**PROTECTION OF STEEL RAILCAR TANK CONTAINING LIQUID CHLORINE FROM HIGH SPEED
IMPACT BY USING POLYHEDRAL OLIGOMERIC SILSESQUOXANE-ENHANCED POLYUREA**

Liguang Cai ¹, Ahmed Al-Ostaz^{1*}, Xiaobing Li¹, Cole Fowler¹, Alexander H.-D. Cheng¹ and

Hunain Alkhateb¹

¹Nano Infrastructure Research Group, Department of Civil Engineering University of Mississippi

University, Mississippi, 38677, USA

* Corresponding author: alostaz@olemiss.edu

ABSTRACT

The ballistic resistance and self-sealing behavior of polyhedral oligomeric silsesquioxane (POSS)-enhanced polyurea (PU) coated TC-128 steel plates subjected to high speed impact were investigated experimentally and numerically using ANSYS AUTODYN. Both experimental and numerical results showed that the POSS-enhanced PU exhibited strong self-sealing properties under high-speed impact and could dramatically reduce leaking of toxic liquid from a hole in the railcar tank. Experimental results and simulation results agreed well for the ballistic limit of POSS-enhanced PU coated and uncoated TC-128 steel plates, with an average error of 5.72%. In terms of the size of hole left after the impact test, although the simulation result for the uncoated TC-128 steel plate was almost identical to the experimental result, the simulation result for the POSS-enhanced PU coating layer was doubled compared to the experimental result, probably due to the mass erosion effect. The POSS-enhanced PU material may serve as a class of effective protective coating layers to reduce the leaking of toxic chemicals from steel railcar tanks.

Keywords: ballistic resistance; self-sealing; POSS-enhanced polyurea; nano reinforcement; AUTODYN simulation.

1. INTRODUCTION

Steel railcar tanks provide a promising way to store and transport toxic liquids such as chlorine [1]. However, the release of toxic liquids from holes in the tanks, caused by accidents or high power impacts, is very harmful to the environment and even has deadly impacts on human health [2-4]. Therefore, the emergence of ballistic protection for these tanks lead to a critical need to develop effective techniques to prevent the leaking of toxic liquids.

In the last few decades, elastomers have been increasingly incorporated into more efficient lightweight protection layers. This is due to their high viscoelasticity, and thus their mechanical properties are strongly rate-dependent [5]. Polyurea (PU) is a type of elastomer that is derived from the reaction product of an isocyanate component and an amine (organic chemical containing amine-NH₂ groups) [6]. PU is an inexpensive and abrasion resistant material, and is an excellent candidate for spray coating applications on large steel plates (e.g., railcar tanks) [7]. It has been found that PU has the capability of sustaining very large deformations, a trait which can be exploited to absorb energy [8]. Therefore, it appears that PU is a promising material for blast/shock mitigation applications.

When used as a coating material, researchers have found that PU can increase the impact resistance of substrates [9-13], and mitigate the blast wave impact [14]. Xue et al. [11] reported that the PU coating provided additional resistance in terms of energy absorption through two mechanisms: (1) the increase in the energy dissipated by the steel plate and (2) the increased energy stored in the polyurea itself. Moreover, PU can stretch to several times its initial length under loading and then almost return to its original dimensions upon unloading [15], which demonstrates the strong self-sealing properties of PU. Therefore, PU is very effective at preventing the leaking of toxic liquids from holes in the railcar tanks when it is used as a coating

to improve the ballistic resistance of railcar tanks and to self-seal the holes in the tank wall if the projectile perforates both the steel tank and PU coating layer.

In this paper, the effect of polyhedral oligomeric silsesquioxane (POSS) on increasing the mechanical properties of PU was studied. TC-128 steel plate is one of the widely used steel materials for railcar tanks. The ballistic resistance and self-sealing behavior of a POSS-enhanced PU coated TC-128 steel plate under high-speed impact was investigated experimentally and numerically. Grujicic et al. [14] investigated computationally the blast wave impact-mitigation capability of polyurea when used as helmet suspension-pad materials. The effect of deformation rate and temperature on the material response of PU was discussed by evaluation of deviatoric stress at the current time t for entire deformation history [16, 17]. In this research, for the numerical simulation, ANSYS AUTODYN was used, and the Ogden 3rd order material model [18] was applied for the POSS-enhanced PU since this model can be applied to materials that have a yield strain up to 700% [19]. For comparison, the ballistic test and numerical simulation results for the uncoated steel plate are also presented in this paper.

2. EXPERIMENTAL

2.1 Materials

In this study, the pure PU used consists of diamine and diisocyanate components that are commercially available. The diamine component is Versalink P-1000 (VP1000), purchased from Air Products and Chemicals, Inc., Allentown, PA, USA. The diisocyanate component is Isonate 143 L, which was purchased from Dow Chemical Company, Midland, MI, USA. Pure PU was made by mixing VP 1000 and Isonate 143L at the weight ratio of 4:1. The mixture was transferred to a Teflon mold (300 mm x 300 mm) and cured at 80 °C for 4 hrs, as shown in Fig. 1.

If bubbles were found in the VP1000, the transferred VP1000 should first be placed in the oven for degassing at around 80 °C for half an hour prior to mixing.

POSS is a class of silicon-based nanochemicals designed to fulfill various mechanical functions. In this study, two types of POSSes with different functionalities were used in PU. Amine POSS (AM0281) has eight secondary amine groups, and epoxy POSS (EP0409) has eight epoxy groups anchored at the eight corners of POSS cage, respectively. The NH groups may react with isocyanate ($-N=C=O$) groups in PU while the epoxy groups may react with amines in PU so that the embedded POSS may have an enhanced interaction with the PU matrix. The POSS compounds were purchased from Hybrid Plastics Inc., Hattiesburg, MS, USA. The PU composites contained a POSS loading of 0, 1, 2, 3 or 4 phr. (The unit phr denotes parts per hundred rubber.)

For the POSS-enhanced PU, POSS was transferred to a disposable plastic cup followed by the addition of VP1000 and mixing. These two components were heated in an oven at 80 °C for one-hour degassing during which they were additionally stir-mixed twice. Then a right amount of Isonate 143L was added and quickly mixed typically within one minute. The mixture was transferred to a Teflon mold (300 mm x 300 mm) to be cured under 80 °C for 4 hours, as shown in Fig. 1. To control the thickness of a sheet, a Teflon U-strip spacer was clamped.

The steel plates for the ballistic test were TC-128 steel, and they were purchased from Clifton Steel Company, Maple Heights, OH, USA. For the POSS-enhanced PU coated steel plate, a Teflon mold was mounted to the plate itself as shown in Fig. 2. Small spacers were used to ensure a uniform coating thickness of 12.7 mm. The resin was poured from the top down into the volume between the spacers. Around the edges, clear tape was used to prevent the viscous

coating from escaping. Once all of the plates were constructed, they were each cured in an oven at 80 °C for 4 hours.

2.2 Tensile test

2.2.1 Test description

Tensile tests were performed for the epoxy and amine POSS-enhanced PU using an Instron 5982 dual column floor model test system at room temperature as shown in Fig. 3(a). Fig. 3(b) shows the PU samples with different loadings of epoxy POSS shown with two white marks. For hyperelastic materials, the grip sections of samples are also stretched during the test, which will cause error in the strain calculation. The video extensometer mounted on an Instron 5982 dual column floor model test system was used to capture the movement of the two white marks on the samples during the testing. Data captured from the video provided a relative gauge length measurement regardless of the absolute movement of the grips, which provided more accurate results for the strain calculation. Another issue with hyperelastic materials is the Poisson's effect at the grip surface, which can cause slippage. This effect was combated with the use of pneumatic grips that supplied a constant pressure along the grip surface throughout the test. Each specimen was secured with grips set at approximately 30-35 psi. As outlined in ASTM D412-06 [20], the strain rate for each test was 0.33/s.

2.2.2 Tensile test results

Fig. 4 plots the ultimate true stress and true strain of PU with different phr of epoxy and amine POSSes. Compared with pure PU, the PU with different concentrations of amine POSS all have smaller ultimate true stresses and true strains while there was a distinct increase in the

ultimate true stresses and true strains when adding different amounts of epoxy POSS. The PU/3phr epoxy POSS, which has the highest material properties, was used as the coating layer for the TC-128 steel plates.

2.3 Ballistic limit test

2.3.1 Ballistic limit test description

The ballistic limit test was performed at H. P. White Ballistic Laboratory in Street, MD, USA. During the test, a standard 0.50 caliber M33 ball was shot into the plates which were mounted on a rigid support structure. The parameters of the 0.50 caliber M33 ball round are tabulated in Table 1. The target plates were secured to a floor-mounted heavy steel rack 7.6 meters from the test barrel. The plates were secured to the rack by C-clamps. A laser leveling device was used to align each shot. Two photoelectric infrared screens, placed three and six meters forward from the barrel, were used in conjunction with a chronograph in order to calculate the average velocity of the projectiles, as shown in Fig. 5. The velocities were manipulated by increasing or decreasing the amount of propellant used in each cartridge.

A 0.50 mm thick sheet of 2024-T3 aluminum was used as a witness plate to determine partial or complete penetration. At least three shots had to penetrate and three had to not penetrate to get the ballistic limit of the plates. So, the plates were shot multiple times, until sufficient data was gathered to quantify an accurate ballistic limit. After the test, the sizes of the holes produced by the impacts were measured.

Fig. 6 shows the configurations of the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates for the ballistic limit tests. A PU/3phr epoxy POSS layer was placed in front of the

TC-128 steel plate in order to seal the hole produced by the bullet impact. The dimensions of the PU/3phr epoxy POSS and TC-128 steel layers are both 300 mm × 300 mm. The thicknesses of the PU/3phr epoxy POSS and TC-128 steel plate layers are 12.7 mm and 19.05 mm, respectively.

2.3.2 Ballistic limit test results

The ballistic test results for the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates are summarized in Table 2. The ballistic limits for the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates were 972 m/s and 971 m/s, respectively. Therefore, the PU/3phr epoxy POSS coating layer did not have a drastic effect on the ballistic resistance of the steel substrates.

Xue et al. [11] reported that when PU is used as a coating layer on the "front side" of steel plate, the stretching, which is the primary energy absorption mechanism of the PU layer, is constrained by the steel plate. This might be one reason that coating layer did not increase the ballistic resistance of the steel plate. However, Roland et al. [13] found that the front-surface elastomer layers can significantly increase the ballistic limit of high hard steel (HHS), which indicates that the hardness of the steel substrate can largely affect impact resistance enhancement for the substrate plate due to an elastomeric coating. Leblanc et al. [21] showed that the thickness of the PU layer on the front surface of a substrate can also play a very important role in improving the performance of curved E-Glass/Vinylester composite panels under explosive loading. Therefore, the impact resistance enhancement for the substrate plate due to the PU coating layer depends largely on the details of the particular impact scenario. Due to the potential reaction between PU/3phr epoxy POSS and chlorine, the ballistic tests for TC-128 steel plate with PU/3phr epoxy POSS layer coated on the back side were not considered in this study.

Figs. 7(a)-(i) display the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates at and after impact. It can be seen from Fig. 7(a)-7(d) that the impact generated a large crater and that the rubber coating was stretched significantly. During impact, the size of the hole in the PU/3phr epoxy POSS coating layer increased first and then decreased. The impact also resulted in the loss of a large amount of mass, as shown in Fig. 7(d). Even so, the crater in the PU/3phr epoxy POSS coating material after the impact was no more than 4.5 mm in diameter as shown in Figure 7(e), while the hole on the back side (steel side) remained about 16 mm as shown in Figure 7(f). Fig. 7(e) also reveals the "brittle" failure of the coating layer which is due to a transition of the coating layer from a "rubbery" state to a "glassy" state induced by the high-speed impact [13]. This "brittle" failure led to a global de-lamination and some material loss during the test. Figs. 7(g)-(i) display the control steel plate after impact. The uncoated TC-128 plate had an average crater diameter of 15 mm or larger either on the front or on the back side.

Hyperelastic materials respond elastically even when subjected to very large strains. No plastic strain remained under the unloading condition after impact. So, the hole should be completely closed after impact. There are many reasons to explain why the PU/3phr epoxy POSS coating layer did not completely self-seal the holes. The primary reason is that the PU/3phr epoxy POSS coating layer exhibits "glassy" behavior under high strain rates [13] and loses the ability to seal holes. Another reason is that PU/3phr epoxy POSS is not a purely hyperelastic material even in its "rubbery" state. There is still some plastic strain after unloading [15]. Also, the formation of small shear plugs at the bullet tip of impact site [22] is another possible reason why the hole cannot seal totally. The large mass loss shown in Figs. 7(a)-(d) should be partially attributed to the shear plugs from projectile. Therefore, a thicker layer of coated elastomer will be desirable to accommodate the mass loss and ensure that the remaining elastomer is enough to

seal the cut-through hole completely. It is anticipated that the result may be dependent on the thickness of the elastomer coating layer along with the diameter of projectile and the impact velocity. Impact with a high-speed projectile could obviously cause “brittleness” in the impacted layer and generate more mass loss of material because the failure occurs at very small strains [13]. Indeed, we observed in another experiment that the layer of PU/POSS rubber (4-6 mm thick) completely sealed the holes from small projectiles (~4.5 mm in diameter) at lower speeds, regardless of complete or partial penetration; however, those results are not reported here.

3. FINITE ELEMENT ANALYSIS

3.1 Material model

3.1.1 Projectile

The two main components of the projectile are a copper jacket and a steel core. During the test, the copper jacket was totally ripped off. This happened because the strength of the copper jacket is so small compared to that of the TC-128 steel plate. In addition, T. Børvik et al [23] found that a brass jacket, which has a much higher strength than a copper jacket, has almost no influence on the ballistic limit of steel targets. So, for all the simulations, the steel core was used to represent the whole projectile.

The equation of state (EOS) of the steel core is linear and defined as:

$$P = ku \tag{1}$$

Where k is the material bulk modulus, and u is the specific volume.

For the strength model, the material properties of the steel core are still uncertain because the required test data are generally not available in the literature. The Rockwell C hardness (HRC) value of the steel core, which is the only known parameter, is equal to 53 and was provided by the H. P. White Company. So, the tensile test data of Arne tool steel with an HRC value equal to 53 was used for the steel core [24]. The bilinear hardening strength model was used to fit the experimental data. The expression of the bilinear hardening strength model is,

$$\sigma = \begin{cases} E\varepsilon & \varepsilon \leq \varepsilon_0 \\ \sigma_0 + E_t(\varepsilon - \varepsilon_0) & \varepsilon > \varepsilon_0 \end{cases} \quad (2)$$

Where E is Young's modulus, and E_t is the tangent modulus.

The failure model for the projectile was not considered at this stage, but the erosion technique was used to represent the failure of the projectile material. This element is deleted from further calculation if the effective plastic strain (EPS) in that element reached a value of 1. The model constants for the projectile are reported in Table 3.

3.1.2 TC-128 Steel Plates

The EOS of TC-128 steel can also be described by (1), which only needs one parameter.

For the strength model, the quasi-static tensile test was performed for the TC-128 steel plate at room temperature and at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The engineering stress-strain curve and true stress-strain curve are plotted in Fig. 8. The piecewise model, a modification model to the Johnson-Cook model (JC model), was used as the strength model for the TC-128 steel plate. For the JC model, the stress can be expressed as a function of strain, strain rate and temperature, ie:

$$\sigma = [A + B\varepsilon_{pl}^n][1 + C\ln\dot{\varepsilon}_{pl}][1 - T_{H0}^m] \quad (3)$$

Where ε_{pl} is the equivalent plastic strain; $\dot{\varepsilon}_{pl}$ the equivalent plastic strain rate; A, B, and C are material parameters (A is the initial yield stress, B is the hardening constant, and C is the strain rate constant); n and m are the hardening exponent and thermal softening exponent respectively; and $T_{H0} = (T - T_{room})/(T_{melt} - T_{room})$ and is the nondimensional normalized (homologous) temperature (the room temperature is T_{room} , and T_{melt} is the melting temperature).

For the piecewise model, the strain rate hardening and thermal softening parts are the same as in the JC model while the strain hardening part $[A + B\varepsilon_{pl}^n]$ in JC model is replaced by a piecewise linear function of yield stress versus effective plastic strain. In AUTODYN software, the strain hardening part of the piecewise model can be obtained with up to ten EPS and yield stress (YS) data points. For the strain rate constant C and thermal softening exponent m, the parameters of weldox 460 E steel, which has almost the same yield strength and ultimate strength as TC-128 steel, are used here [25].

The failure model of TC-128 steel is based on the EPS value. When the EPS exceeds 1, element failure occurs. The model constants for the TC-128 steel plate are summarized in Table 4.

3.1.3 PU/3phr epoxy POSS

The numerical simulation is performed on the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates subjected to impact. It assumes here that the material properties of the base material of the PU/3phr epoxy POSS layer and the bond between the PU/3phr epoxy POSS and

the steel plate are the same [11]. So, the following material models and model constants are applied to both materials.

A hyperelastic equation of state is used for PU/3phr epoxy POSS. Specific heat and thermal conductivity are the two parameters that need to be defined for this EOS. Currently, the hyperelastic EOS can be used in the Lagrange unstructured solver, in which the thermal conductivity had been set to 0. The specific heat of PU/3phr epoxy POSS at 293 K was set as 1240 j/(kg. K) [26].

The PU/3phr epoxy POSS material properties at high strain rates are estimated based on the Xue's study [11] on polyurea at a low strain rate of 0.33/s. Because our PU/3phr epoxy POSS materials exhibited an almost identical stress-strain curve to the PU material at the strain rate of 0.15/s used in Xue's study [11], the stress-strain curve of PU at a strain rate of 10000/s [11] was used for our PU/3phr epoxy POSS material at a high strain rate. Fig. 9 plots the stress-strain curve of PU at strain rate=10000/s by an Ogden 3rd order, and it shows that the model fits the experimental data quite well. The strain energy function for this hyperelastic strength model is defined as

$$\begin{aligned} \varphi = & \frac{\mu_1}{\alpha_1} (\overline{\lambda_1^{\alpha_1}} + \overline{\lambda_2^{\alpha_1}} + \overline{\lambda_3^{\alpha_1}} - 3) + \frac{\mu_2}{\alpha_2} (\overline{\lambda_1^{\alpha_2}} + \overline{\lambda_2^{\alpha_2}} + \overline{\lambda_3^{\alpha_2}} - 3) \\ & + \frac{\mu_3}{\alpha_3} (\overline{\lambda_1^{\alpha_3}} + \overline{\lambda_2^{\alpha_3}} + \overline{\lambda_3^{\alpha_3}} - 3) + \frac{1}{d_1} (J-1)^2 + \frac{1}{d_2} (J-1)^4 + \frac{1}{d_3} (J-1)^6 \end{aligned} \quad (4)$$

Where λ_p is deviatoric principal stretches of the left Cauchy-Green tensor, J is the determinant of the elastic deformation gradient, and μ_p , α_p and d_p are material constants (Here p=1,2,3)

Principal tensile failure strain (PTFS) was applied as the failure criterion for PU/3phr epoxy POSS. If the values of PTFS in the element reach 5.54, then the element cannot sustain any tensile stress. The model constants for PU/3phr epoxy POSS are reported in Table 5.

3.2 Model architecture

Fig. 10 shows the configuration of the PU/3phr epoxy POSS coated and uncoated TC-128 steel plates built in AUTODYN. Lagrange solvers were used to represent the bullet and PU/3phr epoxy POSS, and the numbers of the elements of the bullet and PU/3phr epoxy POSS are 2032 and 10800, respectfully. The TC-128 steel was represented by 14400 particles using a smoothed-particle hydrodynamics (SPH) solver. Interaction between different layers is modeled with a Lagrange-Lagrange interaction. The dimensions of the TC-128 steel and coating layer are 300 mm long $\times$ 300 mm wide for the model. A fixed boundary condition was applied at the top and bottom edge of the steel and coating layer. The impact velocity of bullet was increased from 800 m/s to 1000 m/s to determine the ballistic limit of PU/3phr epoxy POSS coated and uncoated steel plate. Geometry strain is used as the erosion criteria and 3 is the erosion limit for the PU/3phr epoxy POSS. The element is deleted from further calculation if the geometry strain in that element reaches 3.

3.3 Result and discussion

3.3.1 Comparison between the experimental and simulation results

The numerical results in terms of the ballistic limits of PU/3phr epoxy POSS coated and uncoated TC-128 steel plates subjected to high-speed impact are reported in Table 6. The ballistic limit in Table 6 is equal to the average value of the minimum full penetration velocity and maximum partial penetration velocity. For PU/3phr epoxy POSS coated and uncoated TC-

128 steel plates, the ballistic limits are 875 m/s and 955 m/s, respectively. The simulation results slightly overestimate the impact resistance improvement of the TC-128 steel plate after adding the PU/3phr epoxy POSS coating, which is probably due to the neglect of the temperature effect on the material response of PU/3phr epoxy POSS. Fig. 11 shows a comparison of the experimental and numerical results of the ballistic limit. The numerical simulation results agree quite well with the experimental results and the average error is approximately 5.72%.

Fig. 12 shows a snapshot of the uncoated and PU/3phr epoxy POSS coated TC-128 steel plates impacted at a velocity equal to 1000 m/s. For the uncoated steel plate, the hole size increased from 0 to 15.1 mm and then remained constant while the size of the hole left in the PU/3phr epoxy POSS layer increased from 0 to 17.1 mm and then decreased to 9.1 mm. So, the PU/3phr epoxy POSS coating layer exhibited self-sealing properties, even though a small hole remains. The simulation model did not capture the transition of the coating layer from the "rubbery" state to the "glassy" state because of the limitations of the material model. Therefore, for the simulation model, no "brittle" failure behavior has been found for the coating layer after impact

Fig. 13 compares the experimental and simulation results in terms of the size of the hole left in the uncoated TC-128 steel plate and PU/3phr epoxy POSS coating layer. It shows that the simulation results for the uncoated TC-128 steel plate are almost the same as the experimental results while the simulation results for the PU/3phr epoxy POSS coating layer are approximately doubled compared to the experimental results. The overestimation of the size of the hole left in the PU/3phr epoxy POSS coating layer is due to the mass loss which is caused by element erosion. However, the mass of the TC-128 steel plate remained the same when using the SPH solver, which is a meshless technique for which no erosion technique is needed for a large

deformation simulation [27]. So, mass erosion is the reason why the simulation results in terms of the size of the hole left in the PU/3phr epoxy POSS coating layer are much higher than the experimental results while the size of the hole in the uncoated TC-128 steel plate is the same as in the experimental results.

4. CONCLUSION

In this research, the experimental tests and numerical simulations were performed to study the ballistic resistance and self-sealing behavior of PU/3phr epoxy POSS coating layers subjected to high-speed impact. The experimental results showed that although the coating layer did not increase the ballistic limit of the TC-128 steel plate, it exhibited a strong self-sealing property. After ballistic limit tests, the size of the hole left in the PU/POSS coating layer was no more than 4.5 mm, while the hole was 15 mm for the uncoated TC-128 steel plate. The limited size of the holes on the PU/POSS coating layer after impact might be attributed to a significant loss of mass upon high-speed impact. Perhaps the mass loss exceeded the recovery capability of PU/POSS rubber. However, the coating layer could still substantially limit the leaking of toxic liquid from the hole on the railcar tank.

Numerical simulations of the impact of a standard 0.50 caliber M33 ball on PU/3phr epoxy POSS coated and uncoated TC-128 steel plates were conducted using AUTODYN. Close agreements were found between the experimental results and simulation results for the ballistic limit of coated and uncoated TC-128 steel plates and the average error was 5.72%. Also, the simulation results in terms of the size of the hole left in uncoated TC-128 steel plates were nearly in agreement with the experimental results. The simulated hole left in the coating layer was 97.8% greater than the experimental result due to mass erosion. For all the simulations, the effect

of temperature on the PU was not considered, due to the limitation of the built-in material model in AUTODYN. In the future, user-defined material models could be developed and combined with the SPH solver, which could better simulate the impact of a bullet on PU coated TC-128 steel plate in terms of ballistic limit improvement and final hole size.

In summary, the POSS-enhanced polyurea may serve as a promising self-sealing coating material. As an elastomer, it has a very strong ability to restore its original shape. The sealing capacity may be dependent on the size of projectile along with the thickness of the elastomer coating and the speed of projectile, for which further studies will be needed.

5. ACKNOWLEDGEMENTS

Authors acknowledge the financial support received under a subcontract from the Department of Homeland Security-sponsored Southeast Region Research Initiative (SERRI) at the Department of Energy's Oak Ridge National Laboratory for this research work.

REFERENCE

- [1] BJM A, GAM G, D G, K H, LAM J, SR S. Benchmark risk analysis models. 2002.
- [2] Hanna S, Dharmavaram S, Zhang J, Sykes I, Witlox H, Khajehnajafi S, et al. Comparison of six widely-used dense gas dispersion models for three recent chlorine railcar accidents. *Process Saf. Prog.* 2008;27:248-59.
- [3] Saat MR, Barkan CPL. The Effect of Rerouting and Tank Car Safety Design on the Risk of Rail Transport of Hazardous Materials. 7th World Congress on Railway research. 2006.
- [4] Hanna SR, Hansen OR, Ichard M, Strimaitis D. CFD model simulation of dispersion from chlorine railcar releases in industrial and urban areas. *Atmos. Environ.* 2009;43:262-70.

- [5] Roland CM, Twigg JN, Vu Y, Mott PH. High strain rate mechanical behavior of polyurea. *Polymer* 2007;48:574-8.
- [6] Grujicic M, Pandurangan B, Bell WC, Cheeseman BA, Yen CF, Randow CL. Molecular-level simulations of shock generation and propagation in polyurea. *Mater. Sci. Eng., A* 2011;528:3799-808.
- [7] Amini MR, Isaacs J, Nemat-Nasser S. Investigation of effect of polyurea on response of steel plates to impulsive loads in direct pressure-pulse experiments. *Mech. Mater.* 2010;42:628-39.
- [8] Choi T, Fragiadakis D, Roland CM, Runt J. Microstructure and Segmental Dynamics of Polyurea under Uniaxial Deformation. *Macromolecules* 2012;45:3581-9.
- [9] Amini MR, Isaacs JB, Nemat-Nasser S. Experimental investigation of response of monolithic and bilayer plates to impulsive loads. *Int J Impact Eng* 2010;37:82-9.
- [10] Amini MR, Amirkhizi AV, Nemat-Nasser S. Numerical modeling of response of monolithic and bilayer plates to impulsive loads. *Int J Impact Eng* 2010;37:90-102.
- [11] Xue L, Mock Jr W, Belytschko T. Penetration of DH-36 steel plates with and without polyurea coating. *Mech. Mater.* 2010;42:981-1003.
- [12] Mohotti D, Ngo T, Mendis P, Raman SN. Polyurea coated composite aluminium plates subjected to high velocity projectile impact. *Materials & Design* 2013;52:1-16.
- [13] Roland CM, Fragiadakis D, Gamache RM. Elastomer–steel laminate armor. *Compos. Struct.* 2010;92:1059-64.
- [14] Grujicic M, Bell WC, Pandurangan B, He T. Blast-wave impact-mitigation capability of polyurea when used as helmet suspension-pad material. *Materials & Design* 2010;31:4050-65.

- [15] Yi J, Boyce MC, Lee GF, Balizer E. Large deformation rate-dependent stress–strain behavior of polyurea and polyurethanes. *Polymer* 2006;47:319-29.
- [16] Grujicic M, Pandurangan B, He T, Cheeseman BA, Yen CF, Randow CL. Computational investigation of impact energy absorption capability of polyurea coatings via deformation-induced glass transition. *Materials Science and Engineering: A*. 2010;527:7741-51.
- [17] Grujicic M, Snipes J, Ramaswami S, Galgalikar R, Runt J, Tarter J. Molecular-and domain-level microstructure-dependent material model for nano-segregated polyurea. *Multidiscipline Modeling in Materials and Structures*. 2013;9:548-78.
- [18] Ogden RW. Large Deformation Isotropic Elasticity - On the Correlation of Theory and Experiment for Incompressible Rubberlike Solids. *Proceedings of the Royal Society of London A Mathematical and Physical Sciences*. 1972;326:565-84.
- [19] ANSYS AUTODYN version 11.0 what is new? :<http://www.ewp.rpi.edu/hartford/~ernesto/F2010/EP1/Materials4Students/Danyluk/autodyn-new-features.pdf>.
- [20] ASTM D412-06, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension.
- [21] LeBlanc J, Gardner N, Shukla A. Effect of polyurea coatings on the response of curved E-Glass/Vinyl ester composite panels to underwater explosive loading. *Composites Part B* 2013;44:565-74.
- [22] Backman ME, Goldsmith W. The mechanics of penetration of projectiles into targets. *Int. J. Eng. Sci.* 1978;16:1-99.
- [23] Børvik T, Dey S, Clausen AH. Perforation resistance of five different high-strength steel plates subjected to small-arms projectiles. *Int J Impact Eng* 2009;36:948-64.

- [24] Børvik T, Hopperstad OS, Berstad T, Langseth M. A computational model of viscoplasticity and ductile damage for impact and penetration. *Eur J Mech A-Solid* 2001;20:685-712.
- [25] Dey S, Børvik T, Hopperstad OS, Leinum JR, Langseth M. The effect of target strength on the perforation of steel plates using three different projectile nose shapes. *Int J Impact Eng* 2004;30:1005-38.
- [26] Katti KS, Urban MW. Conductivity model and photoacoustic FT-IR surface depth profiling of heterogeneous polymers. *Polymer* 2003;44:3319-25.
- [27] Hayhurst CJ, Clegg RA. Cylindrically symmetric SPH simulations of hypervelocity impacts on thin plates. *Int J Impact Eng* 1997;20:337-48.

Table 1 Parameters of the 0.50 caliber M33 ball round.

Diameter (mm)	Length (mm)	Projectile weight (g)	Velocity (m/s)
12.7	138.4	42.96	914

Table 2 Ballistic test results for PU/3phr epoxy POSS coated and uncoated steel plate.

Configuration	Shot	Velocity (m/s)	Result	Include	V50 (m/s)	Range
Uncoated steel plate	1	927.5	P	N	971	8.8
	2	928.1	P	N		
	3	NR	C	N		
	4	970.8	C	Y		
	5	967.4	P	Y		
	6	976.3	C	Y		
	7	969.6	P	Y		
PU/3phr epoxy POSS coated steel plate	1	968.7	C	Y	972	16.5
	2	951.6	P	N		
	3	959.8	P	N		
	4	975.7	C	Y		
	5	973.5	P	Y		
	6	961.9	P	Y		
	7	976.3	P	Y		
	2	978.4	C	Y		
	3	1023.5	P	N		

V-50: Ballistic limit P: Partial penetration C: Complete penetration Y: Include for V-50 calculation N: Do not include for V-50 calculation

Table 3 Model constants for projectile.

Equation of State				Strength Model			Erosion
ρ (g/cm ³)	K (GPa)	T _o (K)	C _p (j/(kg. K))	G (GPa)	σ_o (MPa)	E _t (GPa)	EPS
7.75	200	300	477	76.69	1,900	15,000	1

Table 4 Model constants for TC-128 steel.

Equation of State				Failure model
ρ (g/cm ³)	K (GPa)	T _o (K)	C _p (j/(kg. °K))	EPS
7.98	181	300	455	1

Strength Model							
G (GPa)	σ_o (MPa)	EPS 1~6					
76	455	0.0004	0.0057	0.03	0.1	0.17	0.2

Strength Model									Failure model
ES 1~6 (MPa)						C	m	T _m (°K)	EPS
448	446	506	646	704	707	0.006	0.893	1800	1

Table 5 Model constants for PU/3phr epoxy POSS.

Equation of State			Failure model
ρ (g/cm ³)	T _o (K)	C _p (j/(kg. K))	PTFS
1.07	293	1240	3.5

Strength Model								
μ_1 (KPa)	α_1	d ₁ (/KPa)	μ_2 (KPa)	α_2	d ₂ (/KPa)	μ_3 (KPa)	α_3	d ₃ (/KPa)
1.443	7.309	1.316e-7	24687.155	0.594	0	25272.918	0.622	0

Table 6 Numerical results in terms of the ballistic limit of PU/3phr epoxy POSS coated and uncoated TC-128 under high power impact.

Configuration	Impact velocity (m/s)	Result	Residual velocity (m/s)	V ₅₀ (m/s)
Uncoated steel plate	860	P	0	875
	870	P	0	
	880	C	49.3	
PU/3phr epoxy POSS coated steel plate	940	P	0	955
	950	P	0	
	960	C	38.7	

P: Partial penetration C: Complete penetration V₅₀: Ballistic limit

Fig. 1. Teflon mold to make pure PU and POSS-enhanced PU sheets.

Fig. 2. Plate shown with spacers, and the mold plate shown before and after casting.

(a)

(b)

Fig. 3. (a) Instron 5982 dual column floor model test system (b) PU samples with different phr of epoxy POSS shown with paint marks.

(a)

(b)

Fig. 4. (a) Ultimate true stress (b) Elongation for PU with different phr of epoxy and amine POSS.

Fig. 5. Experimental set-up of ballistic limit test.

Fig. 6. Configuration of (a) PU/3phr epoxy POSS coated (b) uncoated steel plates for the ballistic limit test.

Fig. 7. (a) Initial impact shown with a large crater. (b) Side view of the projectile penetrating the tested plate. (c) The coated layer was stretched out up to 2 inches upon projectile impact. (d) After penetration, a large amount of polymer is lost. (e) After the bullet impact, the coated PU-POSS rubber closed to the minimal hole. (f) View of the back steel side of the PU-POSS coated TC-128 plate after the ballistic test. (g) Moment of projectile impact on bare TC-128 steel plate. (h) Front side of bare steel plate after shot. (i) Back side of bare steel plate after shot.

Fig. 8. True and engineering stress-strain curve of TC-128 steel.

Fig. 9. Curve fitting for PU/3phr epoxy POSS using Ogden 3rd order.

(a)

(b)

Fig. 10. Configuration of (a) PU/3phr epoxy POSS coated (b) uncoated TC-128 steel plate built in AUTODYN.

Fig. 11. Comparison of the experimental and simulation results of the ballistic limit.

Fig. 12. The snapshot of (a) PU/3phr epoxy POSS coated (b) uncoated steel plate impacted at a velocity of 1000 m/s.

Fig. 13. Comparison of the hole size between the experimental and simulation results.