Stress-Cracking Resistance of Polycarbonate in Contact With Plasticized PVC Compounds

Polymeric polyester plasticizers cause less cracking in polycarbonate than monomeric esters. Certain high-viscosity polymeric plasticizers over 100,000 centipoise and several in the l0,000–25,000 range did not stress crack polycarbonate. However, viscosity is not the only determinant. Chemical type, level of use, polarity and severity of the environment all contribute to crack development in stressed polycarbonate.

Introduction

Polycarbonate has become one of the leading thermoplastics for medical device use. Polycarbonate, an amorphous glassy thermoplastic, is susceptible to cracking or crazing when under stress and in contact with a chemical environment.[1] Much of the polycarbonate molded into medical devices comes in contact with, or is attached to, flexible polyvinyl chloride (PVC). The majority of the flexible PVC compounds used in medical applications are plasticized by monomeric esters. Over a period of time, these monomeric esters migrate readily to the stressed polycarbonate surface and induce crazing and cracking.

This problem has been investigated in the past using a variety of experimental techniques. The method employed in this study was described by Kaufmann.[2] Injection-molded tensile dumbbell specimens of polycarbonate are attached to fixtures that were made to a radius of curvature that causes a defined outer fiber strain.

The migration of monomeric esters to substrates, such as polycarbonate, is well documented.[1,3] Polymeric esters have been investigated less extensively than have monomerics.

In this study, we mixed several types of monomeric and polymeric esters in PVC compound. The polymeric polyester plasticizers varied in viscosity, polarity and chemical structure. The primary objective of this study was to identify the physical or chemical characteristics of a plasticizer or group of plasticizers that would not induce stress cracking of polycarbonate.

Experimental

Flexible PVC compounds of simple composition with various types of plasticizers (Tables I and II) were prepared in a BR Banbury mixer and sheeted on a two-roll mill. The compounds were pressed between aluminum foil and cooled outside the mold. The press conditions were as follows: time - 10 minutes, temperature – 182°C, pressure - 5.7 MPa. Test specimens were 1.90 ± .05 mm.

Tensile dumbbell specimens of a commercially available, fast-cycling polycarbonate resin were tested in this study. The melt flow rate of the resin is 18g/10 min., as measured by ASTM D1238.

Aluminum test fixtures used to induce stress cracking of the polycarbonate specimens had varying radii of curvature, providing a range of strain values from 0.4–1.6 percent (see Figure 1).

The mathematical relationship between outer fiber strain, radius of curvature (R) and thickness (T) is: maximum strain % = $100T/2(R+T)$

For example, if T is 2 mm and the polycarbonate sample is flexed over a test fixture with a 61.7 mm radius, the applied outer fiber strain is 1.6 percent.

The test procedure is to clamp specimens of polycarbonate to the fixtures, thus causing strain. Strips of the PVC compounds were placed in contact with the polycarbonate, and the stacked materials in turn were fastened onto and held down by screw-on clamps attached to the strain fixture. The test samples were placed on the 1.6 percent strain fixture and aged seven days at 70°C in an air oven. Aging conditions were quite severe, but this enabled differentiation as to which plasticized compounds induced the least stress cracking. Polycarbonate tensile specimens not exposed to the PVC compounds were strained at 1.6 percent and checked for stress cracks. These polycarbonate specimens were used for control purposes.

Four PVC compounds from the initial testing were placed on seven strain fixtures that ranged from 0.4–1.6 percent. These compounds were aged 16 hours at 65.5°C. Following exposure, the polycarbonate specimens were checked for crazing or crack development, and ultimate elongation was measured at 25 mm/min on a conventional tensile testing machine. By graphing elongation results versus strain value, the strain limit can then be determined. The strain limit is considered as the highest applied strain at which no cracking, crazing or substantial loss of elongation was observed.

Results and Discussion

Polycarbonate that is molded into medical parts comes in contact with vinyl tubing at connector areas, such as couplings, valves, etc. Molded-in stress is most severe at these points. Several types of materials can cause stress cracking of polycarbonate. In this case, ester plasticizers have been cited as stress-cracking agents.[1,3] Flexible PVC for medical tubing has been traditionally plasticized with monomeric diesters and triesters. The majority of monomeric diester plasticizers used are of the phthalate type.

Monomeric Ester Plasticizers

Several monomerics have been evaluated in the past under a variety of environmental conditions, with the majority causing severe stress cracking.[1,3] In this study, monomeric esters made from varying acids and alcohols were mixed in PVC compound and evaluated for their stress-crack potential. The data shows (Table III) compounds containing diesters di-2-ethylhexyl phthalate (DOP), di-2-ethylhexyl sebacate (DOS), di-2-ethylhexyl adipate (DOA), di-2-ethylhexyl azelate (DOZ) and diisodecyl glutarate (DIDG) cause severe stress cracking to polycarbonate. A triester, tri-2-ethylhexyl trimellitate (TOTM) was also evaluated and found to provide slight improvement over diesters but was still considered an aggressive stress-inducing plasticizer.

Other types of monomeric esters not normally used for this application were evaluated (Table III). Compounds containing epoxidized glycol dioleate, dibutoxyethoxyethyl adipate (DBEEA) and tetraethylene glycol di-2-ethylhexoate all cause substantial cracking and crazing. Thus, the need for a plasticizer that will not migrate and promote stress-crack development in polycarbonate that is in contact with plasticized PVC is evident.

Polymeric Polyester Plasticizers

Polymeric polyester plasticizers in contact with polycarbonate have been investigated on a limited basis. Previous work with polymeric esters has shown that the increased viscosity or molecular weight of polymeric esters compared to monomeric esters causes less marring and cracking of polycarbonate.[4] Even though polyester plasticizers show improvement, a slight amount of edge cracking can lead to complete failure. Polyester plasticizers containing very small amounts of low molecular weight fragments can result in crazing or stress cracking and must be avoided.

The exact composition of the polymeric polyester plasticizers used in this study are proprietary and thus designated by their acid type. They are identified as follows: polyester glutarates (PeG), polyester adipates (PeA) and polyester sebacates (PeS) and by their approximate viscosity (Table II).

The results listed in TABLE IV indicate compounds containing polyester adipates migrate and cause polycarbonate to crack, except for the PeA-150,000 compound. High viscosity, in this case, appears to solve the problem. PeG shows the same trend but at significantly lower viscosities. Polycarbonate in contact with PeG-12,000 and PeG-24,000 compounds show no visible signs of cracking or crazing. The polycarbonate specimens show no evidence of stress cracking when in contact with PVC plasticized by the PeS-160,000 polyester. The compound containing PeS-5,000 induces minimal cracking of polycarbonate.

The visible signs of stress-crack development in polycarbonate are one way of evaluating performance in a specific environment. Polycarbonate has a high degree of elongation for a polymer of its stiffness, and the test values are reproducible for "virgin" material. The measurement of elongation along with appearance will give a good indication of polycarbonate performance when in contact with plasticized PVC material.

The four compounds (PeA-150,000, PeG-12,000, PeG-24,000 and PeS-160,000) that did not induce visible stress cracks were placed on seven strain fixtures ranging from 0.4–1.6 percent. They were tested according to the conditions discussed in the experimental section. The four compounds do not cause great loss of elongation (Table V).

Level of Polymeric Ester Plasticizers

A limited amount of data is available on PVC compounds containing increased levels of polymeric ester plasticizers and their effect on the stress cracking of polycarbonate.[3] Flexible PVC compounds containing 50, 60, 80 and 100 parts per hundred resin of several polymeric polyester plasticizers were placed in contact with polycarbonate strained to 1.6 percent (Table VI). The results show the PeG-3,700 compounds induce more stress cracking in polycarbonate as the amount of plasticizer is increased. Polycarbonate exposed to PeG-12,000, PeG-24,000, PeA-150,000 and PeS-160,000 shows no evidence of stress cracks until 100 PPHR is reached. Even though the data indicates that some polymeric esters can be used at relatively high concentrations in plasticized PVC, careful selection of plasticizer and use level are recommended.

Proposed Mechanism for Stress-Cracking of Polycarbonate by Plasticizer Migration

It is generally accepted that solid glassy polymers, such as polycarbonate, contain microvoids or surface defects. When stress or strain is applied, these microvoids are opened more. A plasticizer can migrate into these microvoids and cause increased crack growth, thus leading to failure. Monomeric ester plasticizers migrate readily from plasticized PVC compounds to polycarbonate, with many factors such as plasticizer type, polarity, temperature, compatibility, etc. controlling the rate of migration.

Polymeric polyester plasticizers show improved non-migration to polycarbonate. It is believed that the molecular chain length and viscosity make it more difficult for polyester plasticizers to migrate through the PVC and penetrate the surface of polycarbonate. In comparing physical properties (Table II) such as viscosity (i.e., molecular weight), plasticizer type and polarity (as it relates to saponification values) of PeA-150,000, PeS-16,000, PeG-12,000 and PeG-24,000, we find that not just one factor but a combination of these factors affect migration rates to polycarbonate.

Conclusions

Polymeric polyester plasticizers cause cracking in polycarbonate to a much lesser degree than monomeric esters. The results show that certain polymeric ester plasticizers of high viscosity (over 100,000 cps), as well as several in the range of 10,000–25,000 cps, did not cause stress cracking in polycarbonate. There are factors other than viscosity that can also affect the stress-cracking problem. Plasticizer chemical type, level of use, polarity, and severity of environmental conditions all play a role in the development of cracking in stressed polycarbonate. These results will be helpful in the formulation of PVC compounds with reduced stress-crack potential.

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References

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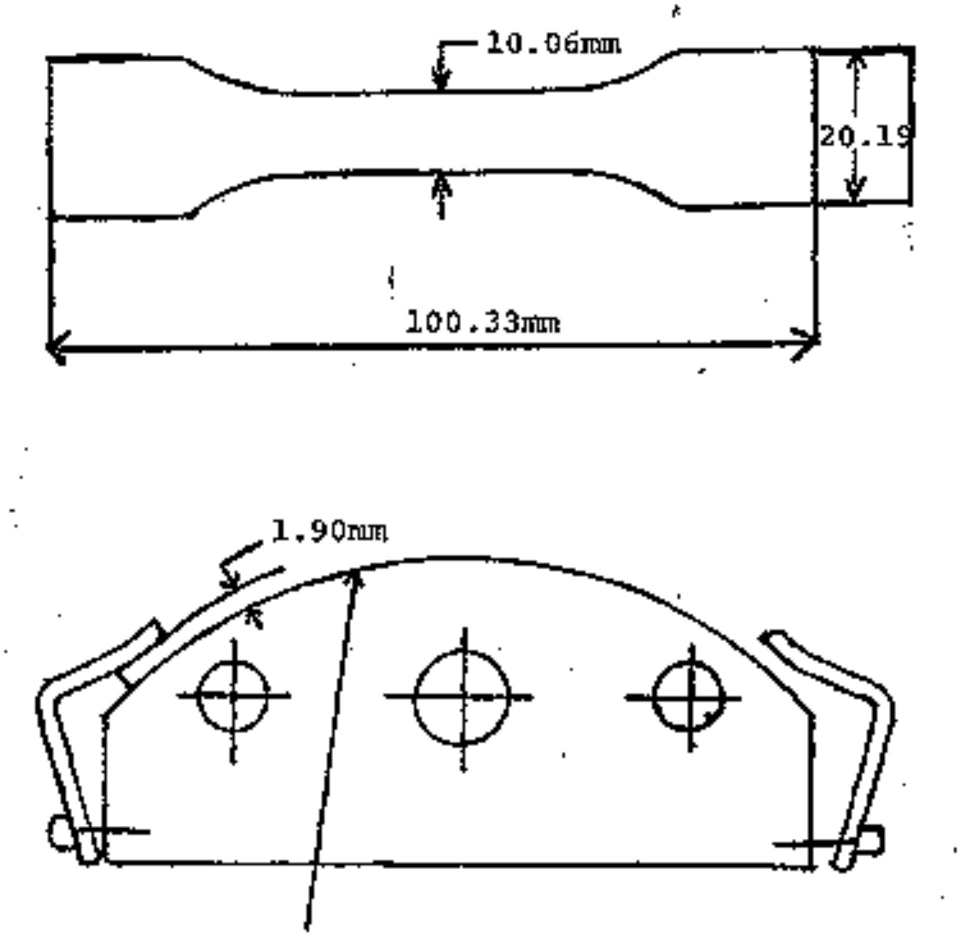

Fig. 1 - 1.6% Strain Fixture and Test Specimen

TABLE I
PVC Compounds with Monomeric Plasticizers [a]

Plasticizer Type:

Di-2-Ethylhexyl Phthalate (DOP)
Di-2-Ethylhexyl Adipate (DOA)
Diisodecyl Glutarate (DIDG)
Di-2-Ethylhexyl Azelate (DOZ)
Di-2-Ethylhexyl Sebacate (DOS)
Tri-2-Ethylhexyl Trimellitate (TOTM)
Epoxidized Glycol Dioleate
Dibutoxyethoxyethyl Adipate (DBEEA)
Tetraethylene Glycol Di-2-Ethylhexoate

PVC Recipe: PVC Resin (I.V.- 1.02) - 100.0, Plasticizer - 60.0, Ba/Cd Stabilizer - 1.0.

TABLE II
Viscosities of Polymeric Plasticizers (a)

Plasticizer Type:	**Apparent Visc. (b) (centipoises)**
Polymeric esters of Adipic Acid (PeA)	7,000
	11,000
	20,000
	22,000
	100,000
	150,000
Polymeric esters of Glutaric Acid (PeG)	3,700
	6,000
	12,000
	24,000
Polymeric esters of Sebacic Acid (PeS)	5,000
	160,000

(a) See PVC recipe - Table I
(b) As measured by Brookfield Viscometer

TABLE III
Effect of PVC Compounds with Monomeric Plasticizers on the Stress-racking of Polycarbonate

Plasticizer	Appearance of Stress Cracks*
DOP	5
DOA	5
DIDG	5
DOZ	4
DOS	4
TOTM	4
Epoxidized Glycol Dioleate	5
DBEEA	5
Tetraethylene Glycol di-2-ethylhexoate	5

***Appearance Code:**
1 = None
2 = Slight
3 = Minimal
4 = Medium
5 = Much

TABLE IV
Effect of PVC Compounds with Polymeric Polyester Plasticizer on the Stress Cracking of Polycarbonate

Plasticizer - Viscosity	Appearance of Stress Cracks*
PeA-7,000	4
PeA-11,000	4
PeA-20,000	3
PeA-22,000	3
PeA-100,000	3
PeA-150,000	1
PeG-3,700	3
PeG-6,000	2
PeG-12,000	1
PeG-24,000	1
PeS-5,000	3
PeS-160,000	1

***See Table III for Code.**

TABLE V
Retention of Elongation at Break, %

Applied Flexural Strain During Exposure, %	PeG 12,000	PeG 24,000	PeA 150,000	PeS 160,000
0	90	100	80	100
0.4	90	90	90	90
0.6	90	80	80	90
0.8	80	90	90	90
1.0	90	60	90	90
1.2	00	80	80	90
1.4	70	90	90	90
1.6	80	70	60	90

TABLE VI
Effect of PVC Compounds with Multiple Levels of Polymeric Polyester Plasticizer on the Stress-Cracking of Polycarbonate

		Appearance of Stress-Cracks*		
PPHR	**50**	**60**	**80**	**.100**
Plasticizer				
PeG-3,700	2	3	4	5
PeG-12,000	1	1	1	3
PeG-24,000	1	1	1	3
PeA-150,000	1	1	1	3
PeS-160,000	1	1	1	2

***See Table III for Code.**

Polymeric Polyester Plasticizers	Trade Name
PeA-7,000	**Paraplex® G-57**
PeA-11,000	**Paraplex® G-56**
PeA-20,000	**Paraplex® G-59**
PeA-22,000	**Plasthall® HA7A**
PeA-100,000	**Paraplex® G-41**
PeA-150,000	**Paraplex® G-40**
PeG-3,700	**Plasthall® P-550**
PeG-12,000	**Plasthall® P-7046**
PeG-24,000	**Plasthall® P-7092**

PeS-5,000
PeS-160,000

Plasthall® P-1070
Paraplex® G-25