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Low-velocity impact behaviour of hemp fibre reinforced bio-based epoxy laminates☆

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ABSTRACT

This work addresses the damage resistance and post-impact damage tolerance of hemp fabric reinforced bio-based epoxy composites subjected to low-velocity impact at energies ranging from the barely visible impact damage (BVID) threshold up to perforation. A comparison is also reported with similar composites in terms of thickness and fibre volume fraction but based on a traditional epoxy matrix. The results confirmed the significant toughness of laminates based on a bio-based epoxy matrix and their superior damage tolerance compared to standard hemp-epoxy laminates, thus highlighting their potential use in semi-structural applications due to an improved interfacial adhesion with hemp fibres.

1. Introduction

The increasing use of composite materials in automotive and aeronautical/aerospace applications, coupled with the depletion of petroleum resources, is stimulating the search for materials and products with the lowest possible environmental 'footprint' with a focus on renewable raw materials. This enhanced awareness has triggered, especially in Europe, a shift towards using natural materials as a substitute for non-renewable synthetic fibres, like glass, in composites based on both thermosetting and thermoplastic polymers [1–4]. For semi- or structural applications, the use of thermosetting matrices is preferred due to their high flexibility in tailoring desired ultimate properties, leading to their high modulus, strength, durability, thermal and chemical resistance as provided by high cross-linking density.

At a first step, the reduction of the environmental impact of composite materials based on thermosets was obtained by the substitution of synthetic fibres with natural ones. Nowadays, researches are based on the replacement of petrochemical components from the matrix with bio-based renewable equivalents. Renewable resources can provide an interesting sustainable platform to substitute partially, and in some cases totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values [5–8]. Thermoset materials represent less than 20% of the total plastic production and epoxy resins account for roughly 70% of the market of thermosetting polymers (not including polyurethanes) [9]. In particular, the global epoxy resins production was estimated to be 2 million tons in 2010 and is projected to reach 3 million tons by 2017 [9]. These figures explain the shift of chemical industry towards a sustainable chemistry with the use of renewable resources in order to synthesize biobased chemicals and products. It is to be emphasized that biobased sourcing does not necessarily imply biodegradability. Recently there is an increasing demand for biobased materials with a strong emphasis on performance and durability. In case of thermosetting materials, the most widely applied renewable resources include plant oils, which are triglycerides (tri-esters of glycerol with long-chain fatty acids) with varying composition of fatty acid depending on plant, crop, season and growing conditions. Recent reviews have focused on the development of cross-linked plant oils and their derivatives for thermosetting applications, such as coatings and resins [10]. Bio-

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Table 1
Key parameters obtained from impact tests on hemp fibre laminates.

Impact energy (J)	Peak force (N)	Maximum displacement (mm)	Absorbed energy (J)
Bio-epoxy			
5	2098.09 ± 62.03	3.84 ± 0.10	2.50 ± 0.06
10	2188.92 ± 63.40	6.18 ± 0.03	8.32 ± 0.10
15	2214.77 ± 49.33	8.60 ± 0.13	14.54 ± 0.01
20	2340.26 ± 74.42	11.02 ± 0.49	19.94 ± 0.04
40	2706.91 ± 37.28	–	29.33 ± 0.08
Traditional epoxy			
5	1765.19 ± 31.79	4.42 ± 0.08	2.64 ± 0.13
10	1873.80 ± 8.36	7.22 ± 0.05	9.51 ± 0.01
15	1970.16 ± 18.62	10.12 ± 0.11	14.91 ± 0.04
18	1980.02 ± 27.27	12.32 ± 0.14	17.84 ± 0.01
40	2462.04 ± 16.78	–	29.86 ± 0.02

based thermosetting polymers can be used as matrices in composites, both for synthetic and natural fibres. It is clear that the goal is the adoption of bio-based thermosetting matrices in the production of fully biobased materials, hence using biobased material also as filler/reinforcement. Natural reinforcements currently account for about 11% of the total volume of fibres used in composites,

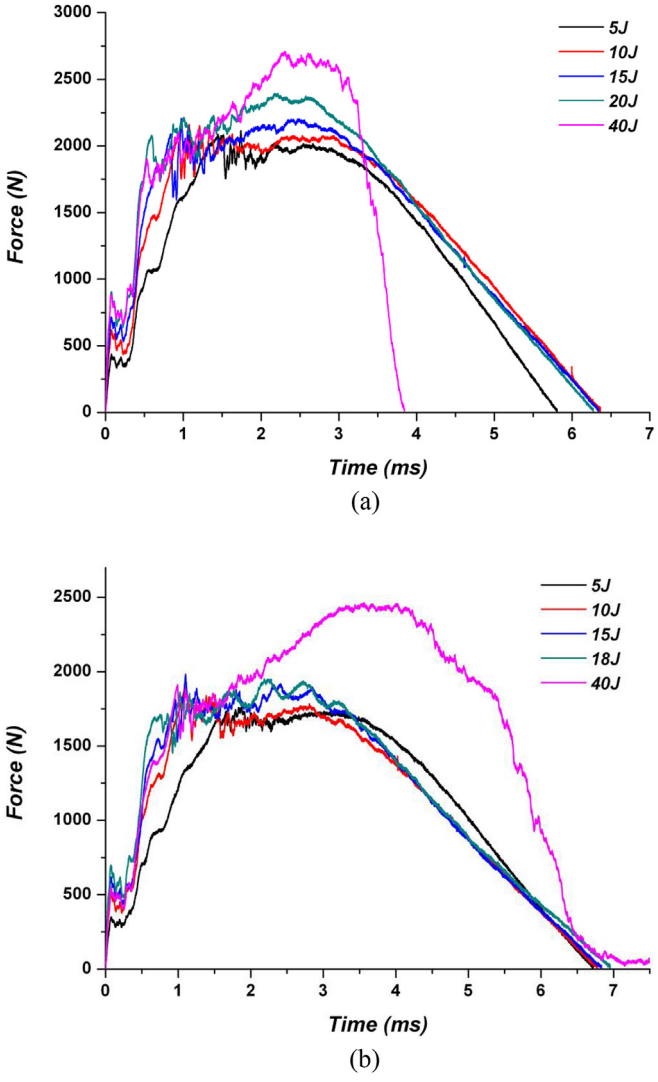

Fig. 1. Typical force vs. time response as a function of impact energy of composites based on (a) bio- and (b) traditional epoxy matrix.

with forecasts estimating 22% by 2020. Among natural fibres, hemp fibre is one of the most inexpensive and readily available bast natural fibre in Europe. It is characterized by high specific mechanical properties together with high cellulose content, which make it a material of choice as reinforcement in polymer matrix composites [11]. Vegetable oils, despite being excellent raw materials for thermosetting biopolymers, due to their availability and inexpensiveness, are usually reported to have limited thermal and mechanical properties because of the low reactivity of aliphatic epoxy groups, which results in poorly cross-linked materials [12]. In this regard, the addition of natural fibres could also partially mitigate their disappointing mechanical performance. At present, despite the growing research studies, available biobased thermoset matrices for structural applications are not known; however, not fully biobased resins but with a significant content of components coming from renewable vegetable materials, having good performance are already marketed (e.g., by Entropy Resins Inc., Eco Green Resins, LLC). Some studies have addressed the physico-mechanical behaviour of composites made with natural fibres and such bio-based resins [12–15], but their properties and their potential use for the manufacturing of natural fibre composites have not been investigated in depth. In particular, the response of such composites to low velocity impact loads is not well known, even though some recent works have addressed such topic for composites based on traditional epoxies reinforced with hemp fibres [16,17]. Such property is very important, because low-velocity impacts by foreign objects during composite structures life may occur during the phase of manufacturing, maintenance, operation and so on. The internal damage produced by impact loads can largely affect their residual mechanical properties even when barely visible impact damage (BVID) is produced. In fact, BVID can result in internal damage such as delaminations and back-face splitting, which can reduce the residual strength by as much as 60%. The inherent variability in natural fibre properties is still limiting the diffusion of natural fibre composites in semi-structural applications, also due to a non reliable understanding of their mechanical behaviour, in particular as regards their impact damage resistance and damage tolerance. The present work addresses the evaluation of the BVID threshold for hemp woven fabric reinforced bio-based epoxy laminates and their residual strength in bending. For the sake of completeness, a similar experimental campaign has been performed on equivalent composites but based on a traditional epoxy matrix, in order to highlight differences and potential limitations of bio-based epoxies.

2. Materials and methods

A plain weave hemp fabric was used with a fibre areal weight of 400 g/m^2 as reinforcement (AssoCanapa srl), while a bio-based

epoxy resin with a bio-based carbon content of 21 wt% (Super Sap® CLR with slow hardener CLS02, supplied by Entropy Resins Inc.) was used as matrix. Super Sap® CLR matrix is a clear modified liquid epoxy resin that, as opposed to traditional epoxies composed primarily of petroleum-based materials, contains bio-renewable materials sourced as co-products or from waste streams of other industrial processes, such as wood pulp and bio-fuels production. The bio-based carbon content is in the range 18.2–25.4% (ASTM D6866, as per supplier's technical datasheet). Eight plies of hemp fabric were stacked in a $[(\pm45)/(0/90)]_{2S}$ configuration, in order to achieve a target thickness of 5(±0.1) mm and a fibre volume fraction of 0.42(±0.01). The specimens were manufactured by hand lay-up and vacuum bagging and were cured at room temperature for 12 h and then post-cured at 80 °C for 15 h.

Coupons (three for each energy level) were impacted at room temperature, according to ASTM D7136 at various impact energies to achieve BVID and perforation. In particular, 5 J, 10 J, 15 J, 20 J and 40 J (perforation) are the five levels of impact energy used for testing. For comparison purposes, similar laminates in terms of stacking sequence, fibre volume fraction and thickness were manufactured with a traditional epoxy resin SR1700 with a slow hardener SD2713 supplied by Sicomin Epoxy Systems. In this case the coupons were impacted at 5 J, 10 J, 15 J, 18 J and 40 J (perforation). An instrumented drop tower (Ceast/Instron 9340) was used for this purpose. Damage was imparted through out-of-plane, concentrated impact (perpendicular to the plane of the laminated plate), using a drop weight with a smooth hemispherical striker tip with a diameter of 16 mm. Rectangular specimens (100 × 150 mm) were supported on a rigid base with a cut-out of 75 × 125 mm. After impact event, the dent depth of each coupon was measured using the contact profilometer Taylor Hobson – Talyscan 150 and the damaged area was measured using an ultrasonic C-scanner (OmniScan MX with standard phased array probe, 3.5 MHz).

Four-point bending tests have been performed in accordance with ASTM D 6272 on a universal testing machine Zwick/Roell Z010, equipped with a 10 kN load cell. A span-to-depth ratio of 16:1 and a cross-head speed of 2.5 mm/min have been used. Specimens have been tested in bending either after their production (non-impacted samples) or after the low-velocity impact tests to measure their residual flexural strength.

Fracture surfaces of composites were investigated by means of Scanning Electron Microscopy (SEM, Philips XL40). The surfaces were sputter coated with gold prior to observation.

3. Results and discussion

The present investigation follows the established methodology for damage tolerance assessment, which consists of four major sequential steps, namely: (i) impact testing, (ii) damage characterization, (iii) determination of static residual strength and (iv) damage tolerance evaluation.

To assess composite's impact damage, it is common to refer to the impact energy (E_i) and absorbed energy (E_a). Impact energy is the kinetic energy of the impactor right before contact with samples takes place, whereas absorbed energy is the energy dissipated by the system through the several mechanisms occurring after the impactor's contact, like elastic deformation, friction, plastic deformation and, most importantly, those peculiar to the material, such as matrix cracking, debonding, pull-out, fibre breakage.

Key impact parameters like peak force, maximum displacement and absorbed energy are summarized in Table 1. Typical force vs. time plots for hemp fibre laminates impacted at different energy levels up to penetration are shown in Fig. 1. These curves for both bioepoxy and traditional epoxy composites exhibited similar features with the presence of two peaks. As reported by many authors

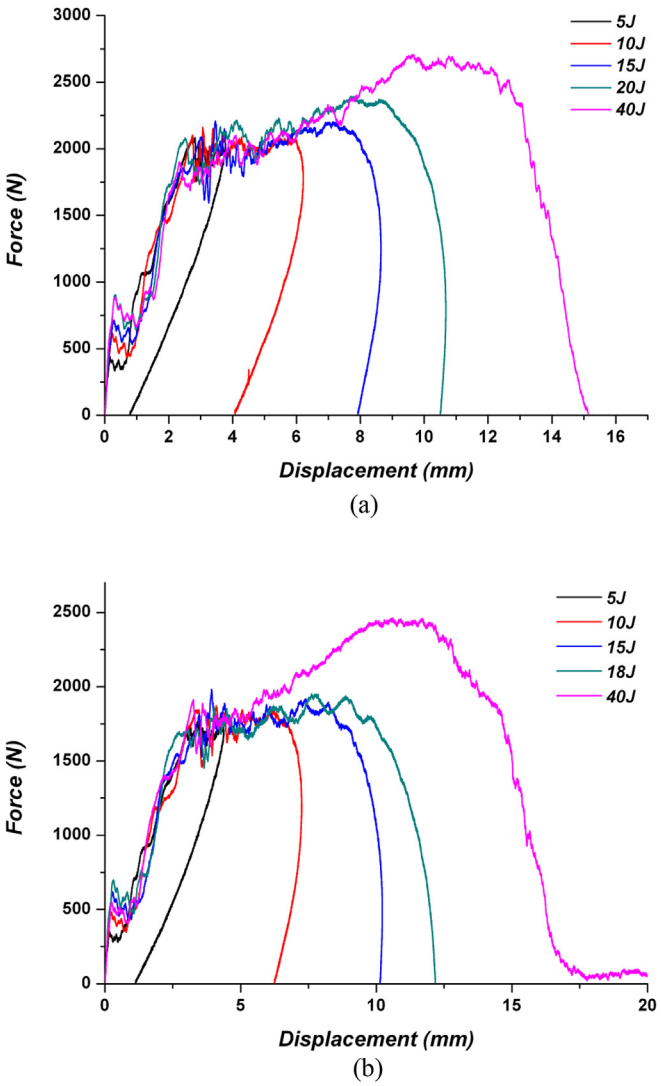

Fig. 2. Typical force vs. displacement response as a function of impact energy of composites based on (a) bio- and (b) traditional epoxy matrix.

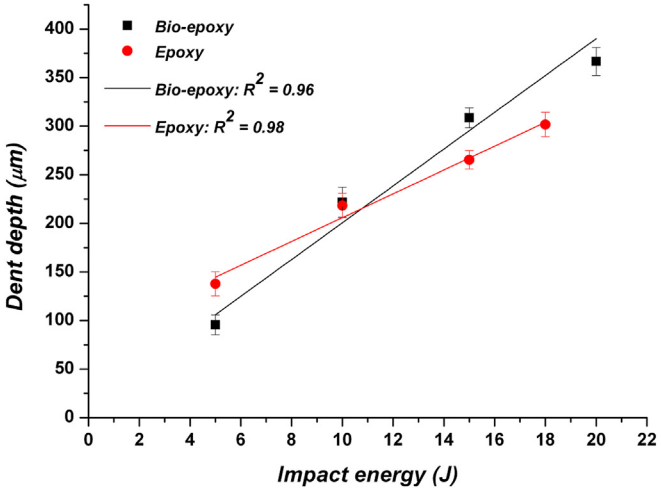

Fig. 3. Dent depth vs. impact energy.

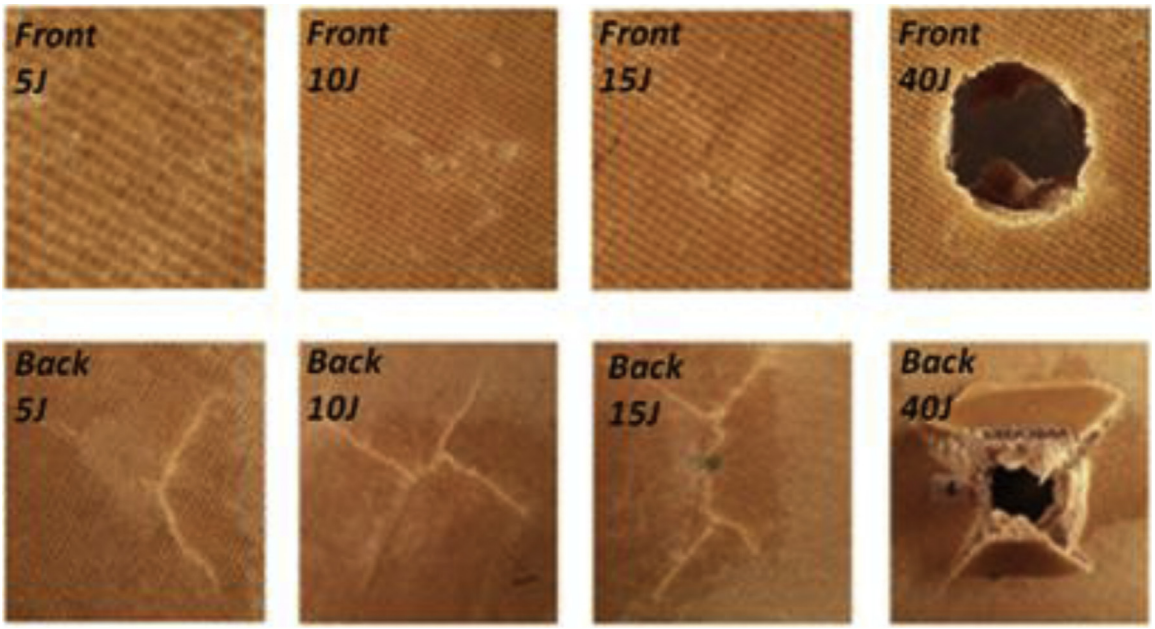

Fig. 4. Close-up views of damage progression on front and rear faces of hemp/bioepoxy composites impacted in the range 5 J–40 J.

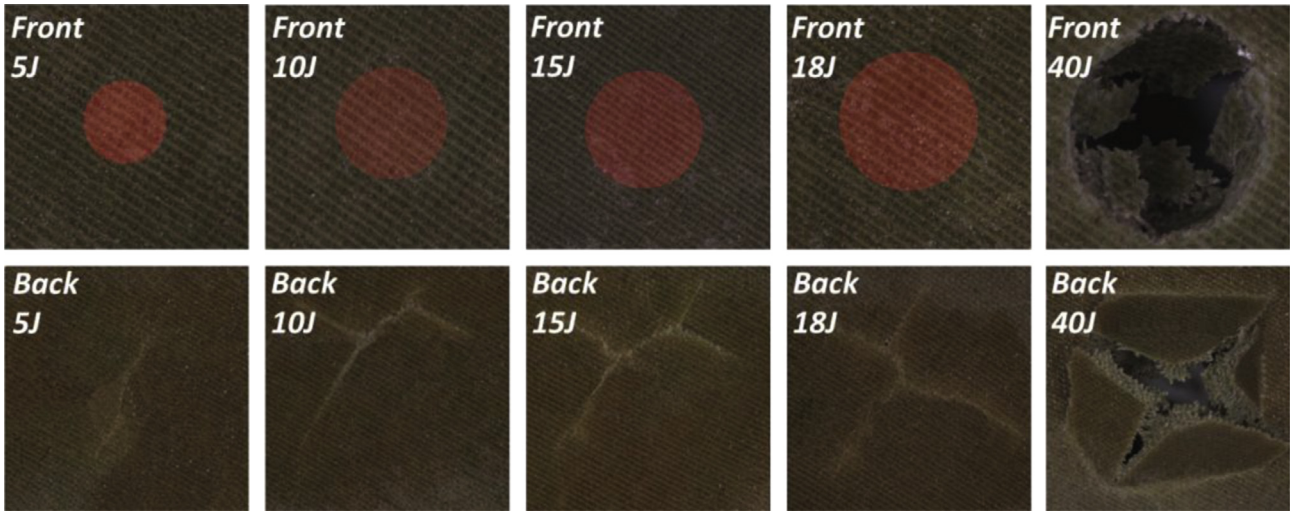

Fig. 5. Close-up views of damage progression on front and rear faces of hemp/epoxy composites impacted in the range 5 J–40 J.

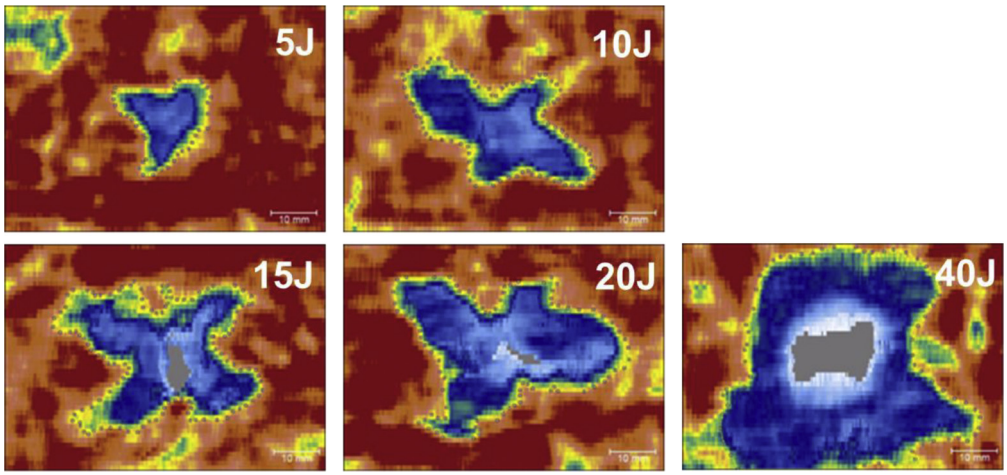

Fig. 6. Ultrasonic C-scan images of composites based on bioepoxy as a function of impact energy.

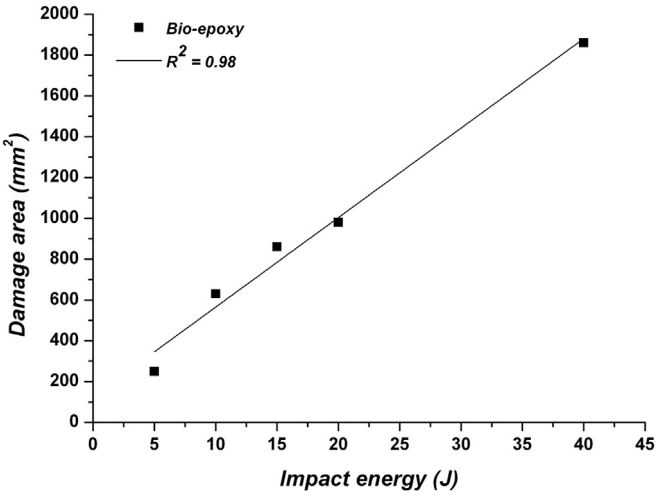

Fig. 7. Projected damage area vs. impact energy.

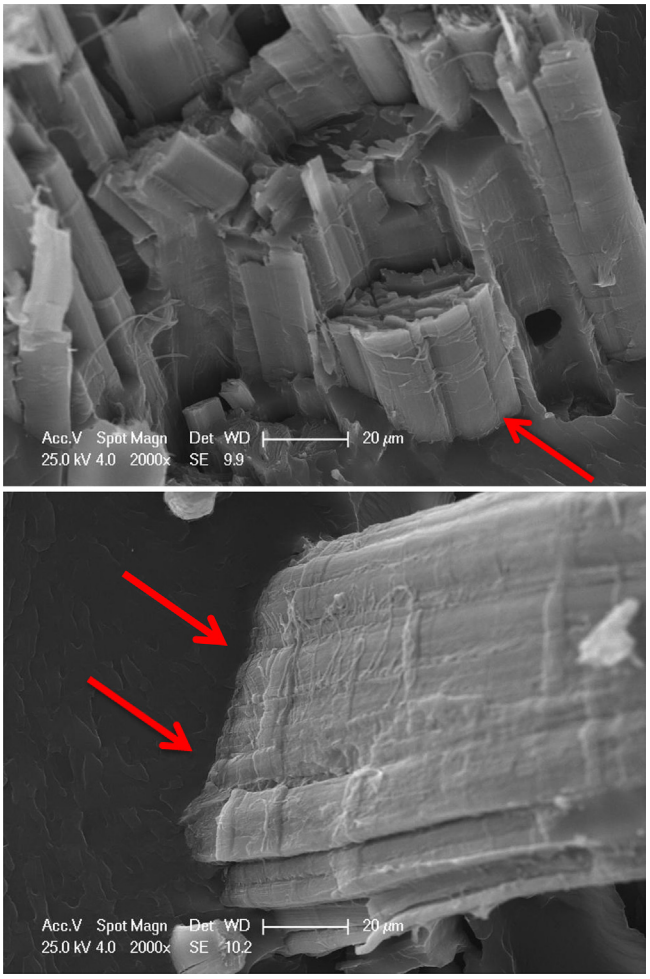

Fig. 8. SEM micrographs showing fracture surfaces of hemp/bioepoxy laminates.

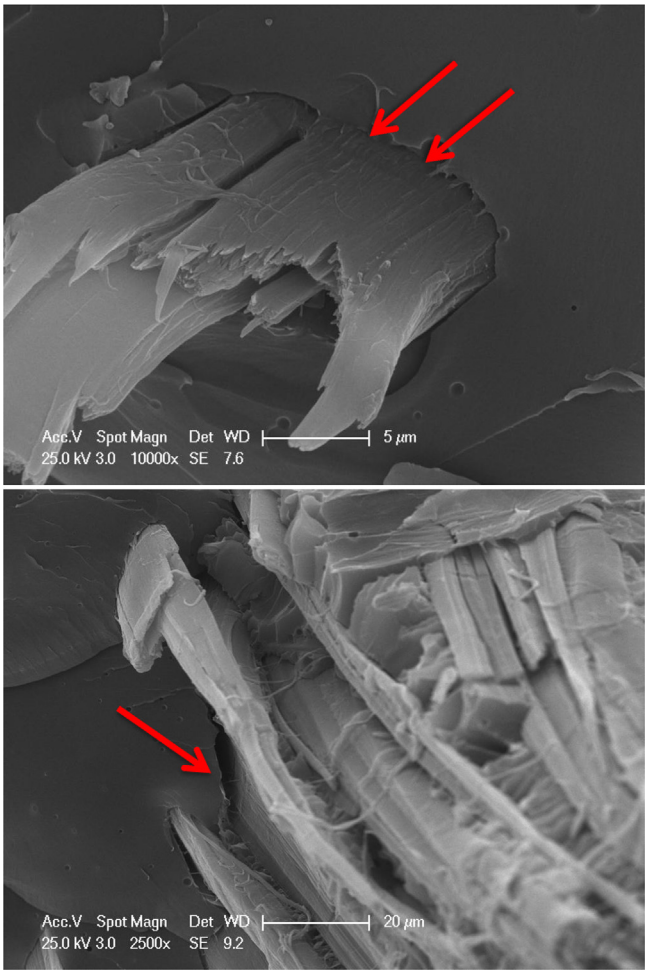

Fig. 9. SEM micrographs showing fracture surfaces of hemp/epoxy laminates.

Table 2
Summary of flexural properties as a function of impact energy and matrix type.

Specimen	Flexural strength (MPa)	Flexural modulus (GPa)
Bio-epoxy		
0 J	107.32 ± 0.28	5.33 ± 0.09
5 J	90.22 ± 7.03	4.77 ± 0.07
10 J	68.49 ± 5.37	4.48 ± 0.11
15 J	60.53 ± 1.86	3.75 ± 0.33
20 J	45.40 ± 4.55	2.55 ± 0.45
Traditional epoxy		
0 J	108.50 ± 1.19	5.26 ± 0.08
5 J	78.30 ± 10.67	4.70 ± 0.17
10 J	63.19 ± 0.81	4.11 ± 0.29
15 J	52.33 ± 0.80	3.58 ± 0.06
18 J	47.44 ± 3.39	3.38 ± 0.06

[18–20], the sudden load drop (incipient damage point) in these curves indicates the occurrence of damage with onset of delamination and sudden loss in stiffness. This threshold load increases with the increase of the incipient impact energy and was slightly higher for the composites based on the bioepoxy. After this incipient failure, the load–time curve went up with oscillations and reached a maximum value. This peak load represents the load that the laminate can tolerate before undergoing major damage and was found to slightly increase with increasing impact energy for both systems. Once the load increased up to the maximum value and dropped suddenly, an irregular plateau with many oscillations followed, which is usually ascribed to the development of severe internal damage. These results confirm, as a whole, the poor damage resistance of natural fibre composites when subjected to low velocity impacts already highlighted in other studies [21,22]. Up to 20 J for bioepoxy composites, penetration did not occur and the impactor rebounded with an energy that is the difference

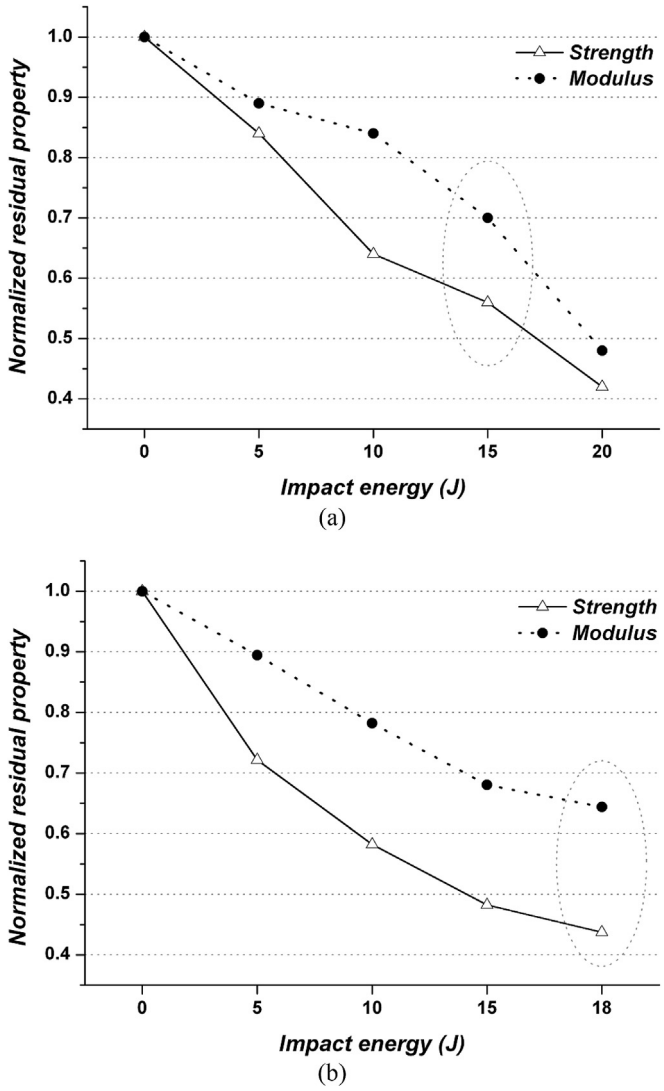

Fig. 10. Normalized residual flexural strength and modulus of hemp fibre reinforced composites after low velocity impact of various energies: (a) bioepoxy matrix and (b) traditional epoxy matrix.

between E_i and E_a. The absorbed energy can be calculated from force–displacement curves (Fig. 2) as the area enclosed within the curve.

The composites investigated exhibited a quite high compliant behaviour which enabled the specimens to absorb energy through high overall deformation and interface failures such as delamination and pull-out. All the curves (with the exception of 40 J-impact) showed a closed pattern, confirming that some elastic energy has been recovered causing the impactor's rebound. It was evident that the area under the curves increased with impact energy, indicating an increase of both absorbed energy and damages in the laminate, thus suggesting that these composites can dissipate a high amount of the impact energy. Similar conclusions can be drawn for composites based on the traditional epoxy matrix.

Dent depth was plotted against impact energy in Fig. 3. At least for the energies tested, dent depth increases approximately linearly with impact energy for both systems (R^2 values ≥ 0.96) which is not unusual in literature [23], even though Caprino et al. [17] recently found a more than linear trend with increasing impact energy for hemp fibre reinforced composites for a wider range of impact energies. Impacts around 15 J for bioepoxy and 18 J for traditional epoxy, fell within the typical BVID regime (being ~ 0.3 mm dent depth the threshold of detectability commonly adopted by aeronautical standards). Interestingly, the ranking of absorbed energy does not correlate with dent depth. Composites based on the traditional epoxy exhibited higher energy absorption through a global ductility (consider for instance the higher displacement during impact tests) that was not observed in laminates based on bioepoxy due to a more pronounced localization of impact damage.

The damage progression in the composite panels with increasing impact energy is shown in Figs. 4 and 5. No visible damage on the front face was detected up to 20 J and 18 J for bioepoxy and epoxy laminates, respectively (in Fig. 5 the red (in the web version) circles represent the indentation area), but matrix cracking and back surface splitting were detected on the back surface, phenomena that were only partially counteracted by the global deformation of the specimens. Comparing Figs. 4 and 5, it is possible to note a slightly more localized damage in bioepoxy laminates.

The ultrasonic phased array testing method was used to evaluate damaged area only for composites based on bioepoxy, which is connected with the energy absorbed by the samples. Fig. 6 shows C-scan images of impacted samples from which it was estimated the extent of damage reported in Fig. 7, where again a positive linear correlation with impact energy was found. The damaged area (in mm^2) at each impact level has to be considered through-the-thickness, being the envelope of damaged areas of each layer. The wide damaged areas suggest that delaminations between different kinds of layers occur with the consequence of improving the energy dissipation. This damage mode, despite being the predominant, is not supposed to be the only one taking place. Interfacial failures, such as debonding and pull-out, are expected to play an important role. These interfacial mechanisms were found to be mitigated by the better fibre/matrix adhesion due to the bio-based content of the resin in comparison to traditional petrochemical equivalent, as confirmed by the SEM micrographs of Figs. 8 and 9. For bioepoxy laminates, no clear gaps between hemp fibres and matrix were observed, whilst they were evident in the case of traditional epoxy laminates. This could explain the highest resistance to impact damage, in terms of incipient damage force and peak load, exhibited by laminates based on bioepoxy matrix and their lower global ductility. In a recent study Marrot et al. [24] performed a detailed multi-scale analysis of the adhesion between commercially partly biobased epoxy and polyester matrices and flax fibres. At the microscopic scale, the debonding test highlighted a satisfactory adhesion for every composite and encouraging mechanical results for the use of partly biobased epoxy and polyester resins in plant reinforced composites were found. In particular it was highlighted the role played by the high hydroxyl groups content due to the amine hardener in partly explaining the significant adhesion obtained for the flax/bioepoxy system. This can apply also to the present case due to the cycloaliphatic polyamine nature of the hardener.

As previously stated, due to the susceptibility of composite materials to impact damage, dramatic loss in residual strength and structural integrity results. In the present work the residual properties were evaluated in bending as this kind of loading introduces a complex state of stress pattern in the specimens and therefore the effect of damage is difficult to be analysed. Table 2 summarizes flexural properties of undamaged and impact damaged composites. Both systems exhibited curves characterized by a yielding stage and a long ultimate deflection, thus suggesting an increase in energy absorption and a good damage tolerance. In order to make comparisons between the different materials easier, the residual strength and modulus values have been normalized by dividing by appropriate flexural strength and modulus values of the

undamaged materials (Fig. 10). As expected, the higher the impact energy, the lower the residual flexural strength and modulus. However, compared with bioepoxy matrix, the composites based on conventional epoxy are more sensitive to impact damage. At the BVID energy (red (in the web version) circles in Fig. 10), the bio-based composites exhibited a decrease in stiffness and strength of approximately 30% and 40%, respectively, which were found to be lower than those suffered by laminates based on conventional epoxy. This outcome is a clear indication that the bio-based composites present the most favourable degradation pattern as they show the best damage tolerance thus implying a better ability to perform post-impact in semi-structural applications.

4. Conclusions

The results demonstrate that hemp fabric reinforced bioepoxy composites offer similar if not superior flexural properties, due to an improved fibre/matrix interface, and damage tolerance compared to those based on traditional epoxy resin. Therefore such laminates can be potential candidates for next generation materials in semi-structural applications, providing end-of-life improvement for products and adequate mechanical properties once established both a stricter control over the raw materials used, an assessment of their reliability along with an optimization of fibre/bioepoxy interface to balance two competing requirements, namely high damage tolerance and high quasi-static mechanical properties.

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