MONOMATRIX THERMOPLASTIC SANDWICH STRUCTURES THROUGH IN-SITU FOAMING TECHNOLOGY

L. Sorrentino[1*], M. Aurilia[2], L. Cafiero[1], S. Cioffi[1], M. D'Auria[1], S. Iannace[1]

[1]*Institute for Composite and Biomedical Materials, National Research Council, Piazzale V. Tecchio 80, 80125 Napoli – Italy*
[2]*Technological District on Polymeric and Composite Materials Engineering and Structures (IMAST), P.le E.Fermi 1, località Porto del Granatello, 80055 Portici (Naples), Italy*
luigi.sorrentino@cnr.it

Keywords: Sandwich, Thermoplastic Matrix, One Step Process, In-situ Foaming.

Abstract
Polymeric sandwich structures are conventionally based on either thermosetting (skin matrix, foamed or honeycomb cores) or thermoplastic (foamed cores) components, bonded through the use of adhesives. A new technology has been developed in the framework of the CESPERT project, which allow the production of a monomatrix thermoplastic sandwich structure in which the core is directly foamed between skins and consolidated without the use of adhesive layers.
In order to show the potential of this technology, a nanocomposite based on poly(ethylene naphthalate), PEN, and expanded graphite, EG, was developed as matrix and a glass fiber fabric was used as reinforcement. PEN is a thermoplastic polyester characterized by a high glass transition temperature (125 °C), comparable to that of PEEK (143 °C), but with a significantly lower melting temperature (265 °C vs 345 °C). Its physical and chemical properties are very promising for applications in transport industry and aeronautics. The polymer was melt blended with expanded graphite by means of extrusion process and its effects on the foaming properties were investigated through solid state foaming process. Reinforced composites were prepared by means of film stacking technique by using the same nanocomposite matrix. Main results of developed technology on morphological, mechanical and impact properties of sandwich structures are presented.

1 Introduction

The growing need to reduce energy and natural resources consumption stimulated materials research towards the development of lightweight structures in transport industries, such as automotive and aeronautics. For this aim, the development of composite and sandwich structures, characterized by high specific strength, stiffness and high impact strength is of great interest.
Sandwich structures are characterized by a very high rigidity obtained through the increase of the moment of inertia. They are conventionally prepared by bonding composite skins with lightweight materials (such as honeycombs or foams) by means of adhesive layers. Composites are used in high performance applications due to the high specific static properties (tensile and flexural moduli, high strength) [1] and are usually based on thermosettings. Thermoplastic polymer could be, however, preferred for composites

preparation because they have high toughness, no chemical reactions during fabrication, short manufacturing cycle, possibility of both scraps recovery and in-use repairing.

Thermosetting polymers are conventionally employed as matrices for cores but the same issues of composite applies. Additionally they cannot be thermoformed after consolidation due to the chemical nature of the polymers [2-3]. Moreover, to produce planar as well as complex shapes, through forming processes, thermoplastic polymers are overall preferable for both skin matrices and cores materials [4]. Thermoplastic cores are gaining ever more attention due to their strong potential advantages over thermosettings (higher productivity, lower raw material cost, recycling, easier welding) [5-6]. Thermoplastics foamed sheets can be thermoformed after the foaming step thanks to the ability to be deformed at high temperatures. Even if thermoforming process is not difficult to be performed on foamed cores, great attention should be paid if a semicrystalline polymer is used [3, 7]. In fact, the presence of crystals enhance the mechanical properties but tends to hinder an adequate flow of macromolecules during forming, inducing residual stresses and strains in the final structure.

Thermoplastic high performance polymers, such as PEEK, PEI, PPS are actually employed as matrices in structural composites in aeronautics applications thanks to their high mechanical and thermal properties (continuous working temperatures between 150°C and 230°C), but engineering polymers, such as PEN, show comparable mechanical properties and good thermal behavior (continuous working temperatures between 125°C and 150°C) at a fraction of their cost. PEN has a glass transition temperature (T_g) included between those of PPS (T_g = 100°C) and PEEK (T_g = 143°C) but its melting temperature is significantly lower (T_m = 265°C), in advantage of processing costs.

In order to prepare monomatrix lightweight structures, the matrix used to prepare the sandwich should also have good foaming properties. Polymeric foams are typically employed for a lot of applications such as packaging, thermal and acoustic insulation, and in the impact energy absorption [8, 9]. The use of a nanofiller, as already demonstrated in literature [10], can increase the T_g of polymers and/or shift their continuous working temperature towards higher values. Furthermore, the presence of nanofillers, in particular graphite, could improve functional, in addition to mechanical, performance and processability. Thermoplastic nanocomposite reinforced with expanded graphite presented an increased nucleation of cells in the foaming process, flame retardant and solvent resistance [11-13].

The aim of this work was to develop lightweight structural composites based on a nanocomposite thermoplastic matrix used for the production of the core in the sandwich structures and for the preparation of fiber reinforced composites. Structural, functional and processing properties of composites and sandwich structures were improved through a nanocomposite matrix developed for both fiber reinforced composites and monomatrix sandwich structures. Expanded graphite was successfully exfoliated in PEN matrix and improvements of its mechanical, thermal, functional and processing characteristics were induced. Finally, an innovative production technology was developed within the CESPERT project to produce monomatrix (same thermoplastic matrix for both core and reinforced skins) sandwich systems characterized by the capability to foam the core at same time of skin consolidation. This approach allows a reduction of the production time since the final sandwich structure is prepared in a single step process.

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 particles (platelets 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.). The nanoparticles

were dispersed in the polymer by using a Haake Rheocord (Thermo, Germany) PTW25P twin screw extruder at 270°C at a screw speed of 40 rpm (5 min of residence time). Nanocomposite matrices with several filler contents (0.1, 0.5, 1.0, and 2.5 vol %) were prepared. A hydraulic press (model P300P, from Collin Gmbh, Germany) was used to prepare samples through compression molding. PEN-based samples were quenched from the melt state to obtain amorphous polymers to be used in the gas solubilization step. All analyzed samples were vacuum-dried at 120 °C for 24 h before thermal analysis, gas absorption, and the foaming process. Graphite dispersion was investigated through an X-ray diffraction (XRD) analyzer at room temperature with a Philips X-ray generator and a Philips diffractometer (type PW1710).

Thermal properties were evaluated with a differential scanning calorimeter (model 2920 DSC from TA Instruments, DE – USA). The crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) were determined by a heating scan from 300°C to room temperature at a heating rate of 10 °C/min. The relative crystallinity (X_c) values were evaluated as the ratio ΔH_c to ΔH°_m, where ΔH°_m is the crystallization enthalpy of the perfect PEN crystal.

Samples before foaming were dried at 120°C for 24 h in a vacuum oven and then saturated for 72 h in a pressure vessel with CO_2 at a pressure of 80 bar and a temperature of 50°C. Gas-saturated samples were removed from the vessel and foamed by means of two different foaming techniques: a) free foaming, in which samples were dipped in an oil bath kept at the desired temperature (from 200°C to 260°C) for the time needed to reach the maximum expansion ratio (between 10 s and 20 s, to avoid foam collapsing), and b) confined foaming in an specially developed mould. The densities of the foams were measured by the water-displacement method according to ASTM D792.

Optical analysis in reflection mode was carried out by using a microscope (BX51 from Olympus, Japan) to investigate the fibers impregnation in the composite and the distribution of particles (detectable with this optical technique) dispersed in the composite matrices. Glass fibre composite samples were prepared by polishing the observation surfaces with wet sandpaper and then with a very fine polishing paste. Scanning electron microscopy (SEM) analysis on the nanofilled foams was performed on cryogenic fractured surfaces with a Quanta 200 FEG from FEI (Eindhoven, The Nederlands). All sample surfaces were gold-coated to render the specimen surfaces conductive.

Flexural properties were measured, according to ASTM D790, by means of a model 4304 dynamometer (SANS, China) on 13x95x3 mm^3 and 22x95x7 mm^3 samples, respectively cut from composites and sandwiches. Impact properties were performed on 45x45 mm^2 samples (same thickness of flexural tests) by using a Fractovis Plus impact testing machine (CEAST, Italy) at different impact energies.

3 Results and discussion

3.1 Matrix preparation and characterization

XRD analysis was performed on nanocomposite samples with filler content higher than 0.1% by weight due to the low sensitivity of XRD apparatus at such low graphite amount. XRD patterns showed a clear peak at 26.7°, the same main peak of expanded graphite (Fig. 1). This is an evidence of 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 100 nm while in 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.
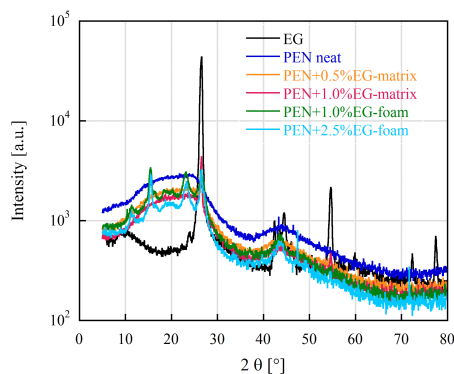
Figure 1. XRD patterns of nanocomposite matrices prepared

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 [14] for HDPE/EG and in [15] for the PA6/EG nanocomposite systems. Fast crystallization kinetics could help to stabilize the cellular structure but also could hinder the matrix expansion.

	Cooling from the Melt state		Max Crystallinity	Amorphous Nanocomp.	Crystalline Nanocomp.	Free Foam ($T_{foam} = 240°C$)	Confined Foam ($T_{foam} = 200°C$)
	X_c [%]	T_c [°C]	$X_{c,max}$ [%]	X_c [%]	X_c [%]	X_c [%]	X_c [%]
PEN neat	13,7	193,6	26,0	0,63	22,94	7,4	21,5
PEN + 0.1% EG	19,9	205,9	24,4	1,15	20,52	18,2	18,6
PEN + 0.5% EG	18,7	205,0	25,6	2,14	20,11	14,9	19,0
PEN + 1.0% EG	17,7	201,6	23,5	2,10	16,72	15,9	16,1
PEN + 2.5% EG	16,7	205,3	21,3	0,20	20,49	14,8	17,9

Table 1. Thermal Properties of matrix and foam samples of PEN Nanocomposites after different processing conditions
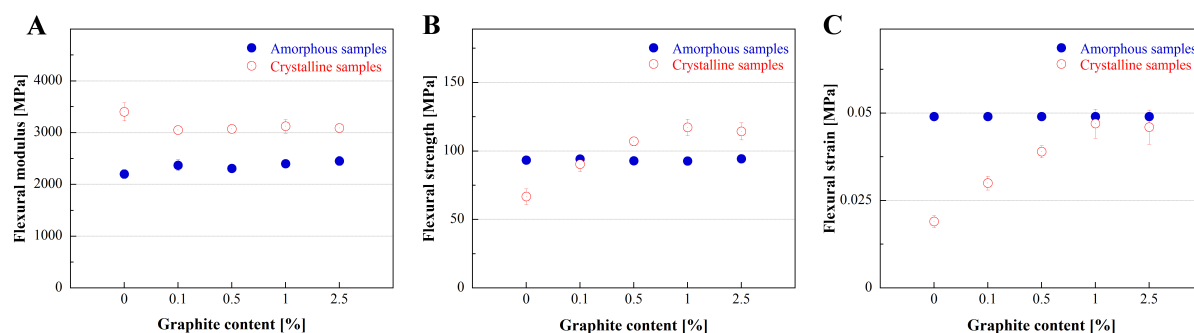

Figure 2. Mechanical properties of unfilled and graphite based nanocomposite matrices: A) Flexural modulus, B) Flexural strength, C) Flexural Strain

EG affected the mechanical behavior (tested at room temperature) of nanocomposites. As evident in Figure 2, nanofilled matrices exhibited higher values of the flexural modulus in the amorphous state. The flexural modulus of crystallized samples showed a different behavior. The flexural modulus of the neat PEN matrix was slightly higher than that of nanofilled samples, due to the reduction of total crystalline phase with the EG increase filled samples with respect to the neat polymer matrix. Nanoparticles induced, on the contrary, an increase of both stress and strain at break.

3.2 Foaming process

The morphology of samples obtained with the free foaming process showed an homogeneous microcellular structure at all compositions but, as evident from Figure 3A and 3B, the presence of graphite increased the number of nucleated cell (of about one order of magnitude), lowering the mean cell diameter from around 20 μm (neat polymeric matrix) to less than 7 μm.

A direct proportionality between the filler content and the number of nucleated cells was not evident in any of the nanocomposite systems. Graphite nanoparticles induced at the lowest filler content (0.1%) an amount of nucleating sites one order of magnitude higher than the amount of nucleated cells evidenced in the neat polymer; a further increase in the nanoparticle content in the matrix did not result in more sites useful for nucleating bubbles. Furthermore, the foaming temperature marginally affected the cellular morphology in samples. After the free foaming process, the crystallinity X_c resulted to be very high in nanocomposite samples with respect to the neat PEN foams (Table I).
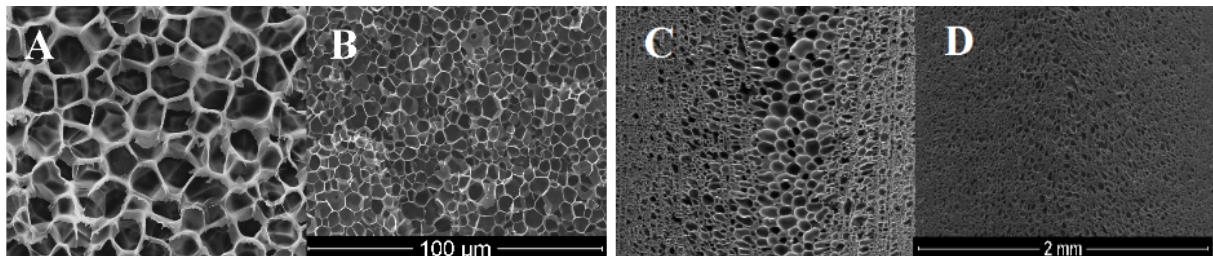

Figure 3. Foam morphologies after free (A – neat PEN and B – 1.0% EG filled PEN; scale of B also applies to A) and confined foaming process (C – neat PEN, D – 0.5% EG filled PEN; scale of C also applies to C)

Also the confined foaming technology allowed a microcellular morphology (Figure 3C and 3D) in all matrices but, as evident in Figure 5, all PEN foams showed a cell size gradient through the sample thickness. In fact, the mean cell diameter in neat PEN foams was about 100 μm at the middle of thickness, while it was around 7 μm at the edge while the mean cell diameters in nanocomposite samples was about 27 μm in the middle and 5 μm at the edge. The different cell sizes in neat and nanocomposite PEN samples were addressed to the nucleating effect of nanoparticles, which reduced the cell size and increased their number. From a mechanical point of view, the increased number of cells and the presence of graphite, aligned along cell walls, effectively reinforced the polymeric matrix, giving higher compression modulus and, in particular, yield stress (raised of about 50%, Figure 4).
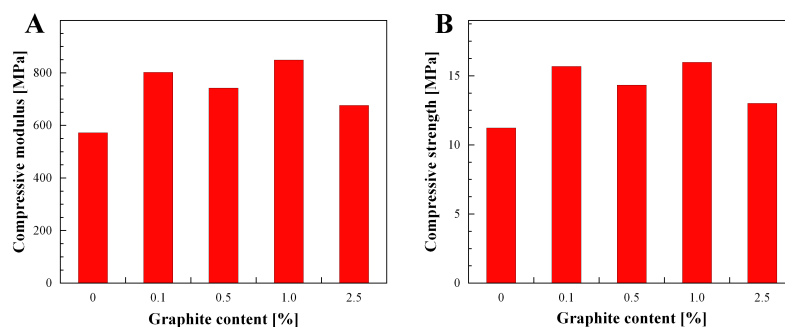

Figure 4. Compressive modulus and compressive strength (at 10% strain) of selected foams

3.3 Fiber reinforced composites

Composites were successfully prepared by using all of the 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 performed on composites has shown a homogeneous impregnation along sample thickness and between fibers (Figure 5A). Furthermore, graphite platelets penetrated the fiber bundles and resulted evenly distributed between fibers as shown in Figure 5B.
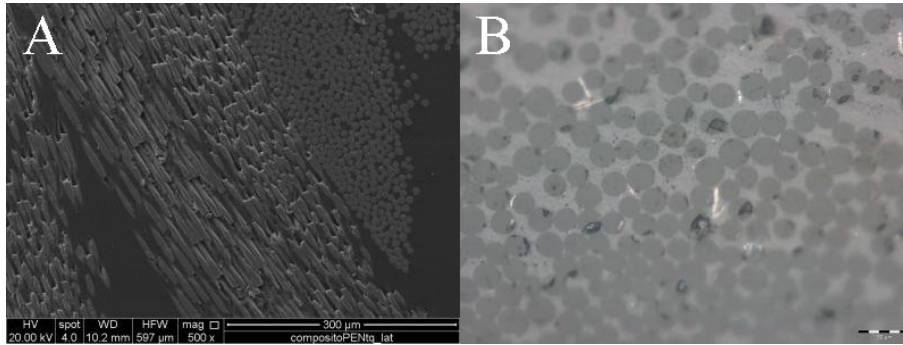

Figure 5. Details of fiber impregnation in the composite based on 1.0% graphite filled matrix: A) SEM image, B) graphite platelet dispersed between fibers

3.4 Sandwich production

The technology for the preparation of sandwich structures was developed within the CESPERT project and allowed the preparation of the foamed core and the bonding with the skins in a one step process, without the use of adhesive layers thanks to the fact that the matrix of the composite skins was made out of the same polymer used for the core. In order to obtain the welding, the polymeric matrix in all stacked components must be in the amorphous state, and the slow crystallization kinetics of the developed matrices was of benefit. The final core density was determined by foaming process parameters. The facings of prepared sandwiches were previously produced by means of the film stacking technique and were realized by alternating 5 layer of polymer and 4 layer of glass fiber fabric. In Figure 6 one of the sandwich samples produced by using the developed technology is shown. As evident from SEM micrographs performed on sandwich samples, the foam morphology developed during the sandwich preparation was homogeneous and microcellular along the sample thickness (Figure 7A). Adhesion of the core with facings was strong and sample failure occurred in the foamed core. SEM image of a skin after failure in the flexural test is shown in Figure 7B.

Figure 6. Sandwich structures based on Neat PEN (a) and the 1.0% EG filled matrix (b)

3.5 Comparison of structural properties of composites and sandwich structures

Flexural and impact properties of both sandwiches and composites (with the same amount of reinforcement) are compared in Figure 8A and 8B, respectively. Composites (based on neat and nanocomposite matrices; density 1.67 g/cm^3; glass fiber content 30%) exhibited higher

values of flexural modulus with respect to those of the sandwiches (based on neat and nanocomposite matrices; density 1.03 g/cm^3; glass fiber content 30%) but specific values (diamond markers), obtained after density normalization, are comparable (Figure 8A). The presence of 1.0% by weight of EG induced an increase of the flexural modulus with respect to the flexural modulus of composites based on the neat matrix. For all prepared systems a theoretical model was used to predict the mechanical properties starting from the structural properties of constitutive materials, taking the hypothesis of prefect impregnation of fibers (for composites) and perfect adhesion between skins and cores (for sandwich structures). A very good agreement was evidenced. Impact properties resulted to be dependent on the fiber reinforcing content, not on the polymeric matrix used (Figure 8B). In fact, absorbed impact energy are quite similar (43J) but stress during impact was significantly lower in the sandwiches with respect to the composites, thanks to the presence of the core.
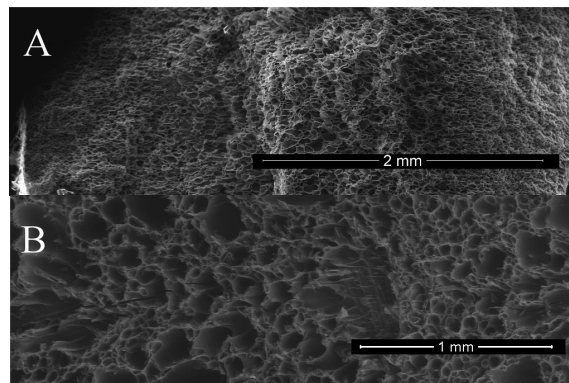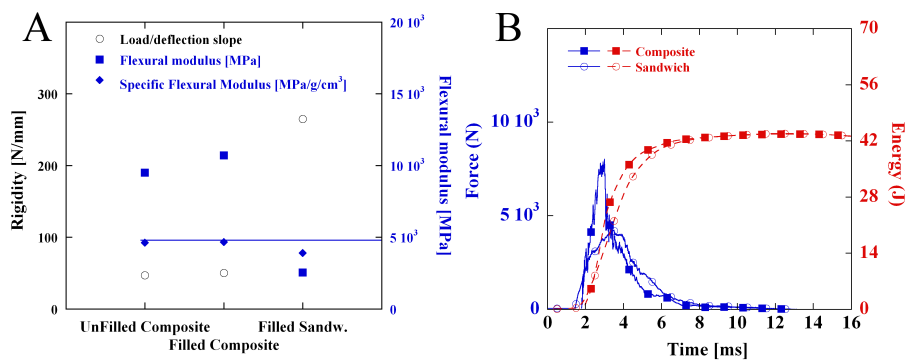

Figure 7. SEM image of the skin after flexural test

Figure 8. Flexural (A) and impact (B) properties of selected composite systems

4 Conclusions

A thermoplastic matrix (PEN) was selected for the production of sandwich structures through an innovative technology which is able to join the composite skins to the core directly during the core foaming without the use of adhesive layers.

Expanded graphite was used as nanofiller for the preparation PEN nanocomposites, which showed improved mechanical properties. Foam samples, prepared by means of supercritical carbon dioxide, exhibited a microcellular morphology at all compositions. When used, EG nanoparticles acted as nucleating agents for bubbles, resulting in a reduction of cell diameters from 10 μm to less than 4 μm. Nanocomposite foams showed higher mechanical properties with respect to solid matrices, because they were able to further exploit the reinforcing effect of both platelets and polymeric crystals by means of the stretching of cell walls during foaming.

Fiber reinforced composites were also successfully prepared by using PEN nanocomposites. The developed nanofilled matrices were also suitable for the production of sandwich structures through the proposed one step process. The surface analysis after failure evidenced a good adhesion between core and facings and the mechanical behavior was in very good agreement with theoretical predictions. Graphite addition into PEN matrices resulted in a slight increase of the flexural modulus of composites and sandwiches, while its effects were not evident upon impact properties. Impact properties of all composite systems showed that the total absorbed energy was only dependent upon the fiber content. Sandwich resulted to be a more efficient structure for impact absorption due to its higher specific absorbed energy, coming from its lower density, and the strong reduction of peak stress during impact.

Acknowledgments

References
[1] Partridge I.K. *Advanced Composites*, Elsevier Applied Science, New York (1989).
[2] Karlsson K.F., Åström B.T. Manufacturing and applications of structural sandwich components. *Composites A, **28***, 97-111 (1997).
[3] Rozant O., Bourban P.E., Månson J.A.E. Manufacturing of threedimensional sandwich parts by direct thermoforming. *Composites A, **32**,* 1593-1601 (2001).
[4] Ning H., Janowski G.M., Vaidya U.K., Husman G. Thermoplastic sandwich structure design and manufacturing for the body panel of mass transit vehicle. *Composite Structures, **80**,* 82–91 (2007).
[5] Breuer U., Ostgathe M., Necitzel M. Manufacturing of All-Thermoplastic Sandwich by a One-Step Forming Technique. *Polymer Composites, **19***, 3, 275–279 (1998).
[6] Akermo M., Astrom B.T., Modelling component cost in compression moulding of thermoplastic composite and sandwich components. *Composites A, **31**,* 319–333 (2000).
[7] Throne J.L. *Technology of themoforming*. Hanser, Munich (1996).
[8] Gibson L.J., Ashby M.F. *Cellular solids: Structure & properties*, Pergamon Press, Oxford (1988).
[9] Gay D., Hoa S.V., Tsai S.W. *Composite Materials: Design and Applications*, CRC Editions, Boca Raton (2003).
[10] Paul D.R., Robeson L.M. Polymer nanotechnology: Nanocomposites. *Polymer, **40***, 3187-3204 (2008).
[11] Sorrentino L., Aurilia M., Iannace S. Polymeric Foams From High Performance Thermoplastics. *Advances in Polymer Technology, **30**,* 234–243.(2011).
[12] Sorrentino L., Aurilia M., Cafiero L., Iannace S. Nanocomposite Foams From High Performance Thermoplastics. *Journal of Applied Polymer Science, 122,* 3701–3711 (2011).
[13] Aurilia M., Sorrentino L., Sanguigno L., Iannace S. Nanofilled Polyethersulfone As Matrix For Continuous Glass Fibres Composites: Mechanical Properties And Solvent Resistance. *Advances in Polymer Technology*, **29**, 146–160 (2010).
[14] Jo G., Naguib HE. Constitutive modeling of HDPE polymer/clay nanocomposite foams. *Polymer*, **48**, 3349-3360 (2007).
[15] Pan Y.X., Yu Z.Z., Ou Y.C., Hu G.H. A New Process of Fabricating Electrically Conducting Nylon 6/Graphite Nanocomposites via Intercalation Polymerization. *Journal of Polymer Science - Part B: Polymer Physics*, **38**, 1626–1633 (2000).