Effects of Moisture on the High-Speed Impact Response of Selected Polyurethane–Polyether Block Copolymers

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Synopsis

Certain aspects of moisture sensitivity for selected polyurethane–polyether block copolymers were investigated. Exposure to ambient conditions tended to raise the impact velocity for projectile penetration and to decrease the brittleness of these materials. High values of relative humidity, whether applied immediately or after a time delay, led to softening and ductile response of an initially brittle formulation. Immediate desiccation of the brittle formulation caused retention of hardness and brittleness, whereas after prior humidification, desiccation removed much water but did not reverse the prior transition to ductile response to impact. Measurements were made of water sorption and desorption exhibited by this brittle formulation.

INTRODUCTION

Although considerable data concerning the effects of moisture on the mechanical properties of nylons have been published,[1] no such body of information exists for polyurethanes. Chemical intuition suggests, given the structural similarities of the amide and urethane groups, that similar effects may hold for them as well. Of the scattered reports that do exist,[2–4] none deals with the effects of moisture on impact response. Early work in this laboratory on the impact behavior of some polyurethane block copolymers seems to support this suggestion of moisture sensitivity.[5] We now report studies which confirm the existence of this phenomenon for this class of materials.

The materials studied were all polyurethane–polyether block copolymers composed of 2,4-toluene diisocyanate (TDI), poly(tetramethylene oxide) (PTMO) of molecular weight about 1000, and 1,4-butanediol (BD). Their idealized structure is given in Figure 1. Variations in y and z was achieved by varying the molar ratios of the components. Deliberate variations in exposure time and relative humidity of the storage environment were found to cause pronounced differences in hardness and in the response to high-speed projectile impact of these materials. A detailed account of these studies is given below.

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EXPERIMENTAL

Synthesis and Casting of Polymer Specimens

Materials. The requisite TDI was obtained from Aldrich Chemical Company and redistilled before use. Anhydrous BD was obtained from GAF and used as received. The PTMO was obtained from Quaker Oats Company. Hydroxyl numbers were determined using the procedure described by David and Staley.[6] Through use of a procedure described by Scholten et al.,[7] the polyols were determined to be acidic, thus requiring no further acidification to prevent gel formation during polyurethane formation.

General Synthetic Procedure. A 500-ml three-neck flask fitted with a mechanical stirrer, an argon source, and a vacuum take-off connected to a vacuum pump was used. The system was purged with dry argon three times and the TDI was introduced, followed by the PTMO. The mixture was stirred under 20 mm of argon at 85°C for 1½ hr. At this point, the vacuum was released using argon, and the requisite amount of BD was introduced. Stirring under 20 mm argon at 85°C was resumed for an additional 5 min. The resulting pale-yellow viscous syrup was used immediately for the preparation of specimens as described below.

Specimen Preparation. The casting syrup described above was poured into a 6 × 6 × ¼-in. cavity which had been milled into a ½-in. sheet of poly(tetrafluoroethylene). The filled mold was placed in an oven and cured overnight at 100°C.

Determination of Mechanical Properties

Specimen hardness was determined with a Shore Durometer, type D. Specimen impact responses were rated in terms of a characteristic projectile impact velocity V_p. This quantity is defined as the projectile impact velocity at which there is a 50% probability of complete penetration of the target specimen. The higher the V_p value, the more resistant the specimen is to projectile penetration. The projectiles were chisel-nosed steel cylinders weighing 1.10 g (shown in Fig. 2). These were propelled from a 4-ft-long cylindrical smooth-bore tube by sudden release (high-speed solenoid valve) of pressurized helium from a gas reservoir connected to the tube. The projectile impact velocities were determined by a pair of printed silver grid-paper screens located in front of the specimen and connected to an electronic chronograph for time-of-flight measurements. All of the V_p results have been normalized to a specimen areal density of 22 oz/ft² (0.67 g/cm²). The overall precision in this determination of V_p is ± 20 ft/sec.

The nature of the response of the polymer specimen to the projectile impact can be characterized by a spectrum ranging from ductile to brittle. High-speed
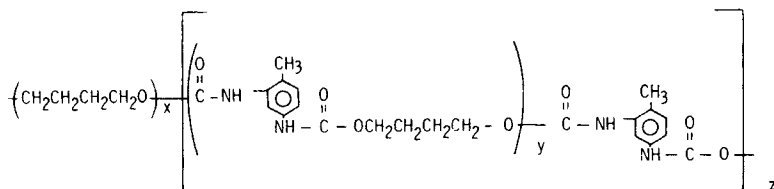

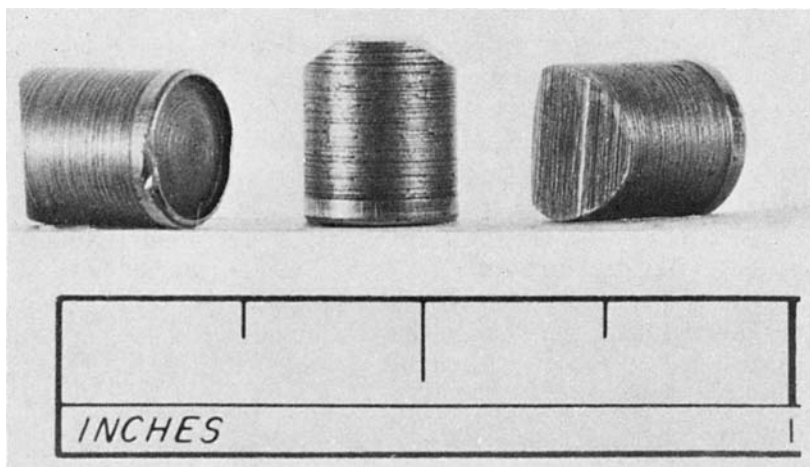Fig. 1. PTMO/2,4-TDI/BD polyurethane block copolymer idealized structure.

Fig. 2. Chisel-nosed projectile for high-velocity impact test.

photography (accomplished with a portrait camera and an Edgerton, Germeshausen, and Grier, Inc., model 502 multiple-microflash system with 1-μsec flash times) illustrates these responses. For example, Figure 3 is a triple-flashed photograph taken just after projectile penetration of a specimen that responded
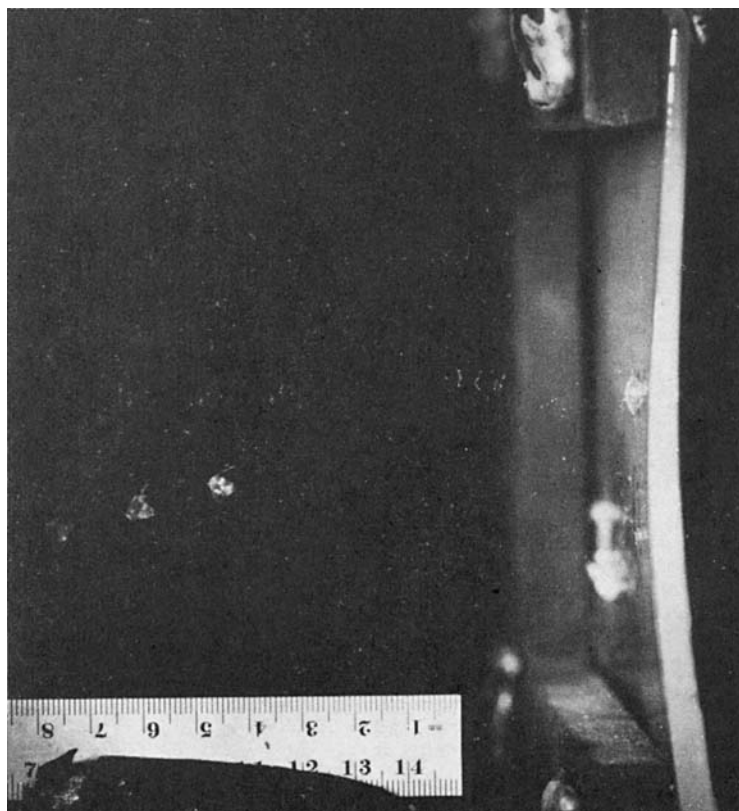

Fig. 3. Triple-flashed photograph showing ductile response to high-speed impact.

to the impact in a ductile fashion.   The three positions of the projectile in flight
are faintly visible to the left of the specimen and in line with the penetration hole;
just below these are seen the three positions of the single smooth plug of specimen
material in flight generated by the penetration.   There is no other damage to
the specimen.   Figure 4 is a similar photograph taken just after projectile pen-
etration of a specimen that responded to the impact in a brittle manner.   To the
left of the specimen a number of irregularly shaped fragments in flight produced
by the impact are seen.   In addition, brittle response is usually manifested by
considerable radial cracking of the specimen together with the presence of a
sizeable crater in the specimen generated by spallation of material from its rear
surface.   The irregularly shaped fragments seen in the photograph are composed
of spalled material.   It should be noted that the definition of V_p is not dependent
upon the type of response, i.e., ductile or brittle, displayed by the polymer
specimen.

RESULTS AND DISCUSSION

Effects of Aging

The effects of aging time at ambient conditions were noted for the impact
responses displayed by a series of polymer formulations encompassing a range
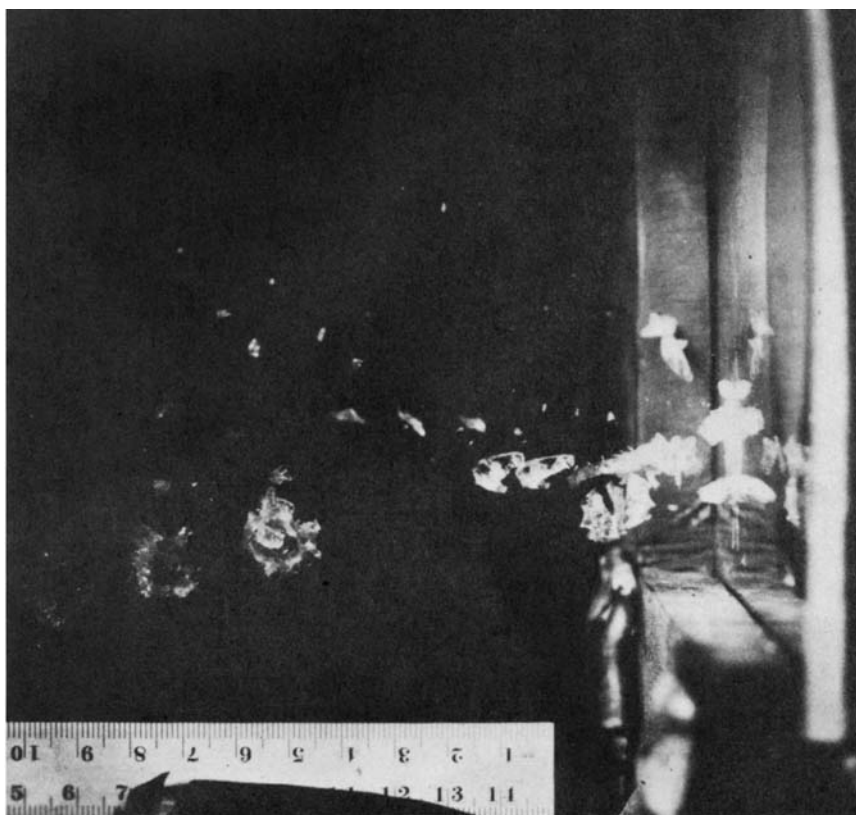of soft segment contents.   It is normally considered that the soft segments are

Fig. 4. Triple-flashed photograph showing brittle response to high-speed impact.

TABLE I

Composition designation	Composition, mole ratio			Soft segment, wt %	Shore D hardness[a]
	2,4-TDI	PTMO, 1070	1,4-BD		
A	5.25	1.00	4.00	45.7	40–45
B	6.30	1.00	5.00	40.9	52–57
C	7.35	1.00	6.00	37.0	63–68
D	8.40	1.00	7.00	33.9	71–76
E	9.45	1.00[b]	8.00	30.1	78–80
F	10.50	1.00[b]	9.00	27.9	78–81
G	11.55	1.00[b]	10.00	26.0	80–82
H	12.60	1.00[b]	11.00	24.3	81–83

[a] Measured more than 60 days after synthesis.
[b] For PTMO 1020.

composed of the PTMO component and that the hard segments are composed of units which contain both the TDI and BD components. This series of formulations is described in Table I.

The V_p values for two sets of aging time (time elapsed between casting of the specimen and the test of its properties) are shown in Figure 5 for this series of polymers. The specimens of low soft-segment content (less than 34 wt %) were found to have considerably lower V_p values and to exhibit pronounced brittleness to projectile impact when tested within 15 days after synthesis, as compared to the results obtained after 60 days or more, when some of the specimens exhibited
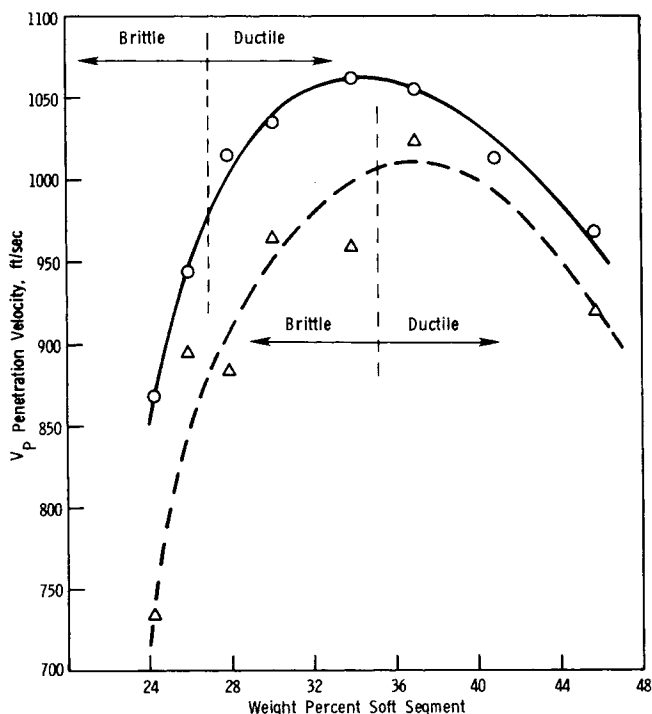

Fig. 5. The V_p penetration velocity as a function of soft-segment content. Tests conducted at two different aging times at ambient conditions: (—O—), at least 60 days; (- -△- -), less than 15 days. Brittle and ductile refer to the nature of the specimen response to projectile impact in the various regions of composition.
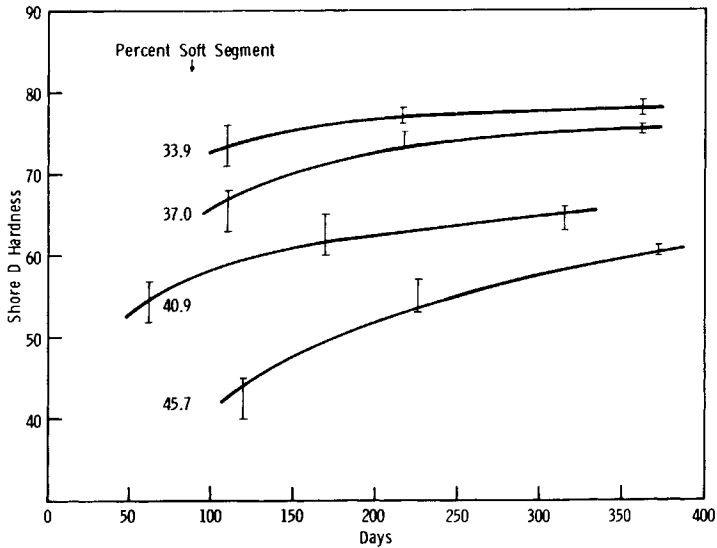
Fig. 6. Specimen hardness as function of ambient aging time after synthesis, for a series of specimens with various soft-segment contents.

ductile response to impact. In contrast, the specimens of high soft-segment content (greater than 34 wt %) displayed V_p values only moderately lower at short aging times than at aging times of 60 days or more, exhibiting ductile response to impact in both cases. For this series of compositions, the maximum V_p occurred in the ductile response region for both aging times.

The hardness of these specimens was found to change over a period of time, as shown, for example, with the specimens of high soft-segment content in Figure 6. There was a continuous increase in hardness between August 1974 and April 1975.

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

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 hardness and impact properties. A specimen of composition D was sawed in half after

TABLE II
Effect of Aging at Ambient Conditions Upon Polyurethane-Polyether Block Copolymer Specimens

Soft-segment content	Composition	V_p Value	Response to impact
Low	H, G, F, E, D	increases considerably	becomes more ductile
High	C, B, A	increases moderately	remains ductile

TABLE III
Effect of Water Vapor Content Upon Properties of Polyurethane–Polyether Block Copolymer
Specimens After 30 Days. Composition D

Storage environment	Shore D hardness	V_p, ft/sec	Response to impact
Ambient	76–79	1054	ductile
Saturated water vapor	66–68	1004	ductile

three days of exposure to ambient laboratory conditions. One piece was stored for 30 more days at ambient conditions, the other piece was stored in a closed container over liquid water (saturated water vapor) for the same 30 additional days. The resultant properties of these specimens are listed in Table III. 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 projectile impact. The saturated water vapor environment caused a drop in the specimen hardness and also led to a significant weight gain (1.4 wt %). In this particular instance, the V_p value was lower for the specimen exposed to the higher moisture content, in accordance with our previous findings[5] that further softening of ductile specimens leads to a decrease in the V_p value.

The second experiment involving relative humidity concerned a comparison between a saturated water vapor environment and a desiccated environment. A specimen of composition E was sawed in half after three days of 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 phosphorous pentoxide for the same 58 days. At the end of this period, the specimens were tested. Their properties are listed in Table IV. The desiccated environment caused this initially brittle formulation to remain brittle with a high hardness. Unfortunately, the V_p could not be determined accurately with such a small brittle specimen. The saturated water vapor environment caused a drop in hardness and a change to a ductile response mode. (Although the response modes in Table IV differed from each other, the corresponding V_p values were roughly equal. This suggests that these V_p values may lie on opposite sides of a possible maximum in a V_p-versus-water content relationship. This is somewhat analogous to the situation shown in Figure 5, where one side of the maximum goes to the brittle region and the other side goes to the ductile region.)

Both of these experiments suggest that ambient moisture is at least partially responsible for the results discussed for Figure 5, i.e., the increased ductility and higher V_p manifested at longer aging times by the specimens. This follows from our previous results[5] which indicated that near the brittle–ductile transition composition a change in impact response of a specimen from brittle toward ductile is frequently accompanied by an increase in V_p value. In the present

TABLE IV
Effect of Water Vapor Content Upon Properties of Polyurethane–Polyether Block Copolymer
Specimens After Conditioning of 58 Days. Composition E

Specimen designation	Storage environment	Shore D hardness	V_p, ft/sec	Response to impact
E_1	desiccated	78–80	>997	brittle
E_2	saturated water vapor	67–71	1010	ductile

case, this transition appears to be caused by exposure to higher relative humidities.

Loss of absorbed moisture may be responsible to some degree for the increasing hardness shown in Figure 6 for four of the test specimens. 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 Fig. 6 because of the staggered dates of specimen synthesis.) The ambient humidities in December and April are generally lower than those in the summer months, so these specimens were probably losing moisture absorbed previously during the summer months of 1974 which immediately followed their syntheses. Additional hardness determinations were made in October 1975 (not plotted in Fig. 6). These showed a drop to values which were approximately equal to the original ones plotted in Figure 6 for August 1974, indicating a second softening owing to the humidity of the summer of 1975. Hence, the specimen hardnesses appear to respond to an annual humidity cycle, such as that determined from weather records at a nearby U.S. Army test facility and shown in Figure 7 as average monthly absolute humidity during a period of 19 consecutive months. (Also plotted here are the average monthly temperatures which were used to convert relative humidity data to absolute humidity values.)

In a third experiment, the two specimens described in Table IV were switched and then conditioned in the opposite environment for an additional 197 days
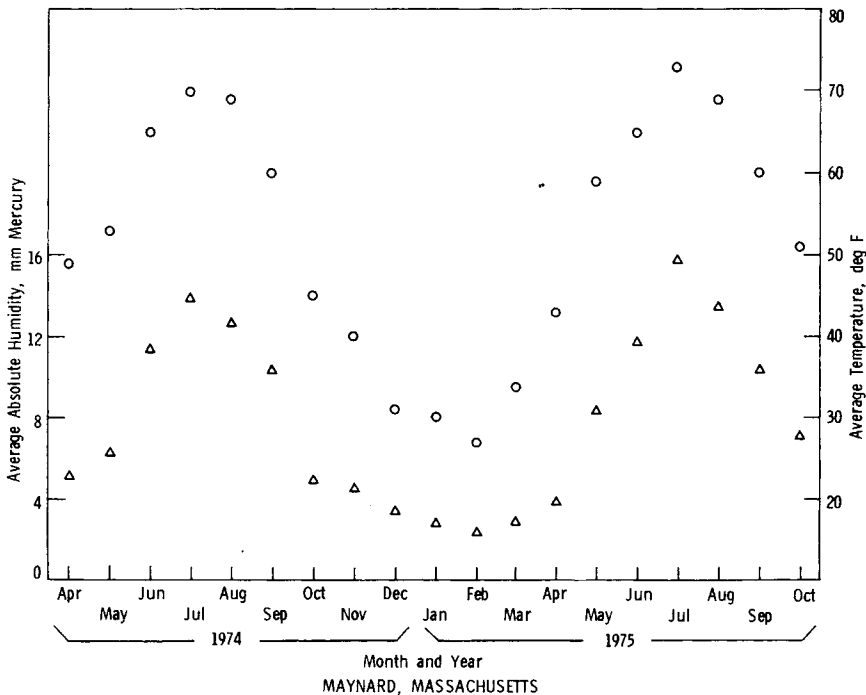

Fig. 7. Average absolute humidity and average temperature during a period of 19 consecutive months, obtained from records of the Maynard (Massachusetts) Central Meteorological Observatory, U.S. Army Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico: (O) outdoor temperature; (△) absolute humidity.

before being tested again. The results are given in Table V. Both specimens responded to projectile 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), 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 projectile impact. For the recently desiccated specimen, this experiment showed a return to a higher hardness and also indicated 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 impact specimens were not weighed during their conditioning treatments, weight determinations, to be described in the next section, were performed on fragments from these specimens and indicated that perhaps 0.5 wt % water remained in the recently desiccated specimen.) It is not known whether the continued ductility of the recently desiccated specimen is due to the remaining small amounts of the originally absorbed water or 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 weight measurements made during the reverse conditioning described above. The measurements were performed on polymer fragments generated during the previous projectile impact testing described in Table IV 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 wt % higher than at the beginning of the 410-day period. The fragment in the desiccated environment lost weight continuously, reaching a value 1.64 wt % 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 8, 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:

$$W = W_0 \,[1 + 0.00355t^{0.433}]$$

For the specimen in the desiccated environment:

$$W = W_0 \,[1 - 0.00184t^{0.459}]$$

TABLE V
Effect of Water Vapor Content Upon Properties of Polyurethane–Polyether Block Copolymer
Specimens After Additional Reverse Conditioning of 197 Days. Composition E[a]

Specimen designation	Most recent storage environment	Shore D hardness[b]	V_p, ft/sec	Response to impact
E_1	saturated water vapor	68–70	987	ductile
E_2	desiccated	78–80	999	ductile

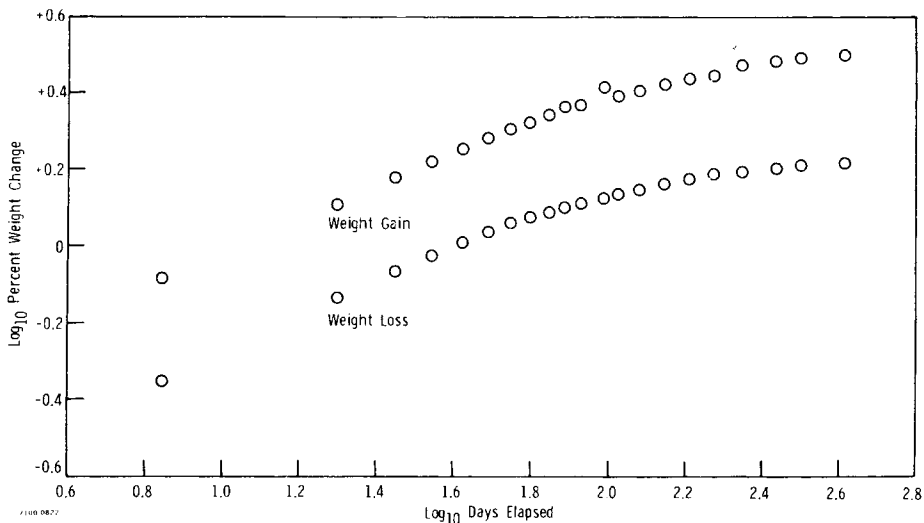[a] Same specimens as those in Table IV.
[b] After 42 days.

Fig. 8. Log–log plot of weight change as function of elapsed time for both humidified and desiccated specimens.

where W = specimen weight in grams, W_0 = initial weight (at beginning of the 410-day reverse conditioning), and t = elapsed time in days.

It is evident that both exponents were in the vicinity of 0.5. According to Meares,[8] 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 that 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 wt %. Assuming that this is entirely due to water pickup, we calculate a molar ratio of water to urethane groups amounting to 31%. (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 wt %. After 197 days of desiccation, the weight loss was 1.54 wt %, indicating that about 0.5 wt % water was retained at the time of the impact testing described in Table V. After 410 days of desiccation, the weight loss was 1.64 wt %, indicating that about 0.4 wt % water remained at the conclusion of these measurements. By a similar calculation, this corresponds to a molar ratio of water to urethane groups of 4%.

SUMMARY AND CONCLUSIONS

(1) With brittle polyurethane–polyether block copolymer formulations, aging at ambient conditions tended to decrease the brittleness and raise the V_p values. Formulations having ductile behavior showed only small increases in their V_p values during aging at ambient conditions because there was no change in mode of response to projectile impact.

(2) The effect 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 projectile impact. Delayed humidification apparently caused the same property changes as immediate humidification. Delayed desiccation (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 projectile impact. The effects owing to environmental moisture thus appeared primarily responsible for the changes noted above for the ambient aging of the brittle polyurethane formulations. It is reasonable to postulate that absorbed water is acting mainly as a plasticizer in this system, as has been noted for nylons,[9] although some chemical changes may occur.

Thus, it has been conclusively demonstrated, at least for this class of polyurethanes, that there exists a significant dependence of mechanical properties upon moisture. In addition to the obvious implications of this phenomenon for applications of these materials, it is apparent that representative mechanical property determinations must be carried out only on materials that have been allowed to reach equilibrium with ambient moisture.

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