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BALLISTIC CHARACTERIZATION OF NANOSTRUCTURED COMPOSITE MATERIALS FOR AEROSPACE APPLICATIONS

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INTRODUCTION

The capability of absorbing energy upon impact is an important feature for structures in a large number of fields. Aircrafts, helicopters, satellites and in general transportation components are faced with impact events that can damage or collapse devices and structures. Generally, materials employed to limit damages due to impact are metals, ceramics and composites based on long continuous fiber reinforcements; however, the increasingly stringent requirement of lightweight components drives investigations towards new advanced composite materials, based on nano-fillers.

In the last decades the research on composite materials have been acquiring importance due to the possibility of increasing the material mechanical performances while contemporary decreasing both mass and volume of the structures. Mass lowering is a "must" especially in military and space applications, since aircraft aerodynamic profile needs to be optimized and because of the high costs of launch and launcher and payload mass constraints. Further, the need to face up to the well know problem of the so called "space debris" has lead many aerospace researchers to look for advanced lightweight materials for ballistic applications.

As far as ballistic properties are concerned, the fiber- reinforced composite materials are increasingly used in the manufacturing of aerospace and automotive structures due to their high strength to weight ratios. Every one of customers wishes good performance and mass production with low cost, but these properties are usually not possible all at once. The aviation industry normally entails components with a high design security without being mainly cost-effective. In the automotive industry the centre of attention is fairly diverse i.e., low cost mass production. The outstanding corrosion resistance of fiber-reinforced polymer matrix-composites makes them predominantly attractive in this latter industry. From a strategic point of view, the objective of this field of research is to improve or replace the heavy, steel Ballistic Protection Systems (BPS) system currently in use on special operations rotary wing aircraft by increasing the survivability of the aircraft, crew, and passengers while retaining a versatile and lightweight system, capable of sustaining multiple round impacts from small caliber weapons at variable ranges and angles of fire. The aircraft must be able to operate in extreme weather and high altitude environments without a significant performance decrease during mission flights due to the presence of BPS. In recent history, research and development has led to great improvements in modern day BPS. Researchers are constantly in search of better materials and systems with which to protect soldiers on the battlefield; whether it is body armor, aircraft or vehicular BPS. The natural human desire for self-preservation and the developments in munitions and threats have motivated individuals throughout history to search for better means of protection.

Among all innovative materials, a promising branch of such research focuses on the polymeric composite materials with inclusions of nanostructures. Polymer nanocomposites are composites with a polymer matrix and a filler with at least one dimension less than 100 nanometers. While some nanofilled composites (carbon black and fumed silica - filled polymers) have been used for over a century, in recent years the dedicated research and development of nanofilled polymers has greatly increased. This is due to our increased ability to synthesize and manipulate a broad range of nanofillers and significant investment by government and industry in this field. Current interest in nanocomposites has been generated and maintained because nanoparticle-filled polymers exhibit unique combinations of properties not achievable with traditional composites. These combinations of properties can be achieved because of the small size of the fillers, the large surface area the fillers provide, and in many cases the unique properties of the fillers themselves. In many cases these large changes in the material properties require small to modest nanofiller loadings. Unlike traditional micron-filled composites, these novel fillers often alter the properties of the entire polymer matrix while, at the same time, imparting new functionality because of their chemical composition and nanoscale size.

As far as ballistic properties are concerned, the interest in developing advanced lightweight materials based on nanocomposites arise from the unconventional behavior of several nanomaterials in terms of impact energy dissipation. A rich and complex vibrational structure, in particular for acoustic phononic modes, gives to nanoparticles the possibility to withstand high external stresses without structural damages. Thanks to a suitable procedure of nanostructures intercalation within organic matrix, is thus possible to manufacture light composite materials with improved capabilities of ballistic protection, via energy spreading from local points over larger areas or by means of the so-called shear thickening effect. Nevertheless, an extensive study on the capability of absorbing energy, in particular by nano-reinforced composite materials subject to high velocity impacts, is not available in the scientific literature. In this scenario, BPS realized by means of composite materials reinforced with carbon nanotubes (CNT) and shear thickening fluid (STF) were identified as those with the highest expectation in terms of performance benefits.

A carbon nanotube is a honeycombe lattice (“graphite sheet”) rolled into a cylinder. The diameter of a carbon nanontube is of nanometer size and the length of a nanotube can be more than 1 μm. The nanotube diameter is much more smaller in size than the smallest carbon fiber obtained so far. CNTs are largely investigated for their exceptional electrical, thermal and mechanical properties. From a mechanical point of view, the nanotubes uniqueness is their stiffness, corresponding to the upper limit of the best carbon fibers (which are commonly used as a strong light-weight material), coupled to an uncommon pliability. At an early stage, the theory stimulated experiments in carbon nanotube physics, since obtaining sufficient quantities of a pure carbon nanotubes has been difficult in practice. The direct evidence provided by electron microscopy for the existence of carbon nanotubes was sensational to many physicist and chemists, and because of this fascination, the field of carbon nanotubes has grown explosively, with many active research groups worldwide working independently or in collaborative research projects. The electrical and mechanical properties of carbon nanotubes have captured the attention of researchers worldwide. Understanding these properties and exploring their potential applications have been a main driving force for this area. Nanotubes are ideal systems for studying the physics in one-dimensional solids. Theoretical and experimental work have focused on the relationship between nanotube atomic structures and electronic structures, electron-electron and electron-phonon interaction effects. Extensive efforts has been taken to investigate the mechanical properties of nanotubes including their Young's modulus, tensile strength, failure processes and mechanisms. Also, an intriguing fundamental question has been how mechanical deformation in a nanotube affects its electrical properties. In recent years, progress in addressing these basic problems has generated significant excitement in the area of nanoscale science and technology. The advantages associated with the use of CNT-reinforced materials are linked to the multifunctional features of such nanomaterials. Recent reviews reported that multi-walled carbon nanotubes as fillers can influence the absorbing energy capacity of polymers and of fiber-reinforced polymer composites. In particular, the high aspect ratio, the dispersion and the chemical modification of the CNT surface may increase the toughness of the composite. The mechanical properties of a nanostructured composite material are strongly affected by the dispersion of the nano-fillers within the polymer matrix, which depends on the interface bonding with the polymeric chains. Based on this consideration, an important role in the energy absorption mechanism of a composite material is played by the functionalization treatments of the filling nanoparticles. Such treatments provide for a chemical modification of the nanoparticles surface, making them compatible with the polymer matrix.

An intriguing issue of nanoscience research for aerospace applications is to produce a new thin, flexible, lightweight and inexpensive material that have an equivalent or even better ballistic properties than the existing Kevlar fabric. A shear thickening fluid is a material with remarkable properties. STF are very deformable materials in the ordinary conditions and flow like a liquid as long as no force is applied. However they turn into a very rigid solid-like material at high shear rates. Shear thickening is a non-Newtonian fluid behavior defined as the increase of viscosity with the increase in the applied shear rate. This phenomenon can occur in micro/nano colloidal dispersions. More concentrated colloidal suspensions have been shown to exhibit reversible shear thickening resulting in large, sometimes discontinuous increases in viscosity above a critical shear rate. Two main causes of reversible shear thickening have been proposed: the order–disorder transition and the "hydrocluster" mechanism. The phenomenon of shear thickening of suspensions in general has no useful applications in industrial production. Recently U.S. Army research lab developed a body armor using shear thickening fluid and Kevlar fabric. These research results demonstrate that ballistic penetration resistance of Kevlar fabric is enhanced by impregnation of the fabric with a colloidal shear thickening fluid. Impregnated STF/fabric composites are shown to provide superior ballistic protection as compared with simple stacks of neat fabric and

STF. Comparisons with fabrics impregnated with non-shear thickening fluids show that the shear thickening effect is critical to achieving enhanced performance.

The goal of the present work is to perform a ballistic characterization of both CNT-based and STF-reinforced nanocomposites by means of an in-house built electromagnetic accelerator. This study fits in a more general research project, the aim of which is to realize, study and characterize several types of nanocomposite materials. These latter are currently manufactured in the DIAEE *SASLab* of 'Sapienza' University of Rome, by mixing the nanoparticles directly within polymeric matrixes in such a way to obtain a material as homogeneous as possible, in order to have a final composite with improved physical/chemical characteristic.

The manuscript is arranged in three main parts.

In the first chapter the nanocomposite manufacturing is described. As far as the CNT-filled polymeric composites are concerned, a carbon nanotube functionalization process by thermal and chemical treatments has been performed, and Scanning Electron Microscopy (SEM) analysis, as well as Raman and FT-IR spectroscopies were used to verify the surface modifications of the CNTs by the added radical groups. Then, the manufacturing of the CNT-reinforced epoxy composite has been carried out, and Differential Scanning Calorimetry (DSC) was used to analyze the polymerization process for the nano-reinforced thermosetting polymer systems. SEM investigations were also performed to assess the nanocomposites quality in terms of nanoparticle dispersion and material homogeneity. Regarding the STF-reinforced materials, STFs have been synthesized in a single step reaction through high power ultrasound technique, and characterized in terms of their rheological properties. The shear thickening fluid is prepared by ultrasound irradiation of silica nanoparticles dispersed in liquid polyethylene glycol polymer. Then, STF-reinforced fabrics have been realized by soaking layers of several types of Kevlar in STF/ethanol solution; the morphology of the as-realized fabrics, in particular for what concerns the STF/fibers interaction, has been deeply investigated by SEM analysis.

In the second chapter the realization and the characterization of the in-house built Coil Gun device for ballistic applications is presented. The realization of such experimental apparatus, and mostly the optimization with a view to space debris testing plane, is quite complex since the fundamental machine parameters have high non-linearity behavior. With the aim to perform an as accurate as possible ballistic characterization, both theoretical issues and experimental preliminary results of the prototypal device are widely presented and discussed.

In the third chapter the results of the ballistic characterization of the realized nanocomposite materials are reported. The response of the manufactured materials to several levels of impact energy is widely investigated. Charpy impact and weight drop tests were performed to obtain a preliminary ballistic characterization of the CNT-

reinforced epoxy composites in the low energy impact range. In order to assess the influence of the nanoparticles content as well as the effectiveness of the nano-filler itself and after chemical treatments, samples with different percentages of functionalized CNTs embedded in two different epoxy resins were tested and compared with samples reinforced by pristine CNTs and micrometric graphite powder. Finally, the response of CNT-reinforced epoxy materials and STF-reinforced Kevlar fabrics was experimentally investigated by Coil Gun ballistic tests at different impact energy: the effects of the nanoparticles on the penetration failure and the impact absorbing mechanism is analyzed and discussed.

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