Original Article

Ballistic behavior of a hybrid composite reinforced with curaua and aramid fabric subjected to ultraviolet radiation


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ABSTRACT

Mobile ballistic armors, particularly those intended for personal protection, are also designed with lowest possible weight. Composite materials are the best choice for this kind of application, especially laminated composites reinforced with high-performance fibers or fabrics. Owing to environmental problems, research works on hybrid composites based on natural instead of synthetics fibers is already a promising line of investigation. These composites, when used outdoors, are exposed to ultraviolet (UV) radiation and some properties and applied behavior may change. Therefore, this work investigated the ballistic behavior of a thermostet polyester resin laminated hybrid composite reinforced with a natural fiber mat and aramid fabric after exposure to UV radiation. The mat was produced with curaua fiber, one of the strongest natural fibers. Infrared spectroscopy analysis and determination of the degree of cross-linking, to identify possible structural changes in the curaua mat, are performed after two different exposure times to UV radiation. The mechanism of failure related to the ballistic impact is analyzed by visual inspection. The results show that the composite is influenced by UV radiation, which affects the ballistic performance due to delamination on the interface of plies as well as chain scission on curaua fibers and increasing crosslinking of the polyester resin. The delamination was attributed to a low interfacial energy between the polyester matrix and curaua fibers.

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1. Introduction

Ballistic armors are designed to resist a specific projectile threat with efficient weight/protection ratio, i.e., highest ballistic strength with the lowest weight. In the case of personal and vehicular protection, the lightness of the armor is of uppermost concern in terms of mobility. Composite materials might be a choice for this kind of application [1,2]. These materials are usually reinforced with fabrics of high-performance synthetic fibers, because of their low density, high Young modulus, high strength and excellent capability for absorbing the projectiles’ kinetic energy [3]. With the current attention to environmental issues, a significant growth of researches on composites reinforced with natural lignocellulosic fibers (CRNF) is revealing advantages that these fibers present when compared to synthetic ones [4–11]. In particular, examples of natural fiber composites are emerging as proposals to produce sustainable materials [12–16]. These examples serve as motivation for possible studies on the use of hybrid composites in different applications, including ballistics.

The development of CRNF with hybrid participation of synthetic fibers in many cases will need environmental effects to be considered. Indeed, humidity, temperature, biological attack and radiation might induce degradation associated with changes in molecular structure, which could significantly impair the composite properties. Ionizing radiation, such as ultraviolet (UV) rays, gamma rays, X-rays, accelerated electrons and ion beam, leads to scission of the main macro-molecular chains as well as crosslinking with the concomitant formation of covalent bonds among synthetic or natural polymers [17]. In particular, UV radiation might significantly affect natural fibers and could also be relevant in hybrid composites due to both fibers scission and crosslink in the polymer matrix [18]. These combined effects decrease the fiber/matrix adhesion and induce delamination. As a matrix-dominated fault mechanism, delamination normally impairs the composite mechanical properties [19]. However, delamination might also play a positive role in the ballistic behavior by dissipating part of the impact energy.

Fig. 1 shows schematically the ballistic failure mechanism proposed by Yu et al. [20] upon the impact of a projectile, from partial penetration to complete perforation.

Partial penetration occurs in two stages. First, the impact produces fiber breaking by shear, Fig. 1(a); after that, the kinetic energy of the projectile is absorbed and its speed decreases due to fiber stretching, bulging and layer delamination, Fig. 1(b). Complete perforation is associated with fiber breaking, which also decreases the projectile speed due to energy absorption and is followed by plastic deformation, showing that ballistic failure is controlled predominantly by both delamination and the tensile stress at break of the reinforcing fibers, Fig. 1(c) [20].

The present work investigated a hybrid CRNF composed of a polyester matrix reinforced with a natural mat made of curaua fiber and an aramid fabric. Among the traditional Brazilian natural lignocellulosic fibers, those extracted from the curaua plant (Ananas ertectifolius) of Amazonian origin, stands out in the engineering applications for its high mechanical strength and stiffness, attributed mainly to the high content of cellulose (70% cellulose content), degree of polymerization (conferred to approximately 21% of hemicellulose 8% of lignin) and low fibrillary angle [6]. Environmental effects associated with photodegradation and biodegradation in EPS/curaua fiber composites [21] as well as accelerated aging on the mechanical properties of curaua/glass fiber hybrid composites [22] have already been primarily investigated. The choice for the synthetic aramid fabric in the present hybrid composite was based in the worldwide application for ballistic protection. In fact, the aramid fabric, Kevlar™ or Twaron™ (commercial trade marks), is known by its superior mechanical properties such as tensile strength, 3600–4100 MPa, and elastic modulus, 131 GPa, associated with relatively low density of 1.44 g/cm³ [23].

In this work, the degradation process in a hybrid polyester composite reinforced with curaua mat and aramid fabric subjected to UV radiation, is evaluated in terms of dissipated energy from the impact of projectile in ballistic tests. The composite performance is also evaluated by physical and chemical analyses. The type of failure, which occurred before and after different times of UV irradiation exposure is investigated to disclose mechanisms responsible for changes in both the microstructure and properties.

2. Materials and methods

Laminated hybrid composites were produced with 6 wt% polyamide aromatic (aramid) fabrics, 34 wt% curaua fabrics and 60 wt% thermoset polyester resin (matrix). Curaua mats were supplied by Pematec Triangel Company, the aramid fabrics by Teijin Aramid Company and the polyester resin by Resinpoxy Company, Brazil. Both curaua mats and aramid fabrics were dried in a stove at 60 °C for 24 h. The curaua

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**Fig. 1** – Behavior of fiber-reinforced aramid composites after impact: (a) and (b) partial penetration; (c) complete perforation [20].
mats were first compressed under 2 ton in a model Sky-15 hydraulic press for better accommodation of the fibers. Rectangular 150 × 120 × 12 mm plies of both curaua mats and aramid fabrics were positioned together with still fluid polyester resin inside a steel mold, according to the distribution of layers schematically shown in Fig. 2. Hybrid laminated composites were obtained after uniaxial pressing under 5 ton of load in the aforementioned hydraulic press. Curing occurred under pressure for 24 h. It is important to notice in Fig. 2 that curaua plies were placed at the surfaces of the hybrid composite plate, just covered by a thin (~1 mm) layer of polyester. In this way, the aramid fabrics were distant ~6 mm from the plate surfaces and, consequently, much less affected by UV radiation.

The exposition of samples to UV radiation was performed by using an accelerated aging system for non-metallic materials with ultraviolet "B" rays (UV-B), following the standard guidelines of ASTM G-154 [24], during 300 and 600 h for both sides, remaining them in direct contact with air. They have been located at 5 cm of distance away from the UV sources emitting a spectrum peaking at the wavelength of 306 nm.

Infrared spectroscopy analyze was performed on an iS90 Smart ITR Spectrometer in the range 400–4000 cm⁻¹. This analysis was aimed at evaluating structural changes in the macromolecules of the irradiated material to correlate the UV radiation times with the possible crosslinking of the thermoset resin (matrix) and chain scission of the curaua fibers. The molecular change of curaua has been studied using the peaks in 1727 cm⁻¹ and 1033 cm⁻¹ that are attributed, respectively, to stretching of the C=O functional group and C–O–C on the molecular chain of the curaua fiber [17].

The amount of polyester resin crosslinked by the action of UV radiation was determined by the calculation of the crosslinking degree, before and after irradiation. This was performed by the extraction of the non-crosslinked resin in a Soxhlet type extractor, following the ASTM D 2765 [25] standard with some modifications. Tetrahydrofuran (THF) grade PA was used as the solvent for 6 h under reflux (189–192 °C) at the rate of 40 drops per minute. Drying of the insoluble gel, after complete extraction of the uncrosslinked components, was performed inside a stove at 110 °C for 12 h until the mass remained constant. The calculation of the insoluble fraction of the material was performed according to Eq. (1), where \( W_s \) is the mass of the non-soluble sample, after drying, in grams; \( W_i \) is the initial sample mass (before extraction) in grams, and \( W_o \) is the mass of the cage.

\[
\text{Degree of crosslinking}\% = \left( \frac{W_s - W_o}{W_i - W_o} \right) \times 100. \tag{1}
\]

The swelling ratio of the polymer matrix was also determined according to Eq. (2). This ratio corresponds to the absorption of the solvent by the polymer, which is directly related to the number of crosslinks present in the polymer [26]. Where \( W_s \) is the mass of the wet sample with the cage.

\[
\text{Swelling ratio}\% = \left( \frac{W_o - W_e}{W_o} \right). \tag{2}
\]

The ballistic tests were carried out according to the NIJ Standard 0108.01 [27] level II (9 mm ammunition), using projectiles fired from a weapon (gun barrel) on targets 5 m away, at an incident angle of 0°. Fig. 3 illustrates schematically the ballistic test setup located at the Brazilian Army shooting range facility (CAEx, Rio de Janeiro).

The ballistic performance of the armor was evaluated considering the energy absorbed by the composite, calculated by Eqs. (3) and (4), using the residual and impact velocity, obtained by Doppler radar model Weibel SL-520P, after complete perforation. For each condition (non-irradiated, irradiated 300 h and irradiated 600 h), five composites were tested, each with one shot.

\[
E = \frac{1}{2} \cdot m \cdot (V^2). \tag{3}
\]

\[
E_L = E_i - E_R, \tag{4}
\]

where \( E_i \) is the absorbed energy, \( E_i \) the impact energy and \( E_R \) the residual energy.

The damage produced by the shot, in terms of the layer deformation, the occurrence of punching or cutting of the yarns and the delamination around the point of impact was analyzed by visual inspection. Scanning electron microscopy...
Table 1 – Degree of crosslinking and swelling ratio of orthophthalic polyester resin before and after UV irradiation.

<table>
<thead>
<tr>
<th>Condition of the polyester resin</th>
<th>Average degree of crosslinking %</th>
<th>Average swelling ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-irradiated</td>
<td>96.4 ± 1.7</td>
<td>1.41</td>
</tr>
<tr>
<td>300 h of UV irradiation</td>
<td>95.6 ± 2.1</td>
<td>1.41</td>
</tr>
<tr>
<td>600 h of UV irradiation</td>
<td>97.1 ± 0.6</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Table 2 – Oxidation indices obtained by the peak intensities of 1639 cm⁻¹ and 1537 cm⁻¹ of aramid fabric, normalized by the peak intensity of 821 cm⁻¹, before and after UV irradiation.

<table>
<thead>
<tr>
<th>Condition of the aramid fabric</th>
<th>Oxidation indices (1639/821)</th>
<th>Oxidation indices (1537/821)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-irradiated</td>
<td>0.527</td>
<td>0.659</td>
</tr>
<tr>
<td>300 h of UV irradiation</td>
<td>0.541</td>
<td>0.746</td>
</tr>
<tr>
<td>600 h of UV irradiation</td>
<td>0.512</td>
<td>0.659</td>
</tr>
</tbody>
</table>

Table 3 – Oxidation indices obtained by the peak intensities of 1727 cm⁻¹ and 1033 cm⁻¹ of curaua mat, normalized by the peak intensity of 2917 cm⁻¹, before and after UV irradiation.

<table>
<thead>
<tr>
<th>Condition of the curaua mat</th>
<th>Oxidation indices (1727/2917)</th>
<th>Oxidation indices (1033/2917)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-irradiated</td>
<td>0.658</td>
<td>3.870</td>
</tr>
<tr>
<td>300 h of UV Irradiation</td>
<td>0.467</td>
<td>1.996</td>
</tr>
<tr>
<td>600 h of UV Irradiation</td>
<td>0.416</td>
<td>1.154</td>
</tr>
</tbody>
</table>

Table 4 – Average ballistic energy as a function of the areal density (µA).

<table>
<thead>
<tr>
<th>Condition of the composite</th>
<th>µA (kg/m²)</th>
<th>Absorbed energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-irradiated</td>
<td>13.36 ± 0.18</td>
<td>140.01 ± 16.24</td>
</tr>
<tr>
<td>300 h of UV Irradiation</td>
<td>13.04 ± 0.02</td>
<td>105.93 ± 13.49</td>
</tr>
<tr>
<td>600 h of UV Irradiation</td>
<td>12.58 ± 0.20</td>
<td>120.51 ± 09.91</td>
</tr>
</tbody>
</table>

(SEM) observations were performed in a model Quanta FEG 250 FEI microscope with secondary electrons operating at 15 kV. Samples were previously coated with platinum.

3. Results and discussion

Table 1 shows the variation of the degree of crosslinking (expressed as percentage of gel) and the swelling content of the orthophthalic polyester resin as a function of the time of exposure to UV radiation.

The results in Table 1 reveal, for all conditions, that only around 4% of polyester resin did not undergo crosslinking during the curing process. This suggests a failure in the production of the composite, i.e., lack of interaction between the curing agent and the liquid resin. It can also be seen that the material exposed to 300 h did not produce more cross bonds than the non-irradiated composite, as shown by the swelling ratio of 1.41 for both conditions. However, after 600 h of irradiation the number of cross bonds increased, as observed by the swelling ratio of 1.34. This raise on links suggests that the UV radiation acts as the initiator for the cure of the monomers not previously crosslinked, just after 600 h, producing a higher amount of crosslinking in the polymer and resulting in a stiffer composite [29]. Actually, this increase in crosslinking makes the resin more brittle, providing a decrease in interfacial energy and increasing the probability of delamination.

The degradation promoted by UV radiation in hybrid CRNFs occurs on the surface of the polyester and curaua fiber macromolecules in a micrometric scale. By contrast, significant changes in the aramid fabric layer were not observed [30]. Table 2 shows the oxidation indices evaluated by the normalized peak intensities for Amide I (1639 cm⁻¹) and Amide II (1537 cm⁻¹), as a function of peak intensity of 821 cm⁻¹, considered unaffected by irradiation [31,32]. It can be seen that the intensities at both peaks varied as compared to the non-irradiated material. This indicates that carboxylic or aldehyde groups were possibly generated after cleavage (C–N) of the main chain. In the case of the 600 h irradiation, this process was attributed to photo-oxidation at the fiber surface [33].

Fig. 4 presents the FTIR spectra of the curaua fabric before and after UV irradiation. In this figure, the intensities of absorbance peak associated with the C=O–C group are shown expressed as a function of the characteristic wave number of the material [34,35]. Table 3 presents the oxidation indices obtained by peak intensities of 1727 cm⁻¹ and 1033 cm⁻¹, normalized by the peak intensity of 2917 cm⁻¹, before and after UV radiation.

According to Table 3, the decrease of both peak intensities suggests the occurrence of scission in C–O–C and C=O groups, giving rise to lower molecular weight. As a consequence, the curaua mat becomes brittle, which affects the hybrid composite ballistic behavior [17].

Table 4 presents the absorbed energy by the hybrid composite before and after UV irradiation on the ballistic tests. Within the respective precisions (standard deviation) both UV irradiation times are associated with similar absorbed energies, relatively lower (<14%) than that absorbed by the non-irradiated samples.

As the Doppler radar did not capture the impact velocity of the projectile at the composite, this velocity was assumed to be the same at the exit of the gun barrel in Fig. 3 [36]. The results in Table 4 show that the ballistic resistance of the composite decreased with UV irradiation and the absorbed energy (E₅), Eq. (4), associated with the same areal density (µA), varies with the increasing UV irradiation time.

The decrease observed in the ballistic performance of the hybrid composite after UV exposure could be mainly attributed to the decrease in the molecular weight of the curaua mat, Fig. 4. A small contribution to this decrease might also be assigned to the increase in the amount of crosslinks of the polyester matrix, shown in the degree of swelling for 500 h of irradiation, Table 1. However, the composite subjected to 600 h of UV radiation presented better ballistic performance than those subjected to 300 h of exposure. This suggests that the possible intermolecular bonds (hydrogen bonds between the natural fiber surfaces/matrix) generated after the UV irradiation, promote a greater rigidity to the surface of the material. This gives rise to intralaminar faults that propagate...
Fig. 4 – Curaua fiber spectra before and after different times of UV irradiation.

Fig. 5 – Cross section of composites after ballistic tests: (a) non-irradiated; (b) 300 h of UV irradiation; (c) 600 h of UV irradiation and (d) SEM micrograph of the 600 h UV irradiated sample.

throughout the composite body and, consequently, result in delamination [17,37].

The macro and microscopic analyses allowed the identification of possible failure mechanisms in the laminated composite. Fig. 5 presents the cross-section of the impacted composite, before and after the UV irradiation.

In this figure, it is observed that complete ballistic perforation occurred for all conditions. In Fig. 5(a) it is also noted that non-irradiated composite absorbed the impact energy through the rupture of the fibers (curaua and aramid), followed by the plastic deformation of the fibers. The SEM micrograph in Fig. 6 shows that the fibers are ruptured with slight stretches at their ends (microfibrils). This confirms the fact that the fibers’ plastic deformation and their tensile strength control this type of failure in both non-irradiated curaua mat and aramid fabric.

By contrast, as shown in Fig. 5(b)–(d), it should be noted that, unlike non-irradiated composites, the irradiated ones have delamination after ballistic impact. This delamination is possibly related to increased crosslinking of the polymer chains after exposure to ionizing radiation, yielding a more rigid and less tough resin. This rigidity, which can be translated into less plastic deformation in relation to the fibers, increases the probability of delamination occurring in the composite [38,39]. This results in energy dissipation upon impact and is, therefore, not considered to be harmful to the ballistic behavior of the composite.
4. Conclusions

- Results of ballistic tests of hybrid polyester matrix composites reinforced with plies of curaua mat, near the surface, and aramid fabric, in the interior of plate samples, revealed the effect of ultraviolet (UV) radiation for 300 and 600 h of exposure.
- The absorbed ballistic energy from the impact of a 9 mm ammunition displayed similar values for both 300 and 600 h UV irradiated composites. These values were found to be around 14% lower than that for the non-irradiated composite.
- UV radiation exposure improved the crosslinking degree of the polyester matrix, which became more rigid with less plastic deformation in association with a decrease in its capacity to absorb the impact energy.
- As for the curaua mats near the hybrid composite surface, fiber macromolecular scission due to UV irradiation causes brittleness of the mat, which reduces toughness but contribute to dissipate the ballistic impact energy by means of fiber/matrix delamination process.

Conflicts of interest

The authors declare no conflicts of interest.

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