Antiplasticization.   III.   Characteristics and Properties of Antiplasticizable Polymers*

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Synopsis

Antiplasticization is applicable to polymers which contain rigid, polar groups and stiff chains, such as many bisphenol polycarbonates and polyesters, 2,2,4,4-tetramethyl-1,3-cyclobutanediol polycarbonates and polyesters, cellulose triacetate, and a commercial poly(sulfone ether).   The stiffness, hardness, and tensile strength of these polymers are increased by antiplasticizers, and the elongation, impact strength, and heat-distortion temperature are decreased.   The stiffness of antiplasticized polymers can be further increased by crystallization.   A clear, hard, stiff, tough, self-extinguishing molding plastic with good electrical properties and improved resistance to stress cracking is obtained by antiplasticizing bisphenol A polycarbonate with 20% Aroclor 5460.

INTRODUCTION

The preceding paper[1] of this series discusses the characteristics of materials which antiplasticize bisphenol polycarbonates.   These additives, which increase the tensile modulus and tensile strength of films and decrease the elongation, consist of molecules which meet certain requirements of polarity, rigidity, and size.   This paper discusses the characteristics of polymers which can be antiplasticized by these additives and describes their effects on the properties of films and molding plastics.   Speculations are also made concerning the mechanism of antiplasticization.

EXPERIMENTAL

All of the experimental polymers had inherent viscosities of 0.6 or higher (measured at a concentration of 0.25 g./100 ml. in chloroform or, if not soluble, in 60/40 phenol–tetrachloroethane).   Polyesters of 2,2,4,4-tetramethyl-1,3-cyclobutanediol were prepared from the diol (Eastman Chemical Products, Inc.) and dimethyl esters of dicarboxylic acids; the polycarbonate was prepared from the diol and diphenyl carbonate.[2]   The polyformal of this diol was prepared with paraformaldehyde.[3]   Bisphenol polyesters were prepared from bisphenols and diphenyl esters.[4]   Bisphenol

A polycarbonate was obtained from the General Electric Co. (trade name Lexan). Other bisphenol polycarbonates were prepared from the corresponding bisphenol and phosgene.[4,5] Poly(2,6-dimethyl-p-phenylene oxide) was obtained from the General Electric Co. A poly(sulfone ether) (trade name Polysulfone) was obtained from Union Carbide Corporation.

Unless indicated otherwise in the tables, films containing the various additives were cast from methylene chloride, dried, and tested as described in our preceding paper.[1] Wideline nuclear magnetic resonance spectra of films were determined at 40 Mc./sec.

Several of the polymers mixed with an additive were injection-molded in a 1-oz. Watson-Stillman injection-molding press to give $1/16$-in. tensile bars and $1/8$-in. flexure bars. The additive was deposited on the polymer particles (10–20 mesh) by dissolving in acetone or cyclohexane and allowing the solvent to evaporate while the mixture was stirred and gently warmed. The particles were then stirred in a flask while heating in a bath at 100°C. for 2 hr. to remove last traces of solvent and permit the additive to penetrate the particles.

ASTM procedures were used for measuring flexural modulus (ASTM D747–61T), tensile strength and elongation (ASTM D1708–59T), Rockwell hardness (ASTM D785–51), and Izod impact strength (ASTM D256–56 Method A). The impact strength of $1^{1}/_8 \times 1/8$-in. buttons was determined on a Tinius Olsen impact tester, which measures shatter resistance. The heat-distortion temperature was the temperature at which 0.2% deflection of a 2 in. span of a $1/8$-in. flexure bar occurred at 264 psi. This was measured in a forced-convection oven.[6]

RESULTS

Amorphous Films

The polycarbonate (Ia), polyterephthalate (Ib), and poly(*trans*-1,4-cyclohexanedicarboxylate) (Ic) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol can be antiplasticized with various classes of additives (Table I).
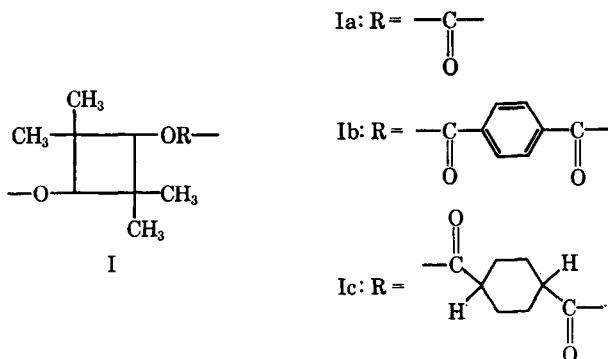

Except for the flexible polysuccinate polymer, which was plasticized, the moduli and tensile strengths of the films were appreciably increased,

and elongations were decreased.   Heat-distortion temperatures were also depressed.

Bisphenol polyesters of aromatic and alicyclic dicarboxylic acids also can be antiplasticized by the same types of additives that antiplasticize bisphenol polycarbonates.[1,7]   One of the best antiplasticizers is Aroclor 5442, and its effect on the film properties of several bisphenol polyesters is shown in Table II.   The flexible polyazelate was plasticized, but the stiff polymers from the cyclic dicarboxylic acids were antiplasticized, i.e., moduli and tensile strengths were increased and elongations were decreased.   The percentage modulus increase due to the Aroclor is also tabulated.

Table III lists the tensile properties of miscellaneous polymers containing additives which antiplasticize bisphenol polycarbonates and polyesters. The polyformal (R = —CH₂— in formula I) was plasticized by Aroclor 5442, but cellulose triacetate and a commercial poly(sulfone ether) (II) were antiplasticized by this additive.   In polystyrene, Aroclor 5442 acted
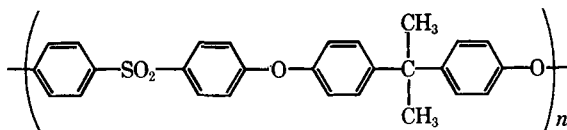
II

as neither a plasticizer nor an antiplasticizer but as a diluent.   Since poly-(2,6-dimethyl-p-phenylene oxide) (III) and poly(methyl methacrylate) were stiffened but not significantly strengthened by the Aroclor, they
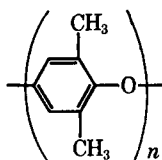
III

were not antiplasticized.   The other additives, poly(styrene glycol) and abietic acid esters, had only diluting or stiffening effects in the various polymers.

Crystalline Films

Crystallization of polycarbonate and polyester films has an effect on the tensile properties similar to that of antiplasticization: increased tensile strength, increased modulus, and decreased elongation.   Crystallization also increases the heat-distortion temperature of the films, whereas anti-plasticization lowers the heat-distortion temperature.   By combining the effects of crystallization and antiplasticization, it is possible to obtain films with (1) a higher tensile modulus than can be obtained by either effect alone and (2) a higher heat-distortion temperature than that of amorphous

TABLE I. Effect of Additives on Film Properties of 2,2,4,4-Tetramethyl-1,3-cyclobutanediol Polyesters[a]

| Diol, % trans | Polyester | Additive | | Tensile properties | | | Heat-distortion temp, °C. |
		Commercial name[b]	Concn, %	Modulus, 10^5 psi	Break strength, psi	Elongation at break, %	
46	Carbonate	—	0	2.1	6,800	13	133
		Aroclor 5442	10	4.1	10,200	3	87
		Aroclor 5460	30	5.4	9,800	3	49
		Aroclor 5460	20	4.1	10,200	3	98
		SAIB	20	3.2	7,100	4	76
60		—	0	2.9	8,000	8	225
		Aroclor 5442	10	4.7	9,500	3	128
		Aroclor 5442	20	5.5	9,800	2	125
		Aroclor 5460	20	4.3	10,300	3	—
		SAIB	20	3.9	8,100	4	—
69	Terephthalate	—	0	2.2	8,300	15	206
		Aroclor 5442	20	3.9	10,700	3	90
		Aroclor 5460	20	3.8	10,500	3	121
		Abalyn	20	3.9	10,300	4	107
69	80/20 Terephthalate sebacate	—	0	2.3	6,700	7	122
90	trans-1,4-Cyclohexanedicarboxylate	Aroclor 5442	20	3.4	7,900	4	55
		—	0	2.0	3,600	2	—
95	Succinate	Aroclor 5442	20	Too brittle to measure			
		—	0	2.4	3,700	3	93[c]
		Aroclor 5442	10	0.1	1,000	212	<30

[a] Polycarbonates from 46% *trans* diol were cast from methylene chloride, the terephthalate polyesters were cast from 80/20 methylene chloride/trifluoroacetic acid, and the remaining polymers were cast from chloroform; [b] the Aroclors were obtained from Monsanto Chemical Co. Aroclors 5442 and 5460 are chlorinated terphenyls containing 42 and 60% chlorine, respectively. SAIB is sucrose acetate isobutyrate from Eastman Chemical Products, Inc. Abalyn is methyl abietate from Hercules Powder Co.; [c] glass transition temperature.

TABLE II. Effect of Aroclor 5442 on Film Properties of Bisphenol Polyesters

$$-O-\!\!\!\left\langle \right\rangle\!\!\!-R-\!\!\!\left\langle \right\rangle\!\!\!-OC-R'-C-\!\!\!\left.\right)_n$$

R	Polyester[a]	Aroclor concn., %[b]	Modulus, 10^5 psi	Increase in modulus, %	Tensile properties		Elongation at break, %	Glass transition temp., °C.
					Yield strength, psi	Break strength, psi		
$(CH_3)_2C$	Azelate	0	1.8	—	3,900	3,000	10	36
		20	0.6	—	400	2,600	169	—
	Cyclohexanedi-carboxylate	0	1.8	—	—	7,000	8	150
		20	4.1	128	—	13,000	4	80
	75/25 Cyclohexanedicarboxylate isophthalate	0	2.1	—	—	7,400	17	—
		20	4.0	90	—	13,000	4	—
	70/30 Cyclohexanedicarboxylate terephthalate	0	2.3	—	—	7,700	13	—
		20	4.3	87	—	13,500	5	87
	60/40 Terephthalate/ cyclohexanedicarboxylate	0	2.7	—	8,700	9,700	15	257
		20	4.8	78	—	15,000	4	181
	Terephthalate	0	3.1	—	9,000	10,200	11	287
		20	5.4	74	—	16,500	4	197

a Ratios of components are by moles. All cyclohexanedicarboxylate polyesters are *trans*.
b Terphenyl containing 42% chlorine from Monsanto Chemical Co.

TABLE III

Effect of Additives on Film Properties of Miscellaneous Polymers[a]

Polymer	Additive		Tensile properties				Glass transition temp., °C.
	Commercial name[b]	Concn., %	Modulus, 10^5 psi	Yield strength, psi	Break strength, psi	Elongation at break, %	
2,2,4-Tetramethyl-1,3-cyclobutanediol polyformal[c]	—	0	1.5	3,200	2,700	15	32
Cellulose triacetate	Aroclor 5442	20	0.3	900	2,400	280	—
	—	0	5.6	13,000	14,100	11	170
	Aroclor 5442	20	6.6	—	17,200	4	143
	Polyglycol 174–500	20	5.6	—	13,900	5	—
Poly(sulfone ether)	Abalyn	20	5.1	12,600	12,400	12	—
	—	0	3.4	—	9,500	4	180
	Aroclor 5442	20	4.5	—	10,900	3	122
Polystyrene	—	0	4.7	—	4,800	1	—
	Aroclor 5442	20	4.5	—	4,100	1	—

Poly(2,6-dimethyl-p-phenylene oxide)	Staybelite Ester 3	20	3.3	—	2,500	1	—
	—	0	3.0	9,000	8,000	10	—
Poly(methyl methacrylate)	Aroclor 5442	20	4.1	—	8,000	3	—
	—	0	4.1	—	8,500	4	—
	Aroclor 5442	20	5.0	—	8,200	2	—
	Abalyn	20	4.4	—	7,500	2	—
Copolymer[d]	—	0	3.7	—	6,800	2	—
	Aroclor 5442	20	4.6	—	7,000	2	—
	Abalyn	20	3.8	—	5,500	2	—

[a] The polyformal, poly(sulfone ether), and poly(phenylene oxide) were cast from chloroform. Cellulose triacetate and poly(methyl methacrylate) films were cast from 90/10 methylene chloride–methyl alcohol; polystyrene was cast from methylene chloride.

[b] Sources and compositions are given in Table I except for Polyglycol 174–500 [poly(styrene glycol) of mol. wt. 500 from Dow Chemical Co.] and Staybelite Ester 3 (triethylene glycol ester of hydrogenated abietic acid from Hercules Powder Co.).

[c] Prepared from diol with a cis-trans ratio of 52/48.

[d] Prepared from 75 mole-% methyl methacrylate and 25 mole-% $COOCH_2CH(CH_3)_2$ / $COOCH_2CH(CH_3)_2$
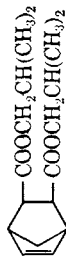
films. Table IV lists several examples which illustrate these different effects with bisphenol A polycarbonate. Crystallization occurred when the films were cast from solvent mixtures in which one solvent or semisolvent boiled above 100°C. (for example, chlorobenzene, o-dichlorobenzene, anisole, acetophenone, methyl benzoate, benzonitrile, and cyclohexanone). Since this solvent evaporated relatively slowly, it was possible for the polymer chains to arrange themselves in a crystalline pattern before the loss of too much solvent made chain movement impossible. Crystallization also will occur in films cast from methylene chloride alone if a closed system is used in which the methylene chloride evaporates slowly. This latter process is appreciably more difficult to control, however.

Merrill and Petrie[8] attempted to plasticize bisphenol A polycarbonate with Aroclor 1254. Since thick (5-mil) films were cast, crystallization took place. They interpreted the increased modulus and tensile strength as being due to crystallinity, but antiplasticization also occurred.

Another example of the combined effects of crystallinity and antiplasticization is tetramethylcyclobutanediol (46% *trans*) polycarbonate contain-

TABLE IV

Effect of Crystallinity on Film Properties of Antiplasticized
Bisphenol A Polycarbonate[a]

Antiplasticizer			Tensile Properties			Heat-distortion temp., °C.
Commercial name[b]	Concn., %	Solvent[c]	Modulus, 10^5 psi	Break strength, psi	Elongation at break, %	
—	—	CH_2Cl_2	3.0–3.3	9,000–9,500	20–90	154
—	—	4/1 CH_2Cl_2–anisole	4.0	11,500	8	220
Aroclor 1254	20	CH_2Cl_2	4.5	11,200	4	91
		5/1 CH_2Cl_2–anisole	5.0	12,800	3	155
—	—	2/1 CH_2Cl_2–anisole	4.1	10,800	6	224
Aroclor 5442	10	CH_2Cl_2	4.5	13,700	4	108
		2/1 CH_2Cl_2–anisole	5.2	12,800	3	174
—	—	2/1 CH_2Cl_2–chlorobenzene	4.0	12,000	6	211
Aroclor 5442	10	"	4.7	12,700	4	168
Abalyn	20	CH_2Cl_2	4.7	12,700	4	87
		5/1 CH_2Cl_2–methyl benzoate	4.9	10,200	3	159

[a] Films cast from methylene chloride alone were amorphous; all other films were crystalline.

[b] Sources and compositions are given in Table I. Aroclor 1254 is chlorinated biphenyl containing 54% chlorine.

[c] Solvent from which films were cast. Ratios are by volume.

ing 20% Aroclor 5442 and cast from 4/1 chloroform–anisole. The amorphous film containing no additive had a tensile modulus of 2.1×10^5 psi and a heat-distortion temperature of 133°C. (Table I). The crystallized, antiplasticized film had a modulus of 5.2×10^5 psi and a heat-distortion temperature of 147°C.

Although films with the highest moduli were those which were both antiplasticized and crystalline, films with the highest tensile strengths were those which were antiplasticized but not crystallized. Of the crystalline films, those containing antiplasticizers generally had the higher tensile strengths.

Films 2 mils in thickness could be tightly creased without cracking, but appreciably thicker films occasionally cracked under these conditions. The tear strength and folding endurance are both better than would be expected, however. A 1.2-mil crystalline bisphenol A polycarbonate film from methylene chloride/anisole containing 10% Aroclor 5442 (Table IV) had an Elmendorf tear strength of 12 g./mil and a folding endurance of 1200 folds.
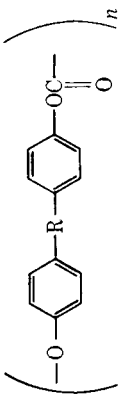
These crystalline films are somewhat hazy but still are transparent. Consequently, they will be limited to applications in which clarity is unimportant.

Molding Plastics

The effects of various additives on the properties of two injection-molded bisphenol polycarbonates are shown in Table V. The Aroclors increased the stiffness (modulus), tensile strength, and hardness of the polymers, but the impact strength and heat-distortion temperature were decreased. The temperatures required for injection molding also were decreased about 50–100°F. Most of the bisphenol A polycarbonate data in Table V were obtained with polymers of inherent viscosity 1.0. When the inherent viscosity was 0.6, essentially the same results were obtained except for modulus, which was somewhat higher, and impact strength, which was somewhat lower. Most experiments were carried out with Aroclors 5460 and 1268 because film results[1,7] indicated that these materials did not stiffen the polymer or decrease the heat-distortion temperatures as much as the other Aroclors. Consequently, it was possible to incorporate enough of one of these Aroclors in the polymer to achieve self-extinguishing characteristics without increasing the rigidity and brittleness too much and depressing the heat-distortion temperature too far.

The compositions of particular interest were those containing 20% Aroclor 5460. When $1/8$ in.-thick flexure bars of these polymers were held for 10 sec. in a Bunsen burner flame (1000°C.), the bars extinguished themselves within 1 sec. after removal from the flame. The composition containing 20% Aroclor 1268 had the same self-extinguishing characteristics but a somewhat lower impact strength. This polymer was colorless, however, whereas the polymers containing Aroclor 5460 were yellow because of the colored Aroclor.

TABLE V. Effect of Additives on Properties of Injection-Molded Bisphenol Polycarbonates[a]

$$\left(-O-\underset{}{\bigcirc}-R-\underset{}{\bigcirc}-O-\overset{O}{\underset{\|}{C}}- \right)_n$$

| R | Additive | | Flexural modulus, 10⁴ psi | Tensile strength, psi | | Elongation at break, % | Rockwell hardness, L | Impact strength | | Heat distortion temp., °C. |
	Commercial name[b]	Concn., %		At yield	At break			Button, in./lb.	Izod, ft.-lb./in. notch	
(CH₃)₂C⟨ ⟩	—	0	2.6	9,000	9,800	67	94	>50	9.1	148
	Aroclor 5442	10*	3.5	12,600	10,800	31	112	14	0.5	98
	Aroclor 5460	10	3.5	10,600	10,600	69	106	>50	0.7	124
		20	3.4	12,000	11,900	64	108	>50	0.7[e]	108
		20*	3.6	12,200	10,000	54	107	24	0.6	111
		30*	4.0	12,200	9,400	45	109	13	—	—
		50*	4.1	—	10,600	7	105	6	0.4	84
	Aroclor 1268	10	2.9	11,200	10,700	58	105	>50	0.4	118
		20	3.6	12,800	11,900	66	111	27	0.3	105
	H-1 Ketone	20	2.4	8,800	9,700	72	93	>50	1.3	132
		20*	2.7	8,700	8,500	87	89	>50	0.6	128
		30*	2.8	8,400	8,100	97	91	>50	0.7	128
⟨cyclohexyl structure⟩	—	0	2.5	11,400	9,600	24	116	—	1.0	225
	Aroclor 5460	20	3.4	—	14,500	10	124	—	0.4[d]	160

[a] No appreciable loss in inherent viscosity occurred on molding. The additive was added to polymer with an inherent viscosity of 1.0 except in experiments designated by an asterisk, which indicates an inherent viscosity of 0.6; [b] Aroclors 5442 and 5460, obtained from Monsanto Chemical Co., are chlorinated terphenyls containing 42 and 60% chlorine, respectively. Aroclor 1268 is chlorinated biphenyl containing 68% chlorine. H-1 Ketone (II) was obtained from Hooker Chemical Co. as a monohydrate and converted to the anhydrous ketone in refluxing toluene by azeotropically removing the water; [c] when the notch was molded into the samples, a value of 0.9 was obtained. Unnotched impact strength was >30 ft.-lb./in.; [d] unnotched impact strength was 9 ft.-lb./in.

The 4,4'-(2-norbornylidene)diphenol polycarbonate (Table V) has considerably less tendency to craze and to stress-crack than bisphenol A polycarbonate, but the resistance of the latter to stress cracking was greatly improved by the Aroclors. When $1/_8$ in.-thick flexure bars containing 10–20% of an Aroclor were bent with pliers about 30 degrees (to introduce stress) and then were immersed in acetone, the bars did not become brittle until after 1–4 hr. Similar bars containing no antiplasticizer cracked and became brittle at the bend in less than one minute after immersion in acetone. Bent norbornylidenediphenol polycarbonate flexure bars containing no antiplasticizer, on the other hand, did not become brittle during immersion in acetone for up to 24 hr.

At frequencies of 0.1–100 kc./sec. and temperatures up to 110°C. with bisphenol A polycarbonate and 140°C. with norbornylidenediphenol polycarbonate (Table V), the presence of 20% Aroclor 5460 has very little effect on the dielectric constant (constant at about 3.0) and dissipation factor (about 0.1 to 0.3%). Lower melting chlorinated biphenyls and terphenyls, such as Aroclors 1254 and 5442, cause the dielectric constant and dissipation factor to increase appreciably as the temperature is raised. The volume resistivity, a measure of insulation resistance of the compositions, is high (10^{16}–10^{17} ohm-cm.).

The bisphenol A polymer containing 20% Aroclor 5460 was particularly tough. The unnotched Izod impact strength at -40°C. also was very high—the samples did not break. Because the polymer was malleable, it did not shatter when struck by a hammer. The heat-distortion temperature, 108–111°C. at 264 psi. is adequate for many applications, and molded pieces do not crystallize even when heated for 24 hr. at 130°C. As a clear, hard, stiff, tough, self-extinguishing molding plastic with good electrical properties, this composition is of unusual interest.

H-1 Ketone (IV) made bisphenol A polycarbonate self-extinguishing with a lower loss in impact strength and heat-distortion temperature than the Aroclor-containing compositions (Table V). This additive is unique in that it does not greatly affect the stiffness, tensile properties, or hardness
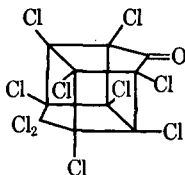
IV

of the molded polymer, particularly when only 20% of the chloroketone is present. As explained in our preceding paper,[1] this compound is not an antiplasticizer because the molecule is too thick.

The properties of injection-molded tetramethylcyclobutanediol (46% *trans*) polycarbonate containing several additives are listed in Table VI. The Aroclors increased the stiffness, tensile strength, and hardness and

TABLE VI

Effect of Additives on Properties of Injection-Molded 2,2,4,4-Tetramethyl-1,3-cyclobutanediol Polycarbonate[a]

| Additive | | Flexural modulus, 10⁵ psi | Tensile strength, psi | | Elongation at break, % | Rockwell hardness L | Impact strength | | Heat-distortion temp., °C |
Commercial name[b]	Concn., %		At yield	At break			Button, in.-lb.	Notched Izod, ft.-lb./in. notch	
—	0	1.8	5,700	5,600	50	72	>50	11.0	112
Aroclor 5442	5	2.6	7,000	6,600	41	96	>50	0.4	81
	10	3.1	—	8,700	8	101	9	0.3	83
Aroclor 5460	10	2.5	7,900	6,800	26	92	12	0.4	103
	30	3.4	—	8,900	7	98	6	0.2	—
Aroclor 1268	5	2.5	6,600	6,400	47	93	44	0.5	91
H-1 Ketone	20	2.1	6,600	5,700	30	90	25	0.6	116

[a] Diol cis/trans ratio was 54/46. Inherent viscosities were 1.0–1.2 before molding and 0.8–0.9 after molding.
[b] Sources and compositions are given in Table V.

decreased the elongation, impact strength, and heat-distortion temperature. H-1 Ketone (IV), on the other hand, was not an antiplasticizer and had little or no effect on the stiffness, tensile properties, and heat-distortion temperature. This polycarbonate did not stress crack in acetone.

Listed in Table VII are the properties of the poly(sulfone ether) (II) containing 20% Aroclor 5460. As shown by the properties, antiplasticization occurred. Both poly(sulfone ether) and antiplasticized poly(sulfone ether) bars containing a 30-degree bend cracked and broke within a few seconds after immersion in acetone. (It was necessary to use tensile bars $^{1}/_{16}$ in. thick for this test because the antiplasticized $^{1}/_{8}$-in. flexure bars were too brittle to bend.)

TABLE VII

Effect of Aroclor 5460 on Properties of Injection-Molded Poly(sulfone Ether)

Aroclor concn., %	Flexural modulus, 10^5 psi	Tensile strength, psi		Elongation at break, %	Rockwell hardness, L	Izod impact strength, ft.-lb./ in. notch	Heat-distortion temp., °C.
		At yield	At break				
0	2.8	9,600	9,100	113	97	0.9	180
20	4.5	—	12,700	11	107	0.4	152

DISCUSSION

Antiplasticizable Polymers

Since the modulus and tensile strength of the following classes of polymers were significantly increased and the elongation was decreased by certain additives, these polymers were antiplasticized: bisphenol polycarbonates[1,7] (Tables IV and V); 2,2,4,4-tetramethyl-1,3-cyclobutanediol polycarbonates (Tables I and VI); 2,2,4,4-tetramethyl-1,3-cyclobutanediol polyesters of cyclic dicarboxylic acids (Table I); bisphenol polyesters of cyclic dicarboxylic acids (Table II); cellulose triacetate (Table III); poly(sulfone ether) (Tables III and VII). These polymers have two characteristics in common: stiff chains and rigid, polar groups.

2,2,4,4-Tetramethyl-1,3-cyclobutanediol polyformal (R = —CH$_2$— in formula I) was not antiplasticized by one of the most effective antiplasticizers, Aroclor 5442 (Table III). The polycarbonate, on the other hand, which contains a carbonyl group instead of a methylene group at R in formula I, was antiplasticized. The reason for this difference is apparently due to the difference in polarity and flexibility of the two polymers—the polyformal is less polar and more flexible than the polycarbonate.

Polystyrene, which has stiff chains but no polar groups, was not antiplasticized (Table III). Poly(2,6-dimethyl-p-phenylene oxide) (III) has stiff chains, and the polymer is stiffened by Aroclor 5442 (Table III), but apparently the oxygen atoms are not sufficiently polar so that the polymer can also be strengthened by the additive.

Poly(methyl methacrylate) and a poly(methyl methacrylate) copolymer were stiffened by Aroclor 5442, but the tensile strength was not appreciably increased (Table III). Unlike the polymers which can be antiplasticized, the polar methoxycarbonyl groups are not in the rigid polymer backbone but are attached to the backbone. Consequently, these groups have a degree of flexibility. All the polymers listed above contain relatively rigid, polar groups because they are in the rigid backbones.

Polymers with flexible chains apparently cannot be antiplasticized. In fact, some compounds which are antiplasticizers for stiff polymers are plasticizers for certain flexible polymers. Aroclors and abietic acid esters, for instance, plasticize various flexible, polar polymers.[9] Rigidity and polarity are required in both the polymer and the additive in order for antiplasticization to occur.

The glass transition temperature T_g of a polymer is a measure of its flexibility, and the polymers which were antiplasticized all had T_g above 100°C. before antiplasticization and above 40°C. after antiplasticization. When sufficient antiplasticizer was added to depress the T_g almost to room temperature, or lower, plasticization occurred (decreased modulus and tensile strength and increased elongation). Examples are the polysuccinate of tetramethylcyclobutanediol (Table I), the polyazelate of bisphenol A (Table II), and the polyformal in Table III. Bisphenol A polycarbonate was antiplasticized by 30% Aroclor 1254,[7] but plasticization occurred when 50% was present.

Antiplasticization can occur in copolymers containing a small amount of a flexible component, but the antiplasticizer is less effective in increasing the modulus and tensile strength of the copolymer than of the more rigid homopolymer. This is illustrated in Table I for polyterephthalate compositions.

Antiplasticization appears to be most effective with polymers having relatively low moduli and tensile strengths in addition to stiff, polar chains. The modulus of tetramethylcyclobutanediol (46% *trans*) polycarbonate in Table I, for instance, was increased 95% (from 2.1 to 4.1 × 10⁵ psi) by 10% Aroclor 5442. The similar polycarbonate from diol with 60% *trans* content had a higher initial modulus and tensile strength, and twice as much Aroclor 5442 was required in order to increase its modulus 90% (from 2.9 to 5.5 × 10⁵ psi). The bisphenol polyesters without Aroclor in Table II are arranged in the order of increasing modulus and tensile strength. As the modulus and tensile strength of the films without the additive increases, the percentage increase obtained with 20% Aroclor 5442 decreases. Cellulose triacetate has a very high modulus and tensile strength (Table III). These properties were increased only 18% and 22%, respectively, by the addition of 20% Aroclor 5442, and poly(styrene glycol) and methyl abietate were not antiplasticizers.

Stress-Cracking Resistance

The surprising improvement in the stress-cracking resistance of bisphenol A polycarbonate when antiplasticized may be due in part to its increased

tensile strength.   Griffith's equation expresses a relationship between tensile strength and surface energy, which is a measure of the resistance of the material to the initiation of the fracture process:[10]

$$\sigma = (2E\gamma/\pi C)^{1/2} \tag{1}$$

σ is the tensile strength, E is Young's modulus, γ is the surface energy, and C is the flaw size prior to fracture of the material.   If this equation is squared and rearranged, we obtain eq. (2):

$$\gamma = \sigma^2 \pi C/2E \tag{2}$$

Therefore, the surface energy, a measure of the resistance to fracture initiation, is proportional to the square of the tensile strength and inversely proportional to the modulus.

We do not know the flaw size C, but by inserting yield strengths and moduli in eq. (2) we can calculate approximations of relative surface energies.   Table VIII lists the results that were obtained with a few polymers.   Also listed are the approximate times for bent molded bars to become brittle in acetone.   The flaw size C probably varies in these samples, but nevertheless, it is noteworthy that there is a rough correlation between solvent stress-cracking resistance and the relative surface energies of similar polymers.   The stress-cracking resistance of bisphenol A polycarbonate was greatly improved by antiplasticization with Aroclor 5460, and the relative surface energy was increased 35%.   The stress-cracking resistance of the poly(sulfone ether), on the other hand, was not appreciably improved by the same Aroclor, and the apparent surface energy was increased only 10%.   The norbornylidenediphenol polycarbonate was superior to the other compositions, and it had the greatest relative surface energy.   The brittleness time of this polymer containing 20% Aroclor 5460 could not be determined because the samples were too brittle to bend,

TABLE VIII
Comparison of Stress-Cracking Resistance and Relative Surface Energies

Polymer	Aroclor 5460 concn., %	Time to brittleness, hr.[a]	Relative surface energy, πC in.-lb./in.[2b]
Bisphenol A polycarbonate	0	<0.02	156
	20	1–3	210
Poly(sulfone ether)	0	<0.02	164
	20	<0.02	180[c]
4,4'-(2-Norbornylidene)diphenol polycarbonate	0	>12	260

[a] Approximate time for an injection-molded polycarbonate bar ($^1/_8$ in. thick) or poly(sulfone ether) bar ($^1/_{16}$ in. thick), permanently bent 30 degrees, to become brittle in acetone.

[b] Calculated from eq. (2) by using yield strengths and flexural moduli from Tables V and VII.

[c] Calculated from break strength since polymer did not exhibit a yield point.

but it should be even more resistant to stress cracking since its calculated relative surface energy is 310 πC in.-lb./in.[2]   The tetramethylcyclobutane-diol polycarbonate of Table VI, which is an alicyclic polymer, cannot be compared in stress-cracking resistance with these aromatic polymers because it is too dissimilar and does not stress-crack in acetone.

It is reported[11] that plasticized bisphenol A polycarbonate has lower resistance to stress cracking than the unplasticized polymer.   Plasticization reduces both the tensile strength and modulus, and we have observed that the tensile strength of plasticized bisphenol A polycarbonate films generally decreases more rapidly than the modulus.   One would think that plasticization would improve the resistance to stress cracking, but the above observation and eq. (2) explain how the reverse can be true.

Mechanism of Antiplasticization

The phenomenon of antiplasticization is not explained by crystallization of the polymers, because these polymers were noncrystalline (except for some which were deliberately crystallized, such as those in Table IV). As reported in our earlier paper,[7] differential thermal analysis curves of polycarbonate films containing Aroclors showed broad endotherms which indicated the presence of forces which were broken by thermal energy. Perhaps these forces were due to interaction between the polar groups of the polymer and those of the antiplasticizer.

Density measurements of the polycarbonate films indicated that the densities were significantly higher than would be obtained by simple addition of the volumes of polymer and Aroclor.[7]   This loss of free volume should restrict the movement of polymer chains and increase the stiffness. The density was also higher when dibutyl phthalate, a plasticizer, was present, but wideline NMR spectra indicated that dibutyl phthalate was mobile in the polymer whereas the Aroclor was not.   Therefore, the Aroclor stiffened the polymer and the plasticizer made it more flexible. H-1 Ketone (IV) is a polar, rigid molecule which is not an antiplasticizer, and it is probably significant that there was no loss in free volume of polycarbonates containing this compound.

When both the polymer and the additive consist of stiff molecules, it is possible for the polymer to be stiffened by the additive but not strengthened. This can occur when either the polymer or the additive is not sufficiently polar.   An example of the former is the poly(phenylene oxide) polymer (Table III) containing Aroclor 5442; examples of the latter are bisphenol polycarbonates containing aromatic hydrocarbons.[1]   Sufficient polarity is required in both the polymer and the additive in order for an increase in tensile strength to occur.   This strengthening action perhaps is due to interaction between the polar groups of the antiplasticizer and those of the polymer.   And, as demonstrated in the preceding paper,[1] the polar additive also must be a relatively thin molecule, perhaps because thick molecules push the polymer chains too far apart and interfere with the attractive forces between chains.

The mechanism of antiplasticization is perhaps a combination of several factors—reduction of the free volume of the polymer, interaction between the polar groups of the polymer and of the antiplasticizer, and a physical stiffening action due to the presence of rigid antiplasticizer molecules adjacent to the polar groups of the polymer. Since the most flexible portions of a rigid condensation polymer are its polar groups (such as carboxylate, carbonate, or sulfone groups), interaction of these polar groups with thin, stiff, polar antiplasticizer molecules should reduce the flexibility. And it would be expected that a polar antiplasticizer molecule containing only one ring would be less effective than a longer molecule containing two or more rings which could stiffen a longer portion of the polymer chain.

Stiff polymers can be internally plasticized by the incorporation of flexible chains in the polymer backbone.[8] Polymers can also be internally antiplasticized by the incorporation of polar groups in the polymer chain. This concept is illustrated in Table IX. The bisphenol polycarbonates containing halogen atoms have the higher moduli and tensile strengths and the lower elongations. The polar chlorine and bromine atoms perhaps interact with the polar carbonate groups to produce the increased strength and rigidity of the polymers. The addition of antiplasticizers (external antiplasticization) lowers the heat-distortion temperatures of polymers, but these halogenated polymers have increased heat-distortion temperatures, a definite advantage of internal antiplasticization. This approach, however, is not nearly as versatile as that of external antiplasticization.

TABLE IX
Properties of Bisphenol Polycarbonate Films
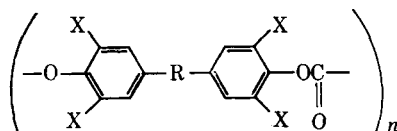
Polycarbonate		Modulus, 10^5 psi	Yield strength, psi	Break strength, psi	Elongation at break, %	Heat-distortion temp., °C.
R	X					
$(CH_3)_2C$	H	3.2	8,800	9,300	50	154
	Cl	4.1	13,400	11,300	27	225[a]
	Br	4.7	15,800	15,700	7	243
	H	3.4	9,800	10,700	40	233
	Cl	4.7	—	14,000	6	300
	Br	4.5	—	16,800	3	306

[a] 2% Distortion at 5 psi. instead of 50 psi.

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Résumé

L'antiplastification est applicable aux polymères qui contiennent des groupes rigides polaires et des chaines rigides telles que le polycarbonate de bisphénol et des polyesters, des polyesters et polycarbonate de 2,2,4,4-tétraméthyl-1,3-cyclobutanediol, le tri-acétate de cellulose et un polyéther sulfone commercial. La rigidité, la dureté et la force à la tension de ces polymères étaient accrues par es antiplastifiants et l'élongation; la force d'impact et la température de distorsion thermique sont décrues. La rigidité des polymères antiplastifiants peut être en outre accrue par cristallisation. Un plastique clair dur, rigide et auto-extincteur avec de bonnes propriétés électriques et résistance accrues à la cassure par tension est obtenu par antiplastification du polycarbonate de bisphénol A avec 20% d'Aroclor 5460.

Zusammenfassung

Antiweichmachung ist bei Polymeren anwendbar, die starre, polare Gruppen und steife Ketten enthalten, wie viele Bisphenolkarbonate und Polyester, 2,2,4,4-Tetramethyl-1,3-cyclobutandiol-polykarbonate und Polyester, Cellulosetriacetat und ein handels-üblicher Polysulfonäther. Die Steifigkeit, Härte und Zugfestigkeit dieser Polymeren werden durch Antiweichmacher erhöht und die Dehnung, Stossfestigkeit und Hitzverformungstemperatur herabgesetzt. Die Steifigkeit antiweichgemachter Polymerer kann durch Kristallisation weiter gesteigert werden. Durch Antiweichmachung von Bisphenol-A-polykarbonat mit 20% Aroclor 5460 wird ein klares, hartes, steifes, zähes, selbstlöschendes Plastomeres mit guten elektrischen Eigenschaften und verbesserter Beständigkeit gegen Spannungsrissbildung erhalten.