COMPARISON OF LOW VELOCITY IMPACT BEHAVIOUR OF THERMOPLASTIC COMPOSITES REINFORCED WITH GLASS AND BASALT WOVEN FABRICS

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Abstract
The effects of interface strength on the quasi-static and low velocity impact behaviour of woven basalt and woven glass/polypropylene (PP) laminates have been investigated and the performances of the resulting composites compared. The fibre/matrix interface strength has been managed by modifying the matrix with a coupling agent (maleated PP) acting as a compatibilizer. Quasi-static flexural tests showed that the compatibilizer improves both flexural modulus and strength, as well as the strain at yield in glass fibre based laminates. On the contrary, for systems reinforced with basalt woven fabrics, probably owing to a specific surface pre-treatment, only limited gains in flexural properties were detected after compatibilizer addition to the matrix.
This consideration is reflected in different effects on the impact strength. An improved interface strength, such that of glass fibre/compatibilized PP samples, lowered the perforation threshold because crack propagation cannot be blocked and matrix or fibre breakage become the main dissipative mechanisms. The reduction of the interface strength allows further dissipative mechanisms (fibre splitting, larger fibre and matrix deformations, frictions) and improves the perforation threshold. In particular, PP/basalt fabric composites showed the highest perforation threshold among all prepared laminates (perforation occurring above 60 J), due to the very weak interface strength and the higher ultimate properties of basalt fibres with respect to glass ones.

1. Introduction

Continuous fibre reinforced thermoplastic composites, based on commodity polymers, are attracting a growing interest due to their fast processability, recyclability, chemical resistance, low moisture absorption and low cost. In addition, their high impact strength is one of the main advantages over thermosets. Many works concerned with the impact response of woven composites have been published [1-5], and the different contributions to the energy dissipation have been described. Among thermoplastic matrices, polypropylene (PP) is considered one of the most promising for many industrial applications [6], mainly because of its low density, good processability and environmental resistance. In addition, PP has a low cost, which strongly increases the performance/cost ratio, and can be reprocessed several times without significant loss of its properties.

Failure of polymer composites subjected to impact loads is related to a vast variety of phenomena, and all the many mechanisms can be exploited to improve the energy dissipation during impact. Matrix deformation and micro-cracking, interfacial debonding, lamina splitting, delamination, fibre breaking and fibre pull-out all contribute to the energy dissipation in the composite structure during the impact [1]. Laminates with unidirectional fibre layers, even if characterized by very high specific stiffness and strength in the fibre direction, are not preferred when the perforation threshold is a main requirement. In fact, their low tensile strength in the direction orthogonal to the fibres makes them very susceptible to impact damages [3]. Woven fabric reinforcements are indeed preferred to unidirectional ones because the interlacing mechanism of fibre yarns (usually in orthogonal directions) reduces the directional sensitivity to loads and improves the energy dissipation through the friction between fibres [2-4]. In structural laminates the adhesion between fibres and matrix is properly addressed to reach high strength values [5,7]. Physical treatments to fibre surface or the addition of suitable coupling agents into the polymeric matrix can be used to enhance the fibre wetting of the matrix, and the chemical or physical interactions between the two composite components. Each method has advantages over the other, but pull-out tests have demonstrated that the strength of the fibre/matrix interface can be improved to a higher extent by means of a compatibilizing agent rather than by only applying a sizing treatment to fibres [7].

Glass fibres, despite their lower elastic modulus and lower resistance to fatigue with respect to carbon fibres, are widely preferred in impact sensitive applications. They couple the higher impact damage tolerance of laminates to a lower raw material cost with respect to carbon fibres [1]. In recent years basalt fibres have gained an increasing attention as possible replacement of the conventional glass fibres [8] due to their advantages in terms of environmental cost and chemical-physical properties. Mineral fibres obtained from basalt rocks are not new, but their suitability as reinforcement in polymer composites is a relatively new issue [9]. The chemical structure of basalt is similar to that of the glass, even though the density is slightly higher (~2.7 g/cm3 compared to 2.54 g/cm3 of glass). The chemical stability of the basalt fibres is better than that of glass ones, especially in an acidic environment. They can also be used in a wide range of temperatures, from –200 °C to +600 °C [8]. From the mechanical point of view, continuous basalt fibres are competitive with glass fibres. The elastic modulus of basalt fibres strongly depends on the chemical composition but it is usually slightly higher than that of glass fibres, while both tensile strength and elongation at break are significantly better [8]. These characteristics make basalt fibres a promising reinforcing material in composites, as confirmed by the growing attentions that they are continuously gaining within the scientific community as reinforcement for both thermoplastic [10,11] and thermosetting matrices [12-14].

Based on the results of Russo et al. [15] who showed that in thermoplastic composites based on PP and glass fibre reinforcement the interface strength between fibres and matrix plays a major role in dissipating energy during an impact, laminates based on basalt woven fabric and PP have been developed to maximize the low velocity impact behaviour. In order to assess the effect of fibre/matrix interface on PP based composites, laminates were produced by changing the fibre/matrix interface strength by including maleated polypropylene. The control of the interface strength was used to balance the energy absorption capabilities with the quasi-static mechanical properties of the mineral fibre reinforced composites prepared. The higher ultimate properties of basalt fibres were exploited to prepare thermoplastic composites able to sustain very high impact loads before perforation with respect to glass fibre based ones.

2. Experimental

2.1. Materials

Polypropylene – PP (MA712 from Unipetrol – Czech Republic with MFI = 12 g/10min) has been used as matrix for the preparation of fibre reinforced composites. Polypropylene grafted with maleic anhydride (PP-g-MA) commercialized under the trade name Polybond 3200 (MFI 115 g/10 min, 1 wt% maleic anhydride; from Chemtura, Philadelphia – PA, USA) was used as compatibilizer to improve the fibre/matrix interface. To this purpose, 2 wt% of this coupling agent was added to the matrix by means of a co-rotating twin screw extruder (Polylab Haake PTW 24/40 with L/D 40:1 from Thermo Haake, Germany). Plain weave type woven fabrics, based on glass (E-type glass fibres, specific mass of 204 g/m^2) and basalt (BAS 220.1270.P with specific mass of 220 g/m^2 supplied by Basaltex-Flocart NV – Belgium) have been used as reinforcement.

2.2. Sample preparation

Films having thickness between 35 and 40 µm of neat and compatibilized PP were prepared using the film blowing technique (extrusion line model Teach-Line E 20 T from Collin GmbH, Ebersberg, Germany). Composite laminates were obtained by the film stacking technique. Alternate layers of PP film and glass fibre fabrics were compression moulded (press model P300P, Collin GmbH, Ebersberg, Germany) according to a pre-optimized moulding cycle [15].
Laminates having 8 balanced fabric layers 0°/90° symmetrically arranged with respect to the middle plane of the laminate ($[(0/90)_4]_s$ configuration) with a target thickness of 1.4 mm and a glass or basalt fibre content of 50% by volume were fabricated. The actual relative percentages of fibre and matrix were evaluated according to the ASTM D 3171-04 on each tested laminate.

2.3. Sample characterization

Fibre impregnation was qualitatively evaluated by means of optical analysis in reflection mode by a microscope (model BX51 from Olympus, Japan). Samples were prepared by polishing the analysed surfaces first with wet sandpaper and then with a very fine polishing paste. Fractured surfaces were sputter coated with a thin film of gold/palladium alloy and observed by using a field emission scanning electron microscope (model QUANTA-200FEG from FEI, Eindhoven, The Nederlands).
Flexural properties were evaluated on samples by means of a universal testing machine (mod. 3360 from Instron, Akron - OH, USA) equipped with a three point bending configuration set according to the ASTM D 790-10. The span was changed according to the actual measured thickness for each sample in order to keep the span-to depth ratio equal to 40:1. Both flexural modulus (E_F) and flexural strength (σ_F) values were evaluated along the 0° laminate direction averaging the results from 5 different samples. The flexural strength was calculated as the stress at 5% of strain for samples which did not show breaking before that strain. Low velocity impact tests were performed with a falling dart machine (model Fractovis Plus, from Ceast, Italy) at impact energies (E_i) of 31 J and 151 J, in order to assure the complete perforation in all laminates. The impactor was equipped with a 22 kN piezoelectric load cell, having mass equal to 6.926 kg and a hemispheric tip (diameter equal to 12.7 mm). The sample holder was a stainless steel ring with 40 mm inner diameter and 60 mm outer diameter, except

that for some basalt laminates for which 30 mm inner diameter was used. For each composite configuration, at least 4 samples 80x80 mm^2 in size were tested.

3. Results and Discussion

3.1. Composite preparation

Processing conditions were optimized for all composite configurations in order to minimize the formation of voids and to keep the fibre volume almost constant among the different configurations. Several inspections with the optical microscope were performed in different positions and a very good fibre impregnation was always detected. Furthermore, SEM micrographs of fractured surfaces showed that the presence of the compatibilizer improves fibre wetting, althogh to a different extent between glass and basalt fibres (Figure 1). In fact, while the presence of PP-g-MA clearly improves the fiber wetting in case of glass fabric reinforced laminates, this effect appears to be much less pronounced for basalt based ones.

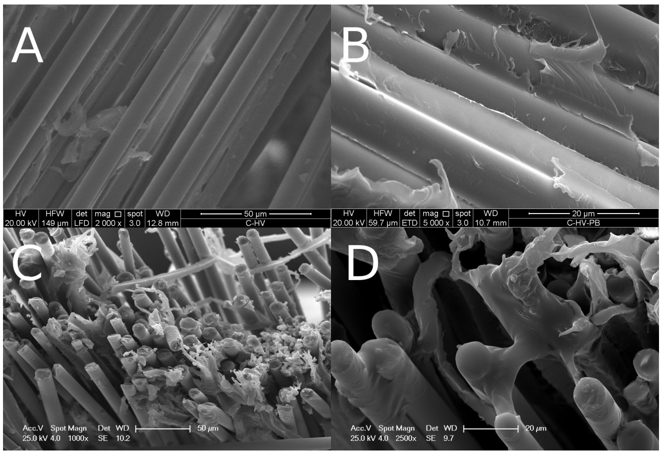

Figure 1. SEM analysis of fibre wetting in the prepared composites: A) glass fibre/not compatibilized PP, B) glass fibre/compatibilized PP, C) basalt fibre/not compatibilized PP, D) basalt fibre/compatibilized PP

3.2. Quasi-static characterization

Flexural modulus and flexural strength of matrices and composites are reported in Table 1. Neat PP matrix samples (coded as M) exhibited a higher flexural modulus with respect to the compatibilized ones (coded as M-PB), which in turn seems to be plasticized by the grafted compatibilizer. Unlike in matrices, the use of compatibilized matrices had positive effects on both flexural modulus and strength of laminates (Figure 2), as a consequence of the enhanced capability to transfer loads from the matrix to fibres through the stronger interface.
Benefits were evident especially in terms of flexural strength and strain at yield with improvements more evident in glass fabric reinforced laminates (coded as GF and GF-PB for neat PP and compatibilized PP samples, respectively) than basalt based ones (BF and BF-PB for neat PP and compatibilized PP samples, respectively) (Table 1). In these latter cases, delaminations, occurring prematurely with respect to glass fibre reinforced samples, were detected as a consequence of the very poor fibre/matrix interactions probably induced by the surface treatment of fibres. Further developments should be made to improve the interface strength through more effective sizing agents, thus allowing a better management of the basalt/PP interactions.

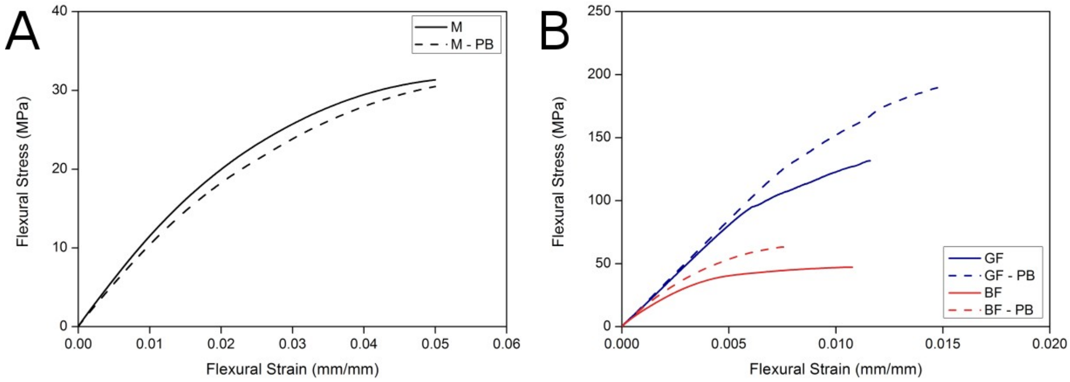

Figure 2. Flexural behaviour of A) matrices and B) laminates

Sample	Flexural Modulus [MPa]	Strain at yield [%]	Flexural Strength [MPa]
M	1409±92	-	31.7±0.8
M - PB	1329±90	-	30.5±0.8
GF	16276±530	1.22±0.16	129.6±8.2
GF - PB	16808±434	1.62±0.15	179.8±9.6
BF	15672±633	1.18±0.14	49.7±3.4
BF - PB	16268±541	0.87±0.12	62.3±2.8

Table 1. Flexural properties of used matrices and laminates

3.3. Low velocity impact characterization

The low velocity impact response of glass and basalt based composites has shown a different dependence on the presence of the compatibilizer with respect to flexural properties. All glass based laminates were perforated at E_i = 31 J impact tests. Compatibilized samples exhibited a perforation threshold (PT) equal to 13 J while for not compatibilized ones PT was 19 J, corresponding to an increase of about 50%. Basalt based laminates were not perforated in this testing condition and showed residual structural properties, as evident from the presence of a peak in the energy/time graphs (Figure 3A).

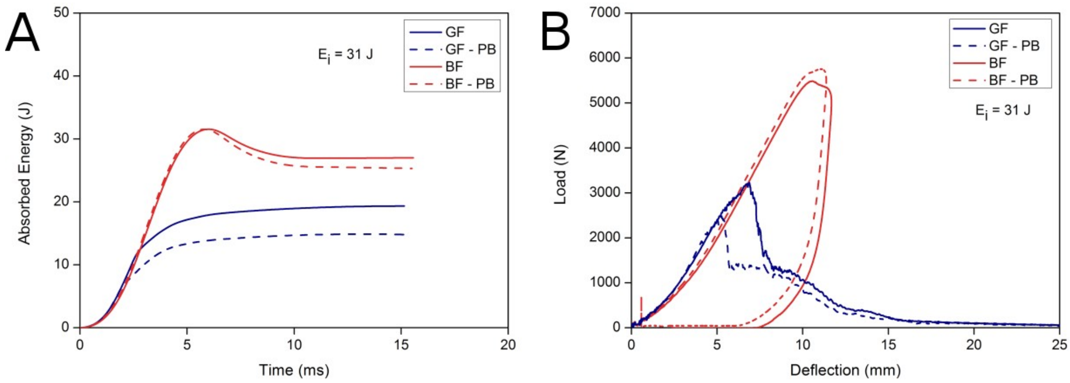

Figure 3. Curves from impact tests at E_i = 151 J: (A) absorbed energy as function of time, B) load versus deflection

The presence of the compatibilizer also affected the load peak (corresponding to fibres breakage occurrence). GF-PB laminates exhibited a load peak of 2.5 kN, while GF laminates were able to carry 3.1 kN load before fibre breakage. The reduced PP/glass interface strength allowed further dissipation mechanisms which helped in dissipating higher impact energy but also protected the fibres from cracks originated in the matrix. Slipping at the fibre/matrix interface permits to achieve higher deflection of the composite and, in turn, higher load bearing. Two main mechanisms should be considered to justify these performances: a) the spreading of the volume involved in fibres slipping increases the energy dissipation in not compatibilized laminates as a consequence of friction mechanisms; b) the reduction of both crack propagation and transmission of complex tensional states from the matrix to the fibres after the interface failure.

Perforation of glass based laminates is also deducible in Figure 3, from the open shape of load/deflection curves. Since basalt based laminates were not perforated, a closed loop was instead exhibited and significantly higher load peaks were detected (5.5 kN for both BF and BF-B samples). This result can be ascribed to the better performances of basalt fibres with respect to glass ones, which did not break. In order to find the PT of basalt/PP laminates, impacts at 151 J were performed, and a reduction of the support inner diameter was used to limit warping phenomena. In this conditions laminates were perforated, and PT values were higher than 60 J, regardless of the presence of the compatibilizer (Figure 4A). The load peak detected was 9 kN, almost three times that of GF laminates. The higher tensile and compressive strengths of basalt fibres play a major role in this remarkable result, considering that GF laminates, also characterized by poor interface strength, are nonetheless perforated at considerably lower energies.

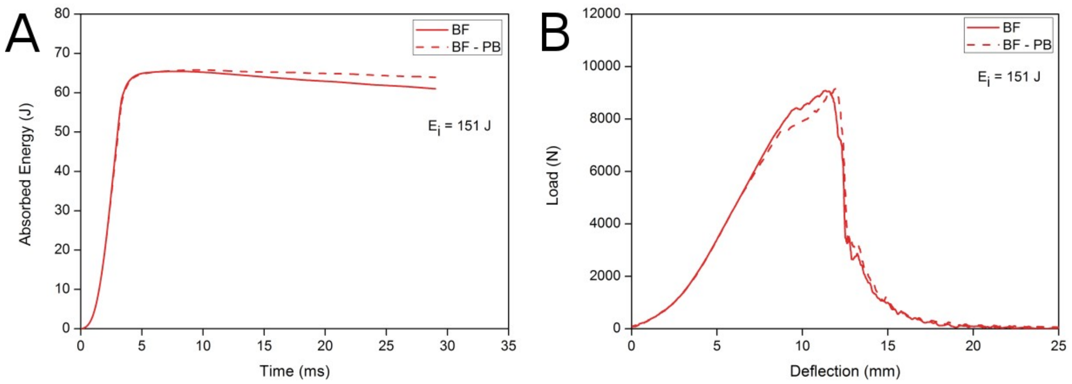

Figure 4. Curves from impact tests at E_i = 151 J: (A) absorbed energy as function of time, B) load versus deflection

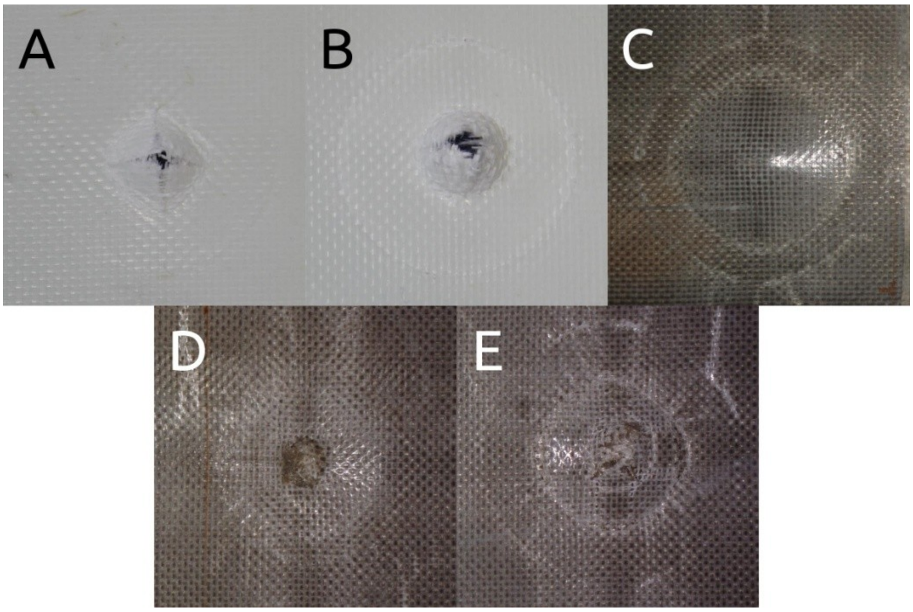

Figure 5. Back surface photographs of tested samples (Impact energy): A) GF-PB (31 J); B) GF (31 J); C) BF (31 J); D) BF (151 J; front surface); E) BF (151 J)

Figure 5 reports the back surfaces of impacted samples. BF laminates showed a very large delamination area (Figures 5C-E) with respect to glass based laminates (Figure 5A and 5B for GF-PB and GF, respectively). In particular, Figure 5C shows how large at E_i = 31 J was the damaged area in a BF laminate, if compared to GF one (Figure 5B). Laminate warping is also detectable in BF and BF-PB samples outside the support imprint (60 mm in diameter) at E_i = 31 J and it is very pronounced at E_i = 151 J (Figure 5D and 5E for front and back surfaces, respectively). This result is a direct consequence of the very wide area involved in dissipating phenomena (delaminations, matrix cracking, fibre slipping) which extends outside the clamping tool before fibres breakage. This behaviour, peculiar to basalt fibres, opens to the production of high performance/cost ratio systems aimed at large energy dissipation applications based on natural fibres and a commodity polymers.

4. Conclusions

Low velocity impact properties of composites made of PP reinforced with glass and basalt woven fabrics have been investigated and the role of the interface strength has been related to the ultimate performances of composites. Laminates prepared with a compatibilizing agent exhibited improved flexural moduli and strengths with respect to analogous systems based on neat matrices, as a consequence of the fibre/matrix interface strength increase. However, basalt based systems showed poor flexural strength also after the compatibilizer addition, due to the basalt fibre sizing treatment, which was not specifically tailored to polypropylene.
The use of a compatibilizer does not translate into better impact properties. The strong interface was responsible for the early starting of fibre failures occurring at small deformations. On the contrary, the weak fibre/matrix interface was responsible for the improved perforation threshold in terms of both absorbed energy at perforation and load peak before failure, since it allowed both larger deformations and crack blocking during the laminate deflection. After impacts at 31 J, not compatibilized glass based laminates showed a 50 % increase of absorbed energy (up to 19 J) with respect to compatibilized ones and an improved load peak before fibre failure. PP/basalt composites exhibited a very high perforation threshold (higher than 60 J) thanks to the better mechanical properties of basalt fibres, which allowed for larger deformations and thus higher energy dissipations through frictions and delaminations.

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