MULTILAYER COMPOSITES WITH SELF-HEALING CAPABILITY BASED ON AN EMAA Ionomer

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1 Introduction

Thermoplastic materials, such as ethylene-methacrylic acid copolymers and ionomers have shown Self-Healing (SH) behavior after ballistic impacts either in low and hypervelocity speed range [1-5].

The SH behavior of these polymers after high energy impacts has been studied and described in several references [1-7]. The repair of damages is autonomous and instantaneous without any external intervention and occurs after impacts with energy high enough to allow the projectile to pass through the material in a very short time.

Ionomers based on ethylene-co-methacrylic acid copolymer (EMAA) are one of the first class of polymeric materials which have been found to exhibit such SH behavior. In view of an extension of the properties range required in different potential applications, SH blends based on ionomers with the addition of different crystalline, elastomeric polymers and modifiers have also been prepared and investigated [8-12]. The use of EMAA based polymers is currently limited to those events that pierce the material; however researchers tried also to investigate the SH behavior of fiber reinforced composites by introducing thin layers of EMAA polymers in the stacking sequence [13].

Despite the SH behavior, these materials cannot be used in primary structural components due to their low mechanical properties. A possible solution to this issue can be the use of EMAA ionomers in multilayer composite structures to improve mechanical performance providing also a SH behavior. These types of structures are very common in many different fields because of their versatility. Multilayer composite structures are widely used in aerospace industry for matching the best properties of different materials. In aeronautical components, sandwich structures are commonly used to increase the flexural stiffness and the ultimate buckling strength with a minimal increase of mass. In space systems, multilayer structures are commonly used to achieve a “multifunctional material” given by the combination of the peculiar properties of each layer. For example, multilayer covering systems with thermal insulation and electromagnetic shielding layers have been developed; for special missions some dedicated layers can be added to primary structures such as ablative heat shield or impact protection for planetary exploration missions.

Furthermore the design of a space structure must take into account the high probability of impact with micrometeoroids or space debris during the operational life of the space system. In recent years, the amount of space debris has increased significantly and nowadays every spacecraft must face almost one orbital maneuver to avoid the collision with major objects. Nevertheless the number of smaller objects (<1 cm), which are difficult to monitor by ground stations, is continuously growing due to space collisions and explosions. In some regions of space environment, incidentally the most interesting for space activities such as the Low Earth Orbits (LEO) region, their concentration is so high that an impact with a spacecraft is almost a sure thing during the operational lifetime [14]. Even if small sized, these objects travel at orbital velocity (~km/s), so that impact events involve a great energy amount and are seriously dangerous for space systems, especially for electronic units and pressurized systems, such as tanks or habitable modules. In this scenario, it is evident how important is the availability of materials which can self-repair after an impact and avoid any pressure leakage. Nevertheless, the rough conditions
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of the space environment limit the usability of many of existing SH materials employed in aeronautic components. For all these reasons, it would be very important to include SH material, such as EMAA ionomers, in multilayer composite structures in order to employ them in space systems. This opportunity could highly increase the reliability of future spacecrafts allowing a longer duration of mission for deep space exploration and a safer environment for astronauts against pressure leakage.

In this research, the SH behavior of ionomer plates and multilayer composites was investigated under different ballistic impact conditions; ionomer plates with carbon foam or with carbon-epoxy backing and aramid fabric/ionomer composites were tested. Aramid fabrics are widely used for flexible ballistic protections thanks to their tenacity and impact energy absorption capacity; aramid reinforced composites and foam cored sandwich structures find extensive employment in rigid armor. Carbon foams present particular mechanical and thermal properties, which make them interesting in a number of structural applications [15-18]. Carbon fiber reinforced composites with epoxy matrix are widely used in many applications, especially in aerospace structures, thanks to their excellent mechanical properties and low weight. The coupling of aramid fabrics, carbon foams or carbon-epoxy composites with polymers able to restore, at least partially, the continuity of the material may significantly extend the performances of such systems ensuring better reliability and response to impact effects.

Ionomer plates have been tested by ballistic puncture tests in a previous research [5]; different conditions were assessed by varying sample thickness, bullet impact velocity (from 180 m/s up to 4000 m/s), bullet shape and diameter. At tested impact speed, EMAA-Na (sodium partially neutralized EMAA) presented self-repair ability up to a specific sample thickness/projectile diameter ratio even at highest impact speeds. Regarding multilayer systems, ballistic tests at the lowest speed prove that self-healing behavior of ionomeric layers can be maintained also in composites. After all impact tests, the healing efficiency was evaluated by applying a pressure gradient at the damage zones. Morphology analysis of the impact sites was also made observing all samples by optical stereomicroscope and scanning electron microscope (SEM) both in the bullet entrance and exit sides.

2 Experimental

2.1 Materials

EMAA based ionomers are available on the market with Surlyn® trade name. Different grades are characterized by different amount of acid group, different cations used for neutralization (e.g Na, Zn, Mg, Li) and different neutralization level.

The EMAA-Na ionomer used in this research (grade Surlyn® 8940) has an acid part content of 5.4 mol% with about the 30% of acid groups neutralized by Na ions. It was provided by DuPont™ Italy in pelletized form. This polymer is characterized by a density of 0.95 g/cm³, a melting temperature of 94 °C and a melt index of 2.8 g/10 min at 190 °C according to the data provided by the manufacturer.

Various materials were used as reinforcement or core, in particular aramid fabric, carbon foam and a carbon/epoxy composite panel. Aramid fabric, STYLE 281 was provided by Seal SpA. Carbon foam, FPA-35, supplied by GraflTech International, is characterized by a bulk density of 0.56 g/cm³. Carbon fiber composite plates were produced using [0/+45/-45/0] stacking sequence of a pre-preg Satin 5H, 285 g/m², fabric obtaining a final thickness of about 1 mm. Cure cycle in autoclave was employed.

2.2 Multilayer sample preparation

After drying ionomer pellets in vacuum at 60 °C for 5 hours, plates of 120x120 mm were produced by compression molding using a hot platens hydraulic press. Pelletized polymer was placed in the mold heated at 180 °C and then pressed in order to obtain samples with thickness ranging from 0.5 mm to 3 mm. A molding pressure of 5 bars was employed with a cooling rate of about 20 °C/min; the pressure was maintained during cooling stage, until the removal of samples.

Multilayer hybrid composites were produced using a similar technique; in the specific, previously produced 1 mm thick polymeric plates were used as outer layers in the stacking sequence (Fig. 1).

All layers, with aramid, carbon foam or carbon epoxy laminate as core, were positioned within the mold and then lightly pressed for 10 minutes at 120 °C in order to allow the adhesion between the different layers.
In case of aramid reinforcement, up to 5 fabric layers were employed and partial impregnation was obtained. Foam slices of 10 mm thickness were instead employed for the production of ionomer/carbon foam multilayer composites. After productions, all samples were stored in temperature and humidity controlled chamber (25 °C/ 50% RH) prior to testing in order to achieve non-variable and stable mechanical properties of the polymeric layers.

2.3 Ballistic tests

Ballistic puncture tests on multilayer materials were performed in a ballistic laboratory by shooting with a shotgun, model Hatsan Optima, 5.65x20 mm bullets through 120x120 mm square samples (Fig. 2). Preliminary test were also performed on pure ionomeric plates of different thickness (0.5, 1, 2 and 3 mm) in order to confirm the SH capabilities under the same test conditions (Fig. 3). The speed of bullets during ballistic tests was measured using an optical chronograph (model CED M2 Millennium) and it ranged between 700 and 730 m/s. All tests were performed at 23±2 °C.

2.4 Healing evaluation

All specimens were observed by optical and scanning electron microscope (Hitachi Ltd., model TM-3000) both in the bullet entrance and exit sides in order to have evidence of hole closures. SEM analyses were also performed to evaluate the morphology of the damaged surfaces of the specimens. To check for the ability of healing, leakage tests were carried out; a pressure difference of 0.9 bars was initially applied by a vacuum pump in a closed chamber, where one side was sealed with the tested polymer plate; A specific-designed device was developed for this purpose [19]. Air tightness through the hole was tested following vacuum decay and by checking for possible flow of a fluid droplet placed at the damage zone with the applied pressure difference. When the hole was healed no appreciable vacuum decay was detected within a specified time range but for non-healed samples vacuum decay was observed within a few seconds.
3 Results and discussion

Previous experiments showed how pure ionomer exhibits a SH behaviour after ballistic impact tests under different experimental conditions [19-21]. Preliminary impact tests on pure ionomer were performed with 5.65 mm diameter bullets fired at 700 m/s and also in these cases the SH behaviour was well maintained. Only the 0.5 mm thickness sample did not show a complete hole closure and hole sealing.

Microscope observations of healed pure ionomeric samples after ballistic tests evidenced a complete hole closure and a clear melted zone in the centre of the crater (Fig. 4); the great energy exchanged during the puncture due to impact, friction forces and deformation causes a local heating above the melting temperature of the polymer, promoting the hole sealing. Damaged area shows also the characteristic striations radially distributed around the crater caused by an intense plastic deformation during projectile passage through the sample. These results are in agreement with the two stage healing mechanism proposed for ionomers, where, viscoelastic recovery is supposed to bring to hole closure in the first stage, while, local melting process leads to full or partial hole sealing in the second healing stage [2,3].

The tested multilayer composites exhibit different responses after ballistic impact, however some common similarities with the previous case can be recognized, in particular for those with aramid fabrics and carbon foam layers.

Regarding multilayer system with aramid fabrics, it can be noted that for all tested samples, having different fabric plies, hole closure occurred (Fig. 5, Fig. 6); however, leakage tests revealed that only sample with 1 and 2 fabric layers show complete and efficient SH behaviour.

The reduced constrain exerted by the fabric in the impact area, allows for ionomeric polymer viscoelastic recovery and efficient healing.

![Fig. 5. Optical image of ionomer/aramid fabric (4 layers) composite bullet entry side area](image)

![Fig. 6. Micrograph of ionomer/aramid fabric (1 layer) composite bullet entry side area](image)
Ballistic experiments carried out on a sandwich made of ionomer plates with carbon foam core, revealed a different behaviour in the self-repairing phenomenon of the ionomeric layers. SH appeared only in the first polymeric layer hit by the bullet (inlet layer). When the bullet passed through carbon foam, the outlet ionomeric layer did not exhibit SH ability, as revealed by leakage tests. It is conceivable that the bullet passage through the first polymer plate and carbon core, reduces its energy so that no re-welding and healing of the ionomer is possible in the outer layer. Another possible cause of no healing of the outer ionomer layer could be attributed to the cloud of carbon microparticles generated during the impact of the projectile with the foam; these particles, deposited on the damaged area, may prevent the repair process. However, also in this case, at least partial hole closure was observed for all tested samples.

Observing the back side of tested pure ionomer (Fig. 7), ionomer/aramid fabric (Fig. 8) and ionomer/carbon foam multilayer composites (Fig. 9) a similar behavior was revealed. Brittle radial cracks appear in all cases indicating a petaling of the material during impacts. The morphology of the damaged area in healed pure ionomeric samples presented petaling phenomenon with a melted zones on the apex of the petals. These melted areas, even if small, are responsible for the sealing of the hole caused by the bullet, thus becoming a crucial factor for the global SH behavior exhibited by the studied material.

On the other hand, non-healed composite samples, still presented petaling phenomena, but did not show a clear melted zone and an efficient SH capability. This behavior suggests that the additional contribution to temperature increment deriving from the friction forces between bullet and impact surface was dissipated in the exit side as consequence of the presence of aramid fabric or carbon foam layers, preventing the repair.
Results of ballistic tests on ionomer/carbon-epoxy multilayer system showed a different response from the previous cases. Although the SH behavior of the EMAA-Na layer was not complete, however a remarkable hole reduction took place even under these testing conditions (Fig. 10-12). Carbon-epoxy composite layer instead present a clear circular hole of about the same diameter of the used projectile. After ballistic tests it can be also observed an extensive delaminated zone around impact sites (Fig. 12).

The presence of a rigid layer, such as the carbon-epoxy composite one, prevents deformation of the ionomer ply. This behavior has effects on the self-repair capability which requires the melting of the polymer in the area of impact. Heat generated by plastic deformation and friction forces consistently give a fundamental contribution to the recovering and sealing of the hole and it seem that limited deformation cause the limitation of such phenomena, thereby preventing an efficient hole closure and repair.
4 Conclusion
In this work, the SH behavior of different ionomeric multilayer systems was explored. Performed ballistic impact tests on multilayer plates showed that SH behavior was in some instance well maintained in the ionomer layers. Similar response after ballistic impact has been shown by ionomer/aramid fabric and ionomer/carbon foam multilayer systems. Hybrid multilayer composites with a carbon-epoxy ply instead, did not exhibit a complete hole closure preventing the self-sealing of the damage after impact. However, a remarkable hole reduction was observed even under these testing conditions. A further study may involve the response of these kind of structures under hypervelocity impact tests in view of possible space applications.
These results encourage the study of ionomeric systems and the development of new complex structures yet able to maintain efficient SH ability suggesting also a number of other potential applications in environments prone to impact damages.

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References


