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SOLVENT ANALYSIS OF STRESSES IN MOLDED
POLYCARBONATE PARTS

Technological Spinoff Report

C.L. Walter, Project Leader

August 1974

MASTER

Prepared for the
United States Atomic Energy Commission
Under Contract Number AT(29-1)-613 USAEC

**Kansas City
Division**

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C. L. Walter
Department 814

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SOLVENT ANALYSIS OF STRESSES IN MOLDED POLYCARBONATE PARTS

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August 1974

Prepared by C. L. Walter, D/814

Specific molded polycarbonate parts were found to stress crack during molding, cleaning, and handling. Cleaning processes were evaluated for their detrimental effects on polycarbonate and revised processes were recommended. The effects of solvents, heat transfer oils, marking methods, and mold releases on polycarbonate were determined. Marking methods presently used and mold releases for polycarbonate were found to be compatible when used properly. A solvent stress analysis method was developed to determine the stress in molded polycarbonate parts.

THE BENDIX CORPORATION

KANSAS CITY DIVISION

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**A prime contractor for the
Atomic Energy Commission**

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SUMMARY

The effects of cleaning alcohols, inks, coolants, solvents, mold releases, and oils on stressed polycarbonate parts have been evaluated. These data in combination with environmental stress data were used to predict the molded-in-stress level of polycarbonate parts. Stress cracking and crazing occur in many thermoplastics, including polycarbonate, when the surfaces are stressed in tension and exposed to certain environments. The data were gathered by holding injection molded test specimens in fixtures at predetermined strain levels, subjecting the test specimens to various environments, and recording the results.

Washing and cleaning methods were studied after it was noted that polycarbonate stress cracked during alcohol cleaning. As a result of these studies, the mandatory use of alcohol as a cleaning agent was dropped and detergent and water were recommended.

Marking methods were investigated to determine their effects on polycarbonate parts. Most of the methods were satisfactory when the stress level in the parts was low.

Coolants used during machining to improve the surface finish and to permit increased feed rate and drilling speed were evaluated for their effects on polycarbonate. Most of the popular coolants were found to contain anti-rust compounds and sulfur--neither of which were compatible with polycarbonate. The use of a low viscosity, highly refined mineral oil was recommended.

Mold releases, commonly used in the production of polycarbonate parts, were evaluated. Those releases specifically intended for use with polycarbonate were determined to be satisfactory when used properly.

Annealing and heat transfer oils were analyzed and evaluated. The highly refined mineral oils or silicone oils were all found to be compatible with polycarbonate. Therminol 66* was the best heat transfer oil evaluated.

The development of a method for analyzing the magnitude of stresses occurring in cracked or crazed polycarbonate parts was emphasized. It was learned that solvents and combinations of solvents could be used to determine the approximate

*All proprietary chemicals, compounds, and materials are listed in the Appendix.

magnitude of stresses within molded polycarbonate parts. Several solvent combinations were tried; the most effective was a mixture of toluol and n-propanol. This mixture could determine a critical stress level from 550 psi (3.79 MPa) to 1400 psi (9.65 MPa). Carbon tetrachloride was another good stress analysis solvent. It had a useful range of 200 psi (1.38 MPa) to 600 psi (4.14 MPa).

DISCUSSION

SCOPE AND PURPOSE

The effect of cleaning media, inks, coolants, solvents, mold releases, and oils on stressed polycarbonate was investigated. These data in combination with environmental stress data^{1, 2} were used in predicting the molded-in stress level of various injection molded polycarbonate parts and evaluating annealing methods for relieving these stresses.

ACTIVITY

Molded polycarbonate parts are affected by external and internal conditions during molding, cleaning, handling, and assembly operations. Many of these conditions will cause stress crazing or cracking. Cracking can occur in many thermoplastics when surfaces are stressed in tension and exposed to certain environments. There is a critical elongation at which crazing or cracking will occur when the surface is exposed to a specific environment while an increasing stress is applied. To initiate a crazing condition, a gaseous or liquid environment must wet the surface or be absorbed by the polymer. The most destructive environments do both^{3, 4}.

Washing and Cleaning Solutions

Stress cracking occurred in polycarbonate parts after they had been washed with alcohol previously thought to be safe cleaning material. In order to determine how and when the alcohol caused the cracking it was necessary to determine the critical elongation of the polycarbonate material. Emphasis was directed toward determining the effect of Formula 30 denatured alcohol, absolute ethyl alcohol, and absolute methyl alcohol. Since other materials were sometimes used in the cleaning process, the effects of tap water, dilute ammonium hydroxide, water and aluminum oxide vapor blast solution, and Carbo-Color 41-R detergent were investigated.

Test specimens were injection molded bars approximately 0.13 by 0.50 by 5.0 inches (3.3 by 12.7 by 127 mm). The bars were held in place (Figure 1) and tested at 1, 2, and 3 percent strain levels* during exposure to a specific

*ASTM D-790

environment. An unstrained specimen was used as a control. A 1 percent strain level is equal to an initial tensile stress of approximately 3400 psi (23.44 MPa). The specimen deflections were determined by the formula

$$D = \frac{rL^2}{6d}$$

where

D is the deflection,

r is the strain level,

L is the length of the span, and

d is the specimen thickness.

SPECIMEN	DEFLECTION (mm)	PERCENT STRAIN LEVEL
1	8.5	1
2	17	2
3	25.4	3

Figure 1. Polycarbonate Surface Stress Analysis Fixture

The deflection required to produce 1 percent strain is 8.5 mm. A strain of 2 percent requires 17.0 mm and 3 percent strain requires 25.4 mm.

When the effects of a volatile liquid environment were tested, the specimens were immersed in the liquid. For non-volatile liquids, an absorbant material was soaked with solution and placed on the specimen. For gaseous environments, the specimen was placed in a closed container of the gas.

The results of the washing and cleaning tests are given in Table 1. This part of the study indicated that alcohols specified for cleaning polycarbonate parts are safe only when the parts have less than 2 percent strain. Mild detergent and water are a better choice. Subsequent to this study the mandatory use of alcohol has been deleted from the polycarbonate material specification.

Marking Inks and Labels

Polycarbonate parts are labeled with ink, vibro-etching, or tags. Only the inking and etching procedures were tested. Vibro-etched specimens were tested with control specimens in various solvents known to craze polycarbonates, such as isopropyl alcohol and methanol. The control specimens crazed at the same time or before the vibro-etched specimens. In all cases the crazing on the vibro-etched specimens started from the edge of the bar and not from the marked area. This indicates that vibro-etching does not cause polycarbonate the craze and might even be slightly stress-relieving on the surface of the part at the marked area.

Two stamp pad inks were evaluated (Table 2). These were Markem GK-6646 and Justrite Slink ink. Both inks can cause polycarbonate to craze. The susceptibility of the polycarbonate to stress crack from Markem ink is dependent on the amount of ink present, or, if the ink is on another component that later comes in contact with the polycarbonate, on how long the ink has dried on that component. Polycarbonate will crack when Slink ink is applied to the opposite side of a thin cellular silicone specimen because the surface of the ink dries and the solvent migrates through the cellular silicone to crack the polycarbonate. The Slink ink is less prone to craze polycarbonate than the Markem ink. The Markem ink will retain its solvent longer and it is the solvent that causes the cracking.

The Markem solvents appear to be more aromatic although this has not been verified. Additional tests have been made on production parts with the Slink ink. Slink ink appears to be acceptable for marking polycarbonate or for use on parts coming in contact with polycarbonate.

Table 1. Effect of Cleaning Media on Polycarbonate

Strain (Percent)	Media	pH	Temperature ($\pm 3^{\circ}\text{C}$)	Time of Exposure	Results
0	Water	6.5	29	64 Hours	No effect
1	Water	6.5	29	24 Hours	No effect
3	Water	6.5	24	7 Days	No effect
1	Water	6.5	57	7 Hours	No effect
3	Water	6.5	57	8 Hours	No effect
1	Water	6.5	74	6 Hours	No effect
3	Water	6.5	74	4 Hours	Crazed
0	Tap water and Ammonium Hydroxide	10.5	26	24 Hours	No effect
1	Tap water and Ammonium Hydroxide	10.5	26	24 Hours	No effect
1	Tap water and Ammonium Hydroxide	10.5	57	6 Hours	No effect
0	Tap water and Ammonium Hydroxide	11.5	26	6 Hours	No effect
1	Tap water and Ammonium Hydroxide	11.5	26	6 Hours	No effect
1	Tap water and Ammonium Hydroxide	11.5	57	6 Hours	No effect
0	Carbo-Color 41 and Water	9	29	8 Months	No effect
1	Carbo-Color 41 and Water	9	29	8 Months	No effect
2	Carbo-Color 41 and Water	9	24	25 Days	Crazed
3	Carbo-Color 41 and Water	9	24	7 Days	Crazed

Table 1 Continued. Effect of Cleaning Media on Polycarbonate

Strain (Percent)	Media	pH	Temperature ($\pm 3^{\circ}\text{C}$)	Time of Exposure	Results
1	Carbo-Color 41 and Water	9	57	6 Hours	No effect
3	Carbo-Color 41 and Water	9	57	9 Hours	Crazed
0	Vapor-Blast Solution	6.5	29	64 Hours	No effect
1	Vapor-Blast Solution	6.5	29	24 Hours	No effect
1	Vapor-Blast Solution	6.5	74	6 Hours	No effect
1	Absolute Ethanol		25	8 Hours	No effect
2	Absolute Ethanol		25	30-60 Seconds	Crazed
3	Absolute Ethanol		25	10-20 Seconds	Crazed
1	Absolute Methanol		25	8 Hours	No effect
2	Absolute Methanol		25	20-50 Seconds	Crazed
3	Absolute Methanol		25	20-40 Seconds	Crazed
1	Formula 30 Denatured Alcohol		25	8 Hours	No effect
2	Formula 30 Denatured Alcohol		25	20-30 Seconds	Crazed
3	Formula 30 Denatured Alcohol		25	10-20 Seconds	Crazed

Table 2. Effect of Marking Inks on Polycarbonate

Conditions	Time to Craze Occurrence at Indicated Percent Strain			
	3	2	1	0
Wet Markem Ink Smear	3 Minutes	3 Minutes	5 Minutes	60 Minutes
Lightly Stamped Markem Ink on Cellular Silicone Against Polycarbonate	15 Minutes	15 Minutes	30 Minutes	No effect
Lightly Stamped Markem Ink on Cellular Silicone (Dried 4 Days) Against Polycarbonate	60 Minutes	210 Minutes	No effect	No effect
Lightly Stamped Markem Ink on Cellular Silicone (Dried 7 Days) Against Polycarbonate	24 Hours	30 Days	No effect	No effect
Wet Slink Ink Smear	3 Minutes	3 Minutes	5 Minutes	20 Hours
Slink Ink from Date Stamp		5 Days	No effect	No effect
Lightly Stamped Slink Ink on Cellular Silicone Against Polycarbonate		No effect	No effect	No effect
Slink Ink Stamped on Cellular Silicone, Ink Side Away from Test Specimen		5 Days	No effect	No effect

Additional marking methods were screened at the 3 percent strain level only. The methods are for those occasions when it is convenient to identify a part between molding and either shipping or placing in the next assembly. The results indicate that good quality pressure sensitive tapes and wax pencils are safe for marking polycarbonate parts. The following materials were tested for their effect on polycarbonate: M&C Specialties Precut Masks, Tuck Masking Tape, Avery Labels, black wax pencils, graphite lead pencils, and 3-M Magic Mending Tape. The precut masks caused polycarbonate to craze at the edge of the mask after 6 days. The other materials had no effect after 11 days.

Coolants

Coolants used during machining and drilling of polycarbonate parts were tested. Coolants are used to permit faster feed and speed rates without melting or greatly stressing the area adjacent to the holes. Coolants also can improve the surface finish of the part and can help achieve nearly burr-free holes. There are two major types of coolants used with plastics: water emulsions and refined mineral oils. Coolants previously or presently being studied are Diamond 55, a refined mineral oil; Cimcool 5-Star, an oil-water emulsion; Johnsons M-54, an oil-water emulsion; Johnsons TL-131, a water soluble and reducible liquid; and Houghton Cut-Max 105, a refined mineral oil.

Diamond 55 and Cut-Max 105 are both low viscosity refined mineral oils. The Diamond 55 contains 0.4 percent sulfur, while Cut-Max 105 has only 0.003 percent. Sulfur containing compounds are known to cause stress cracking of polycarbonate. Cimcool 5-Star and Johnsons M-54 are cutting fluids containing mostly water with small amounts of paraffin oil or glycol as a lubricant, triethanolamine and sodium nitrite as rust inhibitors, and a wetting agent. These fluids are generally diluted with tap water 30 to 60 times by volume and are recirculated and filtered through the machine. The TL-131 is a water solution of isopropyl alcohol, triethanolamine, and glycol, with lesser amounts of several other additives. It is normally used in a 40:1 dilution with water and is used only once before being discarded. This coolant relies upon the evaporative effect in a spray mist for cooling while providing minimal lubrication.

The specimens were exposed to the oils and concentrated coolants by placing a saturated tissue on each specimen. The diluted aqueous tests were made by immersing the specimens and fixture in a container of the solution.

When using a diluted water solution for cooling polycarbonate during a machining or drilling operation the water can evaporate and leave a concentrated film of triethanolamine, sodium nitrite, and other non-volatile compounds on the part. For this reason any part drilled or machined with the water solution coolants or Diamond 55, because of its sulfur content, should be washed with mild

detergent and water immediately. Based on these data, the best choice of a cutting oil or coolant for polycarbonate is Houghtons Cut-Max 105. Table 3 shows the times required for coolants to cause stress cracking in polycarbonate at various strain levels.

Solvents, Mold Releases, and Miscellaneous Chemicals

Polycarbonate parts are exposed to many different mold releases, solvents, and other chemicals between the time they are molded and shipped. Many of these chemicals can cause stress cracking. They were tested to obtain supporting data that would be of value in the later development of a solvent stress analysis test. Tests of mold release chemicals revealed that polycarbonate was tolerant in most cases. When aerosol mold releases caused crazing, it was generally caused by the propellant. Tables 4, 5, and 6 list the effects of chemicals on polycarbonates.

Annealing and Heat Transfer Oils

Since molded-in stresses within polycarbonate parts can be partially relieved by annealing in an oil bath, annealing oils were investigated. Houghton 102 and Gulf 205 oils are highly refined mineral oils having a very high viscosity. The Dow Corning 200 and General Electric SF-96 are silicone oils. These oils are used primarily as dielectric oils in transformers. Their inertness with polycarbonate makes them suitable for annealing molded parts.

Heat transfer oils were also tested. Therminol FR-1 had been used as a heat transfer fluid, but was discontinued by Monsanto because of its adverse ecological affects. The two prime candidates for replacement were Monsantos Therminol 66 and Dows Dowtherm G. Therminol 66 had virtually no effect on polycarbonate, Dowtherm G degraded polycarbonate, and Therminol FR-1 softened polycarbonate upon exposure (Table 7).

Stress Analysis

The final phase of the study was directed toward methods to determine the stress level in molded polycarbonate parts. Several of the classical approaches such as photo-elastic and strain gage measurements were bypassed, since they involve tedious testing or parameters difficult to measure. A literature search and information gained in previous phases of this study yielded several solvents and solvent combinations and techniques to determine the approximate magnitude of stress within molded polycarbonate parts. Methods employing solvents or chemicals known to crack or craze polycarbonates were then investigated.

Text continued on Page 20.

Table 3. Effect of Coolants on Polycarbonate

Coolant	Time to Crack at Indicated Percent Strain			
	3	2	1	0
Diamond 55	20 to 45 Minutes	20 Hours	No effect after 9 months	No effect after 9 months
Cimcool Concentrate	49 Hours	30 Hours	16 Days	34 Days
Cimcool 30:1 Dilution	4 Days	7 Days	No effect after 8-1/2 months	No effect after 8-1/2 months
Cimcool 60-1 Dilution	7 Days	5 Days	No effect after 8-1/2 months	No effect after 8-1/2 months
Houghton 105	No effect at any strain after 18 months			
Johnson M-54 Concentrate	3 Days	4 Days	15 Days	No effect after 8 months
Johnson M-54 40:1 Dilution	11 Days	21 Days	No effect after 8 months	No effect after 8 months

Table 4. Effect of Solvents on Stressed Polycarbonate

Solvent	Time to Crack at Indicated Percent Strain				
	3	2	1	0.5	0
Acetone		Instantaneous	Instantaneous	Instantaneous	1 Second
Benzene		↑	↑	*	*
Xylene		↓	↓	20 Seconds	60 Seconds
Toluol			Instantaneous	10 Seconds	15 Seconds
Amyl Acetate			5 Seconds	8 Seconds	30 Seconds
Petroleum Ether		Instantaneous	30 Seconds	2.5 Minutes	15 Minutes
Isopropyl Alcohol		5 Seconds	60 Minutes	*	*
10:1 n-Propanol and Toluol	5 Seconds	8 Seconds	12 Seconds		
Heptane	3 Seconds	8 Seconds	35 Seconds		
*No effect after 60 minutes					

Table 5. Effect of Selected Chemical Compounds on Stressed Polycarbonate

Material	Time to Crack at Indicated Percent Strain				
	3	2	1	0.5	0
Liquid Glass Cleaner		*	*	*	*
10 Gram Chlorinated Alkaline Detergent per gallon (0.0038 m ³) of water	1 Hour	2 Hours	32 Hours		**
1 Gram Chlorinated Alkaline Detergent per gallon (0.0038 m ³) of water	54 Hours	5 Days	**		**
0.1 Gram Chlorinated Alkaline Detergent per gallon (0.0038 m ³) of water	**	**	**		**
Anti-Rust Oil		5 Minutes	*	*	*
Krylon Spray			3 Seconds	10 Seconds	60 Seconds
Pine Oil Disinfectant		15 Seconds	2 Minutes	15 Minutes	*
Bendix Surfactant Liquid 25I 1.5 percent solution	24 Hours	6 Days	8 Days		9 Days
SBS-61 Soap		*	*	*	*
*No effect after 60 minutes **No effect after 9 days					

Table 6. Effect of Mold Releases on Stressed Polycarbonate

Mold Release	Time to Crack at Indicated Percent Strain			
	2	1	0.5	0
Mold Release* for Nylon	Instantaneous	10 Seconds	30 Minutes	***
Mold Release* for Polycarbonate	Instantaneous	25 Minutes	***	***
Silicone Spray**	Instantaneous	***	***	***
Fluoroglides	3 Seconds	12 Seconds	25 Seconds	2 Minutes
Zinc Stearate	10 Seconds	***	***	***
3M Special Mold Release	***	***	***	***
MS-136**	Instantaneous	Instantaneous	5 Seconds	50 Seconds
MS-122**	10 Seconds	30 Seconds	***	***
*Price Driscoll **Miller Stephenson ***No effect after 60 minutes				

Table 7. Effect of Annealing and Heat Transfer Oils on Stressed Polycarbonate at 25°C

Material	Time to Crack at Indicated Percent Strain			
	3	2	1	0
Dowtherm G Liquid	5 Minutes	7 Minutes	8 Minutes	40 Minutes
Dowtherm G Vapor	4 to 5 Hours	6 to 16 Hours	72 Hours	*
Therminol FR-1 Liquid	16 Hours	30 Hours	48 Hours	96-144 Hours
Therminol 66 Liquid	**	No effect after 240 hours at 0, 1, and 2 percent strain		
Therminol 66 Vapor	No effect after 240 hours any strain			
Houghton 102 Mineral Oil	No effect at any percent strain after 21 months			
Gulf 205 Mineral Oil	No effect at any percent strain after 21 months			
Dow Corning 200 Silicone Oil	No effect at any percent strain after 23 months			
GE SF-96 Silicone Oil	No effect at any percent strain after 24 months			
*No effect after 28 days				
**One of two specimens cracked after 4 hours, the second did not crack until after 240 hours. The first specimen was replaced and did not crack after 120 hours, at which time the test was terminated.				

A solvent stress analysis test received from Mobay Chemical Company was evaluated. The test uses one part by volume of toluol and ten parts by volume of n-propanol. The polycarbonate part is immersed in the solvent at room temperature for 3 minutes, removed, and examined. If no stress crazing or cracking occurs, the part has less than 1400 psi (9.65 MPa) molded-in stress.

A more comprehensive test from Mobay Chemical Company was also used. In addition to the test at 1400 psi it included 1 to 5 parts by volume of toluol to n-propanol with a critical stress level of 1000 psi (6.89 MPa) and 1 to 3 parts by volume of toluol to n-propanol with a critical stress level of 550 psi (3.79 MPa). The mechanism of this test involved an active stress cracking solvent, toluol, and an inert one, n-propanol, as a retarder. By varying the mixture ratio the critical stress level can be changed.

A solvent stress test received from the General Electric Company⁵ used a mixture of ethyl acetate and methyl alcohol in varying proportions to yield critical stress levels from 500 psi (3.45 MPa) for 100 percent ethyl acetate to 3400 psi (23.44 MPa) for 100 percent methyl alcohol. This test also involved immersing the specimen in the solvent for 3 minutes and examining it for stress cracking or crazing.

Carbon tetrachloride is recommended for testing parts having stresses of less than 600 psi (4.14 MPa) (Figure 2).

Acetone has been used to determine critical stress levels of approximately 1100 psi (7.58 MPa). It is not recommended as a test solvent because it will dissolve polycarbonate. Many of the solvents used for stress analysis of polycarbonate parts are flammable and precautions should be taken.

All tests should be performed in a well ventilated hood. When using solvent mixtures, the solutions should be used only once because the polycarbonate absorbs the ethyl acetate or toluol out of the mixture. All test parts should be discarded after testing because of possible absorption of the solvent.

Most polycarbonate parts tested had stresses of less than 1400 psi (9.65 MPa). Those parts with molded-in inserts had very high stresses around the inserts. The toluol and n-propanol mixture is preferred for testing parts suspected of having stresses of 550 to 1500 psi (3.79 to 10.34 MPa). At lower suspected stress levels, carbon tetrachloride is preferred.

A study was performed to evaluate the stress reducing effect of oil immersion annealing at $127 \pm 3^\circ\text{C}$ for 6 hours on injection molded polycarbonate parts, to evaluate different mold temperature cycles, and to evaluate drilling subsequent to molding. Hexane was used to remove the annealing oils because of its high

critical strain level of 2560 psi (17.65 MPa). A toluol and n-propanol mixture and carbon tetrachloride were used for these tests.

Figure 3 shows a 4-inch (102 mm) disc and five connecting blocks photographed between two Polaroid filters. Blocks 1, 3, and 4 were annealed in mineral oil for 6 hours at $127 \pm 3^\circ\text{C}$.

All blocks were then subjected to the carbon tetrachloride solvent test for 10 seconds. Blocks 1, 3, 4, and 5 did not show any signs of crazing or cracking.

Figure 2. Time Required for Carbon Tetrachloride to Stress Stress Crack Polycarbonate at Various Stress Levels

Block 2 cracked as it was removed at the end of 10 seconds. These data indicate that Block 2 was stressed at about 600 psi (4.14 MPa), while the other blocks had less than 550 psi (3.79 MPa) stress.

Three other part configurations have been tested before and after oil immersion annealing with the solvent stress analysis. The tests indicate a reduction in stress after annealing.

In Figure 3, the rainbow color effect is the photoelastic fringe pattern. Each fringe is one complete color change (e.g., blue to blue) and represents a finite unit of stress. Also shown are nodes or black spots where the fringe pattern disappears. The level of stress each fringe represents is difficult to determine since it is dependent upon the molding parameters when the part was produced. The 4-inch (102 mm) disc, having only one fringe except around the gate, is very nearly stress free in the center, with approximately 300 psi (2.07 MPa) around the gate.

Although the stress level is low in both parts, great differences do exist in the number of countable fringes between the blocks and the disc. This makes stress evaluation by counting fringes very difficult.

Figures 4 and 5 show a series of parts tested using solvent stress analysis. Figure 4 shows various views of the part to illustrate its complex shape. Three holes drilled crosswise through the thick area of the part are shown in the top view. This part was studied because of stress cracking problems after molding and subsequent drilling.

The first series of parts that were solvent analysis tested were produced with either a constant mold temperature or a cycled mold temperature (hot during injection and cooled before ejection of the part). The cycling of the mold temperature has an annealing effect on the part and these parts had a significantly lower stress level than the parts using a constant mold temperature. These parts had previously been visually inspected with Polaroid filters and no significant differences could be noted.

Parts that were known to have a low stress level were then drilled under various conditions with different coolants. Significant increases in the stress level of the drilled parts were noted when the parts were tested in carbon tetrachloride.

Parts molded with a cycled mold temperature, from which representative samples indicated a stress level below 500 psi (3.45 MPa), were then drilled. These parts subsequently broke when subjected to carbon tetrachloride (Figure 5). They show that the drilling operation produces stresses above 600 psi (4.14 MPa) around the holes.

Many other part configurations were photographed between Polaroid filters before and after oil annealing, with no visual change in the photos. However,

Figure 3. Birefringent Patterns in Connecting Blocks and a 4-Inch-Diameter (102 mm) Test Specimen

Figure 4. Molded Polycarbonate Parts

Figure 5. Molded Polycarbonate Parts Shown After Immersion in Carbon Tetrachloride

a lower stress in the annealed parts was determined using solvent stress analysis. Similar parts using different molding parameters and tested by solvent stress analysis showed differences in stresses which were not detectable photoelastically. From these data, it appears that the solvent stress analysis test can be used to measure the approximate stress in molded parts.

No differences in stress crack resistance between General Electrics Lexan and Mobay Chemicals Merlon were detected, nor were differences detected among their different grades of polycarbonate.

ACCOMPLISHMENTS

It was determined that the specified cleaning alcohols will craze or crack polycarbonate if the stress level is high enough. An alternate cleaning method of mild detergent and water has been recommended.

A study of marking methods has shown that care must be taken if ink is used. Other methods like vibro-etch and pressure sensitive tape are suitable alternates.

Many coolants or lubricants contain chemicals which will craze polycarbonates. Highly purified mineral oils are the least destructive.

Mold releases for polycarbonates are suitable when applied to the molds properly. The propellant used in aerosols generally degrades polycarbonate.

Highly refined mineral oils and silicone oils are satisfactory for use as an annealing media for polycarbonates. Of the three heat transfer oils tested, Therminol 66 did not adversely affect polycarbonate.

Several stress analysis test methods were developed that would detect a wide range of stress levels in molded polycarbonates. One method will indicate a stress level as low as 200 psi (1.38 MPa).

This analysis technique has been used to evaluate changes in molding and machining processes, and to determine the effectiveness of stress annealing cycles.

REFERENCES

¹Lexan Polycarbonate Resin Handbook. Pittsfield, Massachusetts: General Electric Corporation, Chemical Materials Department.

²Design Manual for Merlon Polycarbonate. Pittsburg, Pennsylvania: Mobay Chemical Company, 1973.

³Roger Kambour, "New Theory Explains Crazing of Plastics," Materials Engineering, Volume 69, Number 2, February 1969, p 64.

⁴G. W. Miller and S. A. Visser, "Mechanism for Solvent Stress Crazing of Polycarbonate," American Chemical Society, Volume 7, April 1967, pp 644-655.

⁵T. A. Tomasetti and F. A. Bauer, Testing of Molded Parts for Residual Molding Stresses. Pittsfield, Massachusetts: General Electric Corporation, Plastics Department, 1973.

Appendix

PROPRIETARY COMPOUNDS USED OR EVALUATED IN THIS STUDY

Avery Label, Avery Label Company, Monrovia, CA
Carbo-Color 41-R, Carborundum Company, Niagara Falls, NY
Cimcool 5 Star Cutting Fluid, Atlantic Richfield, New York, NY
105 Cut-Max, E. F. Houghton and Company, Philadelphia, PA
M-54 Cutting Fluid, S. C. Johnson and Company Incorporated, Racine, WI
Diamond 55 Mineral Oil, Atlantic Richfield, New York, NY
Dowtherm G, Dow Chemical Company, Midland, MI
Fluoroglide, Chemplast Incorporated, Wayne, NJ
Justrite Slink, Louis Melino Company, Chicago, ILL
Krylon Crystal Clear Spray, Krylon Incorporated, Norristown, PA
Lexan, General Electric Company, Pittsfield, MA
Magic Mending Tape, 3-M Company, Saint Paul, MN
Markem GK6646, Markem Corporation, Keene, NH
Merlon, Mobay Chemical Company, Pittsburg, PA
102 Mineral Oil, E. F. Houghton and Company, Philadelphia, PA
205 Mineral Oil, Gulf Oil Corporation, Houston, TX
Pre-Cut Masks, M&C Specialties, Milwaukee, WI
200 Silicone Oil, Dow Corning Company, Midland, MI
SF-96 Silicone Oil, General Electric, Schenectady, NY
SBS-61 Soap, Sugar Beet Products Company, Saginaw, MI

Surfactant Liquid Soap 251, Bendix Corporation, Southfield, MI

Therminol 66, Monsanto Chemical Company, Saint Louis, MO

Therminol FR-1, Monsanto Chemical Company, Saint Louis, MO

Tuck Marking Tape, Tuck Industries, New Rochelle, NY