NACA

RESEARCH MEMORANDUM

EFFECTS OF HIGH DEGREES OF BIAXIAL STRETCH-FORMING ON CRAZING AND OTHER PROPERTIES OF ACRYLIC PLASTIC GLAZING

By I. Wolock, B. M. Axilrod, and M. A. Sherman

National Bureau of Standards

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

May 29, 1953

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

EFFECTS OF HIGH DEGREES OF BIAXIAL STRETCH-FORMING ON CRAZING AND OTHER PROPERTIES OF ACRYLIC PLASTIC GLAZING

By I. Wolock, B. M. Axilrod, and M. A. Sherman

SUMMARY

Following an earlier investigation of the effects of biaxial stretch-forming of polymethyl methacrylate to about 50-percent strain, the effects of higher degrees of forming were investigated. Sheets of commercial cast polymethyl methacrylate were hot-stretched approximately 100 and 150 percent, respectively, and tests were conducted on this material and on unstretched control material. It was found that the tensile strength increased for the 150-percent-stretched material only; this increase was 6 to 12 percent. The elongation at failure was higher for the stretched materials than for the unstretched but decreased as the degree of stretching increased. None of the stretched specimens crazed in the short-time tensile tests. The threshold stress for stress-solvent crazing with benzene was equal to approximately three-fourths of the ultimate strength for the 100-percent-stretched material, as compared with a threshold stress equal to approximately one-fourth of the ultimate strength for the unstretched material. Most of the specimens of the 150-percent-stretched material did not solvent craze at stresses very close to the ultimate strength. Thus, the resistance to crazing increased markedly with increasing degrees of biaxial stretching.

The resistance of the stretched material to surface abrasion was found to be appreciably less than that of the unstretched material.

A theory for the behavior of the stretched acrylic sheet is presented, based on a postulated molecular structure for this material.

INTRODUCTION

Previously reported data (ref. 1) indicated that moderate degrees of biaxial stretch-forming greatly improve the crazing resistance of cast polymethyl-methacrylate sheeting. The results showed that biaxially stretch-forming polymethyl methacrylate approximately 50 percent greatly increased the elongation at failure and the stress and strain at the onset of crazing in short-time tensile tests; in fact most of the specimens tested did not craze in these tests. The forming also increased the threshold stress of stress-solvent crazing about 75 percent. In view of these results, an investigation was made of the effects of higher degrees of biaxial stretching on the tensile, crazing, and surface abrasion properties of acrylic glazing.

This work was performed as one phase of a research program whose purpose is to investigate factors affecting the crazing and strength properties of laminated acrylic glazing. The research is being done at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. The courtesy of Mr. R. E. Leary, E. I. du Pont de Nemours & Co., Inc., and Mr. W. F. Bartoe, Rohm & Haas Co., Inc., in furnishing materials and information for use in this investigation is gratefully acknowledged, as well as the courtesy of North American Aviation, Inc., for permission to use the information cited from their Report No. NA-52-5. The assistance of Mr. Victor Cohen and Mr. Robert W. Mackintosh in conducting these tests is greatly appreciated. The statistical design of the experiments and analysis of the data were supervised by Mr. John Mandel. The X-ray diffraction patterns were made by Mr. H. E. Swanson.

MATERIALS

The materials used were commercial cast polymethyl-methacrylate sheets, Lucite and Plexiglas, of both general-purpose and heat-resistant grades (ref. 2) and were approximately 0.15 inch in thickness. The samples were obtained directly from the manufacturers and consisted of one sheet from each of two production runs for both grades of materials.

APPARATUS AND PROCEDURE

Forming

The vacuum forming apparatus and operation are described in detail in a previous report (ref. 1). Briefly, a sheet of the plastic is heated in an oven to a temperature in the rubbery range, 130° C for the general-purpose-grade acrylic sheet and 160° C for the heat-resistant material. The sheet is removed from the oven and clamped to a flanged cylindrical forming vessel. The vessel is partially evacuated, drawing the sheet down into the chamber in the form of a hemisphere. An open-ended cylinder is inserted into the hemisphere, clamped in place, and air is admitted to the forming vessel, causing the plastic to retract around the cylinder. The formed plastic has the shape of a top hat. Test specimens are taken from the 10-inch-diameter flat top of the formed piece.

A formed hat is shown in figure 1. The sheet was marked off in square grids before stretching so that the degree of uniformity of stretching on the flat top could be observed. The length of the squares on the flat top indicates the degree of stretching when compared with the original length of the squares on the bottom rim. Experiments described in reference 1 showed that the amount of stretching was reasonably uniform over the face of these formed disks.

For the 100-percent-stretched material, one disk was formed from each sheet, making a total of two disks of each sample. For the 150-percent-stretched material, two disks were formed from each sheet, making a total of four disks of each sample. Two standard tensile specimens and two tapered tensile specimens were tested from each disk along with corresponding control specimens from the same respective sheets.

Standard Tensile Tests

The standard tensile tests were made at 23° C and 50-percent relative humidity following in most details Method No. 1011 of Federal Specification L-P-406a. Four 100-percent-stretched specimens and eight 150-percent-stretched specimens of each material were tested along with corresponding control specimens. The specimens were tested in a statistically randomized order and were conditioned at the test conditions for at least 24 hours prior to testing. A testing speed of 0.05 inch per minute was used up to 10-percent strain, at which point the speed was increased to 0.6 inch per minute. Autographic load-extension curves were obtained on the unstretched control specimens with Southwark-Peters extensometers and the associated recorder. The strain gage was also used on the first few formed specimens tested. The knife edges of the gage, however, scratched the surface of the specimens, resulting in a tendency toward premature failure. Accordingly, the strain gage was not used for the majority of the formed specimens, so that load-extension curves were not obtained. The total elongation was measured with dividers for the formed specimens and also for those control specimens which elongated more than 10 percent.

Stress-Solvent Crazing

The stress-solvent crazing tests were conducted on tensile specimens which tapered from a width of 0.500 to 0.333 inch over a 3-inch reduced section. In testing, a specimen was placed under a predetermined load in a hydraulic testing machine and a blotter, saturated with benzene, was pressed against the tapered portion of one face of the specimen for 10 seconds. The extent of crazing along the length of the specimen was noted after removal of the blotter while the specimen was still under load. The stress at the point at which crazing terminated was calculated as the threshold stress for stress-solvent crazing. The extent of crazing on the specimen was taken as that point below which there were no visible craze cracks.

Surface Abrasion Tests

Surface abrasion tests of both formed and unformed material were also conducted in accordance with Method No. 1092 of Federal Specification L-P-406a, using a Taber abraser. Light transmission and haze measurements were made following A.S.T.M. Method D 1003-49T, using a Hunter hazemeter. These measurements were made after 0, 10, 25, 50, 75, 100, 150, 200, and 250 revolutions of the abraser.

RESULTS AND DISCUSSION

Standard Tensile Tests

The results of the tensile tests on the formed and unformed specimens are shown in table I. All of the results are shown graphically in figure 2 along with the results previously obtained on 50-percent-stretched material. A statistical analysis of the data did not indicate any significant sheet-to-sheet variation and the standard errors reported in table I were calculated on this basis. The data did not indicate an increase in tensile strength for the 100-percent-stretched material. There was an increase in tensile strength, however, of about 6 percent for the general-purpose-grade Lucite specimens stretched 145 to 150 percent and about 12 percent for the Plexiglas specimens of both grades which were stretched 165 to 170 percent. The control specimens of heat-resistant-grade Lucite broke prematurely, so that there was no value obtained upon which to base any change in tensile strength upon stretching. The corresponding total elongations were considerably higher for the stretched specimens than for the unstretched, increasing from approximately 7 percent for the unstretched material to approximately 50 and 25 percent for the material stretched 100 and 150 percent, respectively. None of the stretched specimens crazed in the short-time tensile tests, which result might have been expected from the previously reported results on 50-percent-stretched material, whereas the control specimens crazed at the usual strains varying from 2.3 to 3.4 percent for the various materials.

The fracture surfaces of the unstretched specimens and of the previously tested 50-percent-stretched specimens had a mirrorlike area in which, it was postulated, the fracture begins (ref. 1). This mirrorlike area was observed on only a few of the 100- and the 150-percent-stretched specimens (fig. 3). The laminar nature of the fracture surfaces was more pronounced in these highly stretched specimens than in the 50-percent-stretched specimens (fig. 4) and the fracture surfaces were so small and laminar that detection of the glassy areas was usually quite difficult. The influence of orientation on the appearance of fracture surfaces is also shown by the fibrous nature of uniaxially stretched polymers previously noted by Houwink (ref. 3) and Cheatam and Dietz (ref. 4).

Stress-Solvent Crazing

The results of the stress-solvent crazing tests are shown in table II and in figure 2. The specimens of the unstretched materials crazed at stresses corresponding to approximately one-fourth of the ultimate strength upon application of benzene. The threshold crazing stress for the 100-percent-stretched materials was 210 and 160 percent higher than for the unstretched general-purpose and heat-resistant grades, respectively, corresponding to approximately three-fourths and two-thirds of the respective ultimate strengths. Most of the specimens of the more highly stretched materials did not craze upon the application of benzene even at stresses very close to the ultimate strength.

Several stress-solvent-crazed specimens are shown in figure 5 along with a stress-crazed specimen. The craze cracks in the 100-percent-stretched solvent-crazed specimen are finer and more numerous than in the unstretched solvent-crazed specimen. This same effect was noted for the 50-percent-stretched specimens.

Surface Abrasion Tests

The results of the abrasion tests are shown in table III. The light transmission of the formed specimens after abrasion was only slightly less than that of the unformed specimens. The haze of the formed material after abrasion, however, was appreciably higher than that of the unformed material in every case, this increase ranging from approximately 15 to 55 percent. From the data there is a rough indication of increase in haze after surface abrasion with higher degrees of stretching. This was also apparent in working with specimens of the stretched material. The highly stretched tensile specimens were easily scratched when rubbed gently with industrial cleansing tissues or absorbent cotton, which was not true when the same treatment was applied to specimens having low degrees of stretching.

X-Ray Diffraction Patterns

X-ray diffraction patterns were obtained on both stretched and unstretched polymethyl methacrylate, using a recording Geiger counter spectrometer with a copper target and nickel filter. The patterns were similar to those obtained by Krimm and Tobolsky (ref. 5), with halos at Bragg spacings of 6.5 and 3.0A for both the unstretched and the stretched materials, compared with 6.60 and 2.92A reported by the above authors. They attribute the former spacing to interchain interferences and the latter to intramolecular interferences. The height of the 6.5A peak was approximately 30 percent higher for the stretched material than for the unstretched. This would indicate increased orientation in the stretched polymer, which is expected from the nature of the stretching operation. There was a slight decrease noted in height of the 3.0A peak of the stretched samples, but it is questionable whether this change is significant.

Discussion

The mechanism of crazing has been discussed in a previous report (ref. 1). It was postulated that crazing starts at the surface at submicroscopic flaws or weak points. Such weak points may be submicroscopic regions in which the polymer chain segments are oriented normal to the applied stress. In biaxial stretching, the chain segments turn into a position more nearly parallel to the surface, and this angular change is dependent on the degree of stretching. The chain segments do not, on the average, change the angle of their projections on the plane of the sheet with respect to the length or width of the sheet. Bailey (ref. 6) previously made similar statements for polymer chains. As the orientation increases, it may become more difficult for a submicroscopic crack to propagate through the thickness of the sheet, because of the development of "cleavage" planes (ref. 1). The possibility then exists that, in highly formed polymethyl methacrylate, submicroscopic cracks form on the surface of a specimen when a tensile load is applied. The growth of cracks through the sheet is retarded by the planar orientation, however, and the specimen fails before the cracks become visible. Examination of the surface of stretched polymethyl methacrylate with the electron microscope may yield further information on this possibility.

Crazing may be local tensile failure resulting from internal stresses, as postulated by Russell (ref. 7), or may result from other types of surface flaws or defects, which would be points of localized stress concentration. These flaws might be inhomogeneities in chemical composition, such as residual catalyst, or physical surface defects resulting from the casting operation. The importance of flaws in effecting the fracture of other materials has been recognized. Griffith (ref. 8) has proposed a theory of the strength of glass based on the presence of surface cracks. The importance of structural inhomogeneities in the failure of metals has been reported by Epremian and Mehl (ref. 9). They found that inclusions play, by far, the dominant role in the fatigue behavior of metals.

Biaxial stretching probably would alleviate the effects of some types of submicroscopic flaws in cast acrylic sheet, since the material is heated to the rubbery state and then stretched. This would delay the formation of cracks in stretched material.

The orientation of the biaxially stretched material is apparent not only from the previously mentioned X-ray diffraction measurements but also from the laminar structure of the fracture surface of a stretched specimen, as compared with the amorphous appearance of an unstretched specimen (fig. 4). This change from an amorphous to a laminar structure could account for the increase in tensile strength noted for the material stretched 140 percent and more. When the degree of orientation is high enough, the material might act as an assembly of independent laminae parallel to the plane of the sheet, and the force required to rupture a series of such layers would be greater than that required to rupture a single layer of material of the same total thickness. The latter would be typical of the structure of unstretched material.

The increased resistance to crazing offered by biaxially stretched material in stress-solvent crazing tests can probably be explained by similar reasoning and has been discussed in the previous report (ref. 1). Essentially the solvent acts as a plasticizer and allows the chains to be separated more easily, but the postulated molecular structure of the biaxially stretched material would again render the material more craze resistant. When the degree of stretching reaches approximately 150 percent, the specimens fracture before crazing, even upon application of solvent.

The decrease in abrasion resistance of the stretched material may also be due to its laminar structure. The oriented chains that are essentially parallel to the surface may offer less resistance to abrasion than that offered by the randomly oriented chains of the unstretched material.

Possible Use of Stretched Acrylic Sheet

The possible use of prestretched acrylic plastic sheet in aircraft enclosures was suggested in a previous report (ref. 1). Since the report was issued, impact tests have been conducted by North American Aviation, Inc., on a tail gunner's enclosure (ref. 10). During the forming operation, this enclosure is essentially biaxially stretched varying amounts over its area, up to approximately 100 percent at the top of the enclosure. The tests indicated that the shattering characteristics in the highly stretched portions are greatly improved. Failure consists only of a hole approximately the same size as the striking cylinder. Unstretched material, on the other hand, tends to shatter under these conditions. Thus the shattering characteristics of biaxially stretched acrylic sheet suggest that the method for forming enclosures be modified to produce canopies which are stretched over the entire area, including the rim. Besides the improved impact properties, there would also be an accompanying decrease in weight and in tendency to craze.

There are technical difficulties in the forming of prestretched acrylic enclosures which would have to be overcome to make the process commercially feasible. In addition, the decrease in abrasion resistance must be considered, but this may not be serious. Enclosures have been in general use which were essentially highly stretched in certain areas during the forming operation, as in the above-mentioned tail gunner's enclosure, with apparently no serious decrease in abrasion resistance.

CONCLUSIONS

Biaxial stretch-forming of polymethyl methacrylate approximately 100 and 150 percent, respectively, had the following results:

1. The tensile strength did not change for the 100-percent-stretched material but increased 6 to 12 percent for the 150-percent-stretched material. The total elongation increased from approximately 7 percent for unstretched material to 50 and 25 percent for the 100- and 150-percent-stretched materials, respectively. None of the stretched specimens crazed in the short-time tensile test.

2. The threshold stress for stress-solvent crazing with benzene increased from approximately one-fourth of the ultimate strength for the unstretched material to approximately three-fourths for the 100-percent-stretched material. Most of the 150-percent-stretched specimens did not solvent craze even at stresses very close to the ultimate strength.

3. The abrasion resistance of the stretched material, as measured by increase in haze, was significantly less than that for unstretched material.

National Bureau of Standards,
Washington, D. C., October 10, 1952.

REFERENCES

1. Axilrod, B. M., Sherman, M. A., Cohen, V., and Wolock, I.: Effects of Moderate Biaxial Stretch-Forming on Tensile and Crazing Properties of Acrylic Plastic Glazing. NACA TN 2779, 1952.

2. Anon.: Standard Specifications for Cast Polymethyl Methacrylate Sheets, Rods, Tubes and Shapes. A.S.T.M. Designation D 702-46.

3. Houwink, R.: Elastomers and Plastomers. Volume I - General Theory. Elsevier Pub. Co., 1950.

4. Cheatam, R. G., and Dietz, A. G. H.: Effect of Orientation on the Mechanical Properties of Polystyrene. Modern Plastics, vol. 29, no. 1, Sept. 1951, pp. 113-116, 118, 120, 122, 124, 126, 191-192.

5. Krimm, S., and Tobolsky, A. V.: Quantitative X-Ray Studies of Order in Amorphous and Crystalline Polymers. Textile Res. Jour., vol. 21, Nov. 1951, pp. 805-822.

6. Bailey, J.: Stretch Orientation of Polystyrene and Its Interesting Results. India Rubber World, vol. 118, no. 2, May 1948, pp. 225-231.

7. Russell, E. W.: Studies on Polymethyl Methacrylate. Rep. No. Chem. 447, British R.A.E. (Farnborough), Aug. 1948; also see Nature, vol. 165, no. 4186, Jan. 21, 1950, pp. 91-96.

8. Griffith, A. A.: The Phenomena of Rupture and Flow in Solids. Phil. Trans. Roy. Soc. (London), ser. A, vol. 221, Oct. 21, 1920, pp. 163-198.

9. Epremian, E., and Mehl, R. F.: Investigation of Statistical Nature of Fatigue Properties. NACA TN 2719, 1952.

10. Belgen, M. H.: Shattering Characteristics of a Tail Gunner's Enclosure (147-318216) for the B-45A Airplane. Rep. No. NA-52-5, Eng. Res. Lab., North Am. Aviation, Inc., Jan. 2, 1952.

TABLE I.- EFFECT OF BIAXIAL STRETCHING ON TENSILE PROPERTIES

OF POLYMETHYL METHACRYLATE AT 23° C[a]

Material	NBS sample	Biaxial stretch, percent	Tensile strength, psi	Elongation, percent	Stress at onset of crazing, psi	Strain at onset of crazing, percent
Unformed						
Lucite HC201	L1e	---	7,460 ± 30	5.3 ± 0.2	6,950 ± 30	2.7 ± 0
Lucite HC202	L2e	---	(b)	(b)	[c]8,690 ± 140	[c]3.3 ± 0.1
Plexiglas I-A	P1b	---	7,960 ± 20	10.6 ± 1.2	7,110 ± 80	2.3 ± 0
Plexiglas II	P2b	---	9,500 ± 30	7.4 ± 0.8	8,810 ± 100	3.4 ± 0.1
Formed						
Lucite HC201	L1e	100	[d]7,680 ± 190	[d]51 ± 4	Did not craze.	
Lucite HC202	L2e	100	[d]9,310 ± 240	[d]46 ± 2	Do.	
Lucite HC201	L1e	145	7,920 ± 30	30 ± 2	Do.	
Lucite HC202	L2e	150	[e]10,030 ± 30	[e]26 ± 1	Do.	
Plexiglas I-A	P1b	170	[e]8,890 ± 50	[e]25 ± 2	Do.	
Plexiglas II	P2b	165	[f]10,690 ± 50	[f]16 ± 1	Do.	

[a] The tensile tests were made at 23° C and 50-percent relative humidity, in accordance with Method No. 1011, Federal Specification L-P-406a. Testing speed was 0.05 in./min up to 10-percent strain, at which point the speed was increased to 0.6 in./min. All results are the average for eight specimens, unless otherwise noted, plus or minus the standard error.

[b] Seven of the eight specimens tested broke while the stress-strain curve was still rising and did not reach the probable maximum.

[c] Average of the three specimens which crazed.

[d] Average of four specimens tested.

[e] Average of seven specimens.

[f] Average of five specimens (three specimens broke in grips).

TABLE II.- EFFECT OF BIAXIAL STRETCHING ON STRESS-SOLVENT CRAZING WITH BENZENE OF POLYMETHYL METHACRYLATE AT 23° C[a]

Material	NBS sample	Biaxial stretch, percent	Threshold crazing stress, psi
Unstretched			
Lucite HC201	L1e	---	1,760 ± 30
Lucite HC202	L2e	---	2,450 ± 40
Plexiglas I-A	P1b	---	1,710 ± 30
Plexiglas II	P2b	---	2,760 ± 70
Stretched			
Lucite HC201	L1e	100	[b]5,520 ± 30
Lucite HC202	L2e	100	[b]6,260 ± 300
Lucite HC201	L1e	145	Two specimens crazed very slightly at stress of 7,050 psi. Six specimens did not craze at stresses of 7,450-7,750 psi.
Lucite HC202	L2e	150	Six specimens crazed slightly at stresses of 6,700-9,150 psi. Two specimens did not craze at stress of 9,700 psi.
Plexiglas I-A	P1b	170	Seven specimens did not craze at stresses of 8,425-8,650 psi.
Plexiglas II	P2b	165	One specimen crazed very slightly at stress of 9,800 psi. Six others did not craze at stresses of 9,700-10,000 psi.

---

[a] All results are the average for eight specimens, unless otherwise noted, plus or minus the standard error.

[b] Average of four specimens tested.

TABLE III.- EFFECT OF BIAXIAL STRETCHING ON SURFACE ABRASION OF POLYMETHYL METHACRYLATE AT 23° C[a]

Material	NBS sample	Biaxial stretch, percent	Light transmission, percent		Haze, percent	
			Original	Final	Original	Final
Plexiglas I-A	P1b	0 160	92.2 ± 0 91.8 ± 0.1	84.7 ± 0.3 83.8 ± 0.1	0.2 ± 0 .4 ± 0	29.6 ± 1.3 42.8 ± 0.4
Plexiglas II	P2b	0 160	92.3 ± 0 91.8 ± 0.1	86.3 ± 0.1 84.8 ± 0.3	.2 ± 0.1 .4 ± 0.1	22.2 ± 0.3 31.1 ± 1.2
Plexiglas II	P2c	0 56 115	92.0 ± 0 92.0 ± 0 92.1 ± 0	87.1 ± 0.3 85.3 ± 0.6 84.2 ± 0.9	.3 ± 0 .4 ± 0 .3 ± 0	23.3 ± 1.0 28.1 ± 1.8 36.4 ± 5.3
Lucite HC202	L2e	0 70 100	92.1 ± 0.1 92.1 ± 0 92.0 ± 0.1	87.1 ± 0.1 85.6 ± 0.3 85.7 ± 0.1	.5 ± 0.1 .1 ± 0.1 .2 ± 0	23.7 ± 0.2 28.8 ± 0.5 27.3 ± 0.1

NACA

[a] All results are the average for three specimens from the same disk, plus or minus the standard error. The specimens in each group of tests were taken from the same sheet of material. Final measurements were taken after 250 revolutions of the abraser.

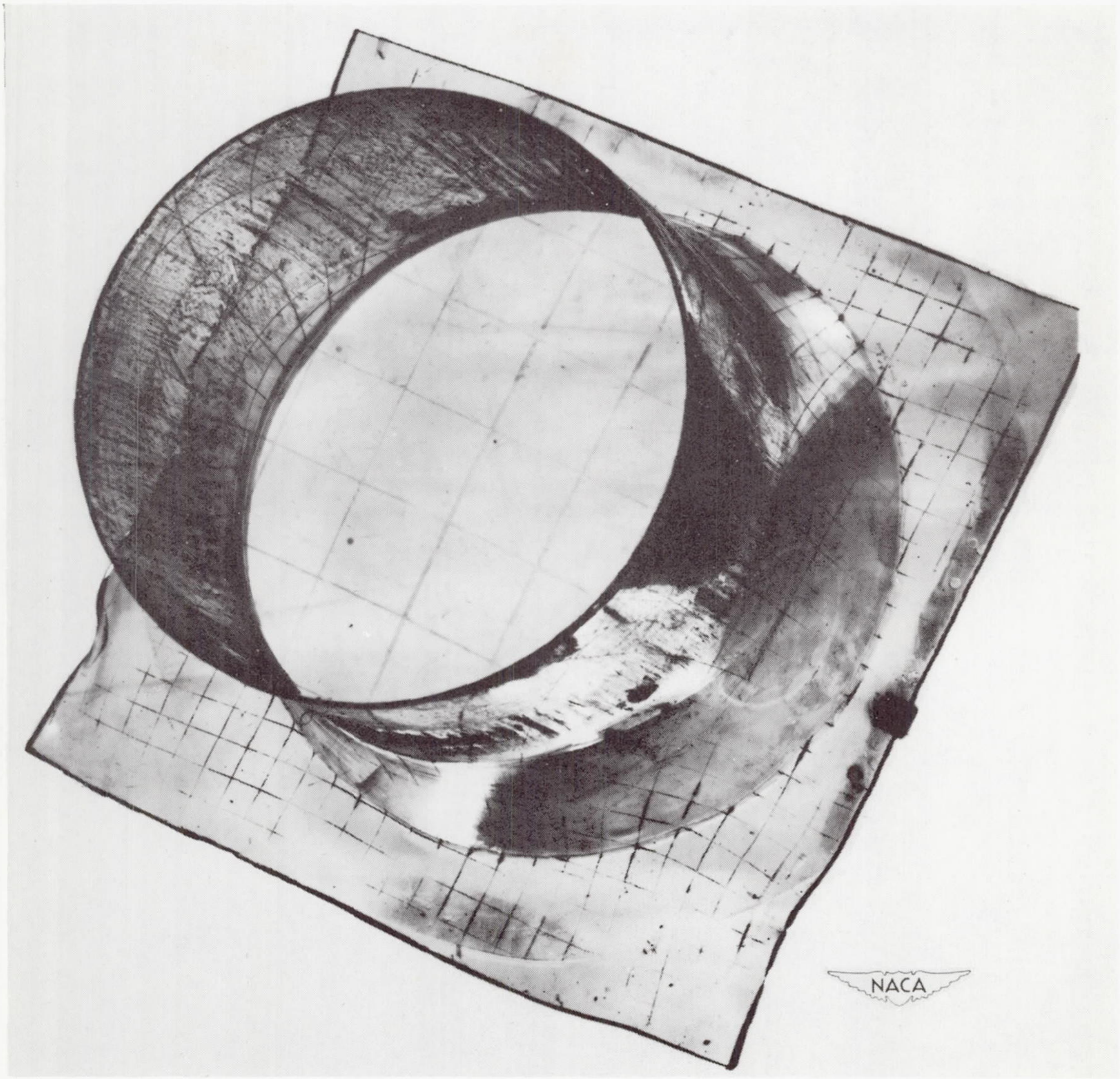


Figure 1.- Sample of formed polymethyl methacrylate as removed from stretching apparatus.

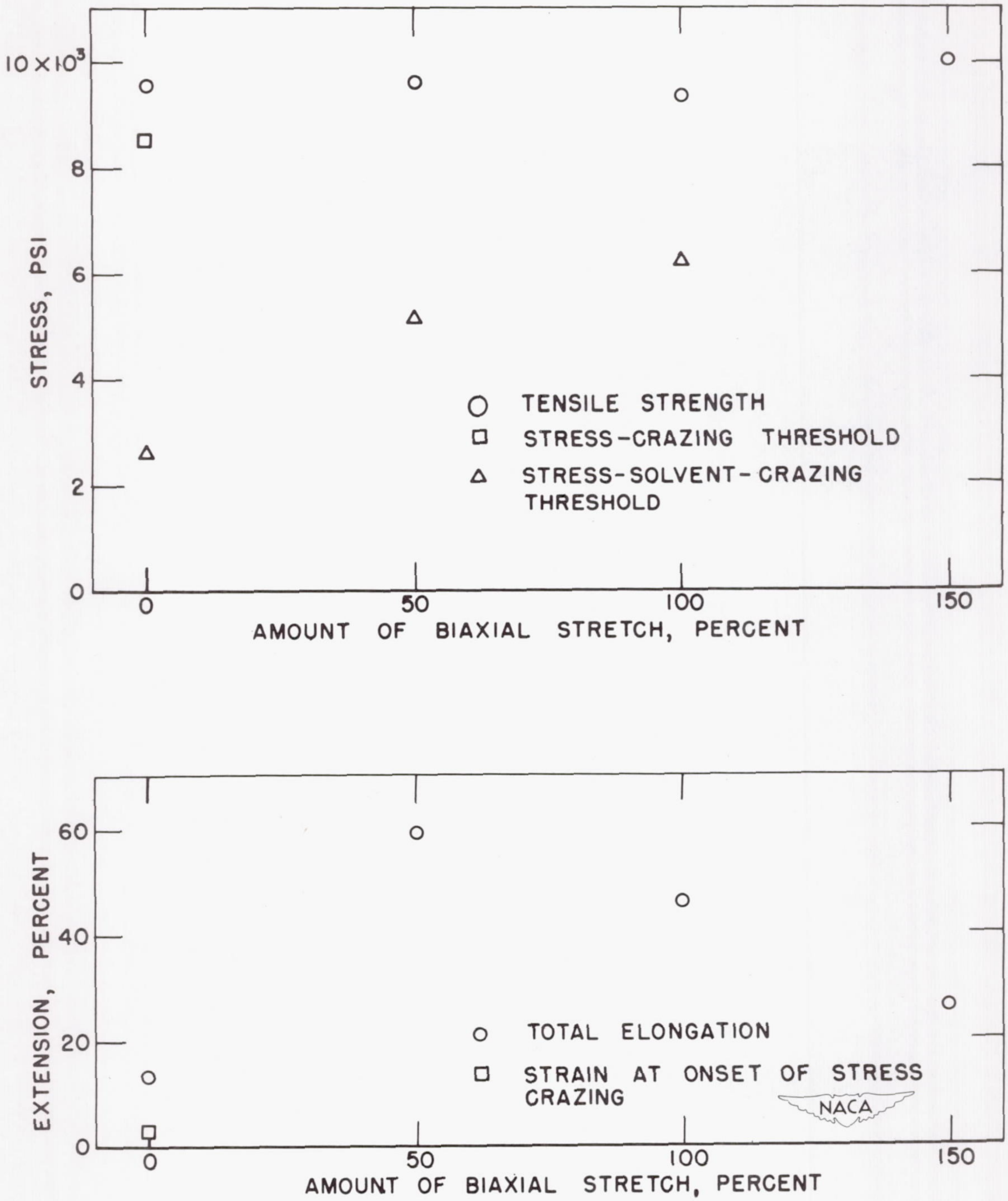


Figure 2.- Effect of biaxial stretching on tensile properties of polymethyl methacrylate at 23° C.

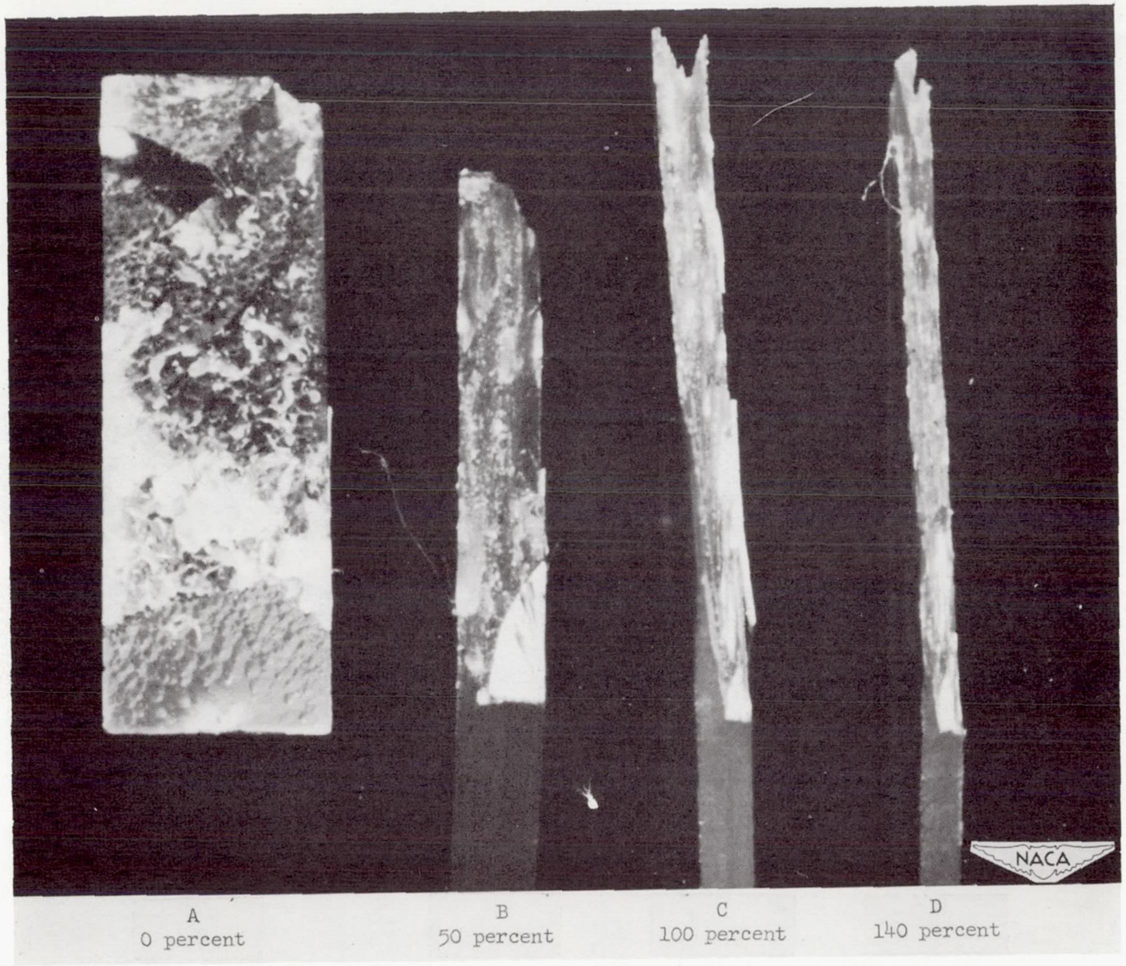


Figure 3.- Top view of fracture surfaces of heat-resistant-grade polymethyl-methacrylate tensile specimens with varying degrees of biaxial stretching. Note mirror areas in lower right-hand corner of stretched specimens and in center of bottom edge of unstretched specimen.

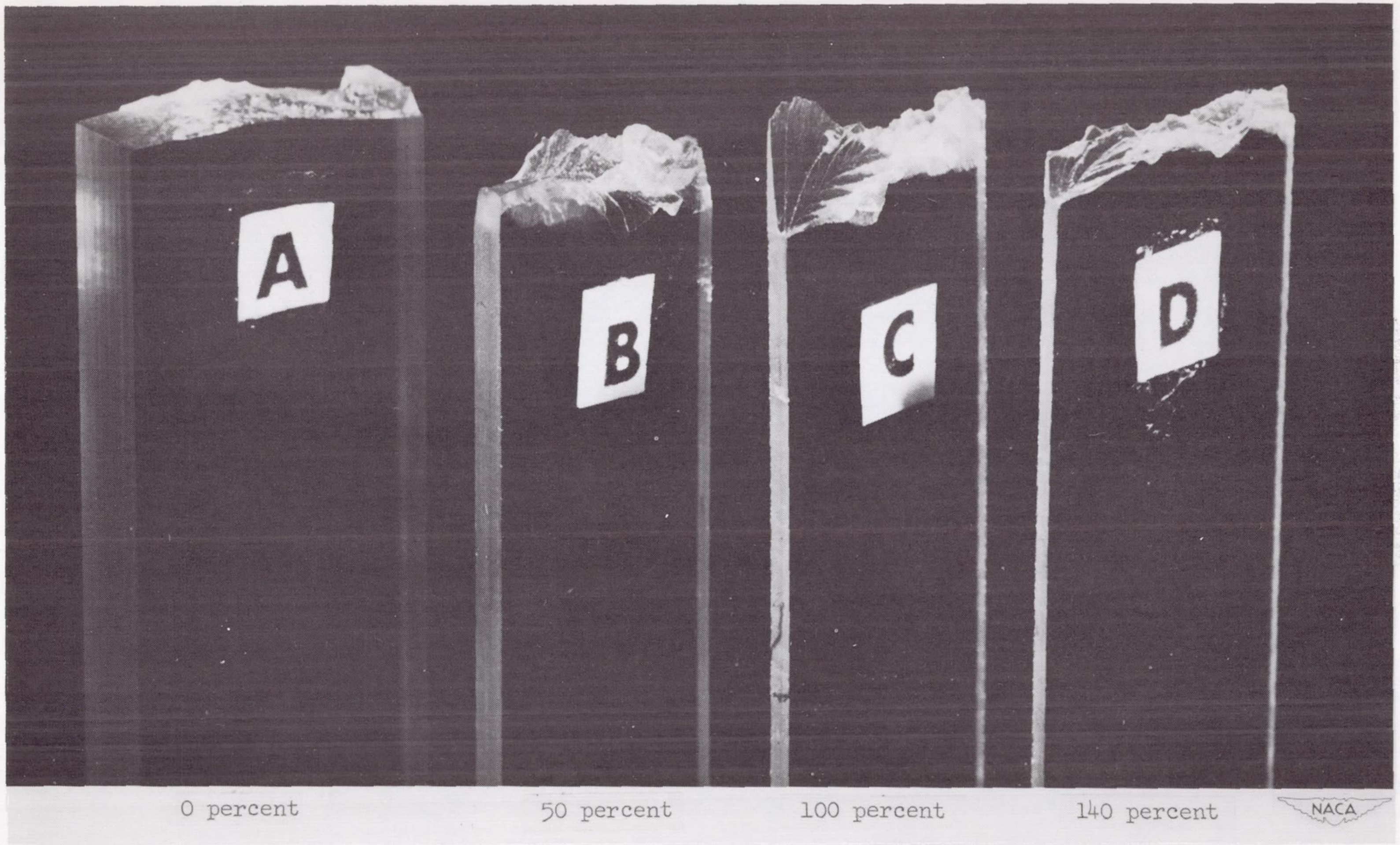
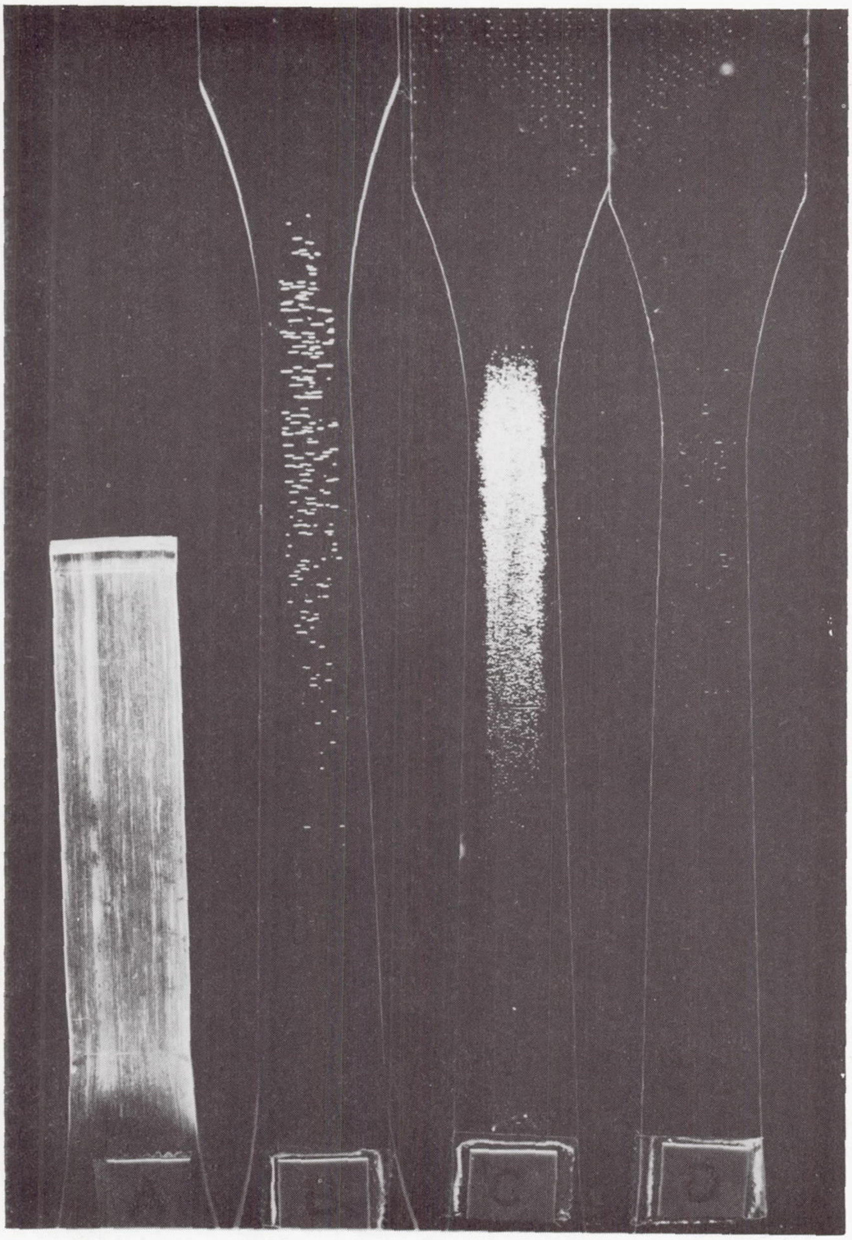


Figure 4.- Side view of fracture surfaces of polymethyl-methacrylate tensile specimens with varying degrees of biaxial stretching.



A Unstretched; crazed during short-time tensile test
B Unstretched; stress-solvent crazed with benzene; maximum stress, 2,400 pounds per square inch
C Biaxially stretched 100 percent; stress-solvent crazed with benzene; maximum stress, 7,000 pounds per square inch
D Biaxially stretched 150 percent; stress-solvent crazed with benzene; maximum stress, 10,000 pounds per square inch

Figure 5.- Crazed tensile specimens of polymethyl methacrylate.