MECHANICAL PROPERTIES AND IMPACT-ENERGY ABSORPTION OF INJECTION MOULDED NANOCOMPOSITE STRUCTURES

Francesco Silva [1], Sophia Sachse [1] and James Njuguna [1*]

[1] *Centre for Automotive Technology, School of Applied Sciences, Cranfield University, Bedfordshire, MK43 0AL, UK.*

[*] *Corresponding Author:j.njuguna@cranfield.ac.uk*

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Abstract

This paper focuses on the improvement of the mechanical properties of polymer composites reinforced with glass-fibres and nano-fillers, and better understanding of the energy absorption mechanism in these materials. Initial experiments focused on quasi-static compression tests of conical structures and quasi-static tensile tests using Instron electro-mechanical universal testing machine. Next, axial dynamic crash of the conical structures was conducted to investigate the influence of the nano-filler on the energy absorption capabilities of the polymer composites. The impact event was recorded using a high-speed camera and the fracture surface was investigated with scanning electron microscopy (SEM). The obtained results indicate an important influence of the filler and the matrix material on the mechanical properties and energy absorption capabilities of the polymer composites.

1. Introduction

In recent years, thermoplastic polymers such as polypropylene (PP) and polyamide (PA6) have been commonly used in the automotive industry, as they indicate an attractive combination of good mechanical properties, processability and low cost [1]. However, application of these materials in load-bearing structures is limited due to their insufficient stiffness and brittleness limits, as well as low impact resistance and energy absorption capabilities [2]. Incorporation of glass reinforcements can provide an enhancement of various mechanical properties, such as stiffness, strength and impact resistance [3]. However, an increase in the mechanical properties, due to the rigid micro-fillers, is usually at the cost of reduced ductility [4]. This effect is caused by the stress concentration regions, which exist in a close proximity of the reinforcement. In case of nano-fillers the stress concentrations are significantly reduced therefore, composite ductility can be maintained at a constant level or even improved, in relation to the neat polymer [5]. Moreover, it has been proved that the addition of nano-sized fillers, rather than micro-sized fillers, can significantly enhance the mechanical properties of the polymeric materials at low filler content [6]. If the filler is in the nano-metric size, an important enhancement can be obtained at content in the range of 0.5-5% [7-9], whereas in case of micro-fillers the reinforcing effect is observed at loadings typically higher than 20% [10]. These unique properties of nanocomposites come from the large number of interfacial effects, existing due to the high surface-area-to-volume ratio of the nano-filler. For spherical nano-particles and nano-fibres this ratio is irreversibly proportional to their radius, and its value can be even up to 1000 m^2/g [11].

In this study mechanical and morphological properties of PP and PA6 composites filled with different nano and micro materials, were investigated. The effect of matrix and filler material, as well as testing speed, on the mechanical properties of injection moulded composites, is discussed in details.

2. Experimental

2.1. Materials

Two types of matrices were utilised to prepare nano-filled materials: Polypropylene (PP) Moplen HP500J from Basell Polyolefins and Polyamide 6 (PA-6) Tarnamid T-30 from Zakłady Azotowe w Tarnowie-Mościcach, Poland. As a nano-filler two different types of silica-particles (SiO_2) and montmorillonite (MMT) for both polar and apolar matrices were selected. This includes: organically modified MMT designed for apolar polyolefin matrices (Dellite 72T from Laviosa); organically modified MMT designed for polar matrices (Dellite 43B from Laviosa); fumed silica with hydrophobic properties (surface modified with dichlorodimethyl silane (DCMS)) for nonpolar polyolefin matrices (AEROSIL 974 from Degussa) and fumed silica with hydrophilic properties for polar polymer (AEROSIL 200 from Degussa). Additionally, four different glass-reinforced composite materials, supplied by MACOMASS Verkaufs AG Germany, were used to prepare nano and glass reinforced composite samples: glass-fibre (GF) reinforced polyamide (MM-PA I 1F30) and polypropylene (MM-PP BI 24), as well as glass-spheres (GS) reinforced polyamide (MM-PA I 1K30) and polypropylene (MM-PP HE25).

2.2. Samples preparation

Preparation of nano and glass reinforced polymer composites was conducted in three main steps: preparation of nano-composite granulate, mixing and extrusion of nano and glass reinforced composite granulate and injection moulding of the macro-samples. In the first step nano-reinforcement and polymeric matrix, all in solid (powder) form, were premixed before extrusion, in order to warrant the highest homogeneity of the composition. Subsequently the premixed materials were fed into the twin-screw extruder. In the second step, granulates of the nano-particle reinforced polymers and glass-fibre reinforced polymers were mixed in the extruder. As a result eight different composite materials were prepared as shown in tables 1 and 2.

Name	PP/GF	PP/GF/GS	PP/GF/SiO_2	PP/GF/MMT
Matrix	PP	PP	PP	PP
1st filler [wt%]	GF [30%]	GF [30%]	GF [30%]	GF [30%]
2nd filler [wt%]	-	GS [12%]	SiO_2 [2%]	MMT [2 %]

Table 1. PP composites

Name	PA/GF	PA/GF/GS	PA/GF/SiO_2	PA/GF/MMT
Matrix	PA	PA	PA	PA
1st filler [wt%]	GF [30%]	GF [30%]	GF [30%]	GF [30%]
2nd filler [wt%]	-	GS [12%]	SiO_2 [2%]	MMT [2 %]

Table 2. PA6 composites

In the third step, tensile bars and crash cones were produced using injection moulding machine (Engel ES200/60 HL ST).

2.3. Tensile test

Quasi-static and dynamic tensile tests were carried out using Instron 5500R electro-mechanical testing machine. All experiments were conducted according to ISO-527 standard, using specimen type A. Five samples of each material were tested, at two different crosshead speeds 0.1 mm/min and 1000 mm/min. The load was measured using a 100kN load cell. In order to measure the displacement a laser extensometer was used.

2.4. Crash test

Quasi-static compression testing of the crash cones was conducted using Instron 5500R electro-mechanical machine, at a crosshead speed of 0.1mm/sec. The load was measured using a 100kN load cell. Impact tests of the crash cones were carried out on a high energy capacity drop tower machine at the velocity of 6.2m/s, corresponding to a 2 m drop height. The impactor mass of 54 kg was constant in all experiments, giving an overall impact energy of 1050J. The load was measured using a 200kN load cell, placed underneath the sample. In order to measure a displacement of the falling mass, the linear variable differential transformer (LVDT) displacement transducer was used, with precision of 0.01mm and maximum displacement speed of 10m/s.

2.5. SEM analysis

The fracture surface of the tensile bars was exanimated with FEI XL30 field emission scanning electron microscope (SEM). The operating voltage was in the range of 10-20 kV and the specimens were gold sputtered to minimise charging of the sample.

3. Results and discussion

3.1. Tensile test

Tensile properties of eight different composites, filled with nano and micro particles, are presented in Table 3. The results show that the mechanical properties of the PP composites have a clear tendency to decrease after the addition of the secondary filler. Modulus, strength and elongation to brake were decreased in almost all samples tested. The biggest drop in all parameters of the PP composite was caused by the presence of GS micro-filler. The negative effect of the secondary reinforcement may be attributed to the properties of the PP material itself. Good bonding between PP matrix and reinforcement is difficult to achieve without an appropriate coupling agent, which assures a chemical coupling between non-polar polymer and polar reinforcement [12]. Another issue associated with PP composites, is good dispersion of nano-reinforcement within a matrix. Usage of untreated nano-reinforcement without a compatibilizer in PP matrix can lead to a bad dispersion and existence of agglomeration regions, which result in a decrease in the mechanical properties of composite materials [13].

By contrast, the effect of secondary filler in PA composites was positive. All samples indicated an increase in tensile modulus. The biggest enhancement was observed in PA/GF/GS (24%) and PA/GF/MMT (10%), and the smallest one in PA/GF/SiO2 (4.7%). The tensile strength of all composites was slightly decreased or remained on the similar level. Elongation to brake was found to increase in materials reinforced with SiO_2 (32%) and to decrease in PA/GF/MMT (2%) and PA/GF/GS (7%) composites. Due to the large strain rate sensitivity of the polymeric materials, a significant difference in the mechanical properties was observed between the samples tested under the quasi-static and dynamic conditions. The material becomes much more brittle, what was observed as a significant increase in stiffness and strength, and on the other hand, a decrease in maximum elongation.

Material	Modulus [GPa]		Strength [MPa]		Elongation [%]	
	Static	Dynamic	Static	Dynamic	Static	Dynamic
PP/GF	6.57	19.28	74.1	102.4	2.8	1.01
PP/GF/SiO_2	5.93	19.03	62.4	90.1	2.9	0.76
PP/GF/MMT	5.93	17.60	61.7	83.7	2.4	0.47
PP/GF/GS	5.75	15.20	47.4	62.8	1.3	0.21
PA/GF	6.92	28.47	116.2	154.4	5.2	1.61
PA/GF/SiO_2	7.25	29.56	105.1	133.3	6.9	2.20
PA/GF/MMT	7.61	31.55	109.7	140.4	5.1	1.31
PA/GF/GS	8.62	32.80	109.9	142.9	4.8	1.10

Table 3. Tensile properties

3.2. SEM Analysis

The fracture surface of the tensile samples tested under the dynamic load was examined using SEM. Figure 1 shows the micrographs of several PP-based composites. On these pictures it is possible to observe that the failure mode is a combination of matrix and fibre cracking, fibre pull-out and debonding. Very little plastic deformation of the matrix is visible, as there are no characteristic deformation paths and fibrous texture of the material. On the other hand, a significant debonding and pull-out of the glass reinforcement is visible, with clean and smooth surface of the glass, indicating poor interfacial adhesion. Comparing the micrographs of nano-reinforced PP/GF and neat PP/GF composites, only a little difference can be observed. This indicates a small influence of the secondary reinforcement on the PP composites failure mode.

The fracture surface of PA-based composites is presented in Figure 2. There is an evident difference in the failure mode in relation to PP-based composites. The fracture is dominated by matrix and fibre cracking, whereas fibres pull out and debonding is of little meaning. The glass reinforcement is covered with polymer residuals, which is a sign of good interfacial adhesion. Moreover, there is a visible difference in the fracture mode between various PA composites. In neat PA/GF and PA/GF/SiO_2 composites the plastic deformation of the matrix is the most evident. An extensive plastic deformation is clearly visible in PA/GF/SiO_2 as a non-smooth texture and characteristic deformation paths. Contrary, in PA/GF/MMT and PA/GF/GS composites, the plastic deformation of the matrix is reduced, due to the transition to more brittle failure. In all PA samples there is a large number of broken fibres, which failed at the same time as the matrix.

3.3. Crashing behaviour

The main observation made from static and dynamic crashing experiments was difference in the failure modes, between various materials tested. The following main fracture modes could be identified and classified: Mode I - progressive crushing with micro-fragmentation and delamination, Mode II - brittle fracture with large fragmentation resulting in catastrophic failure, Mode III - brittle but progressive crushing with medium fragmentation, Mode IV - progressive folding with mushrooming effect. The difference in the fracture mode is clearly visible on the load displacement curves, as the loads induced during the impact are directly correlated with fracture mode and propagation of the cracks (see figures 3 and 4).

Relating the energy absorption characteristic with the crashing characteristics it can be seen that the materials which fail in a progressive manner, with small local cracks induced (modes I and III), were able to absorb much higher energies than those with large continuous cracks (modes II and IV). This is caused by the fact that the fracture mode has got direct influence on the crushing parameters such as: crushing length, value of the peak loads and mean crashing load.

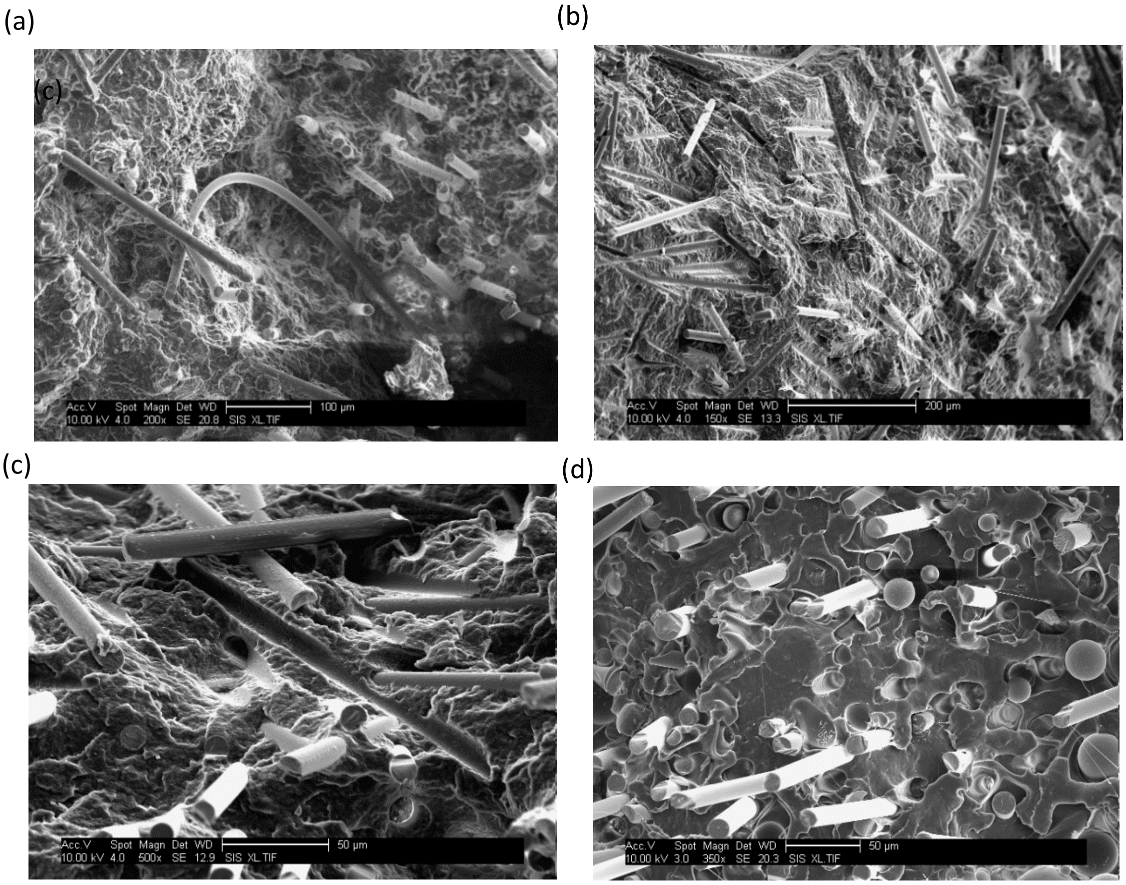

Figure 1: PP composites: (a) neat, (b) SiO_2, (C) MMT and (d) GS

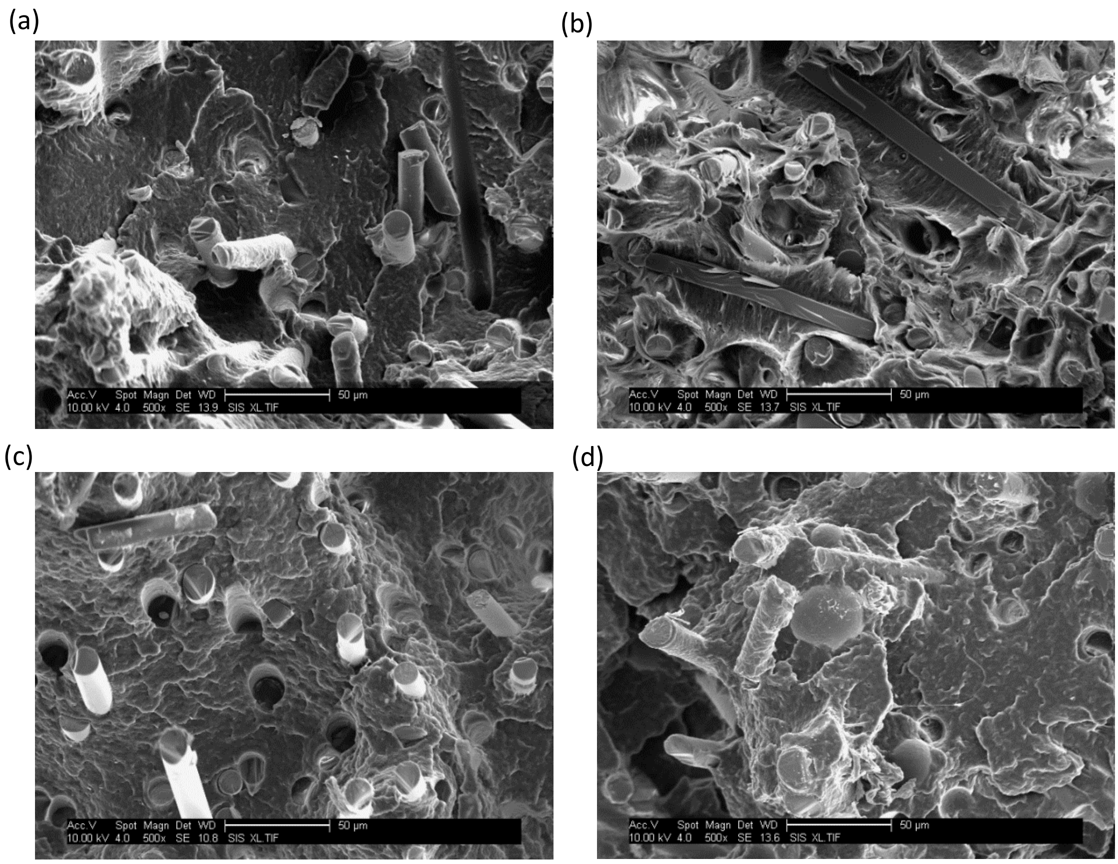

Figure 2: PA composites: (a) neat, (b) SiO_2, (C) MMT and (d) GS

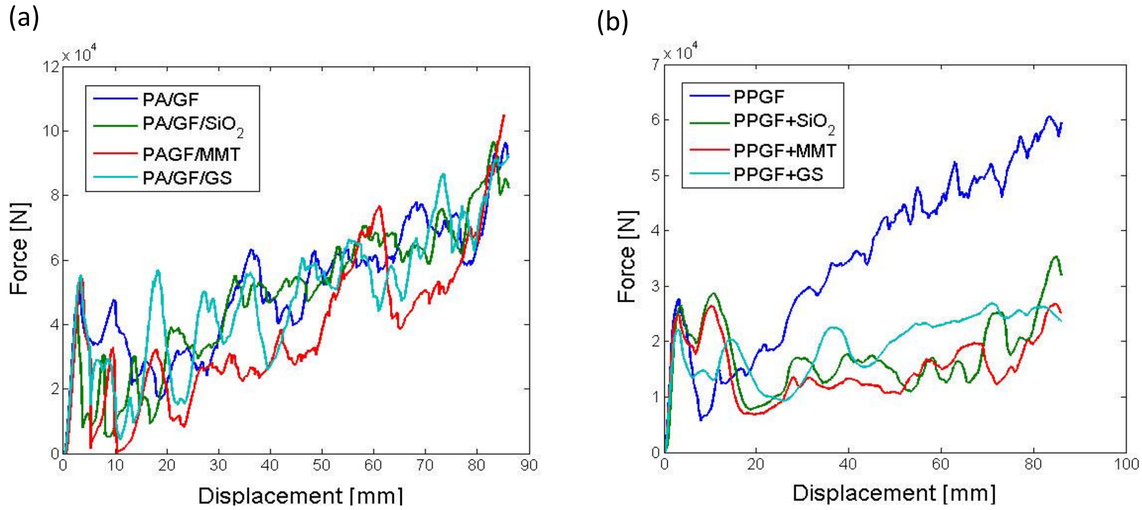

Figure 3: Static load-displacement curves (a) PA composites (b) PP composites

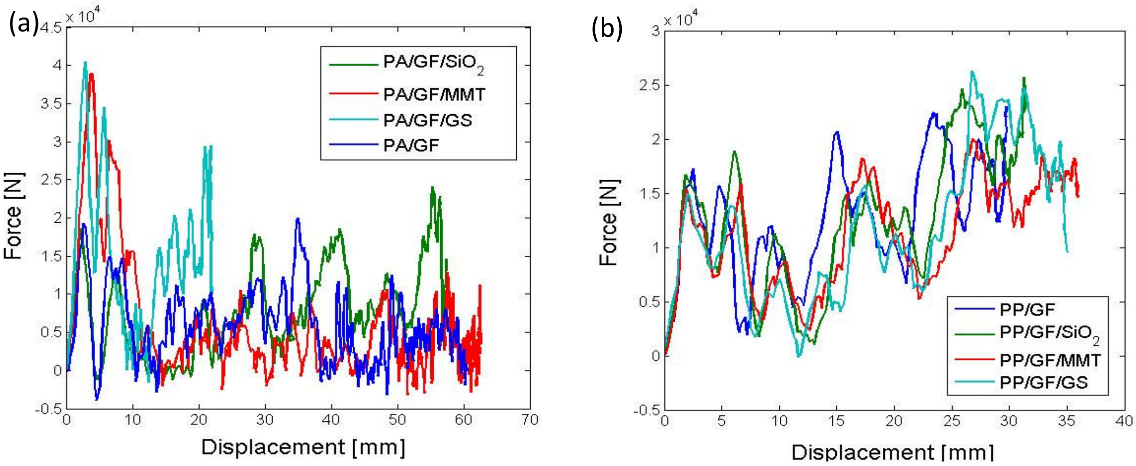

Figure 4: Dynamic load-displacement curves (a) PA composites (b) PP composites

The change in the fracture mode also caused that there was a big difference in energy absorption between the materials tested under quasi-static and dynamic loads. In the static test the energy was the most effectively absorbed in PA composites, whereas in the dynamic test the effectiveness was significantly reduced. In addition, the wakening effect of secondary filler in the PP composite samples, tested under the quasi-static load is much more evident than in samples tested under the dynamic load. A similar trend was observed in the PA composites, in which the addition of secondary reinforcement resulted in reduction of the SEA parameter under the quasi-static load, whereas under the dynamic load the SEA parameter increased, due to the secondary reinforcement.

Comparing the dynamic energy absorption characteristic of different materials it can be observed that secondary reinforcement has got positive influence on the energy absorption characteristics of the PA composites. The SEA parameter increased in both SiO_2 and GS reinforced composite, and remained on the same level in MMT reinforced ones. Neat PA/GF composite failed at relatively low load, in a brittle manner with large longitudinal cracks propagating along the structure. This caused that the energy absorbed by the structure was relatively low. Incorporation of SiO_2 particles did not increase the impact strength of the material but it has changed the way how it fractures. The brittleness of the material was significantly reduced, what was observed as an increase in elongation to brake determined in the tensile test (see Table 3). As a result the strain induced in the structure did not initiate sever cracks, as the non-crashed section of the structure did not reach the failure strain. The opposite behaviour was observed in MMT reinforced composites. In this case the impact strength of the material was increased but at the cost of reduced ductility. That is why the nano-composite became even more brittle than the neat PAGF material. Hence, the strain reached the maximum allowable limit and the crack propagated along the structure, leading to a complete failure of the sample. As a result the energy absorption capability of the material remained on the same level, in spite of the increase in strength and stiffness. The biggest increase in energy absorption capability was found in GS reinforced materials. However, the toughening mechanism was different from that observed in SiO_2 reinforced materials. In this case, both stiffness and impact strength were improved but with reduced elongation to brake. As a result the crushing length of the cone was importantly reduced, due to the high resistance of the material. Hence, the strain did not exceed the allowable limit and the cracks were not initiated in the non-crashed section of the structure.

Material	Crash length [mm]	Collapse mode	Initial peak [kN]	Mean crashing load [kN]	Energy absorbed [kJ]	SEA [kJ/kg]	Change in SEA [%]
PPGF	86	III	29.74	34.75	2.99	49.4	
PPGF/SiO_2	86	IV	26.59	17.86	1.48	24.4	-50.7
PPGF/MMT	86	IV	24.75	15.39	1.29	21.2	-57.0
PPGF/GS	86	IV	22.06	17.66	1.65	26.3	-46.9
PAGF	86	III	47.66	50.44	4.33	58.1	
PAGF/SiO_2	86	III	44.61	45.66	4.15	54.5	-6.1
PAGF/MMT	86	III	54.59	40.65	3.23	42.9	-26.2
PAGF/GS	86	III	55.10	45.74	4.11	51.7	-11.0

Table 4. Quasi-static crashing characteristics

Material	Crash length [mm]	Collapse mode	Initial peak [kN]	Mean crashing load [kN]	Energy absorbed [kJ]	SEA [kJ/kg]	Change in SEA [%]
PPGF	29.79	I	22.99	14.19	0.36	23.6	-
PPGF/SiO_2	31.4	I	25.72	15.41	0.37	22.6	-4.2
PPGF/MMT	36.02	I	20.02	12.86	0.40	20.5	-13.0
PPGF/GS	35.03	I	26.28	13.52	0.40	20.7	-12.3
PAGF	60.5	II	19.99	5.64	0.35	7.7	-
PAGF/SiO_2	57.56	III	26.51	8.98	0.43	9.8	27.0
PAGF/MMT	62.61	II	38.82	4.48	0.37	7.7	0.1
PAGF/GS	22.03	III	40.42	15.58	0.32	22.3	188.5

Table 5. Dynamic crashing characteristics

4. Conclusion

Mechanical properties and crushing behaviour of various polymer composites were studied in this paper. It has been shown that the addition of secondary reinforcement into glass-fibre reinforced polymer composites can have significant influence on the mechanical behaviour of the material. The carried out experiments showed that by changing the matrix and the reinforcement material it is possible to change the micro-mechanism of a crash and therefore control the energy absorption characteristics of the composite. The following general remarks can be drawn, regarding the mechanical properties and energy absorption capabilities of the polymer composites: (i) Secondary reinforcement, in PA composites, leads to an increase in mechanical properties such as strength, stiffness and elongation to brake as well as energy absorption capabilities. (ii) All mechanical properties of PP composites have been decreased after the addition of secondary reinforcement. The possible reason of this phenomenon is bad dispersion of particles and week filler-matrix interphase. (iii) Strength of the material and induced fracture modes were determined as main factors relating the energy absorption capabilities of the composite with the filler and matrix material. (iv) The transition from brittle to ductile fracture mode was clearly demonstrated as a main reason for increased energy absorption capabilities. (v) Two different toughening mechanisms were observed. Firstly, due to the increase in maximum elongation to brake. Secondly, due to the increase in strength and stiffness.

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