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SYNTHESIS AND BALLISTIC EVALUATION OF SELECTED
TRANSPARENT POLYURETHANE BLOCK COPOLYMERS
PART III. FURTHER EFFORTS TO OPTIMIZE BALLISTIC
PERFORMANCE

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
WATERTOWN, MASSACHUSETTS

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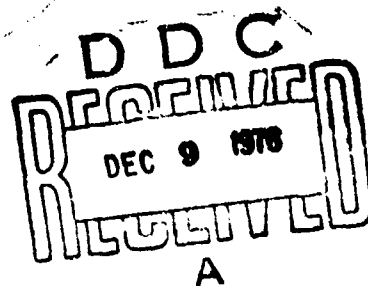
ANTHONY F. WILDE, RICHARD W. MATTON,
JOSEPH M. ROGERS, and STANLEY E. WENTWORTH
POLYMER AND CHEMISTRY DIVISION

September 1976

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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ABSTRACT

In a continuation of previous work with polyurethane block copolymers for transparent armor application, further variations have been investigated in stoichiometry and type of monomer with regard to their effects upon ballistic performance (V_{50}) of the resultant copolymer. For the copolymer composed of 2,4-toluene diisocyanate, polytetramethylene oxide, and 1,4-butanediol, variations in the soft segment/hard segment ratio have led to the composition which gives the highest V_{50} value in this series. Attempts have been made to improve the V_{50} by replacement of 1,4-butanediol with N,N-bis(2-hydroxypropyl)aniline, the substitution of xylylene diisocyanate for 2,4-toluene diisocyanate, the use of a variety of molecular weights of polytetramethylene oxide, and the incorporation of trimethylolpropane as a crosslinking agent. Correlations have been made between composition, specimen hardness, ballistic failure mode, and V_{50} for the polyurethane block copolymers made from these materials.

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A

INTRODUCTION

In previous reports¹⁻³ we have described our efforts to prepare and evaluate polyurethane block copolymers as candidates for transparent armor applications. This work has demonstrated considerable promise for some of these materials, with the best of them having V_{50} of 1062 feet per second (fps), which is within 2% of that of the best such material currently extant for this application. All these materials were prepared from 2,4-toluene diisocyanate (TDI), polytetramethylene oxide (PTMO), and 1,4-butanediol (BD) using varying molar ratios and processing conditions.

In the present work, further variations in formulation of this basic material have been investigated. In addition, several new monomers have been evaluated. The BD was replaced with N,N-bis(2-hydroxypropyl)aniline (Isonol 100). The TDI was replaced with xylylene diisocyanate (XDI), both in formulations containing BD and in those containing Isonol 100. Finally, part of the BD was replaced with trimethylolpropane (TMP) in an attempt to introduce crosslinks.

EXPERIMENTAL

A. Polymer Synthesis and Specimen Preparation

The TDI, PTMO, and BD were obtained and treated as previously described.¹ The Isonol 100 was obtained from the Polymer Chemicals Division of the Upjohn Company and was used as received. The xylylene diisocyanate was obtained from the Takeda Chemical Company and used as received. Although the exact positional isomeric composition was not indicated by the supplier, NMR spectroscopy clearly indicated the isocyanate groups to be on the methyl groups and not attached to the aromatic ring. The TMP was obtained from the Aldrich Chemical Company and used as received.

Polymer syntheses were performed as described previously.¹ Samples containing TMP were prepared by dissolving the required quantity of TMP in the required quantity of BD and adding the solution.

Ballistic test specimens were sheets 6-inches square and 1/4-inch thick. They were prepared³ by pouring the casting syrup from the synthesis into a Teflon mold comprising an open-faced cavity of the specimen dimensions. The filled mold was placed in a 100 C oven overnight to cure the specimen. The resultant polymer sheets were stored at ambient conditions until tested.

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*. Proceedings of the 1974 Army Science Conference, U.S. Military Academy, West Point, New York, v. 3, 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.

B. Testing

Hardness was determined with a Shore Durometer, Type D. Ballistic testing was performed with the standard .22 cal. fragment-simulator projectile impacting at 0° obliquity. The ballistic performances were expressed in terms of the V_{50} value which is the average impact velocity at which the specimen is or is not just barely penetrated completely by the projectile. All of the V_{50} data appearing in this report have been normalized to a specimen areal density of 22.0 oz/sq ft.

RESULTS AND DISCUSSION

A. Variations in Soft Segment/Hard Segment Ratio

1. TDI/PTMO/BD Series: Previous investigations in this laboratory had shown that the ballistic performance of these block copolymers was quite sensitive to the ratio of "soft" material (PTMO) to "hard" material (TDI plus BD).¹⁻³ As long as the specimen failed in a ductile fashion, lower ratios of soft material produced higher V_{50} values. To locate the optimum composition, specimens composed of the standard TDI, PTMO, and BD have now been synthesized with further reductions in the soft segment content to bring it down to 24.3 weight percent. The formulations and properties of the new specimens are given in Table 1. The dependences of V_{50} and hardness upon soft segment content for the entire series are shown graphically in Figure 1. (This includes the data previously presented in Figure 3 of Part II of this series.³)

It is seen that the highest V_{50} value occurs at a soft segment content of about 34 weight percent. Further reductions in the soft segment content cause both a sharp decrease in V_{50} and an eventual change in failure mode from ductile to brittle. Concurrently, the hardness continues to increase slightly. In the brittle response region, therefore, we find that an increase in hardness is accompanied by a decrease in ballistic performance, a trend opposite from that already noted for these materials when formulated to fall well into the region of ductile response to ballistic impact.

2. TDI/PTMO/Isonol 100 Series: Another series of polyurethane block copolymer specimens was synthesized to determine the potential ballistic usefulness of a different type of diol, i.e., Isonol 100. Preliminary small-scale castings of formulations containing TDI, PTMO, and Isonol 100 had been clear, nearly colorless,

Table 1. FORMULATION AND PROPERTIES OF SPECIMENS CONTAINING BUTANEDIOL WITH VARIATIONS IN SOFT SEGMENT/HARD SEGMENT RATIO

Specimen	Composition in Mole Ratios			Soft Segment Weight %	Shore D Hardness	V_{50} * fps	Failure Mode
	2,4 TDI	PTMO 1020	BD				
1187-78A	9.45	1.00	8.00	30.1	78-80	1035	Ductile
1187-78B	10.50	1.00	9.00	27.9	78-81	1015	Ductile
1187-79A	11.55	1.00	10.00	26.0	80-82	945	Brittle
1187-79B	12.60	1.00	11.00	24.3	81-83	869	Brittle

*Tests conducted between 63 and 65 days after casting.

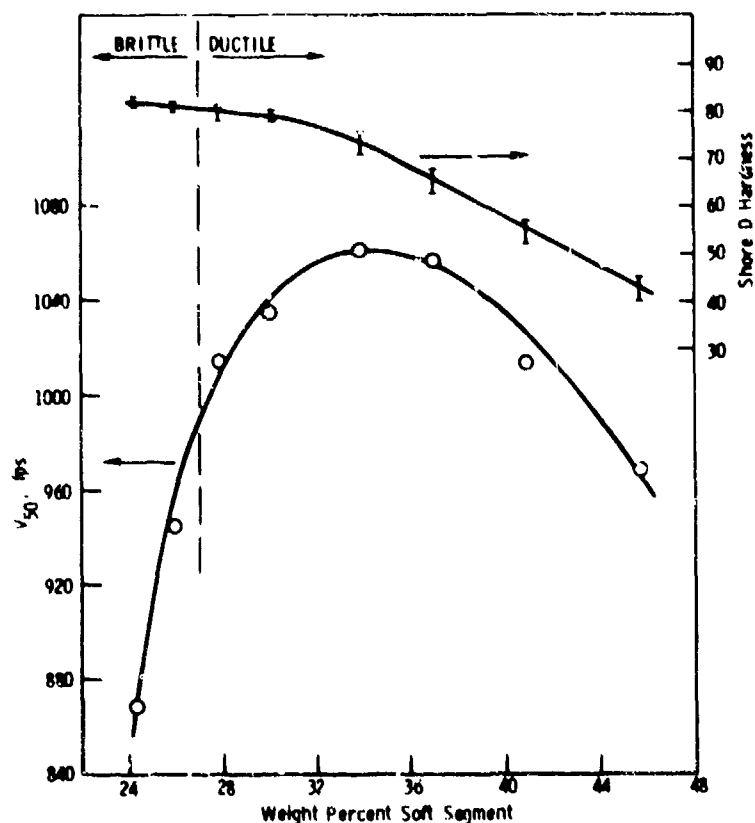


Figure 1. V_{50} and hardness as functions of soft segment content for the butanediol series.

and tough. Ballistic scale specimens were then prepared, covering a range of soft segment contents from 25.9 to 51.4 weight percent. The formulations and properties of these specimens are given in Table 2. The dependences upon soft segment content of V_{50} and hardness are plotted in Figure 2 for this series.

It is evident here that the peak V_{50} value occurs at a formulation just inside the ductile failure region. Further into the ductile failure region a decrease in hardness is paralleled by a decrease in V_{50} . In the brittle failure region an increase in hardness is accompanied by a decrease in V_{50} .

3. Comparisons and Conclusions: To illustrate more clearly the relative ballistic performances of these two series, the two V_{50} curves are plotted together as a function of soft segment content in Figure 3. It is seen that the V_{50} curve of the Isonol 100 specimens is generally lower than that of the BD specimens, and it does not seem likely that there would be any V_{50} values for the Isonol 100 series which would attain the maximum shown here for the BD series.

In summary, for these two series we see that the specimen hardness increases monotonically with decreasing soft segment content, the rate of hardness change becoming less at low soft contents. The dependence of V_{50} upon soft segment content is governed largely by the mode of response to the ballistic impact, i.e., (a) in the brittle response region, the V_{50} decreases with decreasing soft segment content; (b) the highest V_{50} values occur in the ductile response region near the

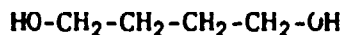
Table 2. FORMULATION AND PROPERTIES OF SPECIMENS CONTAINING ISONOL 100 WITH VARIATIONS IN SOFT SEGMENT/HARD SEGMENT RATIO

Specimen	Composition in Mole Ratios			Soft Segment Weight %	Shore D Hardness	V ₅₀ * fps	Failure Mode
	2,4 TDI	PTMO 1020	Isonol 100				
1187-103C	3.15	1.00	2.00	51.4	38-41	92P	Ductile
1187-104A	4.20	1.00	3.00	42.9	66-69	966	Ductile
1187-103B	5.25	1.00	4.00	36.8	77-79	934	Brittle
1197-105A	6.30	1.00	5.00	32.3	80-81	684	Brittle
1187-105B	7.35	1.00	6.00	28.7	82-83	681	Brittle
1187-105C	8.40	1.00	7.00	25.9	84-85	641	Brittle

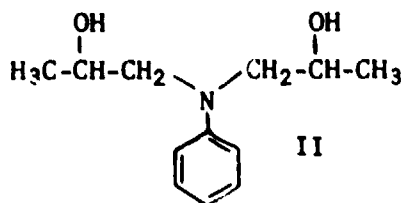
*Tests conducted between 119 and 126 days after casting.

ductile-brittle transition point; (c) farther into the ductile response region, the V₅₀ decreases with increasing soft segment content. This trend has previously been observed for other polymeric systems.^{4,5}

In view of the relative ballistic performances shown in Figure 3, the Isonol 100 series does not appear competitive with the BD series. The ideal ballistic material should have a high degree of hardness to form a rigid structure, yet respond in a ductile fashion to ballistic impact. The BD series approaches this ideal more closely than the Isonol 100 series as seen in Table 3. The desirable ductile responses and high values of V₅₀ occur at greater Shore D hardnesses for the BD series than they do for the Isonol 100 series. A rigorous molecular explanation for these differences is not possible at the present time. A simple comparison of the molecular structures of these two diols shows that BD (I, molecular weight 90) is more compact than Isonol 100 (II, molecular weight 209). By extrapolation it might be expected that even more compact diols, such as 1,3-propane diol or ethylene glycol, might provide polyurethanes with properties yet closer to the ideal material specified above.



I



II

B. Variation of PTMO Molecular Weight

The effect of PTMO molecular weight was investigated by synthesizing ballistic specimens containing PTMO of molecular weights 670 and 2000 to compare with the usual 1000 (nominal) molecular weight PTMO. The specimens were formulated with TDI and BD to give soft segment weight percents nearly the same as one of the standard specimens already investigated. The PTMO 670 specimen was similar in appearance and properties to those described for materials based on PTMO 1000,

- ROYLANCE, M. E., and LEWIS, R. W. *Development of Transparent Polymers for Armor*. Army Materials and Mechanics Research Center, AMMRC TR 72-23, July 1972.
- BAUM, B., STISKIN, H., and WILDE, A. F. *Transparent, Impact-Resistant, Rubber-Modified Acrylic*. Presented at Symposium on Toughness and Brittleness of Plastics, American Chemical Society National Meeting, Atlantic City, New Jersey, September 1974; to be published by the A.C.S. in its *Advances in Chemistry Series*.

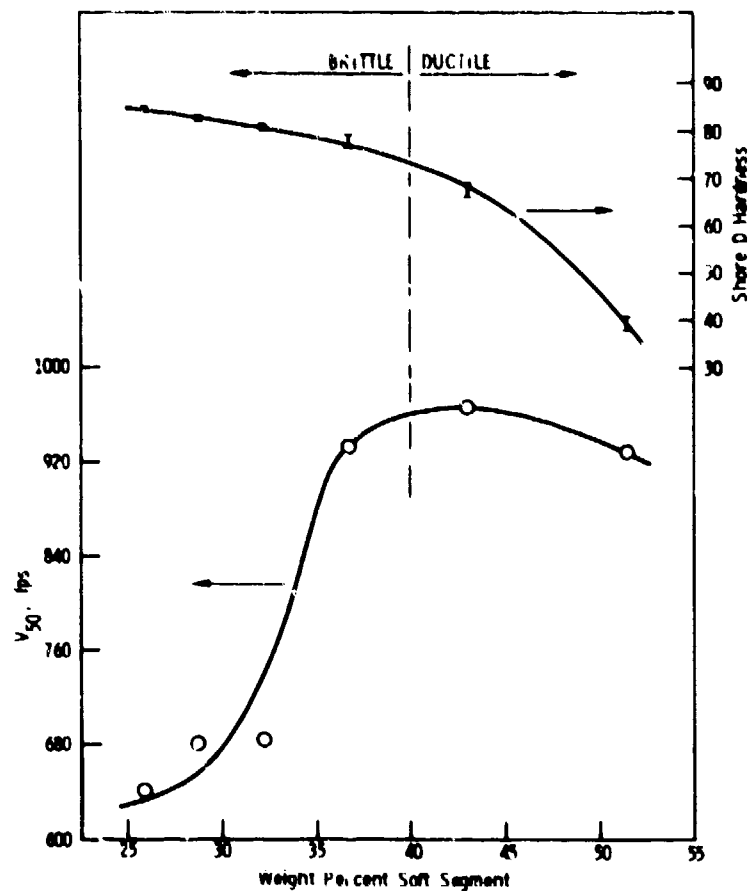


Figure 2. V_{50} and hardness as functions of soft segment content for the Isonol 100 series.

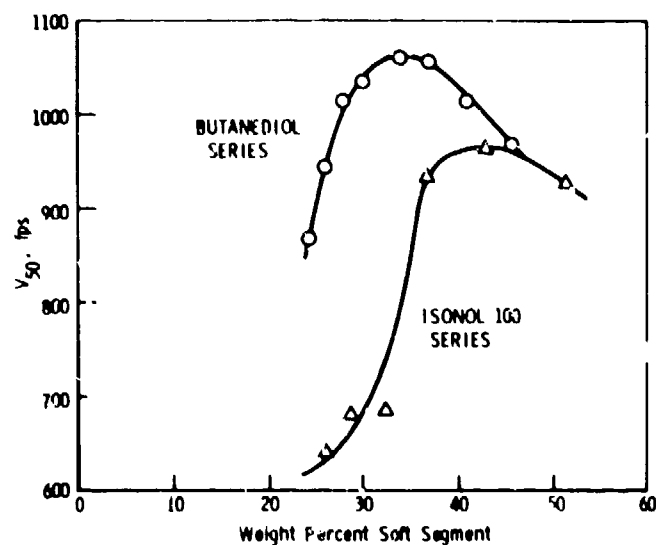


Figure 3. V_{50} as a function of soft segment content for both the butanediol and the Isonol 100 series.

Table 3. COMPARISON BETWEEN BD SERIES AND ISONOL 100 SERIES:
WEIGHT PERCENT SOFT SEGMENT AND SHORE D HARDNESS AT
CHARACTERISTIC BALLISTIC RESPONSE POINTS

Characteristic Ballistic Response Point	BD Series		Isonol 100 Series	
	Soft Segment Weight %	Shore D Hardness	Soft Segment Weight %	Shore D Hardness
Ductile-Brittle Transition	27	80	40	73
V ₅₀ Peak	34	73	43	68

whereas the PTMO 2000 specimen was white, opaque, soft, and flexible. These two specimens are described in Table 4 along with the specimen of PTMO 1070 for comparison. The hardness decreases with increasing PTMO molecular weight; the V₅₀ is greatest for the PTMO 1070 specimen; the ballistic responses are ductile except for a transition to brittle beginning to appear with the PTMO 670 specimen. These relationships are shown graphically in Figure 4.

The opacity, softness, and poor ballistic performance of the PTMO 2000 specimen are quite similar to the characteristics reported by us previously^{1,2} for a 2000 molecular weight PTMO specimen formulated in a somewhat different proportion with TDI and BD. Hence, our conclusions regarding the PTMO 2000 specimen remain the same, namely, that the longer segment length of the PTMO 2000 can crystallize to a degree sufficient to cause loss of transparency. Also these larger or more fully developed polyether domains impart a higher degree of softness or flexibility to the specimen. Figure 4 shows, in a striking fashion, the profound changes produced in the properties of these specimens merely by a change in the size of the molecular units comprising the soft domains.

It is clear that the effects of reducing the size of the soft segment molecular units are quite similar to the effects noted earlier in this report for a reduction of soft segment content. Both variations result in a continuous increase in specimen hardness, a peak in the V₅₀ value, and a ductile-to-brittle transition in ballistic failure mode beyond the V₅₀ peak. Apparently the smaller soft segment units are less able than the large units to exert the influences typical of this separate phase, with the result that the changes displayed in the macroscopic material properties due to smaller soft segment units closely parallel the property changes produced by lower soft segment content.

Table 4. CHARACTERISTICS OF SPECIMENS FORMULATED FROM THREE MOLECULAR WEIGHTS OF PTMO

Specimen	PTMO Mol Wt	Soft Segment Weight %	Specimen Appearance	Shore D Hardness	Age at Test (days)	V ₅₀ fps	Failure Mode
1187-76	670	34.5	Slightly Cloudy	79-81	67	959	Partly Brittle
1011-199	1070	37.0	Clear	63-68	75	1057	Ductile
1187-101A	2000	35.9	Opaque	54-57	32	549	Ductile

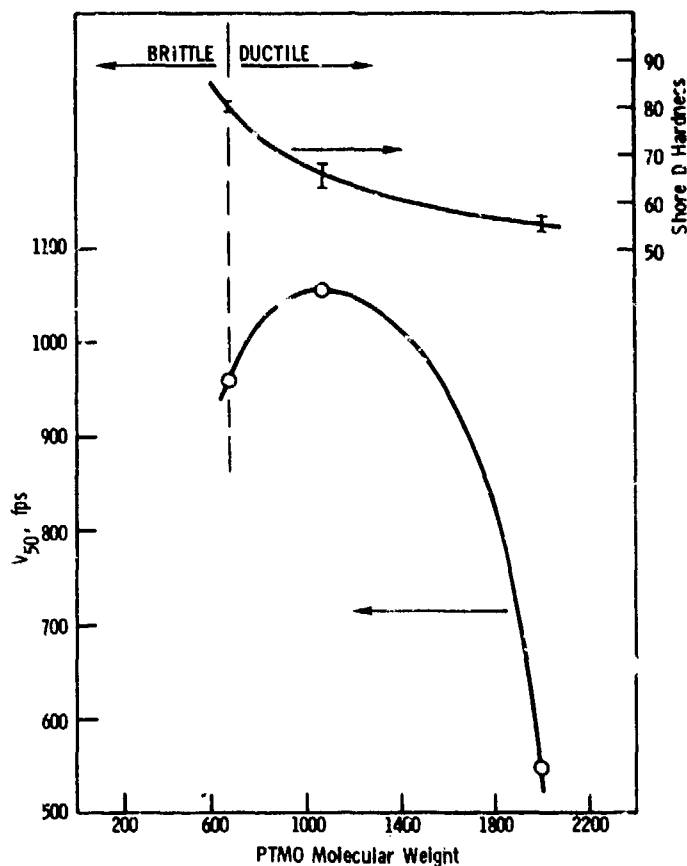


Figure 4. V_{50} and hardness as functions of the soft segment molecular weight.

C. Effects of Trimethylolpropane

To study the effects produced by crosslinking, small amounts of a trifunctional monomer were added along with the BD. This trifunctional material was 1,1,1-trimethylolpropane. The total number of moles of chain extender (BD + TMP) was kept constant. The ballistic specimens were formulated in mole ratios as follows: TDI = 5.25, PTMO 1070 = 1.00, BD + TMP = 4.00. The properties and ballistic performances of these specimens are listed in Table 5.

The specimen hardness increased monotonically with TMP content. However, the responses to ballistic impact appear to be unaffected by this formulation change, i.e., all the failures were ductile in nature and the V_{50} values were slightly scattered but showed no trend with TMP content. The lack of V_{50} change in this region of hardness change is puzzling in view of the results just preceding, and suggests that the V_{50} may be at a maximum at these low TMP contents. If so, a further increase in TMP content might cause an eventual transition to a brittle response with an associated drop in V_{50} . In summary, the use of TMP with this polyurethane formulation has produced no change in response to ballistic impact and therefore does not appear to be a useful modification.

D. Further Variations in Diisocyanate/Diol Mole Ratio

Our previous investigation had indicated that the properties of these block copolymers were significantly affected by small changes in the mole ratio of diisocyanate to diol.³ An additional formulation has now been made and tested. It is included in this report because the total trend now emerging for the effects of diisocyanate to diol ratio is very similar in its general features to the trends illustrated earlier in this report for other types of variations. The specimens in this series were made from TDI, PTMO 1070, and BD in the approximate mole ratios of 5.0, 1.0, and 4.0, respectively, with small systematic variations in these ratios to produce the desired variation in diisocyanate to diol mole ratio. The properties and ballistic performances of these specimens are given in Table 6 and are presented graphically in Figure 5. (This includes the data previously given in Part II of this series.³)

It is evident that increasing values of the diisocyanate to diol mole ratio produce a continuously increasing hardness in the specimens. (A small part of this effect may be due to the concurrent small decreases in the soft segment content.) At higher values of diisocyanate to diol mole ratio the V_{50} goes through a peak and begins to drop. Since both the Shore D hardness and the soft segment content differ considerably from those at the peak value of Figure 1, it seems likely that the peak in Figure 5 is due primarily to the effect of diisocyanate to diol mole ratio rather than to the effect of very small decreases in soft segment content.

We have previously speculated³ that the higher ratios of the diisocyanate may increase the small amount of crosslinking that may occur and/or may change the nature of the interaction between the soft and hard domains in the final block copolymer to produce the observed increases in hardness. It still appears likely that the optimum practical ratio is about 1.05, partly because of the peak in V_{50} value. In addition, lower ratios produce specimens which are too soft for structural use, whereas higher ratios would result in specimens expected to have inferior hydrolytic stability.

Table 5. CHARACTERISTICS OF SPECIMENS FORMULATED WITH DIFFERENT AMOUNTS OF TMP CROSSLINKING AGENT

Specimen	Relative Moles of TMP	Soft Segment Weight %	Shore D Hardness	Age at Test (days)	V_{50} fps	Failure Mode
1011-195	0	45.7	40-45	78	969	Ductile
1187-20	0.2	45.5	44-49	62	909	Ductile
1187-102A	0.4	45.3	57-59	29	942	Ductile
1187-119	0.8	45.0	61-63	29	928	Ductile

Table 6. CHARACTERISTICS OF SPECIMENS FORMULATED WITH VARIOUS DIISOCYANATE/DIOL MOLE RATIOS

Specimen	Diisocyanate/Diol Mole Ratio	Soft Segment Weight %	Shore D Hardness	Age at Test (days)	V_{50} fps	Failure Mode
1011-197	0.95	47.4	19-24	82	830	Ductile
1011-196	1.00	46.5	34-39	77	906	Ductile
1011-195	1.05	45.7	40-45	78	969	Ductile
1187-80A	1.10	44.8	57-60	59	933	Ductile

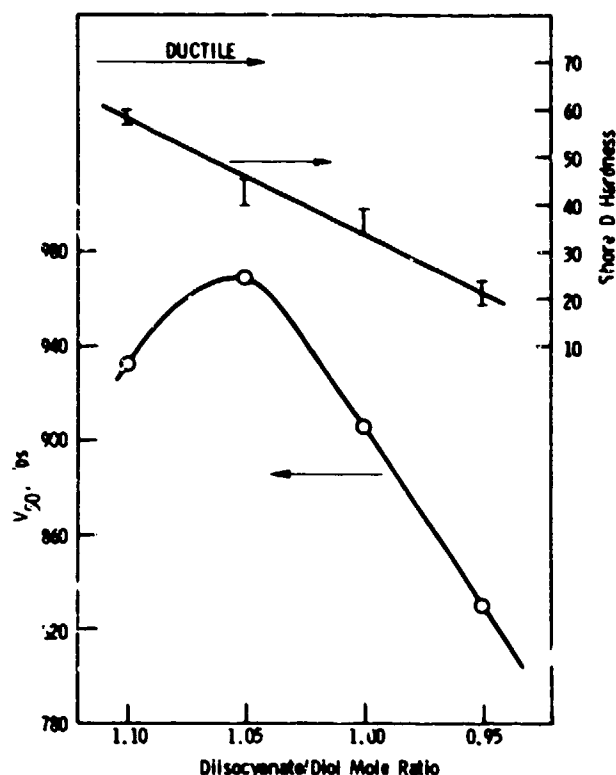


Figure 5. V_{50} and hardness as functions of the diisocyanate/diol mole ratio.

The general features exhibited by variation in the diisocyanate to diol mole ratio are therefore strikingly similar to those observed for variations in soft segment content or in PTMO molecular weight. Well into the ductile failure region, any structural change in the block copolymer which produces a harder specimen also results in an increase in the V_{50} . This trend continues until a peak in the V_{50} is eventually attained. At some point beyond the V_{50} peak, the ductile failure mode changes into a brittle one as the V_{50} continues to decrease from its peak. Evidently the ductile-brittle transition point has not yet been reached in the series depicted in Figure 5 where the hardest specimen is still displaying ductile response to ballistic impact.

E. Polyurethanes from Xylylene Diisocyanate

To investigate the properties resulting from another type of diisocyanate, two specimens were synthesized from xylylene diisocyanate. Here, the isocyanates are located on the aliphatic methyl groups and are thus less likely to yield a

Table 7. CHARACTERISTICS OF SPECIMENS FORMULATED FROM XYLYLENE DIISOCYANATE

Specimen	Type of Diol	Soft Segment Weight %	Specimen Appearance	Shore D Hardness	Age at Test (days)	V_{50} fps	Failure Mode
1187-109A	BD	43.1	Opaque	50-54	22	826	Ductile
1187-108C	Isonol 100	35.9	Clear	55-57	23	902	Partly Brittle

material which would yellow on aging. One specimen contained BD, the other contained Isonol 100. The composition in mole ratios was XDI = 5.25, PTMO 1020 = 1.00, and diol = 4.00. The properties and ballistic performances of these specimens are given in Table 7. Because of the greater molecular weight of Isonol 100 as compared to BD, the Isonol 100 specimen had a lower soft segment content than the BD specimen. The unexpected opacity of the BD specimen is presumably due to a high degree of crystallinity. Apparently, the combination of the XDI with BD increases the tendency of the polymer to crystallize, whereas the lack of symmetry of the Isonol 100 is sufficient to inhibit the development of crystallinity and hence to retain the transparency of the specimen.

Neither specimen provided outstanding ballistic properties. The Isonol 100 specimen had a somewhat lower soft segment content than the BD specimen and was slightly harder, more brittle, and produced a considerably higher V_{50} value. Comparison of these two specimens with similar ones formulated with TDI (Figures 1 and 2) showed the following: (a) with BD, XDI gives a specimen of about the same hardness but much lower V_{50} than does TDI; (b) with Isonol 100, XDI gives a specimen of considerably less hardness and less brittleness but about the same V_{50} as does TDI. From these results it appears that XDI with BD is not as good as TDI with BD, and the XDI with Isonol 100 is no better than TDI with Isonol 100. Since we have previously seen that TDI with Isonol 100 is not as promising as TDI with BD (Figure 3 and Table 3), we must conclude that XDI is inferior to TDI for transparent armor applications, at least in formulations of this type.

CONCLUSIONS

It has been found that V_{50} , specimen hardness, and failure mode are quite sensitive to the following compositional variables: soft segment content, soft segment molecular weight, and diisocyanate to diol mole ratio. For these variables, the maximum V_{50} occurred in the ductile failure region. Well into this ductile region, decreasing specimen hardness was always accompanied by a decrease in V_{50} . The transition to brittle failure always occurred at specimen hardnesses greater than those at the maximum V_{50} . Within the brittle failure region, increasing specimen hardness was accompanied by a decrease in V_{50} value. It has also been found that substitution of Isonol 100 for BD, substitution of XDI for TDI, and incorporation of TMP as a crosslinking agent, individually resulted in either no improvement in ballistic performance or a degradation of ballistic performance, and hence are not useful modifications in polyurethanes of this type for armor application.

It is concluded that the optimum formulation for the TDI/PTMO/BD system in terms of ballistic performance has now been attained. It has been noted during the course of this work that certain environmental parameters such as humidity and temperature exert an influence on the V_{50} of these materials. Thus, it is obvious that further investigation of such parameters is necessary before useful end items can be fabricated from this material. This work is currently in progress.

ACKNOWLEDGMENT

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