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SYNTHESIS AND BALLISTIC EVALUATION OF SELECTED TRANSPARENT POLYURETHANE BLOCK COPOLYMERS. PART IV: EFFECTS OF ENVIRONMENTAL FACTORS UPON BALLISTIC RESPONSE.

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⑩ Anthony F. Wilde, Richard W. Matton,
Joseph M. Rogers, and Stanley E. Wentworth

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ABSTRACT

Investigation has been continued of polyurethane block copolymers for possible application as transparent armor. For a typical formulation, the $V_{(50)}$ ballistic limit velocity exhibited a maximum at room temperature, with lower values at -50 F and +175 F. Aging at ambient conditions tended to decrease the brittleness and raise the V_{50} of these polymers. High values of relative humidity led to softening and ductile response of brittle formulations. Immediate desiccation of brittle formulations caused retention of hardness and brittleness, whereas after prior humidification, desiccation removed much water but did not reverse the prior transition to ductile ballistic response. Incorporation of selected additives had little effect upon the properties of these polymers. Exposure produced changes in weight and hardness which may correlate with humidities and weathering processes; the corresponding changes in $V_{(50)}$ were small and not directly related to these other changes.

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INTRODUCTION

In previous reports[1-4] we have presented results obtained in this laboratory regarding the synthesis, properties, and ballistic performance of a series of transparent polyurethane block copolymers. The purpose has been to investigate the suitability of these polymeric materials as possible candidates for lightweight transparent armor. Although promising ballistic performance was exhibited by certain formulations, we were frequently confronted with the problem of noticeable changes in copolymer properties and performance occurring over periods of time. Because the implications of such changes are of great practical significance, there was need for additional investigation to provide more quantitative information regarding these effects.

This report will describe investigations concerning the effects of temperature, aging, and relative humidity upon the properties of selected formulations of these copolymers. It will also present results obtained with a series of these copolymers, formulated with commercial additives, and subjected to outdoor exposure (with unexposed controls) for periods up to 12 months.

EXPERIMENTAL

A. Polymer Synthesis and Specimen Preparation

The 2,4-toluene diisocyanate (TDI), polytetramethylene oxide (PTMO) and 1,4-butanediol (BD) were obtained and treated as previously described.[1] The additives (Tinuvin 328 and Irganox 1010) were furnished by Ciba-Geigy Corporation and used as received. Polymer syntheses were performed as described in Reference 1. Samples containing additive(s) were prepared by adding the appropriate quantity of molten additive to the TDI/PTMO prepolymer five minutes prior to the addition of the BD to yield the final casting syrup. Ballistic test specimens were prepared as previously described.[4]

B. Ballistic and Hardness Testing

Ballistic evaluation and determination of hardness were performed using the procedures described in Reference 4. All of the V_{50} data appearing in this report have been normalized to a specimen areal density of 22.0 oz/sq ft, and refer to impact at 0° obliquity by the standard caliber .22 fragment simulator projectile.

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1. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *Synthesis and Ballistic Evaluation of Selected Transparent Polyurethane Block Copolymers.* Army Materials and Mechanics Research Center, AMMRC TR 73-53, December 1973.
2. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *The Preparation and Ballistic Evaluation of Transparent Polyurethane Block Copolymers Based on 2,4-Toluene Diisocyanate* in Proceedings of the 1974 Army Science Conference, U. S. Military Academy, West Point, New York, v. III, June 1974, p. 315-329.
3. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *Synthesis and Ballistic Evaluation of Selected Transparent Polyurethane Block Copolymers. Part II: Further Changes in Formulation.* Army Materials and Mechanics Research Center, AMMRC TR 75-6, March 1975.
4. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *Synthesis and Ballistic Evaluation of Selected Transparent Polyurethane Block Copolymers. Part III: Further Efforts to Optimize Ballistic Performance.* Army Materials and Mechanics Research Center, AMMRC TR 76-31, September 1976.

RESULTS AND DISCUSSION

A. Ballistic Performance at Various Temperatures

1. General Methods

Up to the present time, our ballistic evaluations of these polyurethane block copolymers had been conducted only at ambient temperature, i.e., about 70 F to 75 F. A ballistic test facility, which includes a conditioned test chamber, has recently been developed and installed in the Organic Materials Laboratory (OML) at AMMRC. Ballistic test specimens can now be conditioned and then fired in the same chamber at various temperatures.

The test system was developed in accordance with OML specifications by Tenney Engineering, Inc., Union, New Jersey. This was the Tenney Model T5CAS environmental system and attached ballistic chamber. The test specimens are both conditioned and fired in the ballistic chamber which has internal dimensions of 20 by 20 by 25 inches. The temperature range is -65 F to +200 F. The chamber temperature can be changed from +75 F to -65 F in 95 minutes, and from +75 F to +200 F in 35 minutes. The control tolerance is ±1 F after stabilization. Heat is provided by 4000-watt heater banks wired for three steps of heat. Cooling is provided by 5-hp single-stage refrigeration with an air-cooled condenser. The T5CAS environmental system delivers approximately 200 cu ft/min of conditioned air to the ballistic chamber via 20-foot air hoses. At AMMRC the ballistic chamber was fitted with a window 11 by 17 inches, made of ground and polished Lucite 4 inches thick. The interior of the ballistic chamber was then armored with 1/4-inch steel on the side opposite the projectile entrance port. This surface and the remaining inside surfaces of the chamber, including the window, were additionally armored with 1/4-inch sheets of polycarbonate plastic.

A series of ten identical test specimens was synthesized at AMMRC. The formulation in mole ratios was TDI = 7.35, PTMO 1020 = 1.00, BD = 6.00. At the time of ballistic testing the specimen ages ranged from 21 to 24 days. Each specimen was conditioned in the ballistic test chamber for 2 to 4 hours at the specified temperature and was then fired at this temperature. Ten test temperatures were used, ranging from -50 F to +175 F, in 25 F increments.

2. Effects of Temperature

The ballistic performances are presented in Figure 1 as a function of test temperature. The peak value occurred at 73 F. There was generally a smooth drop-off on each side of this peak with the exception of some irregularity at 0 F and -25 F. At -50 F the V_{50} values had dropped to 78% and at +175 F 73% of the peak value. The failure modes are indicated in Figure 1. The V_{50} peak occurred in the transition region, i.e., the region where response to ballistic impact exhibited both ductile and brittle characteristics. This differs from the results indicated in Part III of this series[4] where the V_{50} peaks were all located in the ductile response regions, and where there was little, if any, mixed brittle and ductile response. Although we did not make Shore D hardness measurements at these various temperatures, it seems reasonable to assume that the specimen hardness would increase with decreasing temperature. Referring to Figure 1, one could then surmise that in the brittle response region the V_{50} decreases with increasing specimen hardness, whereas in the ductile response region the V_{50} increases with increasing specimen hardness. This agrees in a general way with the trends noticed in previous work in this laboratory[3,4] for the relationships between specimen hardness and V_{50}.

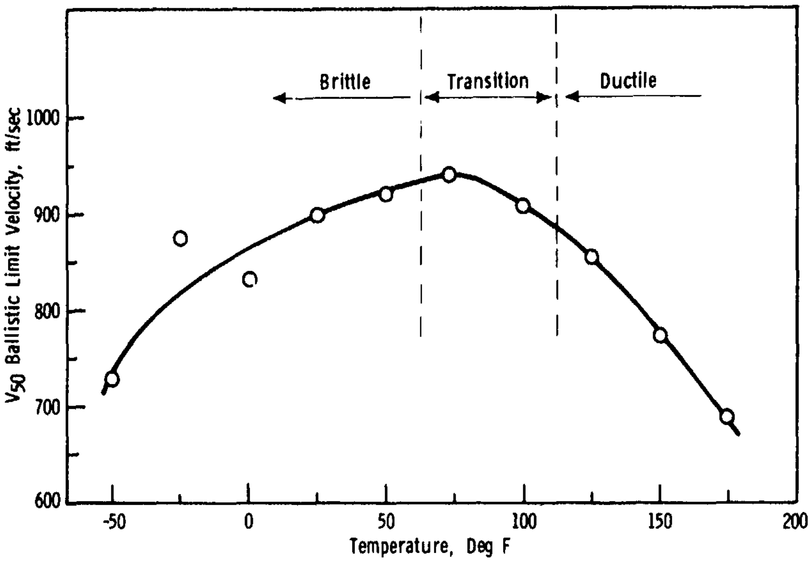

Figure 1. V_{50} ballistic limit velocity as a function of test temperature.

B. Changes in Specimen Properties Due to Aging and Humidity

There have been increasing indications during the course of this work that the ballistic responses of these block copolymers are influenced by the aging time of the specimens, i.e., the time elapsed between casting of the specimen and the ballistic test. In addition, the relative humidity of the storage environment has been found to affect markedly the mechanical and ballistic properties of these specimens. Details of the experimental evidence are now presented.

1. Effects of Aging

The effects of aging time at ambient conditions were first noted in a systematic fashion during previous work with the group of TDI/PTMO/BD ballistic specimens investigated in Part III of this series.[4] A comparison of ballistic performance at two different aging times for these specimens is given in Figure 2 of the present report. The specimens of low soft-segment content (less than 34 weight percent PTMO) were found to have lower V_{50} values and to exhibit considerable brittleness when tested within 15 days after synthesis as compared to the results obtained after 60 days or more. The Shore D hardnesses of these initially brittle specimens showed virtually no change over this same time period (see top curve in Figure 3) even though some of them had changed over to a ductile response to ballistic impact by the time that 60 days had elapsed.

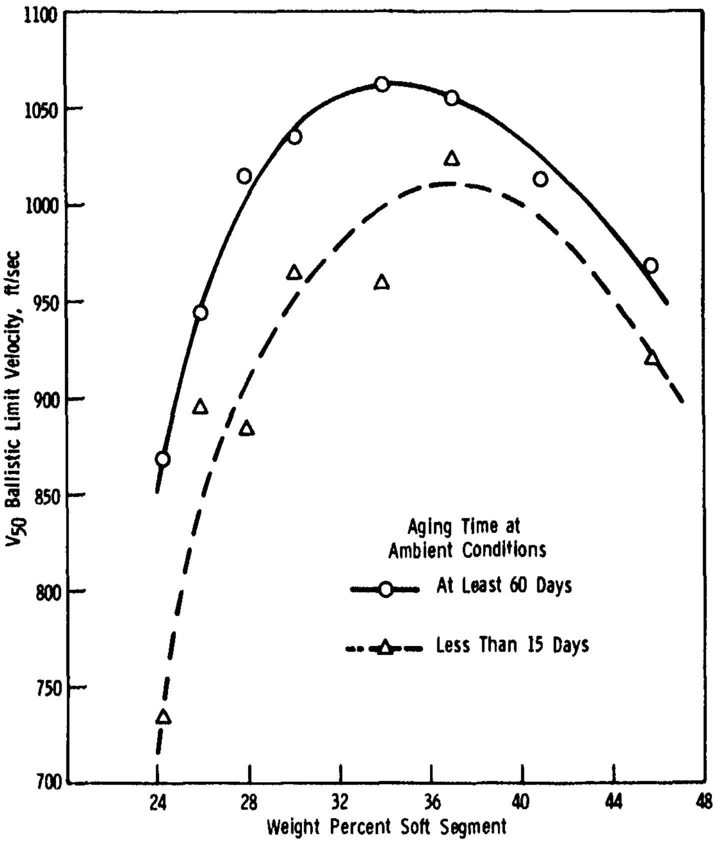

Figure 2. V_{50} ballistic limit velocity as a function of soft-segment content. Tests conducted at two different aging times.

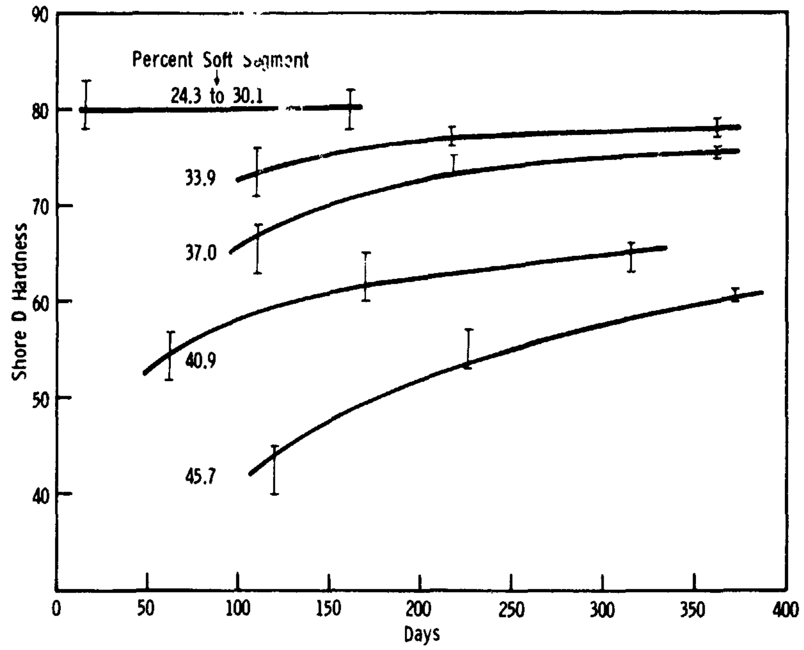

Figure 3. Specimen hardness as a function of aging time after synthesis, for a series of specimens with various soft-segment contents.

In contrast, the specimens of high soft-segment content (greater than 34 weight percent PTMO) in Figure 2 displayed almost as high V_{50} values at short aging times as they did at aging times of 60 days or more. Also, these initially ductile specimens became considerably harder over an extended period of time as shown in the lower curves of Figure 3. During these latter time intervals their V_{50} values remained virtually unchanged.

We have therefore found that with TDI/PTMO/BD block copolymers the effects of aging at ambient conditions are significant and are markedly influenced by the soft-segment (PTMO) content. These effects are summarized in Table 1. Because humidity was strongly suspected to be the principal cause of these effects, the following series of experiments was undertaken.

2. Effects of Relative Humidity

The effects of controlled differences in relative humidity were explored in several ways The first experiment involved comparison of ambient conditions with a saturated water vapor environment in regard to the effect upon mechanical and ballistic properties. A specimen, synthesized at AMMRC (TDI = 8.40, PTMO 1020 = 1.00, BD = 7.00), was sawed in half after 3 days exposure to ambient laboratory conditions. One piece was stored for 30 additional days at ambient conditions, the other piece was stored in a closed container over liquid water (saturated water vapor) for the same 30 days. In the first part of Table 2 are listed the resultant properties of these specimens. Even in the ambient environment there was enough moisture present to convert this initially brittle formulation in 30 days into a material which exhibited ductile response to ballistic impact. The saturated water vapor environment produced lower values in both the specimen hardness and the V_{50}. There was also a significant weight gain (1.4%) for the specimen exposed to saturated water vapor. Again there is evident the same relationship noted many times previously, i.e., within the ductile failure region a decrease in specimen hardness is accompanied by a decrease in the V_{50} value.

The second experiment involving relative humidity concerned a comparison between a saturated water vapor environment and a desiccated environment in terms of their effects upon a polyurethane copolymer material. A specimen, synthesized at AMMRC (TDI = 9.45, PTMO 1020 = 1.00, BD = 8.00), was sawed in half after 3 days exposure to ambient laboratory conditions. One piece was stored an additional 58 days over liquid water (saturated water vapor), the other piece was stored in a desiccator over phosphorus pentoxide for the same 58 days.

Table 1. EFFECT OF AGING TIME AT AMBIENT CONDITIONS UPON SPECIMENS COMPOSED OF TDI, PTMO, AND BD

Soft-Segment (PTMO) Content	V_{50} Value	Response to Impact	Shore D Hardness
Low	Increases Considerably	More Ductile	Unchanged
High	Increases Slightly	Remains Ductile	Increases

Table 2. EFFECT OF WATER VAPOR CONTENT ON PROPERTIES OF POLYURETHANE BLOCK COPOLYMER SPECIMENS

Specimen	Storage Environment	Time in Environment	Shore D Hardness	Normalized V_{50}, ft/sec	Response to Impact
	Ambient	30 days	76-79	1054	Ductile
	Saturated Water Vapor (100% R.H.)	30 days	66-68	1004	Ductile
A	Desiccated (0% R.H.)	58 days	78-80	>997	Brittle
B	Saturated Water Vapor (100% R.H.)	58 days	67-71	1010	Ductile
A	Saturated Water Vapor (100% R.H.)	197 days	68-70*	987	Ductile
B	Desiccated (0% R.H.)	197 days	78-80*	999	Ductile

*After 42 days

At the end of this period, the specimens were tested. Their properties are listed in the second part of Table 2. The desiccated environment caused this initially brittle formulation to remain brittle with a high hardness. Unfortunately, the V_{50} could not be accurately determined with such a small brittle specimen, but it appears that the value for this formulation (30.1% soft segment) would fall somewhere between that in Figure 2 for 15 days aging and 60 days aging when exposed to ambient conditions. The saturated water vapor environment caused a drop in hardness, a change to a ductile failure mode, and a V_{50} slightly lower than that in Figure 2 (1035 ft/sec) for the same aging time under ambient conditions.

Both of these experiments suggest that ambient moisture is at least partially responsible for the results illustrated in Figure 2, i.e., the increased ductility and higher V_{50} manifested at longer aging times. Loss of absorbed moisture may be responsible to some degree for the increasing hardness shown in Figure 3 for the four lower curves. These specimens had been synthesized between April and June 1974. The hardnesses plotted here were determined in August and December 1974 and in April 1975. (The times appear to be staggered in Figure 3 because of the staggered dates of specimen synthesis.) The ambient humidities in December and April are generally lower than in the summer so that these specimens were probably losing moisture absorbed during the summer months of 1974 which immediately followed their syntheses. Additional hardness determinations were made in October 1975 (not plotted in Figure 3). These showed a drop to values which were approximately equal to the original ones plotted in Figure 3 for August 1974, indicating a second softening due to the humidity of the summer of 1975. Hence the specimen hardnesses appear to respond to an annual humidity cycle, such as that measured at a nearby U.S. Army test facility, and shown in Figure 4 as average monthly humidity during a period of 12 consecutive months.

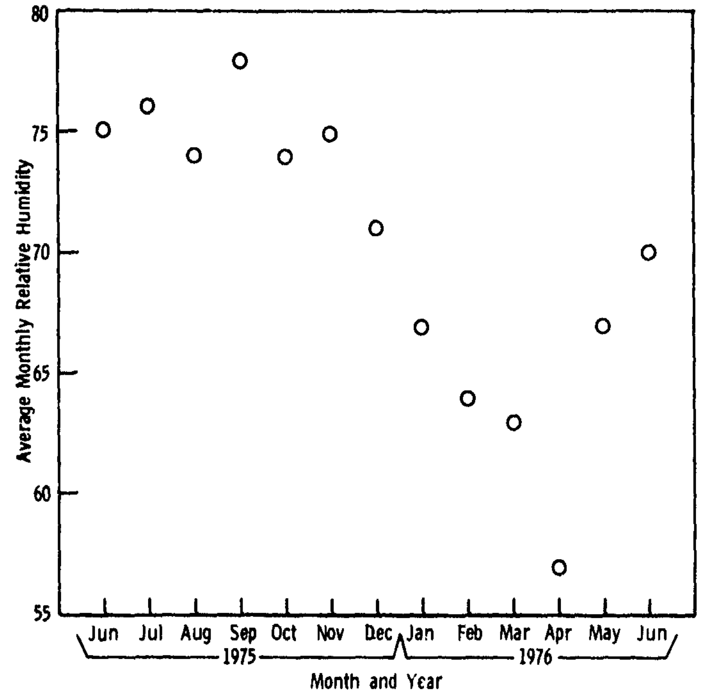

Figure 4. Average monthly humidity during a period of 12 consecutive months, as recorded by the Maynard (Massachusetts) Central Meteorological Observatory, Atmospheric Sciences Laboratory, White Sands Missile Range (New Mexico).

In a third experiment, the two specimens described in the second part of Table 2 were switched and then conditioned in the opposite environment for an additional 197 days before being tested again. The results are given in the third part of Table 2. Both specimens responded to ballistic impact in a ductile fashion. For the recently humidified specimen, this experiment showed that with an initially brittle material kept brittle by water exclusion (for 58 days), the delayed humidification caused the same property changes as did humidification immediately after synthesis, i.e., a lowered Shore D hardness and a ductile response to ballistic impact. For the recently desiccated specimen, this experiment showed that for an initially brittle material, ductility, once achieved by humidification, is difficult to reverse, even after most of the absorbed water is removed. (Although these ballistic specimens were not weighed during their conditioning treatments, weight determinations were performed on fragments from these specimens and indicated that perhaps 0.5 weight percent water still remained in the recently desiccated specimen.) It is possible that the continued ductility of the recently desiccated specimen is due to the remaining small amounts of the originally absorbed water. Alternatively, it could be due to some structural reorganization or chemical modification in the polymer which was facilitated by the presence of water from the original humidification and has persisted throughout the period of desiccation.

The fourth experiment dealt with detailed weight measurements made during the reverse conditioning described above. The measurements were performed on polymer fragments generated during the previous ballistic testing described in the second part of Table 2 which took place after the 58-day conditioning. These fragments were then stored in the switched environment, along with their parent specimens, for the 197-day period described in the above experiment; the conditioning and weight determinations for these fragments were then continued for a total duration of 410 days. The fragment in the saturated water vapor environment gained weight continuously, attaining a value 3.15 weight percent higher than at the beginning of the 410-day period. The fragment in the desiccated environment lost weight continuously, reaching a value 1.64 weight percent lower than at the beginning of the 410-day period. Log-log plots were made of these weight changes as a function of time. As seen in Figure 5, the plots were linear for about the first 50 days. From the slopes and intercepts of the initial linear segments, the following equations were derived.

For the specimen in the saturated water vapor environment

$$W = W_o \left[1 + 0.00355t^{0.433}\right].$$

For the specimen in the desiccated environment

$$W = W_o \left[1 - 0.001845t^{0.459}\right].$$

For both equations,

W = specimen weight in grams,
W_o = initial weight (at beginning of the 410-day reverse conditioning),
t = elapsed time in days.

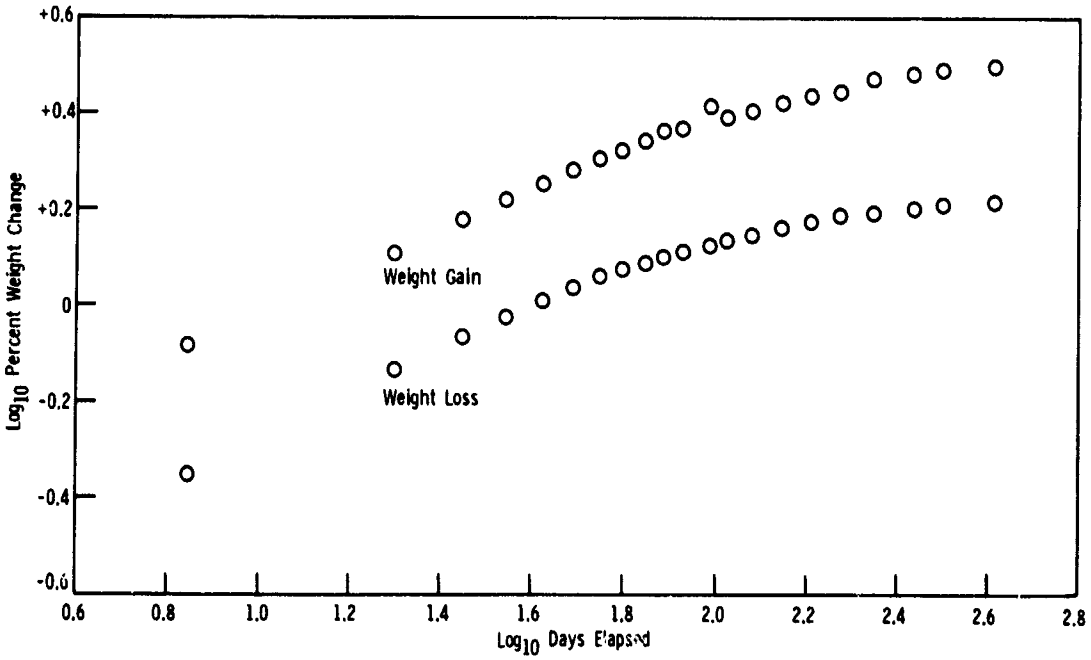

Figure 5. Log-log plot of weight change as a function of elapsed time for both humidified and desiccated specimens.

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It is evident that the exponents were both in the vicinity of 0.5. According to Meares,[5] when the diffusion coefficient of vapors in polymers is independent of the vapor concentration or is an increasing function of the vapor concentration, the fraction of vapor absorbed or desorbed is an initially linear function of the square root of time, providing that the diffusion coefficient is not also a function of time. This suggests that the initial rate-controlling process in our experiments was the diffusion of water vapor into or out of the bulk of the specimens.

At times beyond 50 days, both curves displayed gradually decreasing slopes which may contain other linear segments. At 410 days, when the measurements were terminated, both specimens were still continuing to undergo very slow weight changes.

The fourth experiment may be summarized as follows:

(a) Exposure to a saturated water vapor environment causes a slow but continuous increase in weight for at least a 410-day duration, at which time the gain amounts to 3.15 weight percent.

(b) Desiccation for 410 days is not sufficient to remove all of the water from the previous 58-day humidification. This can be shown by the following. After 58 days of humidification the weight gain amounted to 2.05 weight percent. After 197 days desiccation the weight loss was 1.54 weight percent, indicating that about 0.5 weight percent of water was still retained at the time of the ballistic testing described in the third part of Table 2. After 410 days desiccation the weight loss was 1.64 weight percent, indicating that about 0.4 weight percent of water still remained at the conclusion of these measurements.

C. Changes in Specimen Properties Due to Outdoor Exposure

1. General Methods

A series of polyurethane block copolymers was synthesized at AMMRC to investigate the effects of outdoor exposure for significant periods of time upon the ballistic performance and other properties. The specimens were identical in formulation (TDI = 7.35, PTMO 1020 = 1.00, BD = 6.00), except for small quantities of two additives. The purpose of the additives was an attempt to retard the expected environmental deterioration of the polymer specimens. The chosen additives were Tinuvin 328 (an ultraviolet inhibitor) and Irganox 1010 (an anti-oxidant). The polyurethane specimens contained these additives in various amounts and proportions to give a total of 13 different combinations (listed in Table 3). Four sets of these specimens (52 total) were mounted on racks outdoors at the U.S. Army Natick Laboratories Sudbury Annex, Maynard, Massachusetts, in June 1975. The racks held each 6-inch by 6-inch specimen at the top and bottom edges so that it faced due south at an inclination of 45° to the ground (see Figure 6). Another four sets of these specimens were stored indoors at AMMRC in the dark to serve as controls. All specimens had been weighed just before being placed at their exposure site or their storage location. One set each of the exposed and control

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[5] MEARES, P. *Polymers Structure and Bulk Properties.* D. Van Nostrand Co., Ltd., London, 1965, p. 319-320.

specimens was withdrawn for characterization at three-month intervals, i.e., in September and December 1975, March and June 1976. At these times the specimens were weighed, ballistically tested, and subjected to examination for Shore D hardness and qualitatively by eye for yellowing.

Table 3. AMOUNTS OF ADDITIVES IN EACH FORMULATION

Formulation	Tinuvin 328 Weight Percent	Irganox 1010 Weight Percent	Total Additive Content Arbitrary Units
1	0	0	0
2	0.1	0	1
3	0.3	0	3
4	0.5	0	5
5	0	1.0	1
6	0	3.0	3
7	0	5.0	5
8	0.3	1.0	4
9	0.3	3.0	6
10	0.3	5.0	8
11	0.1	3.0	4
12	0.5	3.0	8
13	0.5	5.0	10

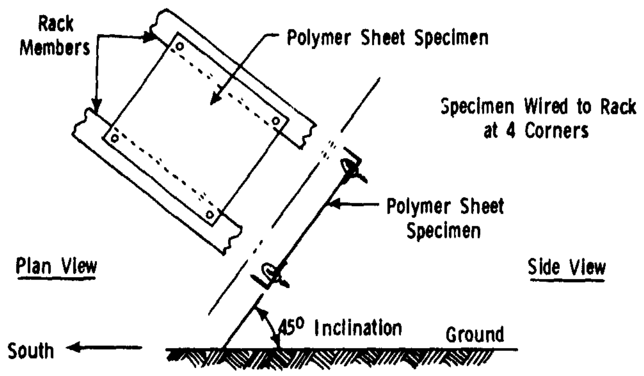

Figure 6. Diagram of specimen orientation for outdoor exposure.

2. Effects of Additive Content

In order to express the test results in quantitative terms, it was necessary for us to specify the additive content in some numerical fashion. Because Ciba-Geigy product literature had recommended additive contents up to 0.5 weight percent for the Tinuvin 328 and up to 5 weight percent for the Irganox 1010, we arbitrarily assigned values of 5 to each of these maximum amounts, with the lower contents scaled proportionately. The total additive contents, computed by this scheme, are given in Table 3.

The weights of the specimens were expressed in terms of the percent gain experienced since the original weighing before exposure. As an example, the weight gain after 12 months is plotted against total additive content in Figure 7 for both exposed and unexposed specimens. In each case the total spread of weight gains is large enough to obscure any trend in the results shown here.

Because of this scattering, it is felt that these data do not represent significant trends. The weight gain data for the 3-, 6-, and 9-month times exhibited a similar lack of significant dependence upon total additive content. When these weight gains were plotted against the individual additive contents, there was a similar scattering and concomitant absence of trends.

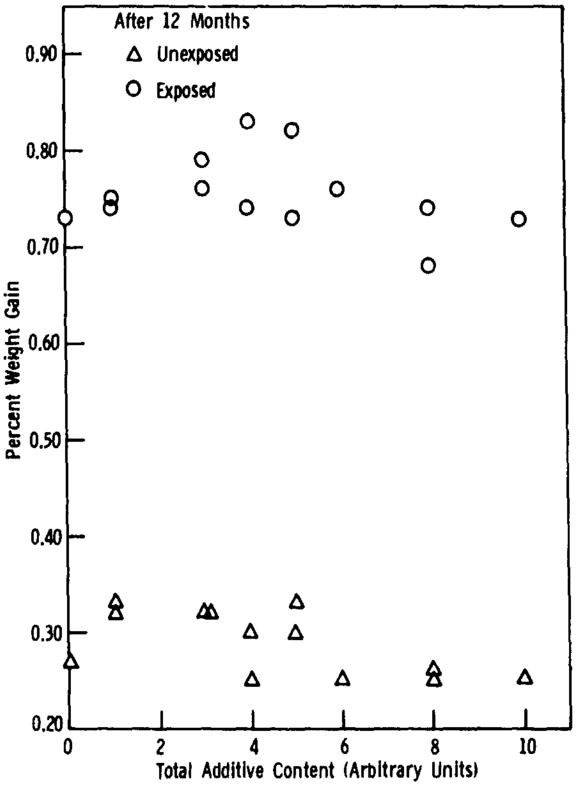

Figure 7. Weight gain after 12 months as a function of total additive content for both exposed and unexposed specimens.

All of the specimens exhibited ductile response to ballistic impact. The V_{50} ballistic limit velocities showed no systematic dependence upon the total additive content. For example, Figure 8 presents the 12-month data for both the exposed and unexposed specimens. Although there appears to be a slight upward trend for these scattered points in each case, least-squares fit of the data to linear expressions indicates a statistical change of only 25 ft/sec per 10 additive units for the exposed specimens and 19 ft/sec per 10 additive units for the unexposed specimens. These are very small effects indeed, amounting to less than 3 percent of the average V_{50} value for each group. The V_{50} results at the 3-, 6-, and 9-month times showed similarly small and scattered changes, with either slight upward trends or no trends in evidence. Plotting of these V_{50} data against the individual additive contents provided no evidence for systematic dependence of V_{50} upon either additive content.

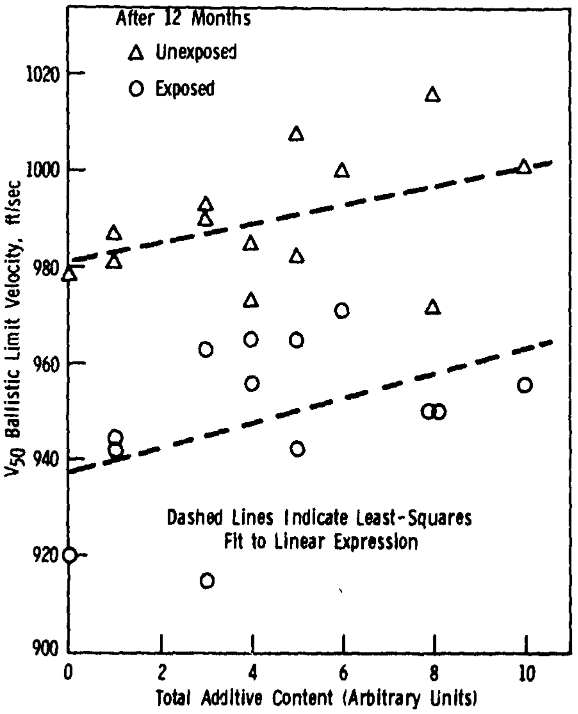

Figure 8. V_{50} ballistic limit velocity after 12 months as a function of total additive content for both exposed and unexposed specimens.

The additives produced no discernible effect upon the Shore D hardnesses of the specimens for the 3-, 6-, 9-, and 12-month times with both the exposed and unexposed specimens; i.e., the hardness values were scattered over a narrow range (averaging 5 hardness units) and displayed no trend with additive content.

The exposed specimens all exhibited a significant degree of yellowing compared to the unexposed specimens. This yellowing was characterized only qualitatively by eye and appeared to be the same for the 3-, 6-, 9-, and 12-month exposures. The exposed specimens with higher additive contents appeared to be slightly less yellow than those with no additives.

3. Effects of Exposure and Time

Because the effects of additive content upon the polymer properties were found to be minimal and somewhat scattered, it was reasonable to consider the data for each set of 13 specimens as a single entity, independent of additive content, and to deal only with averaged properties for each set. The averaged properties for both the exposed and unexposed specimens at the four aging times are summarized in Table 4. These results are also plotted in Figures 9, 10, and 11.

It is seen that exposure (compared to no exposure) produced higher weight gains, lower followed by higher hardnesses, and lower V_{50} values. Exposure also produced a considerable degree of specimen yellowing. Exposure did not affect the ductile response to ballistic impact.

Table 4. AVERAGE PROPERTY OF EACH SET OF 13 SPECIMENS AFTER AGING

	Date of Removal from Exposure Site and Time of Aging			
Average Property	Sep 75 3 Months	Dec 75 6 Months	Mar 76 9 Months	Jun 76 12 Months
Unexposed Specimens				
Percent Weight Gain	0.49	0.39	0.05	0.29
Shore D Hardness	72.6	74.0	76.2	74.7
V_{50}, ft/sec	999	1001	999	990
Exposed Specimens				
Percent Weight Gain	1.12	1.06	0.84	0.75
Shore D Hardness	67.7	73.7	77.1	75.8
V_{50}, ft/sec	930	971	961	949

The effects of time and weathering are complex and cannot be unambiguously interpreted. The specimen weights (Figure 9) increased during the summer months and then decreased until March, suggesting that moisture gain and then loss was responsible and that these changes responded to the seasonal humidity variations illustrated in Figure 4. From March to June the unexposed specimens gained weight, again corresponding to seasonal increases in humidity. The exposed specimens continued to lose weight during this latter period; we have postulated that some of the additive material may migrate to the specimen surface and be mechanically removed by the action of wind and rain, thus more than compensating for any weight increase due to moisture uptake during this period.

The lower initial hardness of the exposed specimens compared to the unexposed specimens (Figure 10) may have been due to the considerably higher water content of the former. We observe from the same figure that during the time from September to March the hardnesses of both exposed and unexposed specimens increased, thus paralleling the apparent decrease in moisture content for this same time period in the fashion discussed for the results appearing in Figure 3, and in good agreement with the average humidity at the exposure site as depicted in Figure 4. The drop in hardness from March to June for the unexposed specimens also paralleled their increased water content. However, the exposed specimens exhibited a drop in hardness during this latter period when their weights were dropping; this may have resulted from an actual gain in water content which was masked by the postulated loss of additives. In Figure 10 we also note that the exposed specimens were increasing in hardness faster than the unexposed ones, overtaking and then surpassing them. Since during this time period the exposed specimens were not losing water any faster than the unexposed specimens, the greater rate of hardness increase of the exposed specimens may have been due to environmentally-induced cross-linking processes occurring during outdoor exposure.

There was no apparent effect of time upon the ductile response to ballistic impact. It is seen in Figure 11 that the V_{50} values did not change very much in relative amounts (less than 4.5%) during the times of these four measurements. The most prominent feature here was the consistent difference between the exposed and unexposed specimens. It did not appear possible to correlate this difference with the totally different relationship between the exposed and unexposed specimen hardness values in Figure 10. However, the weight gain data of Figure 9 did

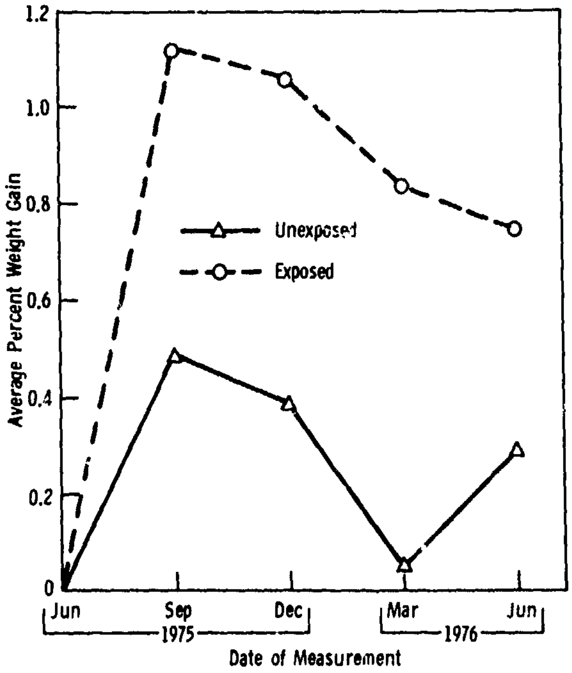

Figure 9. Average weight gain as a function of time for both exposed and unexposed specimens.

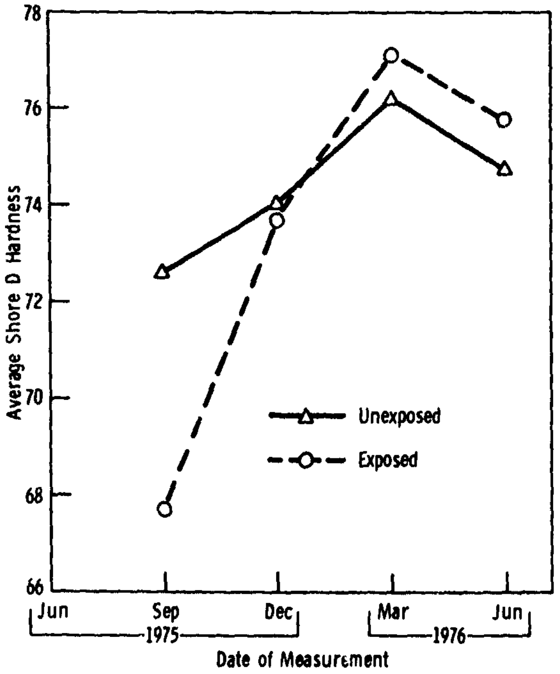

Figure 10. Average Shore D hardness as a function of time for both exposed and unexposed specimens.

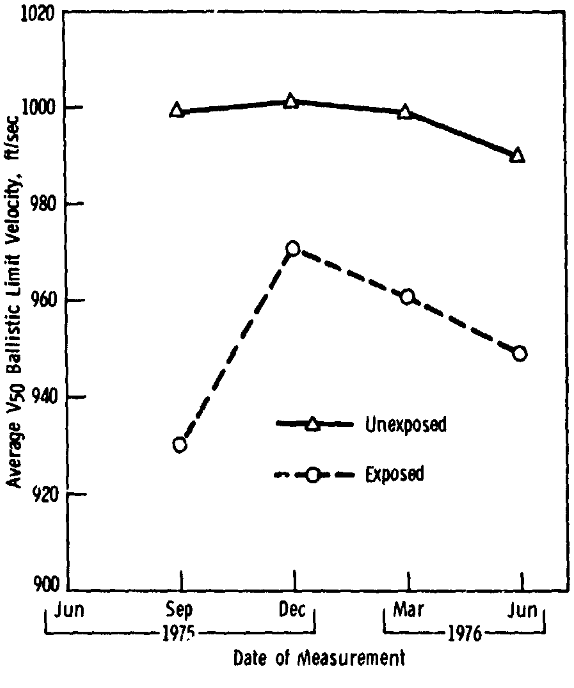

Figure 11. Average V_{50} ballistic limit velocity as a function of time for both exposed and unexposed specimens.

exhibit consistent differences which tended to match the V_{50} results, i.e., the specimens with a consistently higher weight gain (exposed specimens) had a consistently lower V_{50} value. The reasons for this possible correlation are not clear at the present time, although we note that water content exerts an influence analogous to soft-segment content; we have previously observed that with specimens responding to ballistic impact in a ductile fashion, the V_{50} decreased with increasing soft-segment content.[3,4]

SUMMARY

1. The V_{50} ballistic limit velocity was dependent upon the temperature of conditioning and test firing. For the particular formulation examined here, the V_{50} was greatest at room temperature, with significant decreases at both higher and lower temperatures. These trends agreed qualitatively with previously noted effects of hardness upon V_{50}.[3,4]

2. With brittle polyurethane formulations, aging at ambient conditions tended to decrease the brittleness and raise the V_{50} values. Formulations having initially ductile behavior showed only small changes in their V_{50} values during aging at ambient conditions because there was no change in mode of response to ballistic impact.

3. The effects of humidity upon the properties of these polyurethane copolymers was found to be significant. Initially brittle specimens exposed to high relative humidity became softer and more ductile. Exclusion of environmental moisture caused retention of high hardness and brittleness to ballistic impact. Delayed humidification apparently caused the same property changes as immediate humidification. Desiccation (performed after prior humidification) removed much of the absorbed water and led to restoration of the former high hardness, but did not (as far as we have taken it) reverse the prior transition to ductile response to ballistic impact. The effects due to environmental moisture thus appeared primarily responsible for the changes noted above for aging of the brittle polyurethane formulations. It is reasonable to postulate that absorbed water is simply acting as a plasticizer in this system, as has been noted for nylons.[6]

4. For the polyurethane specimens both unexposed and exposed to outdoor environment, the incorporation of Tinuvin 328 in amounts up to 0.5% and Irganox 1010 up to 5.0% has had little effect upon the subsequent properties of the polymers, as determined at the 3-, 6-, 9-, and 12-month times. All specimens responded to ballistic impact in a ductile fashion. Outdoor exposure (as compared to no outdoor exposure) produced higher weight gains, lower followed by higher hardnesses, lower V_{50} values, and significant yellowing of the specimens. Time (of exposure or indoor storage) produced weight changes which appeared in general to follow the annual humidity cycle; time produced changes in Shore D hardness which may have followed seasonal water vapor content and weathering processes; time produced changes in V_{50} values which were small and could not be directly

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[6] KOHAN, I. M. *Nylon Plastics.* John Wiley and Sons, New York, 1973, p. 428.

related to the other property changes observed here. The effects of outdoor exposure were generally deleterious and would hence reduce the applicability of this block copolymer as a transparent armor material in configurations where it would be directly exposed to outdoor environments.

GENERAL CONCLUSIONS

The principal application originally envisioned for these polyurethane block copolymers was as transparent armor material, ideally as a homolithic structure such as an aircraft windshield. Initial ballistic tests were very encouraging, giving very high values of V_{50} for the best formulations. However, as the system was refined and attention was turned to practical environmental problems such as those described in the present report, it became obvious that this material was not suitable for environmental exposure, especially with regard to retention of optical integrity. This conclusion effectively precludes application as homolithic transparent armor. It is suggested that this material be considered as a backup for more brittle but environmentally resistant materials such as glass or Plexiglas. In this configuration the worst of the environmental stresses would be avoided.

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