

## Factors influencing the ballistic impact resistance of elastomer-coated metal substrates

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An experimental study was carried out of various factors affecting the ballistic penetration resistance of elastomer/steel bilayers. For blunt penetrators, the contribution of the coating to performance is optimized using the hardest substrates, front surface placement of the elastomer, and (when normalizing by added weight) thin, ca. 2–3 mm, coatings. These results, none of which are predicted by existing models, evince the marked coupling of coating and substrate in the impact response of the bilayer. We also show that nanoparticle fillers have a modest effect on ballistic performance of polyurea coatings, changing the penetration velocity by a few percent or less. This contrasts with the linear dynamic mechanical behavior, which shows much more significant increases in energy absorption due to nano-reinforcement.

**Keywords:** ballistic impact resistance; elastomer coatings; metal substrates; polyurea

### 1. Introduction

Recent years have seen extensive efforts to improve the performance of armor against ballistic and explosive assault [1]. One important development has been the use of elastomeric coatings on hard substrates to minimize both penetration and blast damage [2–8]. Several elastomers have been shown to function well in this application, and the coating itself can be comprised of different materials [7]. The main requirement is that the polymer undergoes its viscoelastic phase transition upon impact; this means that the frequency of the segmental dynamics of the polymer must correspond to the impact frequency [9]. This empirical discovery is supported by a recent transient, non-linear dynamics finite-element analysis [8]. The impact-induced phase transition effects large energy absorption, which increases the resistance of the material to penetration. Other properties of the coating useful for better performance remain to be explored and, to date, most applications of elastomeric ballistic coatings employ polyurea (PU).

Polyureas are formed from the reaction of isocyanates with polyamines. There are no by-products, and the reaction takes place sufficiently fast that the obtained

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material is unaffected by the ambient temperature and humidity during its formation. The extensive intermolecular hydrogen-bonding of PU, much stronger than H-bonding in polyurethanes, yields “tough” elastomers [10]. The glass transition zone of PU is unusually broad due to the heterogeneous morphology [11], and the glass transition temperature can be controlled by adjustments in the reactants and their stoichiometry [12]. These properties afford a means to ensure that the impact frequency falls within the frequency range of the segmental dynamics, activating the viscoelastic transition. For conventional elastomers, the frequency of the segmental dynamics is determined primarily by the glass transition temperature [13]. For ballistic penetration, impact frequencies are on the order of  $10^5 \text{ s}^{-1}$ , which, for ambient temperature performance, requires the glass transition temperature of the coating to be at least ca.  $-60^\circ\text{C}$ , with higher values required for an optimal response if the breadth of the segmental dispersion is narrow [7,9].

The work herein focuses on polyurea and butyl rubber coatings on metal substrates, identifying characteristics of elastomer–metal bilayers that underlie their ballistic performance. These characteristic properties must be addressed by models that purport to describe or predict the behavior of the bilayers for armor applications. We present recent experimental findings on the effect of the substrate material, specifically its hardness and thickness, the coating location (front or back side), and the relevance of the transient hardening and transverse spreading of the impact force by the coating.

It is common to reinforce elastomers for mechanical applications with hard filler particles, such as carbon black, silica, or more recently nanoparticles. Since substantial concentrations ( $\geq 20\%$  by volume) of conventional fillers are required, their use is contrary to an important advantage of polymer coatings for armor – low weight. However, nanoparticles have very large specific surface areas, so that polymer reinforcement can be achieved at very low concentrations. Since the continuous phase of the soft (predominantly polyamine) domains in PU is inherently reinforced by hard isocyanate domains, the addition of nanoparticles does not change the properties of polyurea as much as homogeneous, single phase elastomers [14]. There have been some recent studies of the effect of added nanoparticles on the properties of polyurea [14–17], and herein we evaluate their effect on ballistic performance.

## 2. Experimental

Results are reported for two coating materials, a vulcanized butyl rubber (Butyl365 from ExxonMobil) compounded with 75 phr N234 carbon black, and a polyurea. For most tests, the latter was formed by the reaction product of a modified methylene diphenyl diisocyanate (Isonate 143 L from Dow Chemical Co.) and polytetramethylene oxide-di-*p*-aminobenzoate (Versalink P1000 from Air Products). Selected experiments, where indicated, used a very similar polyurea provided by Speciality Products Inc., based on oligomeric oxypropylenediamine and diphenylmethane 4,4'-diisocyanate. The nanoparticulates used were: multiwall carbon nanotubes (MWCNT), NC3100 from Nanocyl having an average length of  $1.5 \mu\text{m}$  and a 9.5-nm diameter; nanoclay (Cloisite 10A, montmorillonite modified with a

quaternary ammonium salt; and polyhedral oligomeric silsesquioxane (POSS) functionalized with trisilanolphenyl, from Hybrid Plastics. The concentrations were chosen to optimize conventional mechanical properties without significant particle agglomeration, as determined in a prior study [14]. The particles were incorporated into the polyamine by mechanical mixing, with a solvent (methanol or ethanol) used as necessary to maintain a manageable viscosity. After removal of the solvent, the material was mixed with isocyanate, then poured onto steel substrates to form the coated ballistic test pieces. Dispersion of the particles was assessed from measurement of the low strain dynamic modulus [14]. Additionally, for the nanoclay, intercalation of the polymer into the silicate layers was confirmed by X-ray diffraction [14]. Dynamic mechanical testing of the materials was carried out with an Anton Paar 502 rheometer using a torsional geometry; sample dimensions (mm): width = 12.5, length = 50, thickness = 1.6. A nitrogen atmosphere was maintained during testing.

The ballistic tests were carried out at ambient conditions, following Mil-Std-662F. A rifled Mann barrel fired 0.50 caliber (12.7 mm diameter) fragment-simulating projectiles (fsp) made of steel having a Rockwell C hardness equal to 30. The velocity of the projectile, controlled by changing the quantity of gunpowder, was measured with a pair of tandem chronographs. The penetration velocity (V-50) was determined as the average of the lowest velocity that gave penetration of the target and the highest velocity that did not. Typically testing was carried out until these quantities differed by no more than 15 m/s. Various substrate materials were evaluated: four grades of steel, A36, RHA (MIL-DTL-12560), HHS (MIL-DTL-46100), and UHHS (“ultra” high hard steel); three aluminum alloys, 6111, 6011, and 7075; and titanium (grade 2). For the nanofiller evaluation, however, the only target used was a 5.3-mm thick “high hard steel” (HHS) substrate (Brinell hardness = 500), with a front coating of the elastomeric polyurea. The latter had thicknesses in the range 2.5–19 mm.

### 3. Results

#### 3.1. Interaction of coating and substrate

For blunt projectiles, the principal mechanism imparted by the coating, an impact-induced viscoelastic phase transition with consequent large energy absorption, requires rapid compression of the elastomer. In this regard, the primary function of the metal substrate, other than obviously resisting penetration, is to allow rapid compression of the coating, so that the elastomer is perturbed at frequencies commensurate with its segmental dynamics [9,18]. This mechanism is only active when the coating is on the impact side of the target. When on the back side, there is no rapid compression of the elastomer; the only energy dissipation afforded by the coating is that required for the projectile to tear through a rubbery material, which is relative low. Thus, performance falls off drastically when the coating is on the backside of the target (Table 1). This finding applies to blunt projectiles, such as the fsp used herein. Sharper ogives, such as armor-piercing bullets, may give different results [19].

Table 1. Effect of coating placement on ballistic limit (0.50 cal fps; 19 mm PU/6.4 mm HHS).

Coating	V-50 increase due to coating (%)
Front surface	50.3
Back surface	8.8

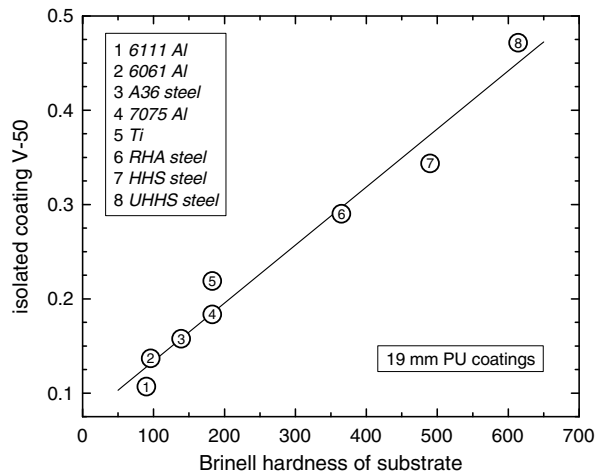


Figure 1. Ballistic penetration velocity of polyurea-coated substrates after subtraction of the V-50 measured for the bare substrate for various substrate metals; values are relative to 7 mm thick RHA. Uncertainty is less than the symbol size. The line is the linear fit (99% correlation coefficient). Substrate thicknesses varied from 2 to 13 mm.

The impact-induced phase transition mechanism implies that the substrate only needs to be stiff enough to avoid out-of-plane bending, which would diminish compression of the coating. Nevertheless, the penetration velocities measured for eight substrate materials having 19-mm PU coatings on the front side reveal an additional effect of the substrate on coating performance. In Figure 1 is the increase of the penetration velocity due to the presence of a coating (i.e. V-50 measured for the coated substrates after subtraction of the corresponding V-50 of the bare substrate) for the different substrate materials. There is a systematic increase in the coating contribution to penetration resistance of the bilayer with increasing substrate hardness. Note the effect is related to the material hardness, and not to the rigidity of the substrate *per se*. This is seen in the V-50 data in Figure 2, showing the ballistic limit measured for the butyl elastomer coating on HHS of varying thickness. The increment due to the coating decreases with substrate thickness (excepting the very thin substrate, which flexed out of plane upon impact, negating rapid compression of the elastomer). The results in these figures demonstrate that there is an effect of the substrate on the coating response; that is, the coating performance is coupled to the mechanical properties of the substrate. Nevertheless, to estimate the isolated effect of

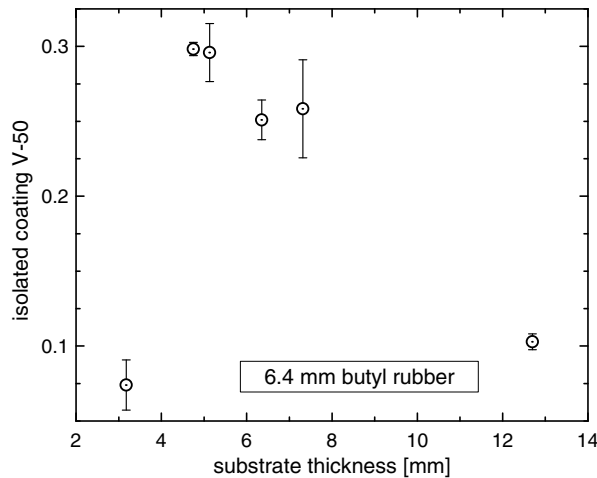


Figure 2. Dependence on substrate thickness of ballistic penetration velocity of coated substrates after subtraction of the V-50 measured for the bare substrate; values are relative to 7 mm thick RHA. Coating was butyl rubber.

the coating on V-50 we assumed that the substrate and coating respective contributions were additive. For this reason the results in Figures 1 and 2 are approximate; however, we can conclude that the coating effectiveness is augmented by harder and thinner substrates. Of course, this refers to the increment in V-50 due to the coating, and not to the ballistic performance of the bilayer.

The interaction between the substrate and coating is also seen in the damage resulting from penetration by the projectile. For example, penetration of uncoated HHS produces a hole about 10% larger than the diameter of the projectile (~14 mm); however, in the presence of a front-side elastomeric coating, this hole in a HHS substrate almost doubles in size, to 26 mm. Similar results were found for softer substrates, although the effect was smaller. For example, the backside hole in the coated Al increased ~40% compared to the size for the bare substrates. This hole enlargement is a consequence of transverse spreading of the impact force by the elastomer, which diminishes the pressure and thereby increasing the velocity required for penetration. This effect can be observed directly by replacing the usual coating (covering the entire front surface of the substrate) with rubber cylinders equal in size to the projectile (see Figure 3). This causes a 25% reduction in the V-50 compared to that of the monolithic coating. The reduction in penetration velocity is a measure of the contribution of lateral spreading of the impact force to ballistic response.

In Figure 4 the penetration velocities measured for the HHS substrate are plotted as a function of coating thickness, for both polyurea and butyl rubber coatings. There is a small increase in performance with increasing thickness, corresponding to about 7 m/s increase per mm of coating; however, extrapolation to zero coating thickness yields a value 35% higher than actually measured for the bare substrate. This indicates that a substantial portion of the energy dissipation occurs in the surface of the coating. Note that the effect is not specific to the coating material; the polyurea and butyl rubber exhibit equivalent behavior. The fact that most of

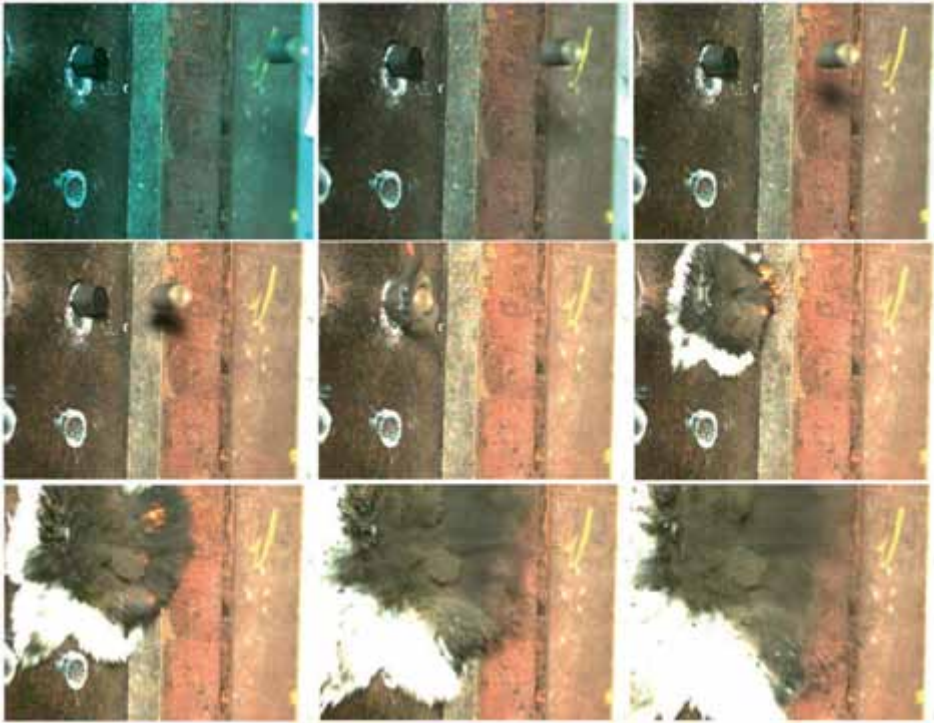


Figure 3. Photographs of 0.50 cal fsp impacting on PU cylinder attached to front face of HHS plate.

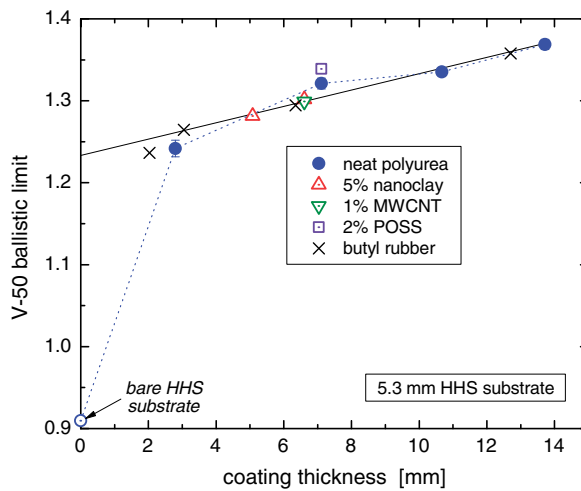


Figure 4. Penetration velocity (relative to the ballistic limit of 7 mm RHA) of steel substrates coated with neat polyurea (filled circles), and PU with added nanoclay (triangles), MWCNT (inverted triangles), and POSS (squares). The solid line is the fit to the neat PU data, which, extrapolated to zero thickness, yields an intercept 35% higher than the V-50 actually measured for the bare substrate (open circle). Also shown are data for butyl rubber (crosses). Error bars are not larger than the symbol size.

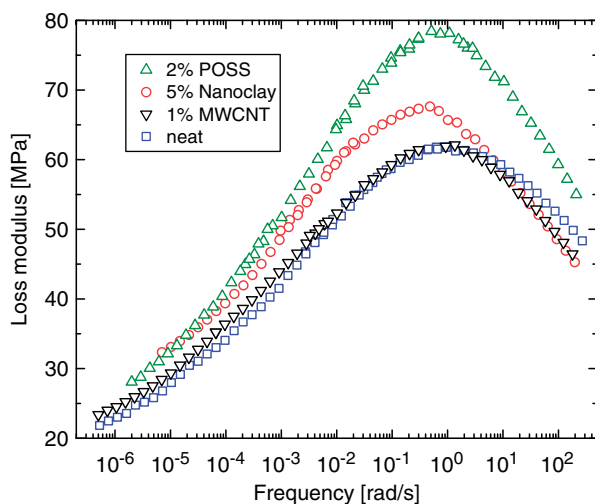


Figure 5. Loss modulus master curves for neat polyurea and the three nanocomposites. The reference temperature is  $-65^{\circ}\text{C}$  for the neat PU; data for the other samples were shifted along the abscissa to make the peaks coincide.

the energy absorption and spreading transpires in the initial 2–3 mm of the polymer can be exploited by using a design with multiple bilayers [7].

### 3.2. Nanoparticle reinforcement of the polyurea

Since small filler particles can affect the segmental mobility of polymers [20–27], and this aspect of the elastomer chain dynamics is related to ballistic properties, we measured the dynamic mechanical response in the glass transition region of the polyurea with various nanoparticles. Master curves of the loss modulus are displayed in Figure 5. These data are obtained in the linear regime, so while an accurate reflection of the frequency of the segmental dynamics, they provide no information on the non-linear response of the coatings to impact.

The area under the loss peaks is a measure of the energy dissipation of the materials. The dispersions are very broad, extending to very high frequencies, which makes integration of the peaks inaccurate. However, since the peak breadths are equivalent (full width at 0.8 maximum =  $4.0 \pm 0.25$  decades), to assess energy dissipation in the neat PU and the nanocomposites, we can compare the peak heights, which are roughly proportional to the peak areas (Note that if the deformation of the coatings was limited by their modulus, the loss tangent, rather than the loss modulus, would be the more appropriate metric of their relative energy dissipation. Near the peak of the loss modulus, the storage modulus of the nanocomposites is about 20% higher than that of the neat polyurea). The results are listed in Table 2, where it is seen that only POSS causes a substantial increase in mechanical energy loss, equal to 24%. This same PU nanocomposite showed a 20% higher toughness compared to neat PU in low strain rate ( $0.06\text{ s}^{-1}$ ) tensile

Table 2. Glass transition of polyurea nanocomposites.

Coating	$T_g$ (°C)	Peak $G''$ (MPa)	V-50 <sup>a</sup>
Neat	-68.7	62	1.30
5% Nanoclay	-68.7	67	1.29
2% POSS	-63.9	76	1.34
1% MWCNT	-63.2	62	1.30

Note: <sup>a</sup>Relative to 7 mm RHA.

measurements [14]. Unlike the other nanoparticles, POSS reacts with the isocyanate and, therefore, alters the crosslinking chemistry and incorporates itself into the PU network.

The penetration velocities measured for the various nanoparticle filled PU coatings over HHS are included in Table 2 and Figure 3. Changes in V-50 due to the nanoparticle reinforcement are negligible. The only (barely) significant effect is from the PU/POSS, which effects a 2.5% increase in penetration velocity. This is not necessarily a consequence of particle reinforcement, since the crosslinking chemistry is affected by POSS, and changes in mechanical properties of the PU can be obtained by varying the stoichiometry of the reactants [12] or varying the processing method [28]. In any case, this increase in V-50 corresponds to an increase in absorbed kinetic energy from the projectile that is five times smaller than the change in the mechanical loss measured at either high (Table 2) or low [14] strain rates; in other words, there is no correlation of the ballistic properties with either low strain/high rate or high strain/low rate mechanical properties of the coating. We can ascribe this disconnect to the effects of strain nonlinearity, which are large [29–31] and rate-dependent [11] for this material. The value of linear dynamic testing is to ensure that the mechanical loss is at its maximum for frequencies relevant to ballistic impact [9]; however, dynamic mechanical properties cannot be used for quantitative predictions of V-50.

#### 4. Conclusions

Various mechanisms have been proposed for the improved resistance of polymer-coated hard substrates to ballistic penetration: delayed onset of necking in the metal [32,33], changes in stress wave propagation [34], viscoelastic phase transition [7–9], etc., but these putative contributions to performance have not been quantified, due to the lack of a comprehensive model of the bilayers under ballistic loading. The difficulty in developing a theory or model can be attributed to three complicating aspects of the elastomer response. (i) The material undergoes a phase transition at a strain rate that depends both on temperature and pressure. Substantial modifications in the physical and mechanical properties of the coating are brought about by this physical change of state. (ii) The polymer is viscoelastic; moreover, the frequency of the material response falls within the polymer segmental relaxation dispersion, for which the rate dependence of the physical properties is greatest. (iii) The mechanical response is highly non-linear, transitioning from a neo-Hookean regime, to yielding and plastic flow, to an upturn in the modulus prior to failure [18,29]. (iv) Polyureas



are intrinsically heterogeneous, with a morphology that changes with both the rate and extent of deformation [30,31]. Furthermore, interaction between the polymer coating and substrate, evidenced by the coupling of the ballistic response to substrate hardness and the anomalous dependence of V-50 on coating thickness, are additional difficulties that make characterization of the individual contributions to the response [35] less directly useful in modeling ballistic properties. Reflecting the difficulty of modeling, we note that among the many efforts to date [4,8,32,33,35–37], none have predicted the effect of substrate hardness (Figure 1), substrate thickness (Figure 2), or coating thickness (Figure 4) on ballistic performance.

The results presented herein show that large energy absorption in the coating due to the viscoelastic phase transition [7–9] is augmented by lateral spreading of the impact force, the latter arising from the transient hardening of the polymer. The failure mechanism of the substrate, shear plugging, is unchanged; however, the area of the plug is larger when the elastomer is present on the front face of the target. This reduces the pressure and thus increases the resistance to penetration.

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