizers on the tensile behavior of PC are presented in Figures 1–7. Figure 1 shows the relationship between the breaking strength (σ_b) and the concentration rate of potassium (K) and nickel (Ni) stabilizers. Although the effect of both stabilizers on PC is similar, the effect of potassium is more prominent. σ_b increased with potassium stabilizer until it reached 0.5% and then the stress decreased with the further addition of K stabilizer. On the other hand, small amounts of nickel stabilizer did

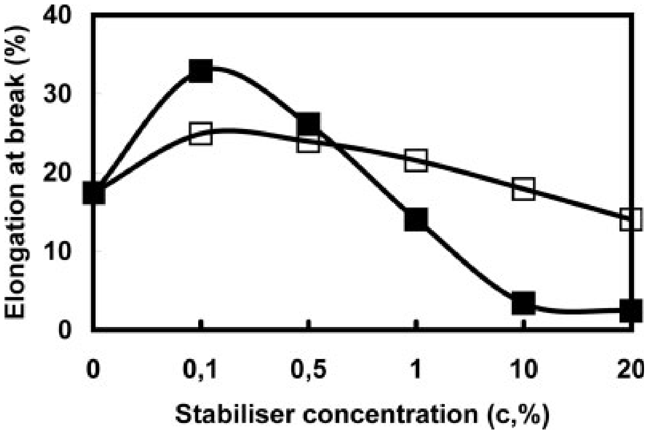


Figure 3 The relationship between the elongation at break of PC and stabilizer concentration for (■) K and (□) Ni.

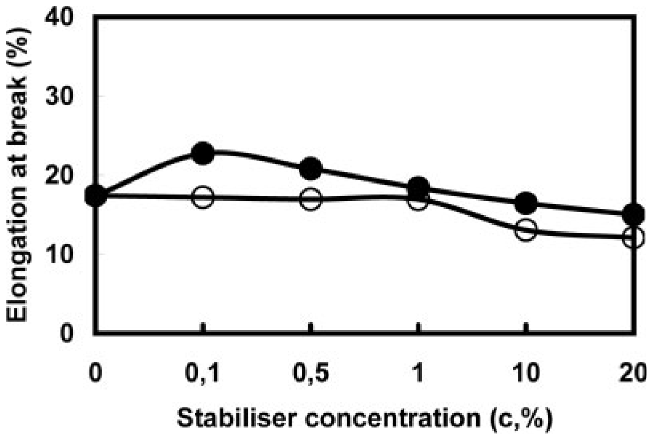


Figure 4 The relationship between the elongation at break of PC and stabilizer concentration for (●) Fe(II) and (○) Fe(III).

not have an effect on the breaking strength of PC, and as the stabilizer concentration is further increased the stress steadily decreased. The decrease in σ_b (between maximum and minimum values) was about 30 and 22% for potassium and nickel stabilizers, respectively.

Figure 2 shows the effects of Fe(II) and Fe(III) stabilizers on the breaking strength of PC. Although both stabilizers had a negative effect on the breaking strength for all concentration rates, Fe(II) had almost the same effect as Ni. The decrease in σ_b was 30% for Fe(III) and 20% for Fe(II) as concentration rate increased from $c = 0$ to $c = 20\%$.

The relationship between the elongation at break, ε (%), and the potassium and nickel stabilizer are presented in Figure 3. The effects of the stabilizers on PC were similar to that of breaking stress. Elongation at break initially increased with the concentration rate of potassium and then decreased with the further increase of stabilizer. ε decreased from 33% ($c = 0.1\%$) to 3% ($c = 20\%$). Nickel did not have a significant effect on ε. The elongation at break was around 18–24% for all concentration rates. Figure 4 shows that the iron stabilizers did not significantly affect the ductility of PC. For both stabilizers ε was in a range of 15–22% for all concentration rates.

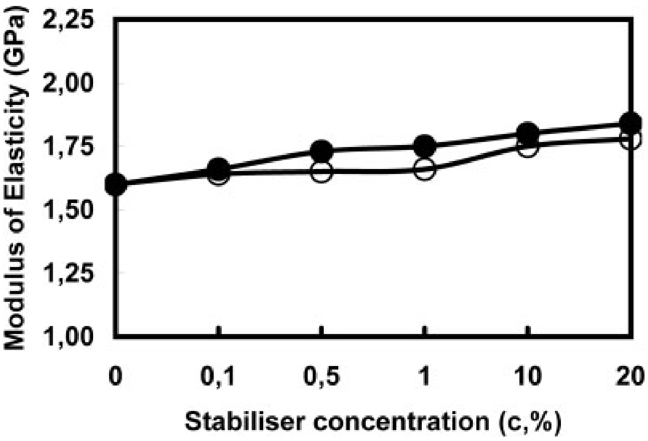


Figure 6 The relationship between the modulus of elasticity of PC and stabilizer concentration for (●) Fe(II) and (○) Fe(III).

The modulus of elasticity E increased with potassium stabilizer until the concentration rate reached 0.5%, and then E steadily decreased with the further increase of c (see Fig. 5). On the other hand E increased slowly and steadily with the nickel stabilizer. The increase in E was about 13%. Figure 6 shows that the phosphinic iron stabilizers Fe(II) and Fe(III)) have a modest positive effect on the modulus of elasticity. E increased steadily with the increase of both stabilizers. The total increase was about 15%. Figure 7 shows a typical tensile behavior of pure and potassium stabilizer added PC.

The mechanical properties have showed a dependence on the level of concentration rate, but the most dramatic effect was exhibited by K. The effect of K on the

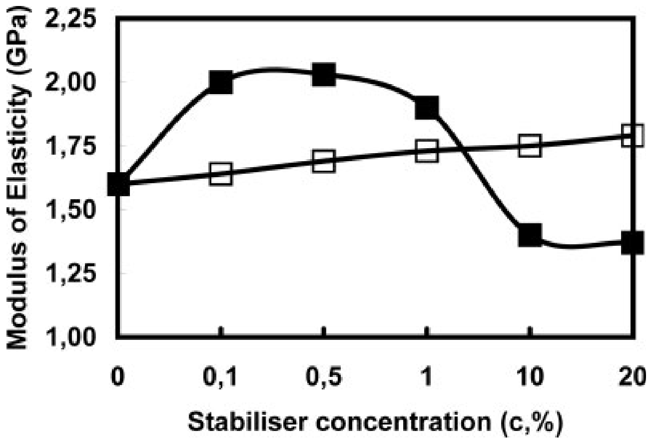


Figure 5 The relationship between the modulus of elasticity of PC and stabilizer concentration for (■) K and (□) Ni.

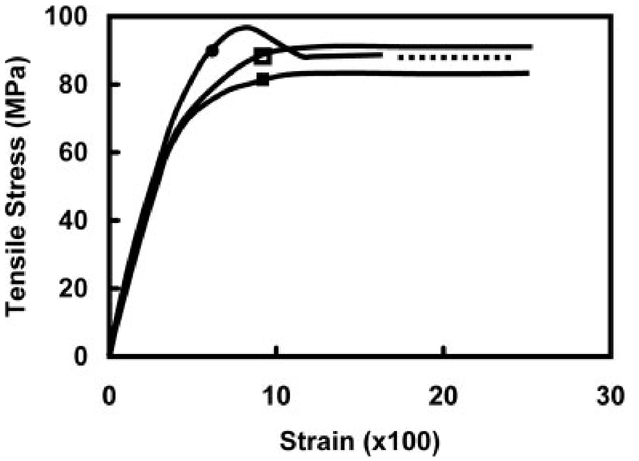


Figure 7 A Typical tensile behavior of PC with (●) no stabilizer, (■) 0.1% K, and (□) 0.5% K.

breaking stress, elongation at break, and modulus of elasticity was similar. All the mechanical behaviors initially increased at smaller stabilizer rates and then decreased with the addition of higher concentration rates ($c > 1\%$). Therefore, it can be concluded that only small concentration rates of phosphinic potassium has a beneficial effect on the behavior of PC. On the other hand, the increase in both E and ε is an unexpected result as the ductility is expected to increase with the decrease of the modulus of the elasticity. The modulus of elasticity E slowly increased while the ductility decreased for the other three stabilizers. It can be concluded that the presence of metallic stabilizers (Ni, Fe(II), Fe(III)) caused an increase in E and decrease in ε.

The causes of different effects of these stabilizers on the mechanical behaviors need explanation. It is important to remember that the oxygen atoms in the phosphinic acid are negatively charged. It is probable that the stabilizer particles, placed along the molecular chains of PC, attracted the positively charged polar units of the neighboring polymeric chains and as result, a more compact structure is obtained. This mechanism operates only at small rates of concentrations that cause the initial improvement in the tensile behaviors.

The stabilizers seem to have two different effects. While the presence of the small rates of stabilizers enhance the attractive polar forces between the polymer chains and enhances the tensile behavior, higher concentration rates PC chains are pushed away from each other by the bulky (bushy) stabilizers. The sizes of the metallic stabilizers increase with the numbers of valence electrons, and as a result, the stabilizers became too bulky (high molecular volumes). At higher concentration rates, the bulky nature of these molecules cause significant steric changes in the main polymeric chains, inhibiting a better packing and therefore causing a reduction in the mechanical properties. Therefore, it may be concluded that these two conflicting effects control the behavior of the stabilized PC.

The different effects of the different stabilizers may be explained in this way: while the potassium phosphinic acid had only one oxygen atom to attract PC molecules, Ni, Fe(II), and Fe(III) based stabilizers had higher number of oxygen atoms that increases the inter molecular forces and is responsible for the initial improvement of mechanical behavior.

It is also probable that as the stabilizer concentration rate was increased, the dispersed acid metallic particles were agglomerated and started to behave like Griffith flaws, which caused a decrease in breaking strength and elongation at break.

The stabilizers had a similar effect on the thermal properties of PC. Table II shows that higher stabilizer concentrations decreased the mass loss temperature. It means that the polymer with higher stabilizer concentrations have started to decay faster than pure PC.

Thermal properties

The thermal properties of PC are presented in Table II. The resistance of the polymers to the degradation was affected by the presence of weaker bonds.[26] The table shows that the thermal stability of PC slightly increased with the addition of small amounts of K stabilizer ($c = 0.1\%$) and then decreased for higher concentration rates. The rest of the stabilizers had a negative effect on the thermal behavior of PC for all concentration rates. It is interesting to observe that the

TABLE II
Thermal Properties of Pure and Stabilizer Added PC

		Thermal stability (°C)			
No	Compositions of PC	Beginning of mass loss	2% mass loss	10% mass loss	50% mass loss
1	PC	360	390	433	476
2	PC + 0.1% K	370	400	435	470
3	PC + 0.5% K	310	330	390	450
4	PC + 1% K	300	315	360	427
5	PC + 3% K	210	248	285	340
6	PC + 0.1% Ni	360	380	420	468
7	PC + 0.5% Ni	320	360	405	460
8	PC + 1% Ni	320	350	380	445
9	PC + 3% Ni	320	345	378	445
10	PC + 0.1% Fe(II)	360	375	405	440
11	PC + 0.5% Fe(II)	335	350	375	415
12	PC + 1% Fe(II)	270	312	365	408
13	PC + 3% Fe(II)	250	290	343	385
14	PC + 0.1% Fe(III)	330	365	410	458
15	PC + 0.5% Fe(III)	310	365	399	440
16	PC + 1% Fe(III)	310	348	380	413
17	PC + 3% Fe(III)	320	342	372	404

TABLE III
The Tensile Properties of the Heat-Treated PC (after 30 min at 200°C)

		As-moulded			Heat treated for 30 min at 200°C		
No	Compositions of PC	Breaking strength (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)	Breaking strength (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)
1	PC	88	17.4	1,6	64	3.5	4
2	PC + 0.1% K	91	32.9	2	54	8.6	1.3
3	PC + 0.5% K	95	26.1	2	40	2.4	1.6
5	PC + 0.1% Ni	88	24.9	1,6	52	4.7	1.4
6	PC + 0.5% Ni	86	24	1,7	48	3.8	1.5
8	PC + 0.1% Fe(III)	79	17.2	1,6	28	2.6	1.2

influence of the stabilizers on the thermal stability of PC is similar to their influences on the mechanical behavior. Probably, the presence of large concentration increased the free volume of the polymer by increasing the intermolecular distances and thus caused the material to decay at lower temperatures.

The mechanical properties for heat-treated specimens are presented in Table III. They are significantly lower than those of the as-molded ones. The decrease in elongation at break is very significant. Ozden has shown that[27] heat treatment imparted brittleness on PC. It is clear that the heat treatment introduced brittleness in PC. It is important to identify whether this brittleness is caused by crosslinking of PC or some other effects. The lower values of breaking strength and modulus of elasticity for the heat-treated specimens meant that the heat treatment could not have introduced crosslinking, because crosslinking would be expected to impart a much higher modulus of elasticity. The crosslinking of the molecules would render elongation more difficult and hence enhance the modulus of elasticity. The highly crosslinked polymers are usually rather brittle with small elongation at break. Therefore, the reason for the observed mechanical deterioration after heat treatment is probably different.

It is widely known that the distance between the chains depend on their polarity.[28,29] As the distance between the molecular chains decreases, the polarity increases or *vice versa*. The polar forces become predominant when the distance between the main molecular chains are 3–4 Å.[29] We have shown in a previous work[24] that polycarbonate stabilized with phoshinic acid had an intermolecular distance macro chains equal to 5.21 Å. The introduction of salts of phoshinic acid moved the chains apart. In the present case, bulkier metallic salts are expected to have a stronger effect on the separation of the chains as the Van der Waals volumes (V_w) of phoshinic acid is much smaller than those of the metallic phosphinate metallic stabilizers.

Therefore, it may be argued that chain breaking following the heat treatment combined with the separation effect of the bulky stabilizers and reduced the mechanical properties of heat treated PC.

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 the stabilizer added polymer. It is thought that the phosphinic metallic acid particles along the main molecular chain were also broken after

TABLE IV
Oxygen Index for PC

No	Compositions of PC	Oxygen index (%)
1	PC	26.5
2	PC + 0.1% K	27.5
3	PC + 0.5% K	29
4	PC + 1% K	29
5	PC + 3% K	25.5
6	PC + 5% K	23
7	PC + 10% K	22
8	PC + 15% K	21.5
9	PC + 20% K	22.5
10	PC + 0.1% Ni	25
11	PC + 0.5% Ni	23.5
12	PC + 1% Ni	24
13	PC + 3% Ni	24.5
14	PC + 5% Ni	24.5
15	PC + 10% Ni	27
16	PC + 15% Ni	27
17	PC + 20% Ni	27
18	PC + 0.1% Fe(II)	26
19	PC + 0.5% Fe(II)	28
20	PC + 1% Fe(II)	29.5
21	PC + 3% Fe(II)	31.5
22	PC + 5% Fe(II)	35
23	PC + 10% Fe(II)	35.5
24	PC + 15% Fe(II)	34
25	PC + 20% Fe(II)	33
26	PC + 0.1% Fe(III)	26
27	PC + 0.5% Fe(III)	28.5
28	PC + 1% Fe(III)	29.5
29	PC + 3% Fe(III)	30.5
30	PC + 5% Fe(III)	32
31	PC + 10% Fe(III)	32
32	PC + 15% Fe(III)	31

TABLE V
The Environmental Effects of Different Acid and Bases on the Polycarbonate at 20°C

No	Compositions of PC	Time, t (10^4 s)	% Mass loss in 10% NaOH	% Mass loss in 40% NaOH	% Mass loss in 10% H_2SO_4	% Mass loss in 96% H_2SO_4
1	PC	8.6	+1.19	−18.3	+0.05	+1.02
2		43.2	−0.57	−87.9	−0.05	+13.5
3		86.4	−0.96	–	−0.22	+31.4
4		129.6	−1.77	–	−0.22	+40
5		172.8	−2.5	–	−0.53	+42.9
6		216	−3.16	–	−0.43	+54.4
7	′	259.2	−3.64	–	0.6	+59.9
8	PC + 1% K	8.6	+0.23	−28.6	+0.98	+2.72
9		43.2	−0.54	–	+0.74	+28.4
10		86.4	−0.85	–	+0.74	+59.5
11		129.6	−2.24	–	+0.74	+76
12		172.8	−3.39	–	+0.49	+89.1
13		216	−4.48	–	+0.49	+97.1
14		259.2	−5.41	–	+0.49	+125.6
15	PC + 1% Ni	8.6	−0.11	−16	+0.2	+1.33
16		43.2	−0.64	−65.2	+0.2	+16.8
17		86.4	−1.01	−96.5	+0.2	+5307
18		129.6	−2.03	–	+0.2	+56.4
19		172.8	−3.09	–	+0.15	+86.5
20		216	−4.06	–	+0.15	+96.8
21		259.2	−4.86	–	−5.31	+97.2
22	PC + 1% Fe(II)	8.6	−0.2	−15.4	+0.34	+2.55
23		43.2	−1.36	−55.1	+0.48	+20.6
24		86.4	−2.17	−93.1	−0.19	+44.6
25		129.6	−3.54	–	+0.19	+46.1
26		172.8	−4.86	–	+0.15	+68.9
27		216	−6.31	–	+0.1	+76.7
28		259.2	−7.68	–	+0.1	+79.4
29	PC + 1% Fe(II)	8.6	+0.1	−16.6	+0.15	+1.59
30		43.2	−0.95	−63.1	+0.19	+18
31		86.4	−1.14	−94.9	0	+44.5
32		129.6	−2.28	–	0	+41.3
33		172.8	−3.37	–	−0.05	+63.1
34		216	−4.47	–	−0.19	+79.5
35		259.2	−5.22	–	−0.19	+87.5

The (−) means that the polymers completely dissolved.

heat treatment and this phenomenon led to the poor mechanical and thermal performance.

To assess the effects of the stabilizers more thoroughly, the oxygen index results for PC were presented in Table IV. The results indicate that the most significant changes in oxygen index were obtained with the phosphinic iron stabilizers. This is an expected result. Since the iron molecules are susceptible

TABLE VI
The Mechanical Properties of PC Subjected to Acidic Environment at 20°C for 25.92×10^5 s

No	Compositions of PC	Breaking strength (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)
1	PC	77[a]	6.3[a]	1.4[a]
		122[b]	12.1[b]	1.9[b]
2	PC + 1% K	48	4	1.7
		61	3.6	1.7
3	PC + 1% Ni	61	4.3	1.6
		84	16.8	1.8
4	PC + 1% Fe (II)	47	3	2
		77	5.9	1.7
5	PC + 1% Fe (III)	66	3	2.4
		71	5.4	1.5

[a] Subjected to 10% NaOH.
[b] Subjected to 10% H_2SO_4.

to oxygen molecules, the polymer itself absorbs some part of the oxygen molecules and the oxygen index rises.

When the pure and additive added PC are inserted into diluted acids and alkalis, they are observed to be resistive to the chemical environmental effects (see Table V). The effects of the acids and alkalis were measured for 1, 5, 10, 15, 20, 25, and 30 days. The presence of the stabilizers did not significantly influence the resistance to the environmental effects. On the whole, the effect was negative for bases.

Table VI shows the effects of the bases and acids on the mechanical behavior of PC. The pure and stabilizer added PC were kept at an aggressive environment for 30 days and they were subjected to tensile tests. There were significant reductions in breaking stress. It was observed that the effect of base was more significant. The presence of the stabilizers seems to have decreased the tensile behavior of PC in the aggressive media.

CONCLUSIONS

The mechanical and thermal behavior of PC were affected by the presence of the four phosphinic metallic stabilizers (potassium, nickel, Fe(II), and Fe(III)). The mechanical properties were sensitive to the presence of small amount of stabilizers. At high concentration rates of stabilizers (>1%) the mechanical properties deteriorated. Potassium caused an initial increase and then a steady decrease in breaking strength, ductility, and modulus of elasticity of PC. Nickel and iron stabilizers caused a steady increase in E while they decreased the breaking stress and ductility.

The increase in E was caused by enhanced organization of chains as a result of polar forces between molecule caused by large amounts of nickel and iron stabilizers and by the better organization of chains. The heat treatment at 300°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 affected at higher stabilizer concentrations. This was probably because of the increased free volume of the polymer.

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