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# COMPOSITE COATINGS WITH HIGH VIBRATION DAMPING PROPERTIES

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**Abstract.** *The concept of using elastomeric coatings for improving the ability of existing structures to dissipate energy due to severe impulsive loading or critical shaking conditions was investigated by many researchers in the past and is still an area of considerable interest. In recent years, polyurea has been successfully applied as a coating material for such a purpose demonstrating a remarkable improvement of the survivability of structures subjected to severe shock and impact conditions. In this work the improvement of the damping properties of polyurea was proposed. The dynamic properties of this polymer were enhanced by reinforcing it with two classes of fillers in the form of short fibers and ceramic particles. We present the results of the experiments that we carried out on the reinforced polyurea materials and we compare them to those of the pure polymer. Particularly, the behavior of the reinforced materials in dynamic conditions showed that these composites have improved mechanical properties and especially higher damping characteristics with respect to those presented by the pure (non reinforced) elastomer. These properties are highly desirable for the dissipation of the energy released by an impact event.*

## 1 INTRODUCTION

The first appearance of polyurea was reported in 1948 [1]. The interesting advantage of using polyurea over polyurethanes is its higher melting point and generally higher thermal properties compared to polyurethanes and the fast curing process which allows the products to have excellent mechanical properties just a few hours after curing. Even though the cost is an important parameter, the high chemical resistance and almost complete insensitivity to humidity presented by polyurea have certainly contributed to its large diffusivity in the market specifically for coating applications since the early 1990's. In those years the spray-on polymer technology was in fact introduced and it is today the technique used to produce polyurea coatings.

The two-component polyurea typically does not contain any solvent or volatile organic products and it is normally processed by equipment that reproduces a high pressure and a desired temperature for spray applications. Due to recent improvement of fabrication techniques, polyurea is today one of the most recent and successful materials developed in the coating industry. The success of polyurea in this field is certainly due to many factors which include the fast curing time, even at low temperatures, the almost complete insensitivity to moisture, the high chemical resistance, the excellent mechanical properties such as the high flexibility, tear and abrasion resistance, tensile strength, as well as the low flammability and excellent durability if compared to polyurethanes.

Since their massive production, polyurea coatings started to be looked at with an extreme interest for coating structures and components exposed to severe dynamic and impulsive loadings caused, for instance, by explosive events either underwater or in air. The interest came from the observation that in the presence of such severe conditions the application of an elastomeric coating on the structure improves the dissipation of the event energy, thus limiting considerably the damage to the structure. Full scale explosive tests performed in the past demonstrated that coating the interior surfaces of the walls of a retrofitted building with polyurea could successfully prevent the failure, collapse and fragmentation of the structure, even in the case of a close detonation [2-4]. Among these works, the dynamic response of circular and rectangular thin metallic plates to impulsive loads was studied both numerically and experimentally [5-6]. Particularly, some works carried out by Mock et al. [7] demonstrated that a layer of polyurea backing a metal thin plate exposed to an impact retarded the failure of the metal due to the absorption of the energy released by the event. These results were also confirmed in the studies [8-9]. Based on these experiments, in general, it can be said that these layered systems demonstrate to increase the resistance at failure of the steel plate preventing its fracture. The explanation resides on the behavior of the elastomer which undergoes very high deformation in favor of the dissipation of the impulsive energy. These dissipative phenomena were observed and commented in this work [10]. The whole result is that the onset of failure of the thin metallic plate, i.e. the necking, seems to be postponed in time due to the viscoelastic characteristic behavior of the elastomer and to its phase transition process from rubber-like to glass-like consistency; phenomena which always depend on the loading conditions imposed. The microstructure and behavior of polyurea was proven to be, in fact, strongly pressure-strain dependent [11-12].

In this experimental work we focused on the quantification of the improvement of the dynamic properties with special attention to the damping characteristics of poluyrea which was reinforced with two different types of fillers. The improved ability of dissipating energy of the reinforced materials was demonstrated by comparing their dynamic properties with those of the pure elastomer. The dynamic characterization of these materials was conducted in order to support the conclusions made in previous experimental observations [13] where a few representative samples consisting of thin metallic plates coated with reinforced polyurea were subjected to high strain rate impact. The results demonstrated that these materials increased the survivability of the samples. The evaluation of their dynamic behavior was considered as an effective way to quantify and characterize the damping ability of these new materials and also a way to explain the phenomena observed in previous experimental studies.

## 2 MATERIALS AND EXPERIMENTS

### 2.1 Materials and samples preparation

The polyurea used in this work was Versathane P1000 and it was derived from the combination of the following components: multifunctional Isonate® 143L and high molecular weight oligomeric amine, Versalink® P1000. In this study polyurea was reinforced with two types of fillers namely commercial milled E-glass fibers, with nominal fiber length of 0.8mm and alumina powder with 0.3μm average particles diameter. The desired amount of fillers was first added to the blend resin component and the mixture was stirred for several hours in a reaction vessel kept continuously under vacuum in order to evacuate the air bubbles present in the liquid. The isocynate component was degassed in a separate flask, also under vacuum, and added to the rest of the mixture at later time. The overall material fabrication time required therefore approximately 15 seconds for mixing all the components together and extra 20 seconds for casting the desired samples.

The samples were of two types. One type consisted of rectangular shape samples made for dynamic mechanical analyses. The samples were cut from 1mm thin and 6cm by 6cm square sheets that were made by pouring the polymer in a Teflon open mold. Another type consisted of a few steel plates coated with the polyurea reinforced materials for high strain rate impact tests. The coating of the plates was done by pouring the polymer mixture directly on a circular open cavity present on one side of the steel plates. The details of the geometry of this particular type of samples are given in the following paragraph. All the samples cured into a chamber in a controlled level of humidity (<10%). The two representative materials whose improved damping properties are discussed in this paper consisted of a polyurea reinforced with 5.7% volume fraction of alumina particles and of 9% volume fraction of milled glass fibers respectively.

### 2.2 Materials characterization

High strain rate impact tests on the reinforced polyurea materials were carried out in a previous research [13] at the University of California San Diego. The experiments were conducted on circular steel plates coated either with the pure or the reinforced polyurea. A few samples per material type (steel plates with either milled glass fibers or alumina reinforced polyurea coatings) were prepared at that time to verify if the steel plates coated with these materials could sustain higher impact energies by showing no evidence of fracture after the impact than steel plates coated with the pure polymer. The circular metallic plates, as the one shown in Figure 1a, were designed following the guidelines presented in a previous study [9]. Each steel sample was machined from 4.77mm thick steel sheet in circular plates of 76mm diameter. The samples presented a central section of about 1mm thickness and 57mm in diameter. This specific design was found to be optimal in order to avoid catastrophic shear failure at the edges of the plate. Some of the samples were coated with pure polyurea and others with reinforced polyurea. The coating process was conducted in a controlled humidity chamber to prevent the moisture from compromising the bond of the material to the metal surface. Each plate was measured and weighted before it was coated. The coating process consisted of pouring the polymer into the inner section of the sample in such a way that a thick layer of the polyurea materials fully covered the central part of the sample until reaching the level of the rim.


Figure 1: Samples for impact tests: a) DH-36 steel plate's geometry; b) steel plate coated with alumina particle-polyurea ($V_f$=5.7%) composite and c) steel plate coated with milled glass-polyurea ($V_f$= 9%) composite.

To reproduce the effects caused by a shock wave due to an underwater explosion and transferred to a steel structure, a 25.4mm thick cylinder of polyurethane material with 75mm in diameter was placed in front of the sample so that the impact force generated by a projectile could be transmitted first to the polyurethane and afterwards to the steel plate, Figure 2.

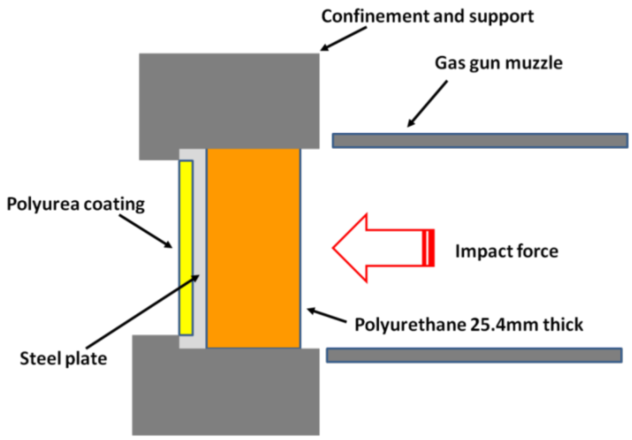


Figure 2: The schematic presents the configuration of the sample in the high speed impact testing system and the way the impact force was transmitted to the steel plate through a cylindrical block of polyurethane of 25.4mm thickness.

In previous investigations reported in the work [14] it was successfully proven that the stress pulse transferred to the plate through the polyurethane, matched the pulse transmitted to the sample when water was used. The sample with the elastomer coating on the surface opposite to the impact, as shown in the schematic of Figure 2, was placed inside a cylindrical steel confinement part of the impact test apparatus, also known as *gas gun*. This cylindrical chamber presented at its end a cavity of a smaller diameter where the rim of the sample leaned against it in a simply supported mode leaving the central part, coated with polyurea or reinforced polyurea, exposed to the impact and free to deform. The projectile was shot by a gas gun at a velocity which was accurately measured by looking at the signals recorded using magnetic sensors located at known distance in the barrel. The projectile had a steel ring built at its end, functioning as a magnetic tail, which triggered the sensors during its course through the barrel allowing to record its velocity. The set up is clearly described in the more recent work [15]. The projectile's impact velocities were calculated to be in the range of 60 to

74m/sec. The kinetic energy resulting from the test was simply calculated by the following equation:

$$E = \frac{1}{2} m_p v_p^{\,2} \tag{1}$$

where $m_p$ is the mass of the projectile and $v_p$ its velocity as measured by the sensors. The energy calculated in (1) was assumed to be fully absorbed by the sample during the impact and its effects on the materials were qualitatively estimated by comparing the failure modes observed for all these samples. The failure mode was associated with the projectile's impact speed (m/sec) and its kinetic energy divided by the thickness of the sample (J/cm). The improvement, in terms of impulsive load bearing capability of the steel plate, was therefore estimated by comparing the kinetic energy transferred to the plate and calculated by the equation (1) normalized by the thickness of the sample. Overall, 2 samples per type were tested and two different coating thicknesses (3.7mm and 2.2mm) were considered.

The dynamic properties of the materials were measured by using a dynamic mechanical analyzer, (DMA), TA Instruments. Milled glass fiber and alumina-polyurea samples were prepared for single cantilever beam tests. The average width of the samples was 6mm while the length was fixed at 17.5mm due to the clamps geometry. The experiments were performed at fixed maximum 1% strain. Storage and loss moduli of these materials were determined as a function of the temperature and frequency. The damping ability of the materials was finally evaluated by observing the trend of the ratio of the loss modulus to the storage modulus, known also as the material's Tan δ [16]. The experiments were conducted by applying a temperature ramp from -120°C to 70°C at the constant rate of 0.5°C per minute while the frequencies were changing from 0.1 to 20Hz. Three samples per type were measured.

## 3 RESULTS AND DISCUSSION

### 3.1 Impact tests

From the analyses of the results of the impact tests it was first confirmed that a layer of polyurea backing a steel plate impacted with the same kinetic energy (per unit thickness) as the one that induced a *catastrophic* failure of a bare steel plate significantly improved the absorption of the impact energy and, in all cases, prevented the failure of the sample. A *catastrophic* failure such as the one shown in Figure 3a was attributed to samples, with or without coatings, where a large central opening was displayed after the impact. A moderate failure, such as the one in Figure 4a, was attributed to those cases where the steel plate after the impact was highly deformed and presented evidence of cracks at the center. Finally, no failure was attributed to those samples which presented a large deformation but no evidence of cracks, as reported in Figures 3b, 3c, 3d and Figure 4b.

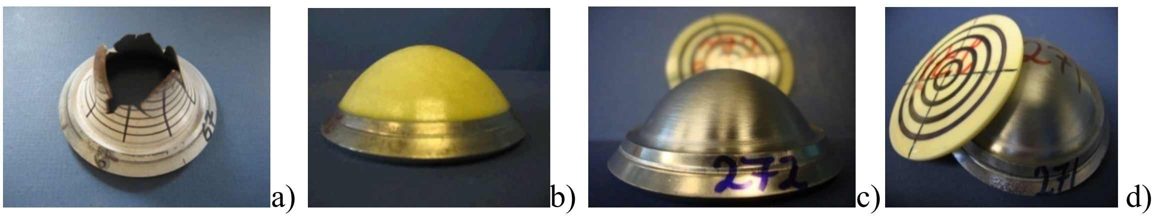


Figure 3: Comparison of the impact results of some representative samples with 3.77mm coating thickness: a) failure of steel plate S67 without coating at 15347 J/cm as reported in previous experimental results [11]; b) milled glass polyurea backing the steel plate MG249 impacted with the energy of 16573.7 J/cm; c) milled glass

fiber polyurea coating the plate MG272 impacted with 20805 J/cm energy; d) alumina reinforced polyurea coating the plate AL271 impacted with 21000 J/cm energy.

In Figure 3a, the reference steel sample impacted with the kinetic energy of 15347 J/cm reported a severe failure, while the sample coated with milled glass fiber-polyurea shown in Figure 3b, displayed high deformation but no fracture when impacted with the energy of 16573.7 J/cm. In this specific case, Figure 3b, in addition to the improved impact resistance, milled glass fiber-polyurea composites demonstrated the unique ability of remaining perfectly attached to the surface of the plate after the shock event. The highest impact resistance was displayed by samples coated with the alumina reinforced polyurea material. In fact, as shown in the Figure 3d one of these samples survived the impact after being shot with the energy of 21000 J/cm. This was the highest impact energy recorded in these experiments. No steel plate coated with pure polyurea or milled glass fiber-polyurea survived at the same impact energy.

A comparison made with the failure of a sample with the pure polyurea coating is presented in Figure 4. The plate coated with the pure polyurea, Figure 4a, presented a moderate damage at the impact energy of 17945J/cm, while the plate coated with the milled glass fiber polyurea, in Figure 4b, survived when impacted with the energy of 19272J/cm.

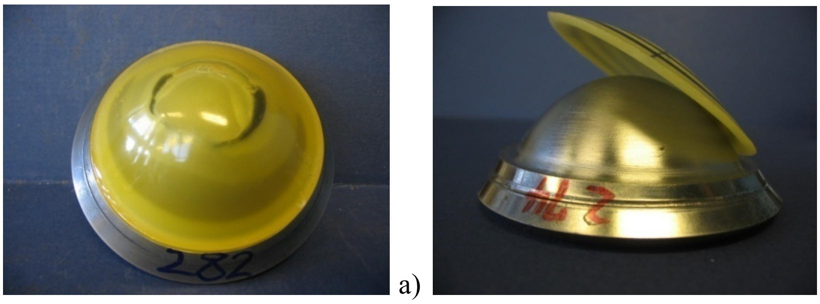
a) b)

Figure 4: Two representative samples where the thickness of the coatings was 2.2mm. a) Moderate failure of steel plate coated with pure polyurea at the impact energy of 17945 J/cm; b) milled glass-polyurea coating a steel plate impacted with the energy 19272 J/cm.

Overall, the improvement in terms of impact resistance of the samples was estimated to be 27% higher if compared to tests conducted on bare steel plates and 15% higher with respect to plates coated with the pure polyurea material. The improvement was observed to be consistent for samples with different coating thicknesses (3.7mm and 2.2mm).

It is certainly true that more experiments are necessary to confirm the improvement and some of the results can be questionable due to the small number of samples tested. However, these results gave a qualitative idea of the benefit that these materials may have over the pure polymer. The classification of the improvement was sought at later time by analyzing the measurements reported in the next section.

### 3.2 Dynamic analyses

The materials' typical dynamic properties are shown in Figures 5 and 6. Figures 5 displays the behavior of milled glass fiber-polyurea composite (MG), and alumina-polyurea composite (AL) compared with those of the pure polymer. The plot shows the behavior of these materials at the selected frequencies of 0.1, and 1Hz for clarity. To highlight the different behavior of these materials we compared the dynamic behavior of both elastomeric composites with the pure polyurea by showing, in Figure 6, the trend of the ratio of the loss modulus to the storage modulus (=Tanδ) which better presents the increased damping ability of a material. In fact, the higher Tanδ the higher the part of the modulus that is responsible for the dissipation of the energy transferred to the material (the loss modulus).

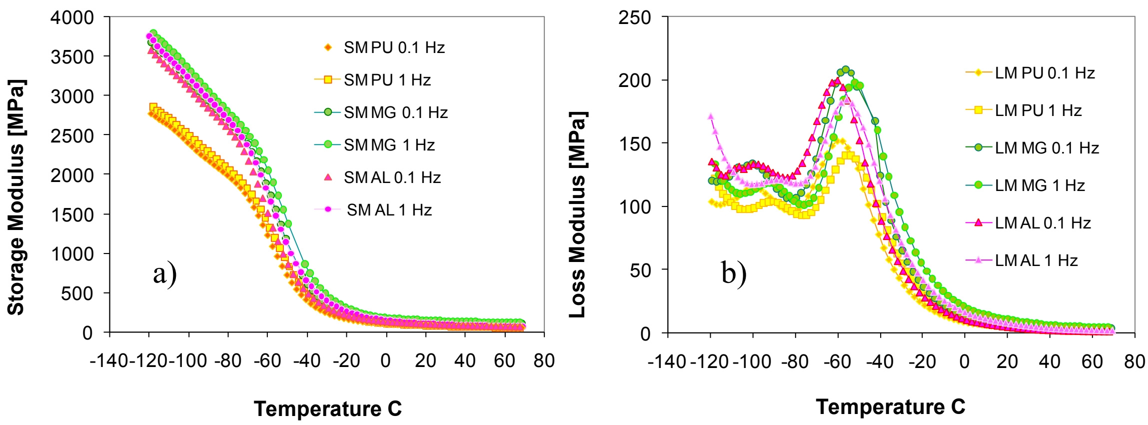


Figure 5: Dynamic properties of the reinforced polyurea compared with thepure polyurea: a) storage modulus and b) loss modulus of polyurea (PU), milled glass-polyurea (MG) and alumina-polyurea composite (AL), plotted at the selected frequencies of 0.1 and 1 Hz.

From Figure 5 we can observe how the storage modulus of polyurea could be remarkably higher, up to 30%, when the material was reinforced. At the same time, the loss modulus increased in the case of the reinforced materials up to almost 20% if measured at the peak displayed by its trend. The peak value for the trend of the loss modulus occurred at the glass transition temperature of the material. For the pure and the reinforced polyurea materials the peak of the loss modulus moved towards higher temperatures with the increase of the frequency. In proximity of the glass transition temperature it is known that the polymer changes its behavior from glass-like to rubber-like behavior and therefore dissipation phenomena dominate in this temperature range.

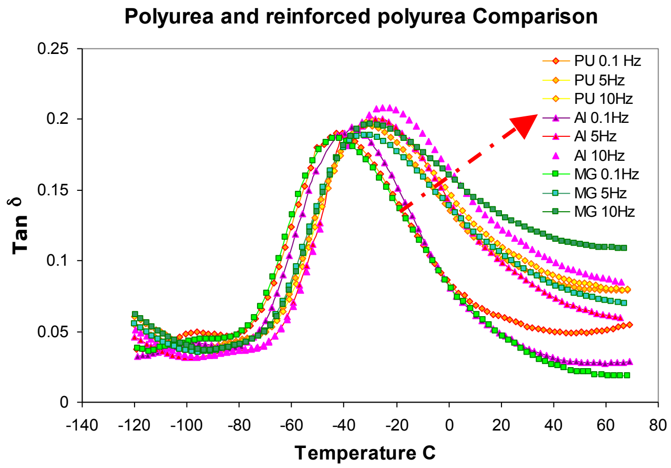


Figure 6: Tan δ of the milled glass fiber and alumina-polyurea composites compared with those of the pure polyurea at the selected frequencies of 0.1, 5, and 10Hz.

The ratio of the loss modulus to the storage modulus (=Tanδ) whose trend is shown in Figure 6, also represents the dissipation characteristics of these materials. From these measurements, and particularly by looking at the trends of these materials at the same frequency, it is clear how the damping properties of the two reinforced polyurea composites were higher than that of the pure polyurea and the improvement became really significant at frequencies above 5Hz. By considering the storage modulus, it is also evident how the strength of these composite materials increased remarkably (in the range of 30%) compared with that of the pure polyurea. We can therefore conclude that the dynamic response of polyurea coatings subjected to high frequency pulses, like a shock impulse caused by a close detonation underwater, can be improved due to the higher damping characteristics resulting from the addition of a proper amount and type of the fillers.

## 4 CONCLUSIONS

The impact response and the dynamic characterization of a reinforced polyurea elastomer were presented in this work. Specifically, the improved damping properties of the polyurea elastomer were obtained by reinforcing the polymer with milled glass fibers and alumina particles. Various samples were fabricated for impact testing and dynamic analyses (DMA). The properties of these materials in multi-temperature and multi-frequency experiments were determined and compared to those of the pure polyurea elastomer. In a previous experimental investigation, a few steel samples coated with pure polyurea and with reinforced polyurea were impacted by a projectile whose speed was in the range of 60 to 75m/s. From the observations made on the failure modes of the steel plates subjected to impact we concluded that when a thin layer of reinforced polyurea material was backing a steel plate and the plate was then impacted with the same kinetic energy (per unit thickness) as the one that induced a failure of a steel plate coated with the pure polyurea, the plate presented a high deformation but did not fail. The explanation of these results was given by assuming that the energy dissipation ability of these materials increased considerably by adding the fillers. The confirmation of this assumption was obtained at later time by characterizing their dynamic properties. From these experiments we observed that the loss and storage moduli of alumina and milled fiberglass polyurea composites were generally higher than those of the pure polyurea. The increase was remarkable at low temperature but the effects could be clearly noticed also at temperatures above 20°C. The damping ability of these composite materials, well depicted by the trend of the measured Tanδ, was found to be generally higher than that of the pure polyurea and its value increased considerably with the increase of the frequency. This particular result led us to conclude that the energy of high frequency pulses such as those transferred by impact events to a structure or component can be better dissipated if the polyurea coating is reinforced.

Given the variety of reinforcements available, further studies and experiments are needed for the optimization of these materials damping characteristics.

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## REFERENCES

[1] R. Hill, E.E. Walker, Polymer Constitution and Fiber properties. *Journal of polymer science*, **3**(5), 609-630, 1948.

[2] K.J. Knox, M.I. Hammons, T.T. Lewis, J.R. Porter, Polymer Materials for Structural Retrofit. Force protection branch, Air Expeditionary Forces Technologies Division, Air Force Research Laboratory, Technical report, Tyndall AFB, Florida, 2000.

[3] J.E. Crawford, Modeling blast-resistant protection systems composed of polymers and fabric. Karagozian & Case, Technical report.

[4] J.E. Crawford, L. Shengrui, Design and implementation of protective technologies for improving blast resistance of buildings. *Enhancing Building Security Seminar*, Singapore, 2005.

[5] G.N. Nurick, J.B. Martin, Deformation of thin plates subjected to impulsive loading-A review, Part I: theoretical considerations. *International Journal of Impact Engineering*, **8**(2), 159-170, 1989.

[6] G.N. Nurick, J.B. Martin, Deformation of thin plates subjected to impulsive loading-A review, Part II: Experimental Studies. *International Journal of Impact Engineering,* **8** (2): 171-186, 1989.

[7] W. Mock, E. Balizer, paper presented at the Polyurea Properties and Enhancement of Structures under Dynamics loads, Airlie, VA, 2005.

[8] M.R. Amini, J.B. Isaacs, S. Nemat-Nasser, Effect of polyurea on the dynamic response of steel plates. *Proceedings of the 2006 SEM Annual Conference and Exposition on the Experimental and Applied Mechanics*, s54p03, 2006.

[9] M.R. Amini, Effect of Polyurea on the dynamic response and fracture resistance of steel plates under impulsive loads. PhD thesis, University of California San Diego, 2007.

[10] Z. Xue, J.W. Hutchinson, Neck retardation and enhanced energy absorption in metal-elastomer bilayers. *Mechanics of materials*, **39**, 473-487, 2007.

[11] J. Yi, M.C. Boyce, G.F. Lee, E. Balizer, Large deformation rate-dependent stress-strain behavior of polyurea and polyurethanes. *Polymers,* **47**, 319-329, 2006.

[12] A.V. Amirkhizi, J. Isaacs, J. McGee, S. Nemat-Nasser, An experimentally-based viscoelastic constitutive model for polyurea, including pressure and temperature effects. *Philosophical Magazine,* **86**(36), 5847-5866, 2006.

[13] F. Ghezzo, Materials with integrated distributed sensing. *Cellular Concepts for the mitigation of localized high intensity dynamic loads Conference*, University of California Santa Barbara, 26-28 March, 2008.

[14] S. Nemat-Nasser, J.B. Isaacs, J.E. Starrett, Hopkinson techniques for dynamic recovery experiments. *Proceedings of the Royal Society of London A*, **435**, 371-391, 1991.

[15] M.R. Amini, S. Nemat Nasser, J.B. Isaacs, Experimental investigation of response of monolithic and bilayer plates to impulsive loads. *International Journal of Impact Engineering,* **37**, 82-89, 2010.

[16] J.D. Ferry, *Viscoelastic properties of polymers*. Wiley, 3rd Edition, 1980.