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Applications in Blast, Shockwave, and Penetration Mechanics

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3.2 Impact-Resistant Elastomeric Coatings

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3.2.1 Introduction

The United States Air Force in 1999 demonstrated the effectiveness of elastomeric polyurea (PU) sprayed on the foundation of buildings in mitigating the effects of a bombing [1]. Fragmentation, which refers to the debris broken from the structure and propelled by the blast, is second leading cause of death when a building is bombed. The PU coating adheres to the structure and remains intact during an explosion, suppressing fragmentation. An additional, unexpected benefit of the coating was reduction in the standoff distance; that is, how close an explosion had to be in order to destroy the building. A few years later the United States Marine Corps adopted a similar idea to increase the ballistic resistance of light vehicles. A different polyurea (called "Dragonhield"), with properties comparable to the Air Force material, was sprayed on High Hard Steel (HHS, MIL-DTL-46100E) and used as the initial means to uparmor High Mobility Multipurpose Wheeled Vehicles in Operation Iraqi Freedom [2].

PU has processing advantages, in particular a rapid rate of reaction, which proceeds independently of ambient conditions and thus facilitates field-application of coatings. However, the mechanism underlying the performance enhancement was unknown, including whether polyurea offers unique advantages over other polymers for infrastructure protection and armor applications. Of course, the extensive hydrogen bonding in PU confers "toughness"; however, at the high strain rates (approximately $10^5/s^{-1}$) of ballistic deformation, it is not obvious whether conventional measures of the mechanical properties of rubbers have any relevance. Moreover, the modulus of PU can span a range from moderately soft (Shore A durometer < 60) to very hard (Shore D ~ 75), so that the term polyurea per se does not describe the material.

An investigation was undertaken at the Naval Research Laboratory to determine the characteristics of soft polymers essential to performance as an armor coating. To address this issue, a systematic study of various rubbers as coatings on steel armor was evaluated. The range of properties included: elastomers with enhanced mechanical hysteresis, achieved by polymer type (e.g., rubbers having intrinsically large internal friction coefficients); both unfilled ("gum rubbers") and compounds incorporating reinforcing filler such as carbon black; elastomers with high glass transition temperatures (but still below ambient in order to be rubbery at room temperature); and both amorphous and strain-crystallizing rubbers.

3.2.2 Experimental Methods

The procedure for the ballistic tests followed Mil-Std-662F, using 0.50 cal fragment simulating projectiles (FSPs) with a Rockwell C hardness of 30. A rifled Mann barrel was used, with the projectile velocity changed by varying the amount of gun powder. These velocities were measured with a pair of chronographs, and the V-50 was calculated as the average of the lowest velocity for full penetration of the projectile through the target and the highest velocity for nonpenetration.

The substrates for tested coatings were of either HHS or ultra high hard steel (UHHS; MIL-DTL-32332). Sulfur-vulcanized butyl rubber or polyurea were used for the coating material. Except where noted otherwise, the PU was prepared from Isonate 143L (Dow Chemical) and Versalink P-1000 (Air Products). Additional tests were also conducted on laminates, consisting of alternating rubber and metal layers (of variable number and thickness).

3.2.3 Results

3.2.3.1 Mechanism of Ballistic Mitigation

Penetration by a projectile of the elastomeric coatings entails some bond breaking (chain scission), but otherwise chemical changes are negligible. This was shown by obtaining samples from the immediate periphery of the hole in a polyurea coating penetrated by a 0.50 cal fsp. The material adjacent to the impacted region:

1. was completely isotropic; SAXS showed no evidence of orientation. This is consistent with results from mechanical tests, indicating zero residual strain (permanent set) in the material for strain rates exceeding approxiamtely 20 s^{-1} [3];
2. had a reduced crosslink density, reflected in a 10% increase in swelling volume when immersed in a good solvent. This reflects the bond breakage during penetration;
3. exhibited no change in either the microphase-separated morphology or crystallinity; the endotherms in calorimetry measurements corresponding to phase dissolution and melting were identical to those in samples taken far from the impact locus.

From these results, we conclude that the mechanism giving rise to improved ballistic performance of elastomer-coated steel substrates is primarily a physical, and thus reversible, process.

The characteristic distinguishing good coatings from those imparting minimal improvement is the glass transition temperature of the polymer (Figure 3.2.1). This correlation can be understood from comparison of the ballistic impact frequency to the frequency of the polymer segmental dynamics. The former is approximated by the ratio of the bullet speed to the coating thickness, yielding values on the order of 10^5/s^{-1}. The segmental dynamics depend on both the glass transition temperature, T_g, of the polymer and the test temperature. We expect, in accord with Figure 3.2.1, that polymers for which T_g is in the range from around −50 to 0°C will have segmental dynamics occurring on the time scale of the ballistic impact [4]. This matching of perturbation rate with the inherent material frequency (resonance condition) causes large energy dissipation, as the polymer undergoes its viscoelastic glass transition. After the transient impact, the coating returns to its original rubbery state. Since the segmental dispersion is several decades broad, there is insensitivity to projectile speed. In addition to the correlation of V-50 with T_g, an indicator of the significance of the impact-induced phase transition mechanism is the mode of failure. Failure of coatings that yield only modest improvements in V-50 is accompanied by large stretching and tearing (i.e., rubbery behavior), resulting in a substantial damage zone. For good performing rubbers, however, the damage to the coating due to ballistic penetration is limited to a hole smaller than the bullet diameter. These different failure modes are illustrated in the photographs in Figure 3.2.2 taken after penetration by a 0.50 cal fsp.

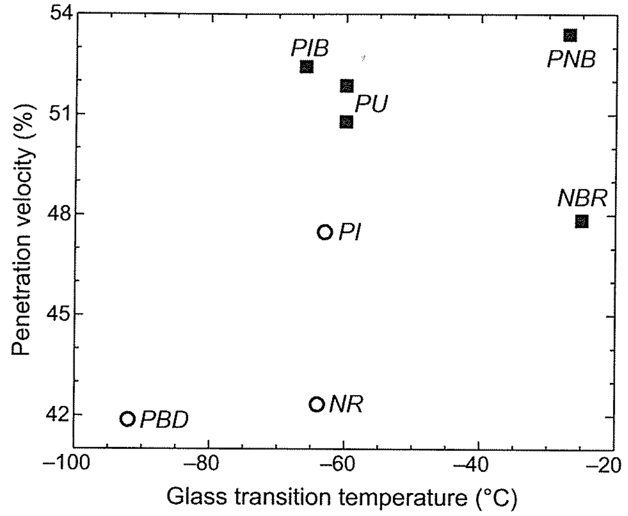

Figure 3.2.1 Improvement in ballistic performance (0.50 cal fsp) of HHS steel plates versus the glass transition temperature of the front-surface coating. Failure mode was "rubbery" (open circles) or brittle-like (solid squares). PBD,1,4-polybutadiene; NR, natural rubber; PI, 1,4-polyisoprene; PU, polyureas (differing stoichiometry); PIB, butyl rubber; NBR, nitrile rubber; PNB, polynorbornene.

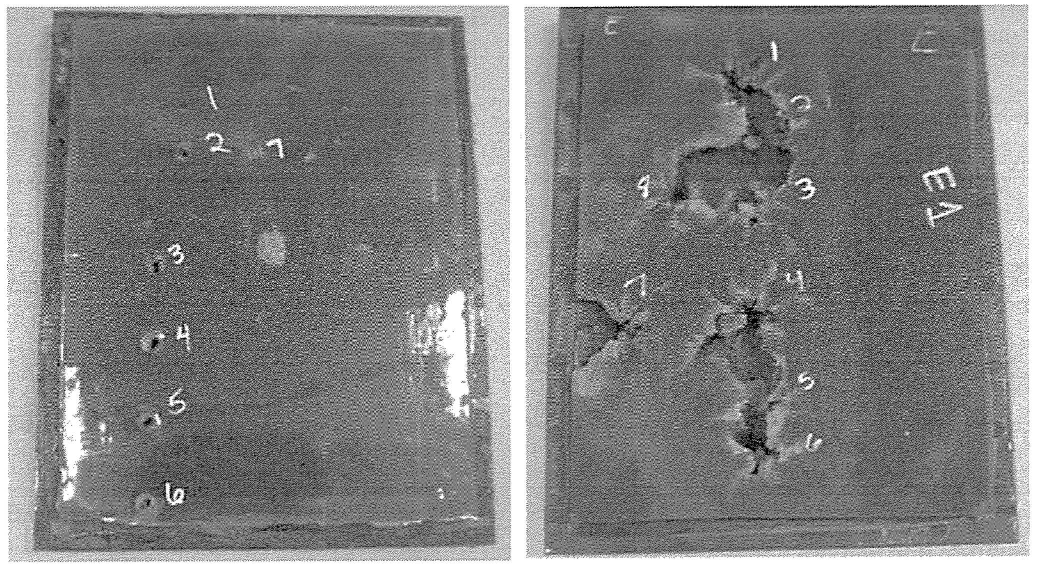

Figure 3.2.2 Front side photographs of HHS steel plates after penetration by several rounds of 0.50 cal fsp (left) polyurea (right) 1,4-polybutadiene.

A second consequence of the impact-induced phase transition, besides large energy absorption, is a transient stiffening of the coating by roughly three orders of magnitude (from MPa, the modulus of a rubber, to GP, that of a glassy polymer). The higher projectile velocity required to penetrate a coated steel substrate corresponds to a kinetic energy about 3 kJ higher than for penetration of the bare substrate. If this is entirely absorbed by the coating, the energy density in the polymer is approximately 4 GJ/m^3 (assuming the impact area equals the bullet diameter). This energy density corresponds to a loss modulus in the GPa range, which is the magnitude associated with glassy behavior. Actually, the stiffening of the polymer causes a lateral spreading of the impact force, which reduces the pressure, further mitigating the effect of the projectile. The impact force was directly measured on the backside of test plates using Digital Image Correlation. As seen in Figure 3.2.3, the force decays over a broader distance when the coating is present. Consistent with this lateral dispersion of the force, the hole in the steel substrate is larger when a coating is present on the front side (Figure 3.2.4).

To quantify the relative contributions of energy dissipation and force spreading, ballistic tests were carried out on plates for which the monolithic coating was replaced by cylinders having a diameter equal to that of the bullet. This precludes lateral displacement of the force. The results, shown in Table 3.2.1, indicate that 30% of the effect of the coating is due to reduction in the impact pressure due to transverse spreading of the force.

Reduction of the weight of armor can be accomplished by minimizing thickness, but of course this affects performance. Shown in Figure 3.2.5 are ballistic results for two elastomer coatings as a function of the coating thickness. The interesting feature, shown as well by PU coatings, is the large increase in V-50 through coating thicknesses of 2 – 3 mm. Beyond that the change in performance is more modest, although still increasing. Of course, the thickness of the substrate has a large effect as well.

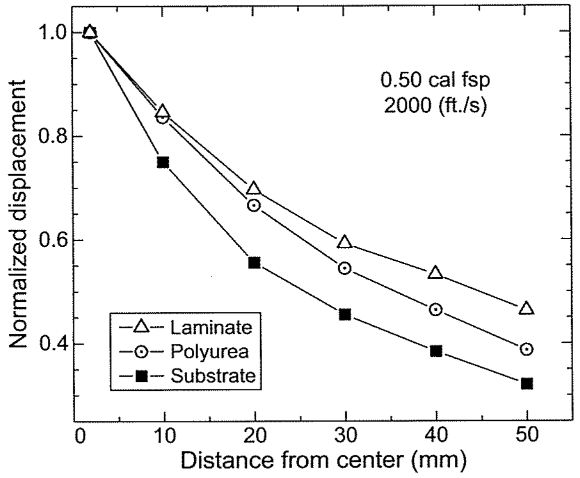

Figure 3.2.3 Maximum out-of-plane displacement on the backside of 0.24" HHS normalized by the displacement measured at the impact locus: bare steel (squares), with a 3 mm PU coating (circles), and with a PU/aluminum laminate on the front side (triangles).

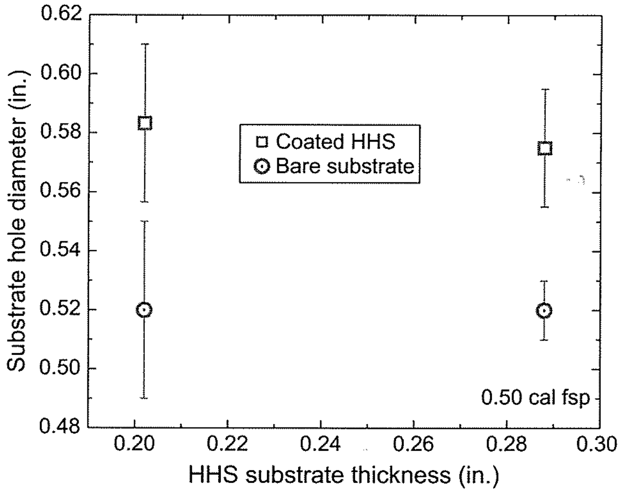

Figure 3.2.4 Comparison of hole size in steel substrate with (squares) and without (circles) PU coating.

3.2.3.2 Effect of Substrate

The mechanisms described above for the coatings, a consequence of the ballistic impact frequency falling with the segmental loss dispersion of the polymer and thereby inducing a viscoelastic phase change, do not directly involve the steel substrate. Rather, the latter's role is simply to ensure the coating is rapidly compressed. Consistent with this is the fact that the ballistic performance was found to be independent of the method of attachment of the coating to the substrate. Adhering the coating with glue, the use of screws, or simply clamping the polymer in place were all found to give equivalent V-50s. Nevertheless, there is some interaction between coating and substrate arising from their close contact. This can be gleaned form in Figure 3.2.6, showing V-50 results for PU coatings against two HHS substrates, having respective Brinell hardnesses equal to 486 and 555. (Note that MIL-A 46100 for HHS specifies a Brinell hardness in the range 477 to 534.) There is a significantly higher V-50 measured for the PU coatings on the harder HHS.

To further elucidate the effect of the substrate, ballistic tests were carried out on the PU coatings on various metals. Assuming additivity of the contributions of each component (which presumes no interaction), the V-50 measured for the substrate was subtracted from that for the coating or substrate bilayer. This difference, representing the isolated contribution from the polymer, is plotted versus substrate hardness in Figure 3.2.7. (These results are for 19 mm thick substrates, which is much thicker than optimal, in order to include older data in the graph.)

Table 3.2.1 Replacing continuous PU coatings with cylinders

Target	V-50 (ft./s)
Bare HHS substrate	2053
Monolithic coating	2866
Cylinders	2616

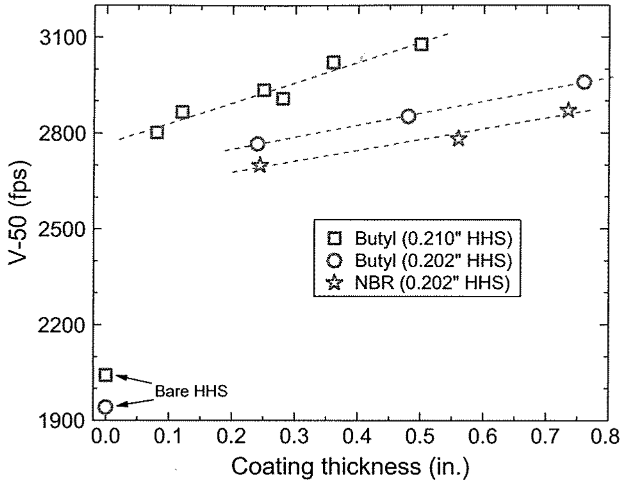

Figure 3.2.5 Ballistic performance (0.50 cal fsp) of steel substrates with coatings of butyl or nitrile rubber. The slopes of the linear range beyond ~0.1" are 340 ft./s per inch (0.202" HHS) and 630 ft./s per inch (0.210" substrate).

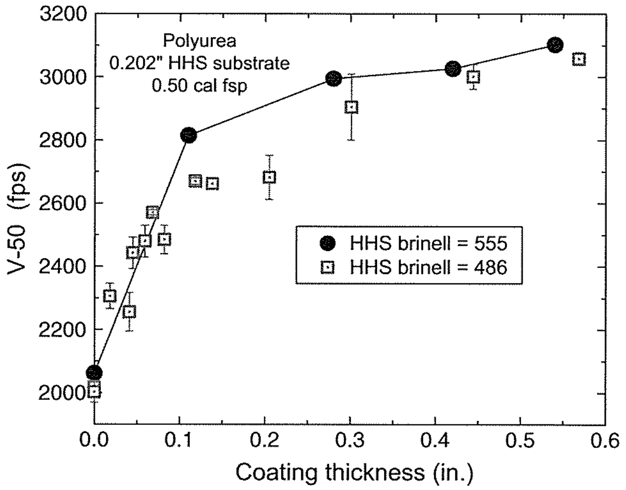

Figure 3.2.6 Ballistic performance of polyurea coatings of varying thickness on HHS of two different Brinell hardnesses; the harder substrate gave better performance. Note the general effect of polymer thickness is similar to the other elastomers in Figure 3.2.5, with most of the performance enhancement due to the first couple mm of coating.

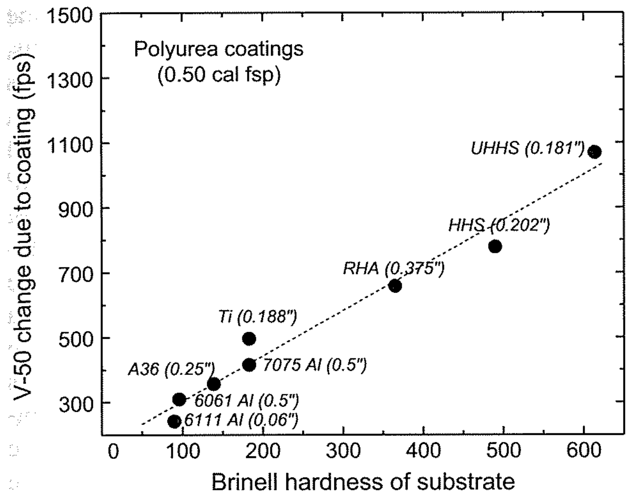

Figure 3.2.7 Isolated contribution of coating to V-50 calculated assuming additivity of coating and substrate. Data have been normalized to 0.75″ coatings. The line through the data is the linear fit, with a Pearson's correlation coefficient of 0.97.

There is a strong correlation between Brinell hardness of the substrate and the V-50 increase due to the coating. Note the control parameter is the substrate hardness, not its bending stiffness; for example, the improvement due to the polymer is uncorrelated with substrate thickness (or the ballistic performance of the substrate absent a coating).

Figure 3.2.8 shows collected ballistic results for coated steel substrates, with variations in the thickness of the coating and substrate. For any areal density (weight per unit area of the bilayer), the penetration velocity of the coated substrate exceeds that of the bare substrate. Included in the figure are data for Rolled Homogeneous Armor (RHA), taken from MIL-DTL-12560 or Gooch and Burkins (2014) [5], a softer steel in long use for military armor. The hardest available substrate was an UHHS (Brinell hardness ≥ 570), and it can be seen that bilayers using UHHS have the best performance, in some cases providing performance equal to bare RHA with more than a twofold reduction in weight.

Although harder substrates improve the contribution of the coating, the V-50 for the bilayer may not be optimized, since of course it depends on the penetration resistance of both the polymer and the steel. An approach to circumvent this limitation is to introduce a thin, very hard layer between the substrate and coating. In this manner the polymer "sees" a hard surface, but the substrate per se can be selected for best V-50 performance. One indication of the utility of this method is the higher V-50 obtained when rust is removed from the substrate prior to application of the coating (Table 3.2.2); removal of this soft rust layer improves the performance of the bilayer.

Preliminary experiments in which a hard coating (e.g., nitride, chrome, etc.) was deposited on the steel substrate prior to addition of the polymer coating yielded further increases in V-50 of almost 10%.

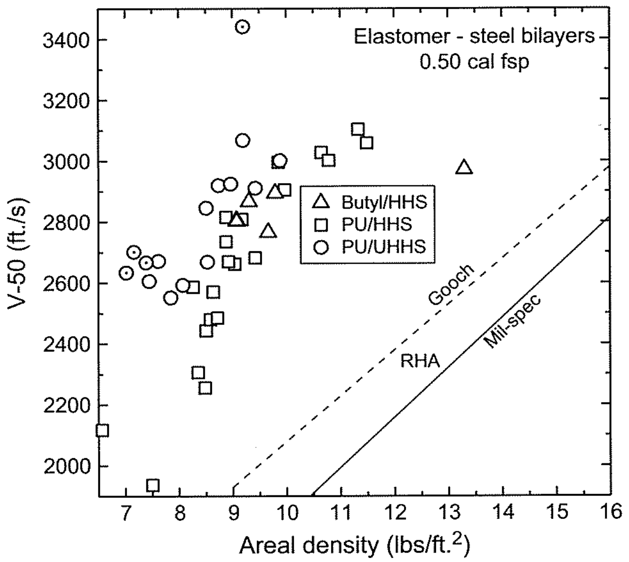

Figure 3.2.8 Penetration velocity of bilayers of butyl rubber over HHS (triangles), and polyurea over HHS (squares) or UHHS (circles). The designs differed in thickness of either the coating or substrate. The lines are results from the literature for RHA (dashed line[5]; solid line from MIL-DTL-12560. The dotted circles are data for bilayers with V-50 equivalent to RHA with a weight reduction of at least a factor of two.

3.2.3.3 Coating Material

Comparing the data in Figures 3.2.5 and 3.2.6, it can be seen that the performance of butyl rubber and polyurea are very comparable. This shows that the characteristic features of PU (polarity, proliferous hydrogen bonding, phase-separated morphology with rigid, small domains) that recommend its use

Table 3.2.2 Effect of rust on bilayer performance (0.11″ PU coatings; 0.50 cal fsp)

Substrate	V-50 (ft./s)	
	Oxidized Surface	Sandblasted
HHS (0.20″)	2735 ± 14	2776 ± 4
UHHS (0.21″)	2795 ± 40	2858 ± 13

in applications where mechanical toughness is paramount, are irrelevant to ballistic mitigation. A high (but subambient) T_g is the essential property of the material. Nevertheless, efforts were directed to improving the material performance through the use of filler reinforcement [6]. Conventionally, elastomers are reinforced with fairly large particles such as carbon black or silica. When 50 phr (parts per hundred parts rubber) N234 carbon black was added to butyl rubber, the V-50 of the bilayer increases about 5%. Polyurea is an ideal nanocomposite, having dispersed hard domains; nevertheless, PU compositions were prepared with low levels of various nanoparticles: nanosilicates (Cloisite 10A), multiwall carbon nanotubes, and polyhedral oligomeric silsesquioxane (POSS). The effect of the reinforcement on the segmental dynamics and ballistic performance was modest. Only the POSS yielded a substantial increase in the magnitude of the mechanical loss peak (almost 30% more energy absorption); however, V-50 of HHS bilayers was only 3% higher than for the neat (unfilled) PU coating.

3.2.3.4 Multiple Bilayers and Laminates

The curious relationship between ballistic performance and coating thickness (Figure 3.2.5), whereby the first few millimeters of coating provide most of the performance gain, suggests the use of multiple bilayers and laminates. Indeed, various configurations involving many repeated layers of metal and polymer have been shown to yield large increases in V-50 at constant areal density [7], The only limitation is that the substrate must be sufficiently thick to avoid out-of-plane flexure, which would diminish the rapid compression of the polymer. An additional mechanism is believed to be operative in such designs, the repeated impedance mismatch between layers. This causes multiple reflections of the pressure wave, increasing its effective path length and hence the dissipation, as well as temporally dispersing the wave.

3.2.3.5 Armor-piercing (AP) Defeat

The results presented above apply mainly to fragment-simulating projectiles, although the technology is also applicable to ball ammunition. The requirement is that the projectile rapidly compresses the rubber coating against a rigid substrate, inducing the viscoelastic phase transition. Unlike the relatively blunt tip of FSP and ball ammunition, AP bullets have a sharp, hard ogive, which cuts and tears the coating, reducing its effectiveness. To overcome this, an AP round must be either rotated or fractured. This can be accomplished by embedding ceramic objects, such as spheres, in the polymer. Ceramic is harder in compression than the steel alloy comprising the AP bullet's core, and thus is able to break up the round. Additionally a spherically shaped ceramic occlusion induces some obliquity, which helps to negate the sharp tip. Conventional use of ceramic suffers a drawback due to its low tensile strength. When the pressure wave reaches the back side, it reflects as an extensional wave. Since the wave speed is typically 3–4 times faster than the projectile velocity, the reflecting tensile wave destroys the ceramic before the incoming bullet has been completed eroded as it traverses the ceramic. This limits the effectiveness, necessitating the use of thicker ceramic. The problem can be overcome with discrete ceramic objects embedded in polyurea or another ballistically effective elastomer. Such an elastomer contains the ceramic as it fractures, so that the fracture particles remain in place. This leads to multihit capability.

The approach has been successively implemented to defeat both 0.30 and 0.50 cal AP bullets. For example, embedded alumina spheres with a Dyneema substrate were able to meet a United States Army Long-Term Armor Strategy (LTAS) specification requiring stopping multiple 0.30 AP rounds. Using a HHS substrate, designs incorporating ceramic spheres in PU passed STANAG 4241 and 4496 specifications, which include stopping multiple 0.50 cal AP rounds.

3.2.4 Summary

For blunt projectiles such as FSPs, the ballistic penetration resistance of steel can be improved more than twofold by application of an elastomeric coating to the strike face. More than one mechanism contributes to the enhanced performance: (1) because the coatings have high (but subambient) glass transition temperatures, their segmental dynamics occur on the timescale of the ballistic impact. This "resonance" condition gives rise to large absorption of the projectile kinetic energy. This mechanism is largely independent of the chemistry of the coating (e.g., polarity, H bonding, filler reinforcement). (2) The impact-induced viscoelastic transition causes transient hardening of the coating at the impact site. This spreads the force laterally, reducing the local pressure and thereby reducing the penetration. (3) Involving an interaction between the coating and substrate that is currently undetermined but likely involves impedance mismatching, harder substrate surfaces enhance the contribution of the coating to the measured penetration resistance. However, greater flexural rigidity (from thicker substrates) has no effect on coating performance per se.

Since the contribution of the coating levels off for thickness beyond a few millimeters, increases in performance can be achieved by multiple bilayer coatings. The limitation of multiple bilayers is the requirement that the substrate be sufficiently rigid to preclude out-of-plane bending. A variation of this approach is to replace the homogeneous coating with alternating thin layers of the polymer and a metal such as aluminum.

AP bullets impose additional requirements of the armor. We have found that discrete ceramic, for example in the form of spheres, functions optimally when contained by an elastomer that is effective as a neat coating. Multihit capability can be achieved, which is not possible with conventional armor designs incorporating ceramic.

Acknowledgments

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3.3 Adhesive and Ultrahigh Strain Rate Properties of Polyurea Under Tension, Tension/Shear, and Pressure/Shear Loadings with Applications to Multilayer Armors

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3.3.1 Overall Structure and Executive Summary of the Chapter

Our research on polyurea started nine years ago. In the beginning, the research was motivated by the desire to find a durable adhesive to join AL-6XN stainless steel plates and E-glass composite sections for lightweight ship construction that could withstand static and dynamic loads during ship operation. To that challenge, a polyurea chemistry was designed that resulted in failures within the E-glass composite section, away from the joint, when the bonded specimens were separated using a double cantilever beam (DCB) experiment. Additionally it was shown that