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Polyurea coatings for enhanced blast-mitigation: a review

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Elastomeric coatings are being advocated as excellent retrofit materials for strategic applications, particularly for blast mitigation and ballistic protection. Polyurea, an elastomer formed by the reaction of isocyanate and amine, possesses hard domains dispersed randomly within the soft domains, forming a heterogeneous landscape with a nano-segregated microstructure, with each domain exhibiting its own characteristic glass transition temperature. Commercialised in the late eighties, this relatively new entrant in the field of elastomers has received enormous attention in view of its excellent blast mitigation properties and ballistic protection. Although the literature is abundant with studies demonstrating the potential of polyurea for retrofitting applications, the underlying mechanism behind its exceptional properties has not yet been fully comprehended. The ballistic protection ability is attributed to the dynamic transition from "rubber to glass", which occurs when the material is subjected to extremely high strain rates, while the blast mitigation potential is attributed to a phenomenon more commonly referred to as "shock wave capture and neutralization". Since the blast mitigation and ballistic protection ability is decided by the hard and soft domains of polyurea, respectively, the polymer needs to be tuned for a particular application through judicious choice of the raw materials. The current article reviews the relevant publications in the field of polyurea-based retrofits including their preparation, characterization, properties and applications in the context of blast mitigation and ballistic protection.

1. Introduction

In the wake of terrorist threats, enormous attention is nowadays being directed towards designing of strategic buildings, where such a possibility is even remotely envisioned. Unfortunately, the majority of the structures existing today were not originally designed to endure dynamic loads, which are characterized by their impulsive nature, transmitting extremely high-pressures *ca.* 10 to 10^3 kPa. On the other hand, static loads are time independent, presumably acting on the structure for infinitely extended time durations (*e.g.* gravity loads). Time dependent dynamic loads are classified on the basis of their relative intensity and frequency. Natural dynamic loads like those

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induced by earthquakes exhibit strong time dependencies and continue for a much longer duration as compared to blast loads. Detonation, on the other hand, being an extremely short duration phenomena (~ms) falls under the category of high intensity as well as high frequency load and in view of the associated inertial effects, the resulting damage is often unpredictable.

Terrorist attacks usually take the form of small bombings, which lead to structural damage, generating high velocity fragments; the extent of damage being dependent on the amount of explosive employed. It is also generally accepted that the structural disintegration and propulsion of the debris result in more casualties as compared to the pressure, heat or other events associated with explosion.[1,2]

In order to reduce the extent of damage, one of the solutions envisaged involves enhancing the strength of existing structures, which in turn can be achieved through retrofitting. The solution has to be economically viable both in terms of material cost as well as maintenance expenses. In addition, miscellaneous factors cannot be negated, particularly maintenance of floor space, non-interruption of existing services and non-requirement of skilled technicians for installation. This paper reviews the materials and methods, commonly employed for improving blast resistance of buildings, with an emphasis on elastomeric spray-on polyurea coatings.

2. Existing solutions to improve blast-mitigating performance

Maintaining a sufficient stand-off distance is undoubtedly the most effective way of protecting any structure from damage resulting from blast loadings, the underlying reason being the rapid decrease in overpressure with increasing stand-off distance.[3] This can be achieved with bollards, fences and walls, but is impractical in urban environments where space is often unavailable. Other arrangements include fixing catcher systems on the inner face of walls, which prevent fragments from entering the occupied space.[4] This can be achieved by covering the entire wall with a fabric securely anchored both at the floor as well as ceiling. However, since no structural strength is provided by this technique, special arrangements have to be made for load bearing walls. In addition, this technique is not befitting for structures where openings are essential, particularly doors and windows, as the fabric needs to span continuously without interruption for optimal protection.

The ability of a structure to withstand blast loads can also be enhanced by increasing its mass and ductility, which can be achieved by additional reinforced concrete for concrete structures and larger sections for steel structures. However, this requires ensuring the ability of existing structure to withstand the additional weight requirements prior to installation.[5] Alternately, external-strengthening techniques using composite laminate/steel jacketing have also been attempted. Lengthy installation times and vulnerability to corrosion, which lead to increased maintenance costs are additional disadvantages associated with this technique.

Another alternate solution involves retrofitting the structure with additional light-weight layers, *e.g.* fibre reinforced polymer (FRP) and elastomeric coatings.[6] The primary requirement of

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the retrofitting material is to possess enough resilience to deflect and hold back the structural debris in place, thereby providing sufficient response time for the inhabitants to take suitable protective measures in the event of explosion.

2.1 Retrofitting with fibre reinforced plastics

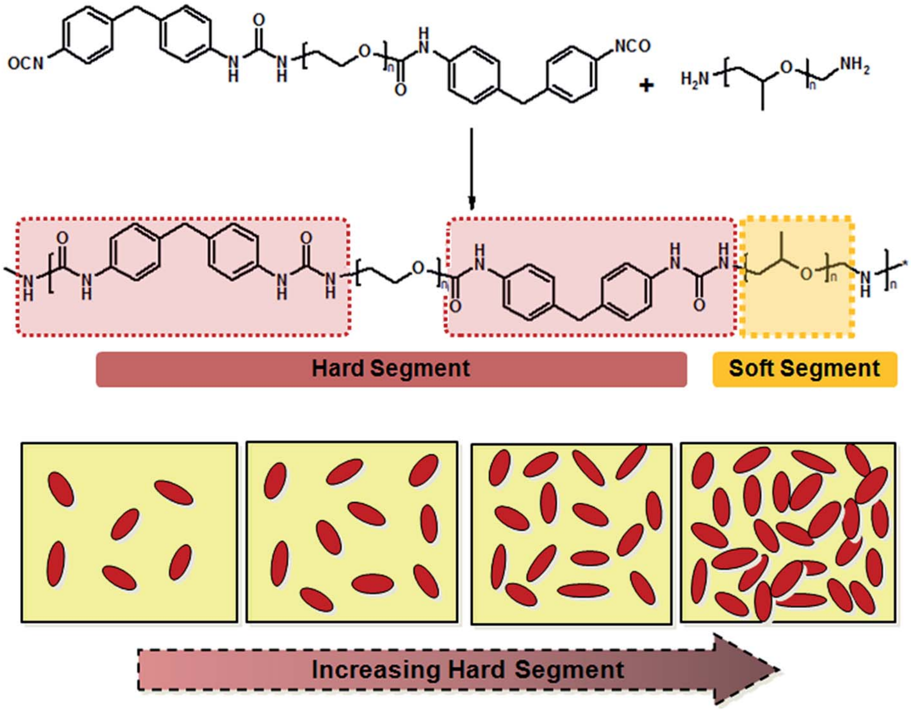
With rapid advances in the field of Fibre Reinforced Plastics (FRP), affordable high strength composites are now available and are being explored for blast mitigating applications.[7–9] The corrosion free characteristics and ease of applicability bestow these materials excellent candidature for retrofitting applications.[6] FRPs possess obvious advantages in terms of mechanical properties and being lightweight, the additional strength requirement of the existing structure is rather lenient. The reason most commonly cited against the use of FRPs includes its high apparent material and installation cost as compared to other materials. However, a direct comparison on a unit price basis may not be appropriate if transportation costs are included during comparison. FRPs can often compete with conventional materials if the comparisons include through-life costs. Carbon,[10] glass,[11] aramids[9] and their hybrids are the most commonly used fibres, with epoxy being the most widely used matrix.[12–18] Studies reveal that in general, FRPs exhibit bending failure, but nonetheless contribute positively towards structural blast strengthening.[4,19,20] FRPs, however, have their own set of limitations. For example, in some situations, the excessively thin sheets of the material require an impractical number of layers or wraps on the structure to function effectively. Besides, in cases of close-in detonations, the strain demand of the strengthening material is beyond the capacity of FRPs.[7] Another drawback of FRP strengthening is that it may lead to a premature brittle failure, such as through FRP de-bonding and FRP-concrete delamination when subjected to high intensity blasts.[21]

2.2 Spray-on coatings

Another approach, which has emerged as an economically viable solution in the context of blast mitigation is the application of elastomeric coatings as a retrofit.[22,23] Among the many desirable properties of any retrofitting polymer, the most important include ease of application, rapid cure time, adhesive properties and excellent mechanical properties, particularly strength and elongation. Elastomers, when subjected to blast and impact loads tend to exhibit high strain to failure, thereby absorbing or dissipating the energy arising from dynamic loads.[24–26] US Air Force was the first to demonstrate the potential of this approach by coating polyurea on building walls. US Navy subsequently extended the use of these coatings to enhance the penetration resistance of structure and vehicles under the impact by blast-fragments and projectiles,[25] a much cited success story being the up armouring of high mobility multipurpose vehicle (HUMVEE).

3. Polyurea coatings

Polyurea is an elastomeric polymer formed by reacting an isocyanate (N=C=O) with amine (NH_2) by a step growth polymerization process. Commercialized in the late eighties, this sub-category of elastomers can be designed to exhibit a wide range of mechanical properties, from soft rubber to hard plastic by judicious choice of the raw materials. A representative reaction between the amine and isocyanate and the resulting microstructure is presented in the Scheme 1.



Scheme 1 A schematic illustrating the reaction of diisocyanate with diamine.

Polyurea spray coatings exhibit rapid cure even at sub-zero temperatures (in view of the high reactivity of isocyanates with amines), exceptional physical properties such as high hardness, flexibility, tear strength, tensile strength, chemical and water resistance. The reaction is rapid with gel times measured in seconds, which means the reaction proceeds largely independently of ambient temperature and humidity, facilitating application of polyurea under diverse conditions. Polyurea are reportedly 100% solids, a feature which renders them compliant with the strictest Volatile Organic Compound (VOC) regulations.[27] It is however, to be noted that the term, "Zero VOC", does not necessarily mean complete absence of solvents, as many commercial formulations do contain reactive diluents, which do not fall under the category of volatile organics *e.g.* alkylene carbonate included in A part (isocyanate). The rest of the additives, especially colouring agents and adhesion promoters are included in the B-part consisting primarily of amines. It is to be noted that polyurea formulations do not require catalysts, which are indispensable ingredients in polyurethanes (formed by reaction of isocyanate with polyols).

An important concern associated with polyurea coatings is the requirement of rapid mixing of the reactants, an issue which has been overcome using a suitable mixing module by impingement at high pressures. The viscosity of both the components (isocyanate and resin) need to be almost equal (difference less than 100 mPa s), which mandates a heating arrangement, with higher viscosity reactants requiring higher pressures for spraying. It is to be noted that the spraying pressure and reaction temperature of the reactants greatly affect the properties of the product formed.

The micro-structure of polyurea comprise of two distinct domains;[28] hard domains, formed by hydrogen bonded polar urea linkages (–NH–CO–NH–) and possibly π-stacking of aromatic moieties, if the polyurea is prepared using aromatic diisocyanates. The soft domains, consist of well-mixed hard and soft long chain aliphatic chains.[29–31] It is to be noted however, that discrete hard domains are formed only when the molecular weight of the soft segment cross a particular threshold. In the case of lower amines, the nano-segregation process results in the formation of a fully percolated hard domain phase. Hydrogen bonding between the urea linkages leads to the formation of nanometre-sized ribbon-shaped hard segments[32] which exhibit a super-ambient glass-transition temperature and are relatively ordered or crystallized. The soft domains on the other hand possess sub-ambient glass transition temperature, usually lower than −30 °C.[32] The soft-segment molecular weight can also have a profound effect on the nano-segregation process, affecting both the extent of segregation and the degree of ordering/crystallization within the hard domains.[33]

It is the strong hydrogen bonding within the hard segments which is responsible for the high melting point exhibited by polyureas. A study on the thermo-mechanical measurements from a series of homologous polyurethane and polyurea materials, was performed, which quantitatively elucidated the role of the urea linkage with respect to the property distinctions between urethanes and ureas. The high melting point of polyurea is a result of the high Cohesive Energy Density (CED), which is defined as the ratio of the energy of vaporization (ΔE_{vap}) and molar volume (V_{m}).[34] The effect of increasing chain length on the melting point of a homologous series of polymers is presented in Fig. 1. Among the polymers shown, polyurea, polyamide and polyurethanes possess high CEDs as a result of their higher degrees of hydrogen bonding. The urea linkages, being resistant to hydrolysis, bestow polyureas with excellent resistance to alkali and acids.[35]

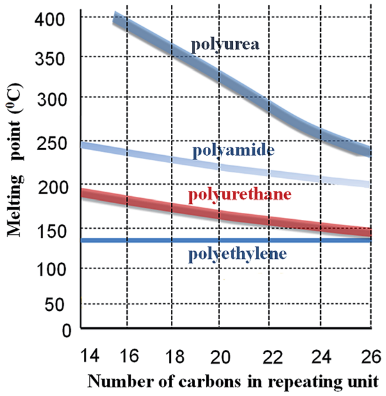


Fig. 1 Effect of hydrogen bonding on the melting point of different classes of polymers.[36]

Non-chain extended polyureas, do not have any covalent inter-chain cross-linking, and hence are often referred as thermoplastic cross-linked elastomers.[37,38] However, depending upon the amount of higher-functionality isocyanate and amine, the polyurea structure may be designed to possess varying degree of covalent inter-chain cross-linking. It is this segregated microstructure which led researchers to explore the potential of polyurea in specialized fields, including linings in personnel-protective gear and as suspension pad material for minimizing traumatic brain injury (TBI).[39–42]

3.1 Quasi-static and dynamic mechanical properties of polyurea

In view of the enormous potential of polyurea in specialised applications, studies with reference to understanding their mechanical response under static and dynamic loads have been performed.[37,39–41,43,44] Defining a loading regime is essential to quantify the strain rate to which a material is subjected to. Extremely low strain rates ($<10^0\ \text{s}^{-1}$) as achievable by using universal testing machine, where the inertial effects can be largely neglected, is referred to as quasi static regime. Characterising elastomers at high strain rates is a difficult proposition, even at small amplitudes and conventional dynamic mechanical spectrometers are limited to low frequencies. Although time-temperature super-positioning (TTS) is often invoked to extend the effective frequency range of data, the results are considered rather inaccurate for measurements in the glass transition zone.[45–47]

High strain rate studies are performed using the split Hopkinson pressure bar.[48,49] It is to be noted, however, that in view of the low impedance of polyurea, classical methods of performing split Hopkinson testing lead to erroneous results, and several modifications have been suggested. These include: use of sensitive piezoelectric sensors, hollow transmission bars and lower impedance polymeric pressure bars in addition to pulse shaping techniques. A comparative study of all these modifications has also been performed, which led the researchers to conclude that polymeric pressure bars of polymethylmethacrylate (PMMA) and hollow aluminium transmission bar are most suitable for high-strain rate characterization of polyurea.[49,50]

It has been realised that there exists a large gap between the low strain rate tests and the SHPB data. To address this issue, a drop weight tester was developed, which was capable of achieving large tensile strains at intermediate strain rates.[51] The developed facility was found to be capable of generating material properties free of artefacts due to inertia, inhomogeneous strains, and irregular strain rates.

It is to be noted that the highest strain rate possibly generated by SHPB system is limited to 10^4 s^{-1}. To extend the time-frequency scale, compressive relaxation experiments on polyurea using quasi-static tests have been performed under varied temperatures (-49 °C to 22 °C) which was subsequently used to construct a relaxation master curve over a reduced time range of 10^{-10} to 10^{-7} s, using the time temperature superposition (TTS) principle.[52] The validity of the same was demonstrated using simulation and SHPB measurements.[53] Subsequently, the applicability of this principle was contested,[54] and dielectric spectroscopy measurements were conducted[55,56] which allowed characterisation over much higher frequency range (10^{-2} to 10^6 Hz) and elevated pressures. To achieve even higher strain rates, laser spallation techniques have been developed, which use laser-generated high amplitude acoustic stress pulses of sharp temporal rise and fall times ($\sim10^{-9}$ s) to dynamically load thin samples to excessively high strain rates[57] ($\sim10^7$ s^{-1}). This technique has recently been used to subject polyurea to ultra-high strain rates, and the studies have clearly highlighted the potential of polyurea films in high energy absorption (50–65%) under high strain rates.[58]

It is to be noted that generally the mechanical behaviour of all viscoelastic materials is strain rate sensitive.[53] Upon application of stress to any such material, certain sections of the elastic soft domain tend to rearrange, which in turn leads to generation of "back stress" in the material. During unloading, it is these accumulated stresses, which results in the return of the polymer to its original form, as shown in Fig. 2.

The effect of increasing strain rate on the mechanical response of polyurea is presented in Fig. 3. As can be seen, an apparently appearing ductile polyurea (under quasi-static regime) tends to exhibit higher modulus as the strain rate increases. At low strain rates, the polymer has enough time to respond to the applied load and with increase in the loading rate, these segmental motions are practically frozen. In general, this change in the material response (from ductile to brittle) is not associated with much energy absorption. However, in the case of polyurea, this very region encompasses a dynamic transition[56,59] and therefore a lot of blast energy is absorbed and in certain cases, dissipated. It can also be assumed that this transition should be relatively easier for polymers which possess T_g closer to the test temperature. However, in certain cases where T_g is not especially high, a rubber–glass transition is still induced, a feature which has been attributed to the existence of a broad transition zone. This large breadth implies that even above the T_g, a large number of segmental modes are still active at frequencies associated with the rate of impact. This implies that the glass transition mechanism remains operative at temperatures well above T_g.

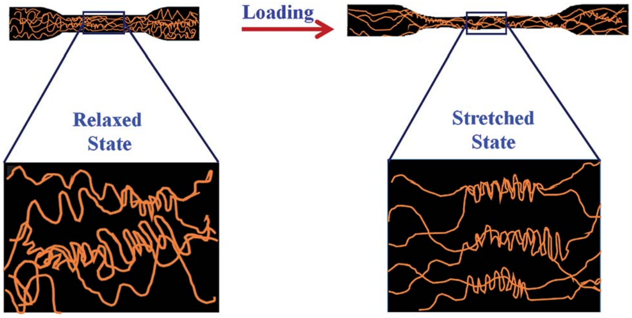


Fig. 2 Micro-structural changes in polyurea upon tensile loading.

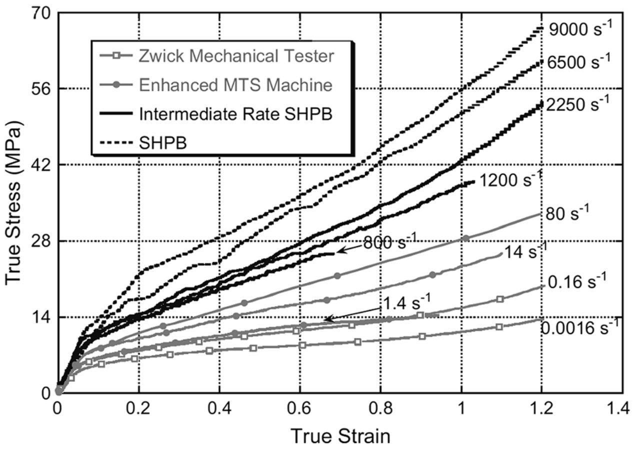


Fig. 3 Uniaxial compression stress–strain behaviour of polyurea ranging from 10^{-3} s^{-1} to 9000 s^{-1} (each SHPB curve is labelled by its true strain rate of 0.6). Reproduced with permission from Elsevier.[43]

The mechanical response of polyurea displays material constitutive non-linearity which shows in terms of high strain hardening at large strains, strain-rates as well as pressures.[33] The large strain stress–strain behaviour of polyurea shows strong hysteresis,[60,61] cyclic softening in addition to strong rate-dependence.[62] This unique combination of properties of polyurea is clearly a result of its complex nano-scale microstructure[61,63–71] which in turn rationalizes its superior performance in blast-/shock-wave-mitigation applications.

The micro structural changes occurring during the deformation of polyurea have been studied with techniques like wide angle XRD, small angle X-ray scattering and time resolved FTIR.[72,73] With increasing deformation, rotation and orientation of hard segment lamellar domains towards axis of elongation has been observed. This is also associated with stretching and shearing of soft segment chains. At very large strains (>300%) the hard segment domains were observed to reassemble to form fibrils.[73]

The data obtained from quasi-static and high strain rate studies have been used to develop several constitutive models for polyurea.[74–76] In a recent review, many of these models were used to construct shock-Hugoniot relations which in turn, were validated with appropriate experimentations. It was reported that while different material models yield vastly different relations, predictions of most of the models are in reasonably good agreement with their experimental counterparts.[77]

3.2 Retrofitting with polyurea: effect on underlying substrate

The following section summarizes the findings related to retrofitting of structural element with polyurea coatings.

3.2.1 Retrofitting Unreinforced Masonry structures. Preliminary investigations undertaken by the Air Force Research Laboratory (AFRL) dealt with the application of polyurea coating towards strengthening of masonry structures and light weight steel structures.[1] It was the positive outcome of this investigation, which paved the way for this technique to be evaluated on other types of structural materials,[78,79] like steel, FRPs *etc.* When polyurea reinforced masonry structures were subjected to explosive blast loadings, the elastomeric coating was found to undergo large deflections.[2] Although severely fractured, the coating reportedly improved the blast resistance of the masonry wall by containing the debris.

The success of this preliminary testing incited researchers towards exploring the potential of other polymers as retrofits.[2] Extruded thermoplastics, although possessing higher strength and modulus, were not taken up for further studies, in view of the inconvenience associated with their installation. Brush-on polymers were rejected in view of their brittle nature and lengthy curing time. Of the spray-on polymers, pure polyurea was selected based on its strength, flammability resistance and economic viability.[2] Subsequent blast studies indicated that coating polyurea on the interior face of unreinforced masonry (URM) walls improved blast mitigation ability of the structure and was particularly beneficial towards containment of fragments. While the application of polyurea on both sides of the wall improved the capacity of the wall against blast loads, it was not considered worthwhile to merit additional cost.[80] These studies indicated that polyurea coated walls (~6 mm thick) withstood peak pressures greater than 400 kPa (60 psi) for one-way action walls as compared to a capacity of less than 35 kPa (5 psi) for URMs. It is however to be noted, that the search for the most appropriate polymer for the purpose of blast mitigation is still not over. If suitable techniques can be developed, whereby tough thermoplastic polymers can be made to adhere to the substrate, higher levels of blast mitigation may be expected. This is definitely an area, which will attract the attention of researchers in the near future.

Explosive tests have been conducted on URM walls with window or door openings, where polyurea has been coated only on a single face of the wall not confronting the blast.[80] The primary aim was to understand the failure and behaviour and establish the underlying failure mechanisms. It was proposed that the propagation of stress waves through walls led to fracture of weak sections. Localized large stress in the mortar–block interface led to the tearing of the polymer coatings at sites nearest to the supports. Flexural compression led to the fracture of front face of the shell of a few blocks. This was followed by tensile mode polymer tearing when the wall flexed and mortar joints cracking followed by debonding of the polymer coating at the boundary to the host structure.

Subsequently, an equivalent single degree-of-freedom (SDOF) model was expounded to simulate the dynamic response of polyurea-retrofitted walls subjected to blast loads. The model was based on coupling of the bending and membrane resistance of the Concrete Masonry Unit (CMU).[81] For the purpose of validation, a blast trial was conducted (peak pressure: 5.8 kPa and pulse duration 20 ms) on a wall (3.05 × 3.05 m × 19.4 cm thick) which was spray coated with polyurea (2.1 mm). The wall recorded a deflection of ~178 mm during the trials. Interestingly, the apparent disparity between the prediction of deflection from the analytical model and the finite element code decreased as the maximum deflection of the wall increased between 1 to 2 times of the wall thickness.[81]

In another study[82] three different types of retrofits were evaluated on a 1/4th scale models of conventional 203 mm CMU walls, with all the retrofits being placed on the backside of the wall: FRP (1 mm), polyurea coating (3.2 mm) and hot-dipped galvanized steel sheet (1 mm). Although all the retrofitted walls failed during the tests, polyurea and FRP were found to be more effective in containing the fragments and debris inside the structure.[82]

Later, Hrynyk *et al.* evaluated the efficacy of two schemes, *i.e.* a spray-on polyurea retrofit and a glass fibre reinforced polymer (GFRP)–polyurea composite (GFRP grid embedded in polyurea matrix), towards strengthening framed URM infill walls. Static load (one way arching action) was applied in order to simplify the testing program. A total of 8 URM walls were evaluated, of which 2 were constructed of clay brick (CL) units, 3 were constructed of CMU and the remaining 3 were constructed from masonry units produced from Wood-Fiber Fly Ash (WFFA). While all the retrofitting schemes exhibited improvements in energy dissipation capabilities, the polyurea retrofit was found to be the most effective in the context of energy dissipation and containment of fragments of the collapsed walls.[83]

3.2.2 Application on steel structures and plates. Ever since Defence Science and Technology Organisation (DSTO), Australia reported the efficacy of polyurea coating towards improving the blast resistance of steel plates[84,85] studies on ballistic protection of steel using polyurea has been extensively reported.[39–42] In a representative study, D36 steel plates (36 mm thick) were coated with different thicknesses of polyurea coatings and subjected to dynamic loads resulting from explosive charge (0.5 kg pentolite, 61 mm stand-off). Steel plates reportedly undergo ductile fracture through void nucleation, growth and coalescence, ultimately leading to the formation of dimpled fracture surfaces.[86] Polyurea coating was found to substantially improve the blast resistance of steel plates, where retrofitted plates recorded much reduced deformation as compared to the bare plate.[87] As expected, the degree of deformation was found to decrease with increasing polyurea thickness.[85] Studies on the application of polyurea onto armour grade steel plates and an examination of resulting failure modes have also been performed.[26] The effect of increasing thickness and locations of the polyurea on the blast mitigating ability was of particular interest. The studies clearly suggest that in comparison to increasing the steel thickness alone, increasing the thickness of polyurea is more efficient towards absorbing energy and preventing fragmentation.[26] A detailed numerical and experimental program of rigid projectile penetration through polyurea coated DH-36 steel plates was subsequently performed by Xue *et al.*[88] A positive contribution from the polyurea coating in terms of improving resistance against ballistic impact when applied at the back face of the plates was observed.

Several computational and experimental assessment of ballistic effects on high strength structural steel plates retrofitted with polyurea have been performed.[89,90] Further, a set of reverse ballistic test was devised to assess the effect of polyurea coating on the dynamic response of steel plates.[91–93] All the studies revealed that retrofitting with polyurea led to positive outcomes, in terms of failure mitigation and energy absorption, when it was applied on the back face or the unloaded face of the plate. It was interesting to note that the same coating, when applied on the blast-receiving face increased the destructive effects of the blast, which was attributed to the strain rate sensitivity of polyurea. It was proposed that the stiffness of polyurea increased manifolds (10–20 folds) when subjected to increasing pressure. This led to an impedance match of the polyurea with the steel plate thereby causing more energy to be transmitted to the underlying plate, leading to more damage. On the other hand, when polyurea coating was applied on the back face, the steel plate absorbed substantial amount of energy with a relatively smaller fraction being transmitted to the polyurea coating. The authors concluded that in the event of polyurea coating application on the blast-facing side of the sample, its presence may actually enhance the destructive effects of the blast, the actual scenario depending on the bond properties between the two materials at the interface.[91–93]

In a separate study, however the experimental results indicated that the variation in coating location, either on front (blast-facing) or back face, did not cause any major effect to the maximum displacements recorded in the panels. Contrary to observation of Amini *et al.* the plates which were coated on the blast-facing side, indicated lower kinetic energy as compared to the panels which were coated on the back or on both faces. The researchers considered it to be more worthwhile to apply polyurea coating on the blast-facing side. It was also suggested that the optimal ratio of the polyurea and steel for effective blast protection required further investigation, since there exists an upper limit in terms of polyurea thickness *versus* their effectiveness in terms of the deflection and kinetic energy.[94]

3.2.3 Application on composite sandwich systems and structures. Fracture mitigation of polyurea coatings on composite substrates has also been studied extensively. Experimental investigations have been carried out to characterize the effect of polyurea coatings on E-glass reinforced vinyl-ester (EVE) composites subjected to blast loadings.[25] Permanent deformation, fiber breakage and delamination are primary amongst the numerous mechanisms responsible for blast-induced failure of fiber reinforced composite materials with the extent of damage increasing with increasing blast pressure amplitude.[95–97]

The studies clearly suggest that composite materials prepared by sandwiching polyurea coatings between two composite skins are more effective as compared to neat composites and the polyurea plates. However, mechanisms responsible for the advantageous behaviour are not yet clear, and mandate more studies.

The dynamic behaviour of sandwich composites of EVE facesheets and Corecell™ A-series foam with a polyurea interlayer was subsequently studied under blast loadings using a shock tube.[98] The materials used were identical, with the only difference being the location of the polyurea interlayer. The results indicated that the application of polyurea behind the foam core and in front of the back facesheet led to reduction in the back face deflection, particle velocity, and in-plane strain, thereby improving the overall blast performance without compromising the structural integrity.

Bahei-El-Din & Dvorak[99–101] studied the mechanical response of composite sandwich plates with a polyurea interlayer under blast loads, where a detailed assessment on the influence of underlying material and their properties on through thickness propagation of the blast waves was conducted. Both conventional (designed as a closed cell foam core construction), as well as modified composite sandwich plate designs, were modelled during the study, assuming a blast pressure of 100 MPa with a positive phase of 0.05 ms on the outer facesheets of the plates. The studies indicated that the conventional plate underwent extensive thinning in the central foam core and the layer separated from both the outer (nearer to blast) and inner facesheets of the plate. However, both the modified designs exhibited significantly reduced deformations.

The effectiveness of polyurea coatings towards improving the blast mitigating properties of hollow composite cylinders have also been investigated in "under-water" conditions.[102] Studies reveal that thick interior coatings significantly reduce the energy released in the pressure pulse by slowing the collapse and softening the initial wall-to-wall contact. In contrast, thick exterior coatings increase this energy by suppressing damage, thereby reducing the energy absorption capacity of the structure.

3.3 Mechanisms underlying polyurea-induced ballistic/blast-mitigation

The fundamental objective behind employing elastomeric polyurea for retrofitting is to minimise the amount of load transferred to the main frame by allowing the wall to fail and dissipate energy, *i.e.* to use the polymer as a catching system. However the basic phenomena behind the ballistic and blast-/shock-wave mitigation capability of polyurea are apparently different, and are hence discussed separately in the following section.

3.3.1 Shock-wave mitigation. The shock-wave attenuation ability of polyurea is believed to be controlled primarily by the hard domains.[30,32,39–42,75,103–109] Presently, there is no general consensus regarding the mechanism underlying polyurea induced shock-wave mitigation. The most accepted mechanisms include the following:

Shock-wave-induced hard domain ordering. Shock-wave-induced hard-domain compaction and ordering has been identified as one, among the many, shock-wave-attenuation and dispersion mechanisms. The extent of this blast-mitigation effect is expected to be directly proportional to the hard-domain volume fraction.[32]

Shock-wave-induced hard domain crystallization/densification. The hard domains of polyurea experience an irreversible compaction and densification with an associated increase in their degree of order upon being subjected to shock-wave loading. These micro structural changes lead to dissipation and absorption of shock-wave kinetic energy and are hence considered to be responsible for the shock-mitigation ability of polyurea.[32]

Shock wave induced hydrogen bond cleavage and formation. Bi-dentate H-bond (Fig. 4) between the urea linkages (bond strength ~21.8 kJ mol^{-1}) results in the formation of a phase separated micro-structure.[110] Exposure to shock loadings lead to the cleavage of these H-bonds, which subsequently rearrange to form more numerous H-bonds within the hard domains, thereby leading to the absorption and dispersion of shock energy.[42,108,111]

Viscoelastic stress relaxation within the hard-domains/soft matrix interfacial regions. Unlike purely elastic substances, viscoelastic materials like polyurea possess both elastic as well as viscous components. It is this viscous component, which endows strain rate sensitivity to polyurea. Purely elastic materials do not dissipate energy (in the form of heat) during cyclic loadings. Viscoelastic material, on the other hand, lose substantial energy, which is evidenced in the form of a hysteresis in the stress–strain curve, with the area of the hysteretic loop being proportional to the energy lost during the loading cycle.[109,112] Representative mechanical response of polyurea under cyclic compression and tensile loadings is presented in Fig. 5, where this hysteresis is clearly visible.

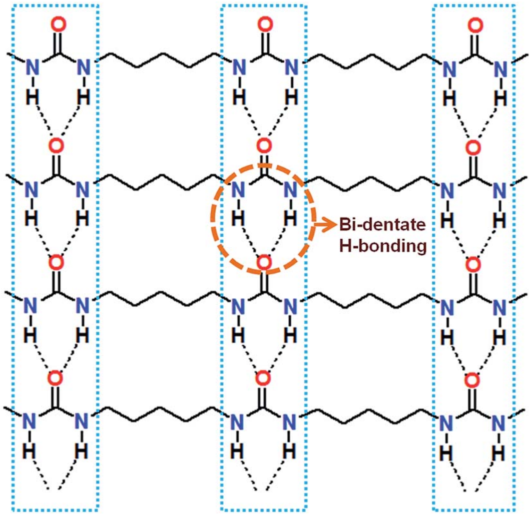


Fig. 4 Hydrogen bonding within the urea linkages in polyurea.

Shockwave-capture-and-neutralization. The ability of a material to mitigate shock waves is related to the shock-wave front profile within the material, more specifically by its width. The shock-wave front is generally broader in materials with higher shock-mitigation capacity. Thus, arrival of a shock-wave to a material boundary/interface is associated with a slow rate of momentum transfer. In addition, shock-waves tend to propagate at much lower velocity in materials with higher shock-mitigation capacity. A dominant shockwave-mitigation mechanism in polyurea is the "shockwave-capture-and-neutralization" phenomenon. Shock waves travel as a single wave in homogeneous materials. However, upon loading of a layered heterogeneous material system, *e.g.* polyurea, a two-wave structure is obtained—a leading shock front followed by a complex pattern that varies with time. This dual shock-wave pattern is attributed to the material architecture through which shock wave propagates, *i.e.* the impedance (and geometric) mismatch present at various length scales, and nonlinearities arising from material inelasticity and failure. This secondary trailing shock-wave (release wave), reportedly catches up with and attenuates the leading shockwave,[33] thereby leading to shock attenuation. A schematic of this process is presented in Fig. 6. Computational studies[33] reveal that larger is the ratio of release-wave speed to shockwave speed, the more efficient is the capture-and-neutralize shock-mitigation mechanism. It is to be noted that the shockwave speed is strongly dependant on the polyurea microstructure and for each shockwave-strength level, an optimum soft-segment molecular weight is optimal. This study clearly indicates that there is enormous scope in terms of designing polyurea for specific applications.

3.3.2 Ballistic protection.

The ballistic-protection efficacy of polyurea, on the other hand, is more due to its soft matrix than to its hard domains.[113] Interestingly, the contribution of H-bonds in this context is rather negligible. The most accepted mechanism behind the ballistic performance is the "rubber to glass second order transition" which occurs in polyurea when it is subjected to high strain rates.[56] Under such conditions, rubbers tend to respond in a glassy fashion, and undergo brittle failure. The reorientation and translational modes of the amorphous segments are unable to respond to the load and "freeze out", leaving behind only the vibrational and secondary motions. These strain rates are comparable to the frequency range of segmental dispersion of polymers having high T_g (but lower than the test temperature), which induces a transition from the rubbery state to glassy state, dissipating significant amount of energy.[59]

Conventionally, brittle fracture does not dissipate such large amount of energy, but in elastomers *e.g.* polyurea, brittleness is a direct consequence of the deformation which encompasses the glass transition zone. However, if the T_g of the elastomer differs from the test temperature substantially, exposure to high strain rates is incapable of inducing this transition and hence the extent of ballistic/blast resistance is much lower than expected.[59]

Dielectric spectroscopy has been used as an effective technique to illustrate the "rubber to glass transition" phenomenon

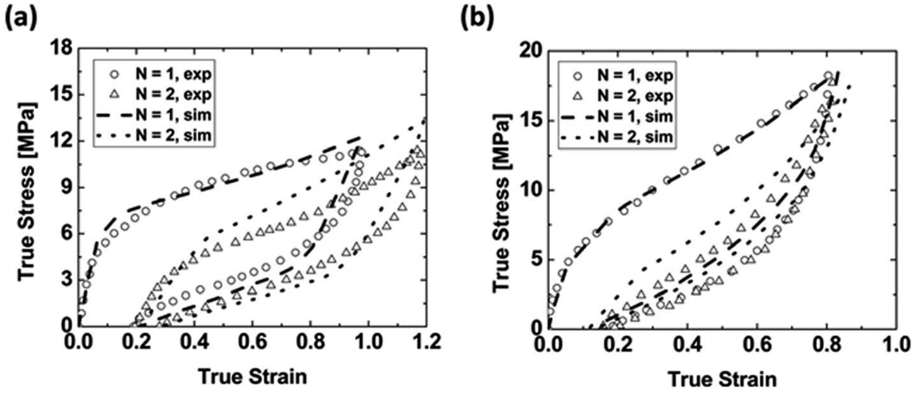


Fig. 5 Cyclic compression and tension data, comparing model results with experimental data (a) stress–strain curves under cyclic compression at a strain rate of 0.1 s^{-1} (b) stress–strain curves under cyclic tension at a strain rate of 0.015 s^{-1}. Reproduced with permission from Royal Society of Chemistry.[112]

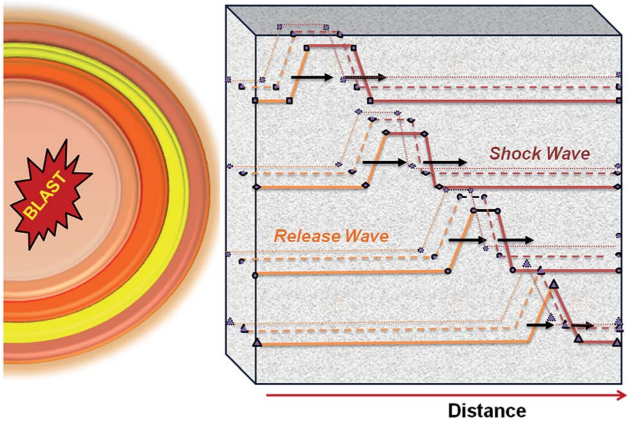


Fig. 6 Shockwave capture and neutralization in phase separated materials.

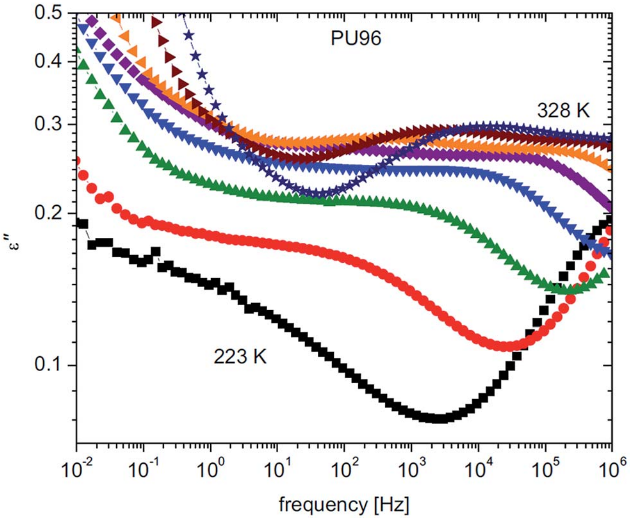


Fig. 7 Representative dielectric loss spectra for dry PU96 at P = 0.1 MPa, for temperatures from T = 223 to 328 K in steps of 15 K. Reproduced with permission from Elsevier.[54]

in polyurea as a function of increasing frequency, which can be considered to be analogous to increasing strain rates. A set of ballistic impact experiments with a complimentary set of dielectric spectroscopic investigations has been performed and representative dielectric loss spectra for polyurea at different temperatures is presented in Fig. 7.[54,59] The transition from rubber to glass results in an increase followed by a decrease in the dielectric loss which appears as a hump in the spectra.[54] It is however to be noted that the frequency associated with this dynamic rubber-glass transition is *ca.* 10^6 Hz, which is only possible under ballistic loadings, and appears to be remote under blast loadings.

4. Conclusions and perspectives

The potential of polyurea in the context of blast mitigation and ballistic protection has been well demonstrated by numerous investigations. It is clear that these interesting properties of polyurea are direct consequence of its composite microstructure, where hard domains (resulting from hydrogen bonding within urea linkages) are dispersed throughout a largely homogenous soft domain. The ballistic performance of polyurea depends primarily on the soft domains while the shock wave mitigation ability is dependent on the hard domains formed due to urea linkages, which effectively means that a polyurea formulation exhibiting blast mitigating properties may not prove to be the most optimal in terms of its ballistic protection ability. The properties of polyurea need to be tuned for a particular application through judicious choice of the isocyanate and amine which also varies the hard segment : soft segment ratio.

Surprisingly, the effect of varying the hard : soft segment of polyurea on the blast performance of polyurea retrofit has not been established experimentally. Although few computational studies are available, experimental validation of the results is still awaited. In addition, data on the dynamic mechanical behaviour of polyureas with varying hard : soft segment ratio as a function of temperature and frequency is also unavailable.[114,115] Presently, a set of parallel DMA studies are essential to justify the assertion that polyurea undergoes a dynamic glass transition at high frequencies, as has been proposed by dielectric spectroscopy. It is also to be noted that all studies in the context of blast mitigation have been performed either on patented formulations or on those containing amine terminated polytetramethyleneglycol. Interestingly, commercial formulations are usually prepared by the reaction of isocyanates with amine terminated polypropylene oxide, which leads to polyureas with much lower glass transition temperatures. Studies on the blast mitigation properties of these formulations definitely mandate the attention of researchers.

It is also to be noted that in view of their discernible heterogeneous microstructure polyureas are not the choicest of materials for preparation of composites. However, inclusion of nanomaterials may lead to substantial improvement in the mechanical properties of the base resin and affect their strain rate sensitivity similar to what has been observed in thermosetting epoxy resins.[116,117] Blending with other materials, especially ionomers[118] can also enhance the toughness and impact resistance of the base polymer appreciably. In view of the same, there exists a distinct possibility of decreasing the thickness of retrofit by introducing fillers; an aspect that needs to be studied in greater detail.[119]

Interestingly, polyurethanes (a reaction product of polyol with isocyanate) also exhibit a similar microstructure as polyurea, but this particular class of polymers has not received attention as far as its potential as blast mitigating retrofit is concerned. Polyurethanes also exhibit a phase separated microstructure, with the hard domains forming as a result of H-bonding between the urethane linkages.[120,121] Polyurethanes have been largely ignored because of the reported absence of strain rate sensitivity. However recent studies have clearly highlighted their potential in the area of blast mitigation[122] and this is a material which definitely deserves further investigation.

Another area which mandate the attention of researchers concerns the scaling up issue.[123,124] In view of the difficulty associated with field trials, lab scale controlled testing are usually performed on scaled down models using a shock tube. However in the absence of scaling laws, there are issues associated with the direct upscalation for practical applications. Further, since it is the adhesion between the polymer and underlying substrate which define the overall behaviour of the retrofitted structure, studies on the effect of surface activation need to be carried out.

It can be concluded that polyurea and polyurethane elastomers hold enormous potential for blast mitigating applications. With ever-increasing terrorist threats, which involve small scale explosions, application of these spray on elastomeric coatings on existing structures will increase in the future. There is practically unlimited choice in terms of design chemistry and optimisation of microstructure through astute choice of raw materials. In view of the above, studies involving exploring the potential of polyureas and polyurethanes will attract the attention of researchers and academicians alike for several years to come.

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