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SYNTHESIS AND BALLISTIC EVALUATION OF
SELECTED TRANSPARENT POLYURETHANE
BLOCK COPOLYMERS

Anthony F. Wilde, et al

Army Materials and Mechanics Research Center
Watertown, Massachusetts

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ABSTRACT

A series of transparent polyurethane block copolymers has been synthesized in-house and cast into sheet specimens for ballistic evaluation. The ballistic performances (V_{50}) were generally superior to polycarbonate and were found to increase with the following independent variations: higher cure temperature, longer room-temperature cure time, higher diisocyanate and diol content, and lower molecular weight (lower weight composition) of the polyether component. These materials generally displayed a ductile response to ballistic impact. Concurrent high-speed photographs served to characterize the transient bowing of the polymer specimen, the velocities of plugs and fragments generated by the impact, and the FSP residual velocity. It is concluded that these materials show considerable promise for transparent armor applications. (Authors)

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INTRODUCTION

For a number of years the Polymer Chemistry Group at AMRC has had a deep interest in the area of polyurethanes. This interest has ranged from fundamental structure-property relationships to applications in the fields of adhesives and flexible packaging. Thus, when it became known that the best of the commercially available transparent armor materials was a polyurethane, it was decided to take advantage of this expertise for our in-house program in transparent armor materials.

A number of custom-synthesized polyurethanes incorporating systematic variations in structure were available for investigation. A cursory inspection of these samples indicated that several of them might have favorable ballistic properties. The best of them, a formulation of 2,4-toluene diisocyanate, polytetramethylene oxide and 1,4-butanediol, was completely transparent, nearly water white (the commercial material is quite yellow), and very tough. It was therefore decided to scale-up the preparation of this polymer and to fabricate it into specimens suitable for ballistic evaluation. The effect on ballistic performance of variation of several synthetic and processing parameters is discussed.

EXPERIMENTAL

A. Polymer Synthesis

Materials. The requisite 2,4-toluene diisocyanate was obtained from Aldrich Chemical Company and redistilled before use. Anhydrous 1,4-butanediol was obtained from GAF and used as received. Polytetramethylene oxide of 1000 and 2000 molecular weights were obtained from Quaker Oats Company. Hydroxyl numbers were determined using the procedure described by David and Staley.¹ Using a procedure described by Scholten et al.,² 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 and a vacuum take-off connected to a vacuum pump and an argon source was used. The system was purged with dry argon three times and the toluene diisocyanate was introduced followed by the polytetramethylene oxide. The mixture was stirred under 20 mm of argon at 85 C for 1-1/2 hours. At this point, the vacuum was released using argon and the requisite amount of butanediol was introduced. Stirring under 20 mm of argon at 85 C was resumed for an additional five minutes. 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-" x 6-" x 1/4-" mold composed of GE RTV silicone rubber compound. The filled mold was placed in an oven, leveled and cured for the desired length of time at the desired temperature. The cured sheets were removed from the mold, wrapped in polyethylene and stored in a desiccator over silica gel at room temperature.

1. DAVID, D. J., and STALEY, N. B. *Analytical Chemistry of the Polyurethanes*, Wiley-Interscience, New York, 1969, p. 289-91.
2. SCHOLTEN, N. G., SCHUHMAN, J. G., and TENHOOR, R. E. *Urethane Polyether Prepolymers and Foams*, Journal of Chemical and Engineering Data, v. 5, no. 3, July 1960, p. 395-400.

B. Ballistic Evaluation and High-Speed Photography

Determination of the V_{50} ballistic limit was accomplished according to standard procedure.³ Impacts were made at 0° obliquity with the standard .22 cal. 17-grain fragment simulator projectile (FSP). Impact velocities were determined with the usual silver grid paper screens and an electronic chronograph. The FSP were propelled from a helium gun designed and built in this laboratory.⁴ The areal densities of the specimens ranged from 19.5 to 24.5 oz/sq ft, hence a value of 22.0 oz/sq ft was selected as a convenient standard for comparison of the ballistic data. Accordingly, the experimentally determined values of V_{50} were normalized to this standard areal density by adjustments of 20 ft/sec per 1.0 oz/sq ft (typical V_{50} dependence of polymeric materials upon areal density in this weight range).

High-speed photographs were taken with 8x10-inch Polaroid type 3000X film in a portrait camera with the shutter opened in the darkened laboratory prior to firing.⁵ Multiple exposures were provided by a series of 1-microsecond light flashes occurring at intervals ranging from 125 to 175 microseconds, the whole group of flashes being synchronized with the impact event. The photographs permitted both the determination of V_R and V_F and observation of the transient specimen response.

RESULTS AND DISCUSSION

A. Summary of Ballistic Results

Based on the preliminary examination of the series of in-house synthesized polyurethanes several formulations were scaled-up and cast into sheets suitable for ballistic testing. The sheets were 6 inches square with thicknesses of approximately 1/4 inch. Each formulation contained 2,4-toluene diisocyanate (TDI), polytetramethylene oxide (PTMO) in one of two nominal molecular weights (as designated by a suffix number), and 1,4-butanediol (BD). Each specimen was subjected to a standard ballistic V_{50} test employing the .22 cal. FSP. The formulations, cure conditions, and V_{50} results are given in Table 1.

For comparison, Table 2 presents the corresponding V_{50} values for a standard commercial polycarbonate and the commercial polyurethane. The former polymer currently offers the best combination of properties in terms of ballistic performance, optical clarity, and commercial availability. The latter polymer currently provides the best ballistic performance at this areal density but is handicapped by a considerable yellow tint. It is seen that all but two of the specimens in Table 1 gave a ballistic performance equal to or better than that of the polycarbonate. These results were very encouraging and have served to suggest possible modifications for further improvements in these materials.

3. MASCIANICA, F. S. *Ballistic Technology of Lightweight Armor - 1973 (U)*, Army Materials and Mechanics Research Center, Technical Report AMMRC TR 73-47, November 1973, Confidential Report.
4. ROGERS, J. M. *Development of a High-Pressure Medium Velocity Helium Gun for Firing 17-Grain Fragment Simulators*, Army Materials and Mechanics Research Center, Technical Report AMMRC TR 72-11, March 1972.
5. WILDF, A. F., ROYLANCE, D. K., and ROGERS, J. M. *Photographic Investigation of High-Speed Missile Impact Upon Nylon Fabric, Part I: Energy Absorption and Cone-Radial Velocity in Fabric*, Textile Research Journal, v. 43, no. 12, December 1973, p. 753-761.

Table 1. FORMULATIONS, CURE CONDITIONS, AND BALLISTIC PERFORMANCE OF ALL SPECIMENS

Specimen	Sample Code	Composition Mole Ratios	Cure Conditions	V ₅₀ [†] and Spread (ft/sec)
1	1011-36	TDI .25 PTMO 1070 1.0 BD 4.0	RT* for 3 days	V ₅₀ = 755 4-shot Spread = 47
2	-38A	TDI 5.25 PTMO 1070 1.0 BD 4.0	100 C Overnight	V ₅₀ = 940 6-shot Spread = 73
3	-39	TDI 6.3 PTMO 1070 1.0 BD 5.0	RT for 5 days	V ₅₀ = 902 8-shot Spread = 34
4	-44	TDI 5.25 PTMO 1090 1.0 BD 4.0	60 C Overnight	V ₅₀ = 899 10-shot Spread = 75
5	-49	TDI 5.25 PTMO 1090 1.0 BD 4.0	RT for 14 days	V ₅₀ = 912 10-shot Spread = 64
6	-52	TDI 6.3 PTMO 2010 1.0 BD 5.0	RT for 8 days	V ₅₀ = 708 8-shot Spread = 50
7	-48	TDI 5.25 PTMO 1090 1.0 BD 4.0	RT for 29 days	V ₅₀ = 928 10-shot Spread = 70

*RT = room temperature

[†]V₅₀ normalized to 22 oz/sq ft

Table 2. BALLISTIC PERFORMANCE OF COMMERCIAL TRANSPARENT MATERIALS

Material	V ₅₀ (fps) Normalized to 22 oz/sq ft
Commercial polycarbonate	850
Commercial polyurethane	1080

From the data in Table 1, selected comparisons can be made to illustrate the effects of specific variables upon the ballistic performance of this preliminary series.

B. Effect of Cure Temperature

Table 3 presents the data pertaining to the series of cure temperatures. The V₅₀ increases with cure temperature, but appears to level off at the higher temperatures. Different cure temperatures were investigated because of the increased tendency to form permanent voids in the specimen at elevated cure

temperatures (perhaps due to expansion of entrapped gases at the higher temperatures). It is evident that the RT cure did not give promising ballistic performance. The deformation of these materials was generally ductile, i.e., no spall or radial cracking was produced, and only one small plug of material was pushed out of the specimen by the FSP. In addition, the ductile penetration holes, as examined after the test, possessed a diameter greater at the impact face than at the exit face. These diameters were less than that of the FSP, thus indicating partial closure of the hole after penetration. The only exceptions to this ductile response were displayed by several of the impacts upon specimen 1; these produced a somewhat brittle response, namely, some radial fracture, with spalling of a number of fragments. The mixed response in this specimen is discussed in more detail below.

C. Effect of RT Cure Time

The results obtained from the series of cure times appear in Table 4. The V_{50} appears to increase steadily with cure time, showing a diminishing dependence at longer times. This phase of the work was undertaken because of the lesser tendency to form voids at RT and the desire to increase the rather undistinguished performance of this RT-cured specimen (1). In this latter regard, the longer cure time did produce a significant ballistic improvement and may indicate one possible route around the problem of excess void formation. The fracture behavior of this series was quite similar to that of the previous series; that is, specimens 5 and 7 showed completely ductile behavior with partial hole closure after penetration.

D. Effect of TDI and BD Content

In Table 5 appear the results for an increase in the relative amounts in two of the components of this formulation. The higher content of TDI and BD caused a marked increase in the V_{50} . Specimen 3 was also harder and less flexible than specimen 1, and displayed a somewhat brittle response to ballistic impact. A majority of the impacts upon specimen 3 produced spall and radial fracture, although a few of them resulted in the usual ductile responses. In a very general way the mixed brittle and ductile response noted for specimens 1 and 3 seems to be related to the chronological order of impact; the first impacts tended to produce ductile failure, whereas the later impacts generally resulted in brittle failure. This apparent trend seemed to outweigh a possible impact velocity dependence of the polymer response; the latter effect was not discernible in these two specimens.

E. Effect of PTMO Molecular Weight

The ballistic results obtained for a variation in molecular weight for one of the components are presented in Table 6. The higher molecular weight PTMO caused a significant drop in the ballistic performance. This specimen was considerably different from the others in that it was a white, opaque material and was a very soft and very flexible specimen. It is believed that the longer segment lengths of the PTMO could crystallize to a size or to a degree of perfection sufficient to cause the observed opacity. At the same time these larger or more fully developed domains of PTMO (the soft segment in these block copolymers) confer upon the entire specimen a greater degree of softness and flexibility. These effects are reinforced by the increased weight percent of soft material in the higher molecular weight formulation.

Table 3. EFFECT OF CURE TEMPERATURE AT FIXED COMPOSITION

Specimen	Cure Temp (deg C)	V ₅₀ (fps)
1	RT	755
4	60	899
2	100	940

Table 4. EFFECT OF RT CURE TIME AT FIXED COMPOSITION

Specimen	RT Cure Time (days)	V ₅₀ (fps)
1	3	755
5	14	912
7	29	928

Table 5. EFFECT OF TDI AND BD CONTENT AT RT CURE

Specimen	Contents in Mole Ratios		V ₅₀ (fps)
	TDI	BD	
1	5.25	4.0	755
3	6.3	5.0	902

Table 6. EFFECT OF PTMO MOLECULAR WEIGHT AT FIXED MOLAR COMPOSITION

Specimen	PTMO Mol. Wt	V ₅₀ (fps)
3	1070	902
6	2010	708

F. High-Speed Photographic Observations

Multi-exposure high-speed photographs of four of the specimens were taken during the ballistic tests. From these photographs it was evident that there was transient bowing of the polymer specimen during the impact if the polymer failure were ductile in nature. The magnitude of this bowing ranged from about 0.3 cm to 0.7 cm. Figure 1 shows a triply-flashed photo taken just after a ductile FSP penetration of specimen 3. The three positions of the FSP are faintly visible to the left of the specimen in line with the penetration hole; just below these are seen the three positions of the single plug of specimen material generated by the penetration. Also evident is the bowing of the specimen.

For the few impacts producing essentially a brittle failure of the polymer specimen, little specimen transient bowing was observed. Figure 2 is a triply-flashed photo taken just after a brittle FSP penetration of specimen 3. Seen to the left of the specimen are a number of irregularly-shaped fragments generated by the impact. There is little evidence of specimen bowing. These results are in agreement with previous ballistic tests performed with plastic/plastic laminates in this laboratory* where the backup plate underwent bowing only if it failed principally in a ductile fashion.

From these photographs it was also possible to estimate the FSP residual velocity (V_R) and the velocity (V_F) of fragments or plugs generated from the polymer specimen (neglecting any out-of-plane velocity components as viewed from the camera). These velocities were plotted as a function of the normalized FSP impact velocities in Figure 3. (For each specimen the impact velocity, V_S , was

*WILDE, A. F., et al. FY-73 Annual Summary, *Development of Transparent Polymers for Armor*. Army Materials and Mechanics Research Center, Watertown, Massachusetts, Internal Report, May 1973.

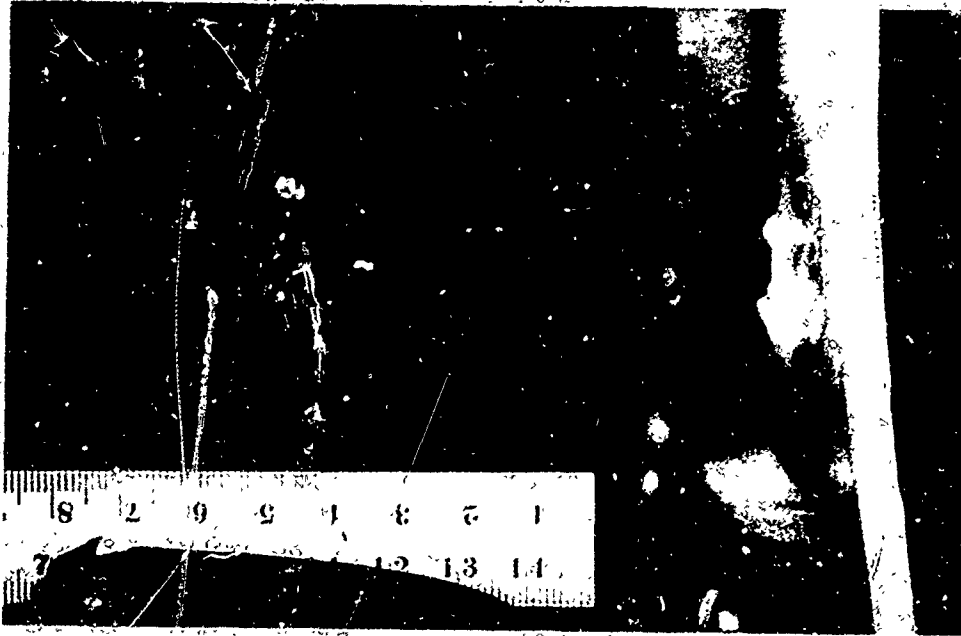


Figure 1. Triply-flashed high-speed photograph just after ductile FSP penetration. 175 μ sec between flashes. 19-066-1184/AMC 73



Figure 2. Triply flashed high speed photograph just after brittle FSP penetration. 175 μ sec between flashes. 19-066-1183/AMC 73

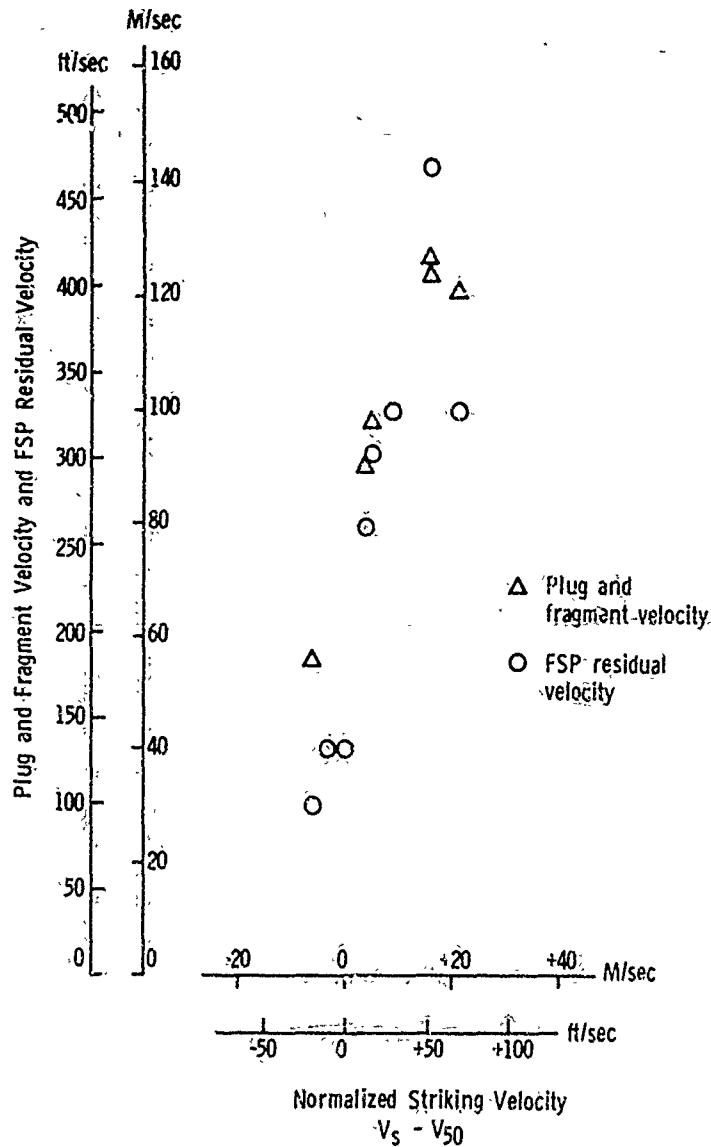


Figure 3. Plug and fragment velocity and FSP residual velocity as a function of normalized FSP striking velocity for polyurethane specimens.

normalized to the V_{50} value for that specimen by expressing the impact velocity in terms of $V_s - V_{50}$.) The plot shows that both V_R and V_F increase very rapidly with V_s in the vicinity of V_{50} and that, in general, V_F exceeds V_R for a given V_s . This latter observation was also reported previously.

G. General Comments

The highest ballistic performance in a commercial polymeric material for application in monolithic transparent armor is provided by the commercial polyurethane referred to in Table 2. This material has a number of useful attributes, namely,

1. high V_{50} value for FSP impact,

2. ductile response to impact (absence of spallation and radial fracture),
3. transparency (although having a considerable yellow tint).

The AMMRC polyurethanes possess qualities which can be enumerated in the same fashion as done for the commercial polyurethane. The AMMRC polyurethanes show the following performances and properties:

1. V_{50} values are generally superior to that of polycarbonate and approach, in some cases, that of the commercial polyurethane.

2. There is nearly always a ductile response to ballistic impact (important because no dangerous secondary fragments are generated and because peripheral damage to the target is minimal, i.e., target integrity and transparency are maintained right to the edges of the penetration hole).

3. These materials exhibit a high degree of transparency, with either a nearly water white or a slightly tinted color.

4. There are some problems with void formation during the cure process; further efforts must be devoted to eliminating these.

From the results discussed in the previous sections dealing with the effects of the four variables upon the ballistic performance, it appears that there is a common trend. In other words, whenever there was an actual (or presumed) increase in specimen hardness or rigidity, there was a corresponding increase in the V_{50} value. (a) higher cure temperature, (b) longer RT cure time, (c) higher TDI and BD content, and (d) lower PTMO molecular weight all resulted in a higher V_{50} value. Variations (a), (c), and (d) definitely produced harder, more rigid specimens; it is presumed that at the time of testing, variation (b) had also produced a similar change in mechanical properties. Therefore, with these materials in this property range, it appears that ballistic performance is improved by treatments or formulations which enhance the hardness or rigidity of the polymer.

CONCLUSIONS

It is concluded that selected polyurethane block copolymers show considerable potential for application in transparent armor systems. Further efforts are planned for the survey of promising chemical variations in polyurethane composition and for the investigation of processing techniques to eliminate the problem of void formation.

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