

POLYESTER BASED NANOCOMPOSITES AS MATRIX FOR LIGHTWEIGHT REINFORCED COMPOSITES

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Abstract

Polyesters like PET and PEN are very interesting as matrix for fiber reinforced composites due to their lower cost with respect to other engineering or high performance thermoplastic matrices and could extend composite applications to lower end markets. They are characterized by high glass transition temperatures (75°C for PET and 125°C for PEN, which are only few degrees lower than those of PPS and PEEK, respectively) and exhibit lower processing temperatures with respect to high performance semicrystalline polymers. To further extend the application range of such polyesters and to solve some of their weaknesses, two nanofillers (a modified MMT clay and expanded graphite) were used to prepare nanocomposites by means of the melt blending technique. The good dispersion achieved was responsible for the improved mechanical and thermal properties of the nanoreinforced matrices and a strong improvement of the thermal stability was also reached, as confirmed by thermogravimetric analysis. The foaming properties of the developed materials were investigated in order to define the compositions and the processing conditions to produce the microcellular structure needed to maximize the mechanical and thermal properties in foams. PEN/graphite nanocomposite system was selected to prepare both glass fiber reinforced composites and foamed composites, demonstrating the feasibility of the proposed approach to produce low cost/high performance lightweight composites with strong specific impact properties.

1 Introduction

Composites are used in high performance applications due to the high specific properties (tensile and flexural moduli, high strength) [1]. Thermoplastic polymer based on composites have high toughness, no chemical reactions during fabrication, short manufacturing cycle, possibility of both scraps recovery and in-use repairing.

Thermoplastic high performance polymers, such as PEEK, PEI, PPS are actually employed in some structural parts in aeronautics thanks to their high mechanical and thermal properties (continuous working temperatures between 150 and 230 °C), but PET or PEN, classified as engineering polymers, show comparable structural behaviors and adequate thermal properties (continuous working temperatures between 70 and 150 °C) at a fraction of their cost. The use of a nanofiller, as already demonstrated in literature [2], can improve the thermal stability of the nanocomposite and/or shift towards higher values the continuous working temperature.

Furthermore, the presence of nanofillers could improve the mechanical performance, both in the elastic region and after yielding, at low contents due to the reduction of the polymeric macromolecular mobility and to the very high surface/volume ratio, which maximize the interfacial interactions between the matrix and the reinforcement.

Among semicrystalline polymers, poly(ethylene terephthalate) (PET) is very interesting due to its combination of low cost coupled with good mechanical properties (e.g., Young's modulus, yield strength) and functional attributes (e.g., chemical resistance, thermal stability). This commends PET for diverse uses in industrial applications such as the reinforcement of textiles, fibers, tires and rubber goods and for food and beverage packaging. Attempts to foam PET were unsuccessful in the past when continuous processing techniques, such as extrusion, were used but the use of chain extenders such as PMDA [3-4], which increased the extensional viscosity, allowed the production of high quality/low density cellular structures. Poly(ethylene 2,6-naphthalate) (PEN) is a high-performance thermoplastic polyester with rigid naphthalene rings and a flexible aliphatic diol unit [5]. Compared with poly(ethylene terephthalate) (PET), this polymer show superior thermal, mechanical, barrier, and chemical resistance properties [5]. These properties make PEN potentially useful, in particular when an high continuous working temperature is needed, in a wide range of applications as either solid matrix or foams [6].

The growing need to decrease the weight such as in automotive, transport and aeronautic industries increased the use of lightweight structures, such as foams or sandwiches, with high specific properties such as flexural strength, high stiffness, good impact strength. The concepts of a) weight reduction through the use of foams and b) the reinforcing effect on the structural properties induced by the presence of fibers were exploited by authors to prepare reinforced foams based on PET and PEN nanocomposites and foamed composite structures based on PEN nanocomposites which showed specific static properties comparable to those of solid composites but exhibited a huge increase of the impact properties.

2 Materials and testing methods

PEN (Teonex TN8065S from Teijin, Japan) was used as semicrystalline polymer ($T_g = 125$ °C, $T_m = 265$ °C). Proprietary expanded graphite (EG) particles (platelets mean width smaller than 65 μm , platelets thickness smaller than 1 μm) were supplied by GrafTech International (TG-741 and its availability exclusively from GrafTech International Holdings, Inc.).

Pellets of Poly(ethylene terephthalate), with intrinsic viscosity of 0.8 dl/g and density 1.3 g/cm³ were kindly supplied by ORV manufacturing Italy (Padova, Italy). A pyromellitic dianhydride (PMDA) with a purity of 97% was supplied by Sigma Aldrich (Milano, Italy). The sodium-Montmorillonite (Na⁺MMT, supplied by Southern Clay Products Inc., now Rockwood Clay Additives GmbH - Moosburg, Germany), with cation exchange capacity of 92.6 meq/100 g, has been modified with the PET monomer bis-(hydroxyethyl terephthalate) (BHET, supplied by Sigma-Aldrich).

Thermoplastic composites samples were prepared by using the film stacking process. Eight layers of glass fiber fabric were stacked between nine layers of polyester films (dimensions: 100x100 mm²) in a mold and then pressed by using a hydraulic hot press (model P 300P, Collin GmbH, Germany). The glass fiber volume content was kept constant in all samples. Glass fiber reinforced foams (3x45x100 mm³) were prepared through a controlled expansion of the thermoplastic matrix by using physical blowing agents preliminary solubilized at high pressure in the polymeric matrix.

The nanoparticles were dispersed in the polymer by using a Haake Rheocord (Thermo, Germany) PTW25P twin screw extruder at a screw speed of 40 rpm. PET and PEN samples reinforced with 0.1, 0.5, 1.0 and 2.5 % by weight of BHET-MMT and EG, respectively, were

prepared. Foams were obtained by using supercritical carbon dioxide as blowing agent and foamed through the solid state foaming technique.

Scanning electron microscopy (SEM) analysis on foams was performed on cryogenic fractured surfaces with a Quanta 200 FEG from FEI (Eindhoven, The Netherlands). All sample surfaces were coated with gold layer before observations to render conductive the specimen surface.

Graphite dispersion was also investigated through an XRD analyzer at room temperature by using a Philips X-ray generator and a Philips diffractometer, type PW1710. The X-ray beam was a nickel-filtered CuK α radiation of wavelength 1.54 Å operated with the voltage generator set to 40 kV and at a current of 20 mA. The diffraction intensity data were collected automatically at a scanning rate of 0.6°/min with 0.02°/s steps from 5° to 60°.

Thermal stability of nanocomposites was studied by thermogravimetric analysis by means of TA Instruments TGA Q5000. Heating occurred under nitrogen flow, from room temperature up to 700 °C with a heating rate of 10 °C/min. Thermal and crystallization behavior was studied using a DSC-Q1000 differential scanning calorimeter from TA Instruments. Samples were cooled from 300 °C to 30 °C at the rate of 10 °C/min under nitrogen purge.

The dynamic mechanical properties were studied by DMA Q800 from TA Instruments, in tensile mode. Flexural properties were performed by means of a SANS 4304 (China) dynamometer on 22x95 mm² samples, cut from foamed and unfoamed composites. Impact properties were performed on 45x45 mm² samples by using a Fractovis Plus impact testing machine (CEAST, Italy) at different impact energy.

3 Results and Discussion

3.1 PET Nanocomposites

Different processing conditions were investigated to maximize the intercalation of nanofiller with the polymer macromolecules. In order to limit the thermal degradation of PET, occurring at long residence times, and to assure enough time for the nanofiller intercalation, the screw speed was then fixed at 55 rpm. The temperature profile for the different heating zones was selected in order to maximize the measured torque and to keep the melt temperature in the extruder metering zone equal to 283 °C. As the amount of clay increased, a decrement of the measured torque values was observed with respect to neat PET, regardless of residence time. In order to avoid viscosity drop during processing, a chain extender (PMDA) was used [3], and new formulations based on non-modified, commercial and BHET modified clays were produced. The chain extension induced by the PMDA was able to compensate the negative effect on melt viscosity induced by the thermal treatment above 280 °C and by the presence of the organoclay modifier. The increased rheological properties in ternary nanocomposites (PET-PMDA-nanofiller) were responsible for the higher mechanical stresses applied to tactoids during the extrusion process, and in turn for the better intercalation.

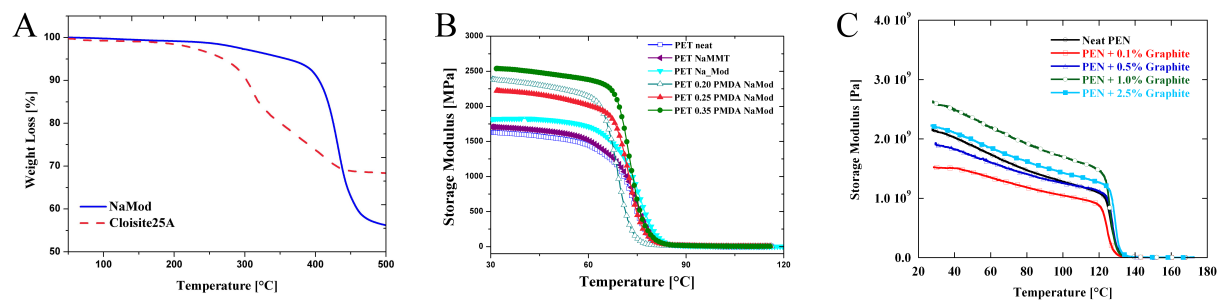


Figure 1. A) TGA curves for commercially organoclay Cloisite 25A and BHET modified organoclay NaMod; B) DMA curves of PET based nanocomposites; C) DMA curves of PEN based matrices

Plots showing the weight loss percentage vs temperature for a commercially available organomodified nanoclay (Cloisite 25A) and that prepared within this work (NaMod) are reported in Fig. 1A. The onset degradation temperature of NaMod is higher than commercial organoclay Cloisite 25A, as a result of the presence of BHET, which preserved the thermal stability of PET based nanocomposites. Nanocomposites prepared by using higher amount of PMDA resulted in an increased storage modulus, because the increased viscosity allowed a better exploiting of the nanofiller reinforcement (Fig. 1B). A commercial foam grade PET was used as benchmark for the foaming process. As shown in Fig. 2B, nanocomposites prepared by using PMDA showed a highly homogeneous morphology, comparable to that shown by the reference foam grade PET (Fig. 2A).

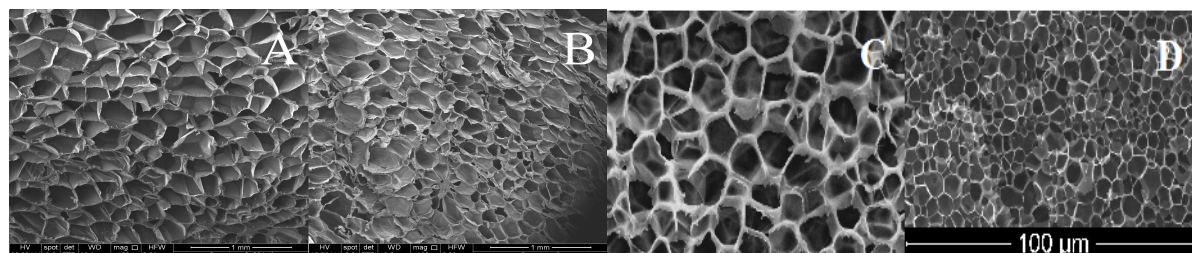


Figure 2. SEM micrograph of the foam grade PET (A), nanocomposite foamable PET (B), neat PEN (C) and 0.5% EG filled PEN (D)

3.2 PEN Nanocomposites

XRD analysis performed on PEN nanocomposites showed a clear peak at 26.7°, the same main peak of expanded graphite. This is due to the presence of not exfoliated graphite clusters. In order to clarify this feature, TEM analysis (not shown for brevity) was conducted on 0.1wt% and 1.0wt% samples. In 0.1wt% samples a good dispersion of the graphite was obtained and graphite platelets presented thickness smaller than 100nm while the 1.0wt% samples showed some clusters were detected confirming the results from XRD analysis. In nanocomposite samples some folded graphite platelets were also detected, in particular at higher filler contents. This filler morphology could be responsible for the lower elastic moduli exhibited in flexural tests of solid nanocomposites with respect to that of the neat polymer and the different behavior measured on foams.

	Cooling from the Melt state		Max Crystallinity	Amorphous Nanocomp.	Crystalline Nanocomp.
	X _c [%]	T _c [°C]	X _{c,max} [%]	X _c [%]	X _c [%]
PEN neat	13.7	193,6	26,0	0.63	22.94
PEN + 0.1% EG	19.9	205,9	24,4	1.15	20.52
PEN + 0.5% EG	18.7	205,0	25,6	2.14	20.11
PEN + 1.0% EG	17.7	201,6	23,5	2.10	16.72
PEN + 2.5% EG	16.7	205,3	21,3	0.20	20.49

Table 1. Thermal properties from cooling scans and relative crystallinity of tested matrices.

Thermal properties of the polymeric matrices were evaluated because of their role in the foaming process. At all concentrations, graphite platelets increased the crystallization kinetics (higher T_c from the melt state during cooling) of the polymeric matrix (Table 1) with respect to the neat polymer, demonstrating that EG acted as nucleating agents for crystals. The increase of graphite content resulted in a reduction of the maximum crystallinity degree after crystallization, as also experienced in [7] for HDPE/EG and in [8] for the PA6/EG nanocomposite systems. Fast crystallization kinetics could help to stabilize the cellular structure but also could hinder the matrix expansion. The use of EG did not result in a decrease of the thermal stability, as experienced in conventional polyester nanocomposites

based on organomodified clays, confirming that EG is a viable nano-reinforcement for polymers having high processing temperature (Figure not shown for brevity).

3.3 DMA characterization of selected nanocomposite samples

The reinforcing effect of nanofiller in PET nanocomposites is evident from the DMA analysis shown in Fig. 1B. The pyromellitic dianhydride (PMDA) does not affect viscoelastic behavior of the PET-PMDA blends, as has also been reported in literature [9], and consequently the increase of storage modulus shown by PET/PMDA/NaMod nanocomposites can be attributed to the better dispersion or intercalation of the nanofiller.

In PEN nanocomposites, DMA analysis showed that the presence of EG increased the storage modulus in amorphous PEN nanocomposites (Fig. 1C). This trend has been confirmed in the mechanical behavior (tested at room temperature) of amorphous matrices, where nanocomposites exhibited higher values of the flexural modulus (FM), while the FM of crystallized samples showed a different behavior (Fig. 3). In fact FM of the neat PEN matrix was slightly higher than that of nanofilled samples, due to both reduction of total crystalline phase (Table 1) with the increase of EG with respect to the neat polymer matrix. Nanoparticles induced in all cases an increase of both stress and strain at break.

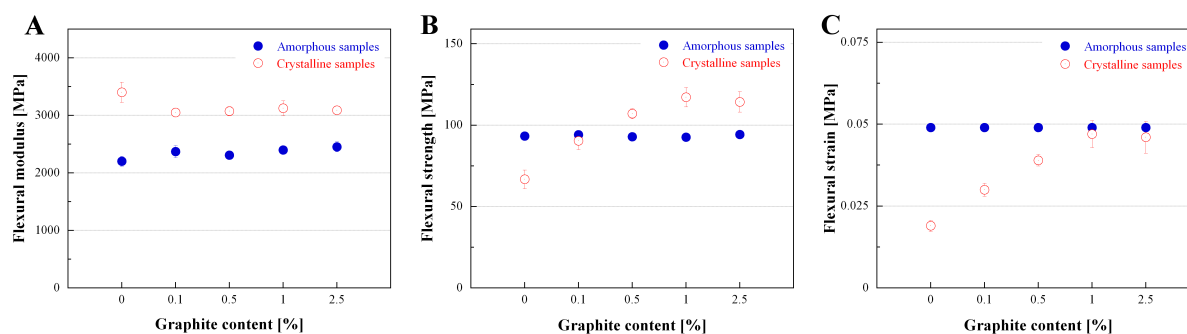


Figure 3. Mechanical properties of unfilled and graphite based nanocomposite matrices: A) Flexural modulus, B) Flexural strength, C) Flexural Strain.

3.4 Mechanical properties of PEN nanocomposite foams

In order to show the potential of thermally stable polyester based nanocomposites as matrix for composites and reinforced foams, PEN/EG nanocomposites matrices were selected to prepare composites and foams. The results of a deeper characterization are shown in the following. The presence of EG into foamed samples resulted in a different trend of the structural behavior with respect to that exhibited by unfoamed matrices. In fact, both compressive modulus and compressive strength increased with the amount of filler. The compressive behavior of the foamed samples with apparent density of $0.46 \text{ g/cm}^3 \pm 0.02 \text{ g/cm}^3$ is shown in Fig. 4. No peak value is evident but at just 0.1wt% of EG content an increase of quite 50% of both mechanical features was measured. The different elastic behavior of foamed samples with respect to solid matrices was probably due to the alignment of the graphite platelets in the cell walls. During the cell growth, the polymeric matrix is elongated and, as a consequence, crystals as well as graphite platelets could align in cell walls, instead of being randomly oriented or folded. A confirmation of this hypothesis was recently reported in [10], where unfoamed graphite reinforced samples exhibited, after stretching, an increase of the mechanical response with respect to unstretched ones.

3.5 Fiber reinforced composites

Composites were successfully prepared by using all thermoplastic matrices by means of the film stacking process. The production process was optimized in order to maximize the

impregnation of glass fiber fabric. SEM analysis (not shown for brevity) performed on composites has shown an homogeneous impregnation along sample thickness and between fibers. Furthermore, graphite platelets penetrated the fiber bundles and resulted evenly distributed between fibers.

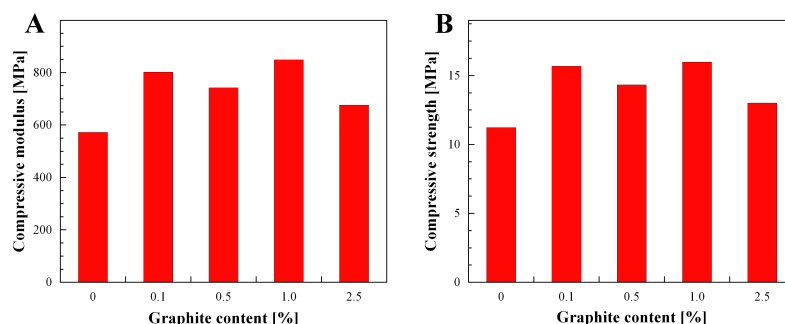


Figure 4. Compressive modulus and compressive strength (at 10% strain) of selected foams

3.6 Foamed Composites

Foamed composites were successfully prepared and exhibited a reduction of density of around 40% with respect to unfoamed composites (referred also as solid composites). The use of expanded graphite allowed the formation of a higher number of nucleated cells in the thermoplastic matrix [11] with respect to neat PEN samples.

Flexural properties of solid and foamed composites are shown in Table 2. As expected, solid composites presented higher flexural modulus with respect to foamed structures. After normalizing these properties with the material density, the differences in the specific modulus between solid and foamed composites are significantly reduced. The flexural strength of foamed composites was also lower than the unfoamed systems. It is worth to note that, after the flexural mechanical tests of foamed composites, the external surfaces showed visible indentation, due to the local plastic deformation of the expanded matrix in the outer surface of samples.

Sample	Density (g/cm ³)	Matrix Density (g/cm ³)	Voids Volume (%)	Flexural Modulus (GPa)		Flexural Strength (MPa)
				Absolute	Normalized	
Neat polyester	1.69			6.8	4.0	134
Polyester + Graph	1.67			6.6	4.0	128
Foamed Neat Polyest.	0.98	0.67	0.42	3.1	3.2	34
Foamed Polyest.+Grap	0.94	0.66	0.43	3.2	3.4	41

Table 2. Flexural properties of samples

Pictures of samples before the impact tests are shown in Figures 5A-5D. Foamed samples after impact are shown in Figures 5E-5F. The external surfaces of solid composites were damaged during impact tests and broken fibers after either low or high energy impacts were observed (Fig. 6). Foamed composites did not show any fiber break but rather a visible surface indentation. On the opposite to impact side of foamed samples a protrusion is evident, more pronounced after high energy impacts (Figure 5F and 5H). Damages after impact for low energy (8.6J) and high energy (42J) impact tests are shown in Figure 6. It is clearly evident that expanded composites (Fig. 6E – 6G) were able to bear the higher impact energy without being penetrated, unlike solid composites (Fig. 6D). Foamed composites were penetrated with an impact energy equal to 61J, 50% higher than the composite with the same amount of reinforcement and 160% higher in case specific properties are considered (Fig. 7).

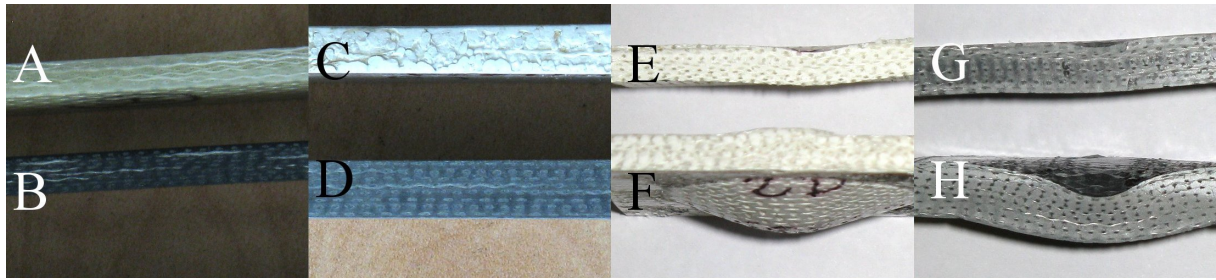


Figure 5. Solid composites (A – Neat PEN, B – EG filled PEN), foamed composites (C – Neat PEN, D – EG filled PEN) and composites after low (E and G samples) and high (F and H samples) energies impacts (E, F – Neat PEN; G, H – EG filled PEN)

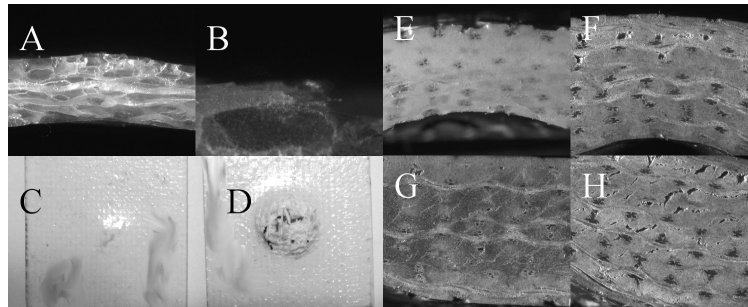


Figure 6. Optical micrographs of impacted samples: A) solid composite (cross section), B) solid composite (detail of broken fibers), C) solid composite (lower surface after low energy impact), D) solid composite (lower surface after high energy impact), E) foamed composite (Neat polyester, cross section), F) foamed composite (Graphite filled polyester, cross section), G) foamed composite (Graphite filled polyester, cross section after low energy impact), H) foamed composite (Graphite filled polyester, cross section after high energy impact)

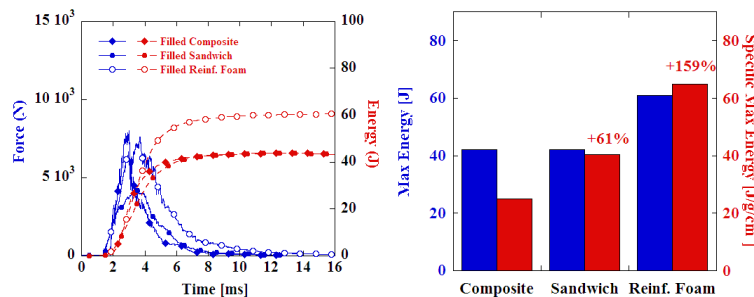


Figure 7. High energy impact response of solid composites, sandwich and foamed composites

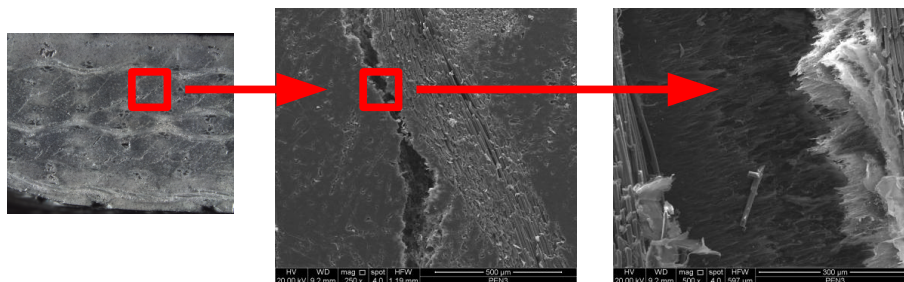


Figure 8. Peak force as function of sample density (High energy impacts)

The improved impact performance of foamed composites can be correlated to the energy absorbed through a complex deformation mechanism that involves both the foamed matrix (combination of compression and shear) and the glass fiber fabric layers. In particular, a large amount of energy is absorbed through i) the plastic deformation of the foamed matrix in a large area around the falling weight (Fig. 8) and ii) larger deformations and accommodation

of fabrics allowed by the reduction of volume permitted by the presence of foams around the reinforcing fibers.

4 Conclusions

PET/organomodified clay nanocomposites and PEN/EG nanocomposites with improved thermal stability and foamability have been successfully prepared. They exhibit increased mechanical properties in both dynamic-mechanical and static characterizations.

Glass fiber fabric reinforced microcellular foams were prepared through a controlled generation of gas bubbles in the thermoplastic polyester matrix with the density of the composites decreased from 1.65 to around 1 g/cm³. The formation of a microcellular morphology in the composite matrix resulted in a slight reduction of the specific flexural modulus but in a strong enhancement of impact properties, giving lower peak force during impact, higher energy absorption and resilience. The remarkable improvement in the impact performance, resulting from the presence of microcellular bubbles within the polymeric phase, avoided sample perforation even at impact energies able to perforate solid composites.

Acknowledgments

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