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Production of Functionally Graded Foams by Solid State Process

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Abstract: *In the present study nano-composite foams were fabricated by mixing thermosetting powders with montmorillonite (MMT) nano-powders at different volume fractions (0%, 5%, and 10%). A first comparison between unfilled and filled foams at various MMT contents was performed in terms of density. Compression tests were also carried out on composite foams to evaluate the mechanical properties (compressive strength and toughness) in dependence of the filler content. Subsequently the same process was used to produce functionally graded nano-foams (FGMs) by compressing tablets with a distribution of MMT filler content along the height. The layering strategy depends on the final application, and is very flexible because the mixing process is carried out at room temperature. Finally, the compacted tablet is already a functionally graded material which will preserve this characteristic after foaming. Indentation tests were performed to evaluate local properties of FGM nano-foams.*

Keywords**:** *solid state foaming, thermosets, montmorillonite (MMT), functionally graded foam.*

1. INTRODUCTION

Porosity in dense engineering materials is often undesirable for load-bearing applications. However, porosity is highly beneficial for weight and cost reduction, damping, thermal insulation and specific strength [1]. Moreover, they are extensively used in several industrial applications: automotive, aeronautic, and naval. In the last years, the attention was focused on these new materials because they combine good mechanical properties and low weight [2].

The method for making foams is straightforward: generating bubbles and stabilizing them within the matrix. There are two major foaming methodologies: soluble foaming (or physical foaming) and reactive foaming (or chemical foaming). The former is generally applied to thermoplastics and involves the mixture of a polymer melt and a blowing agent. The latter is typical for thermosets and involves the addition of reactants for the gas evolution. In both cases, the same three steps are necessary gas implementation, gas expansion and foam stabilization. Different organic solvents (hexane or cyclohexane) are used as physical blowing agents. Alternatively a chemical foaming agent can be adopted so that a gas is released during the cross-linking reaction. In this case, epoxy foam is synthesized with an optimum ratio of epoxy amine blowing

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agent. Moreover, the polymer matrix is always processed in a liquid state by means of plasticators (for thermoplastics) or mixers (for thermosets) [3].

In this paper, a new foaming technology is studied without using any external agent. The epoxy and epoxy-polyester resin to foam are in the form of powder which is compacted in tablets by room temperature compression. Afterwards, the tablets foam in metallic molds by addition of heat. This new technology makes a lot of applications possible and special equipments are not necessary. This foaming process was called "solid-state" foaming for the analogy with a similar process defined for titanium powders [4-5]. The proposed technology allows foaming rapidly thermosetting tablets by means of heat addition only. No blowing agent is necessary as the foaming mechanism depends on the intrinsic resin boiling point. In this way, the selection of the resin powder is critical. In fact it is necessary that the powder has a glass transition temperature high enough to allow the tablet densification by means of cold pressing avoiding any material degradation effect. During boiling, the resin polymerizes and the bubbles inside the foam become stable. However, the resin boiling temperature has to be limited, otherwise the resin burning or thermal degradation would present kinetics faster than the polymerization one. At the end, another critical characteristic deals with the mechanical properties of the cured resin which should be optimal. All these properties can be found in the powders employed for coating. In fact, in this application field, it is important to have high temperature and low time curing systems, in which a low viscosity is necessary in the first heating stage and a complete reaction in the final one. In the proposed foaming process, the compacted tablets are inserted into a muffle at a very high temperature (higher than the burning one) and during the thermal transition from the initial tablet temperature to the muffle temperature, the resin boils and hardens. Boiling is immediate, whereas the polymerization needs time and in this time the bubbles can form. By means of this technology, composite and nanocomposite foams may be produced as well. In fact, before compaction, the resin powder may be mixed with several filler materials such as ceramic or metallic micro and nano-particles. Functionally graded foams may be easily produced by compacting a layered tablet where each single layer is filled with at different particle content. In order to increase the foam strength, different kinds of fillers (Glass, Al, Zn) can be mixed in the matrix powder before the tablet compression [6]. Unfortunately, by increasing the filler content, the foam weight increases excessively and the foaming efficiency decreases. The use of nanofiller, instead, makes possible to reduce drastically the filler content with the advantage of high mechanical performances of the final products. On the same time a low fraction of filler content can avoid the possibility to an excessive increase of the foam weight. In the present study, for the first time, functionally graded nano-composite foams were fabricated by mixing thermosetting powders with montmorillonite (MMT) nano-powders at different volume fractions (0%, 5%, and 10%). A comparison between unfilled and filled foams with various montmorillonite contents was performed in terms of foaming ratio and density. Compression tests were also carried out on composite foams to evaluate the mechanical properties (compressive strength and toughness) in dependence of the filler content. In a typical compression curve of foam, the stress-strain curve can be divided into three parts. In the first part, at low strains, the stress increases almost linearly as the foam behaves rigidly. Subsequently, the bubbles start to collapse and a plateau is reached. This plateau is kept for a wide range of the strain, in which the foam dissipates the energy provided by the compression by means of the bubble rupture. In the last part of the curve, a slight increase of the stress is observed because of the material densification and its inability to dissipate more energy.

2. MATERIALS AND METHODS

A commercial epoxy (EP) and epoxy-polyester (EP-PE) resin (density of 1.44 g/cm^3 and 1.28 g/cm^3 respectively) were used for experimentation. The powder has a fine grain size as it is typical for coating applications. Figure 1 shows the layout of the foaming process.

Due to compaction, the powder can be easily shaped in tablets. Before compaction, the resin powder was mixed with Montmorillonite (MMT) nano-powders at different volume fractions (0%, 5%, and 10%). Figure 2 shows nano-foams that were produced with different content of nano-clay.

The used nano-clay was montmorillonite (MMT) derived from especially purified and natural clay which was modified with quaternary ammonium salt (dimethyl benzylhydrogenated tallow ammonium). The interest in this class of filler depends on

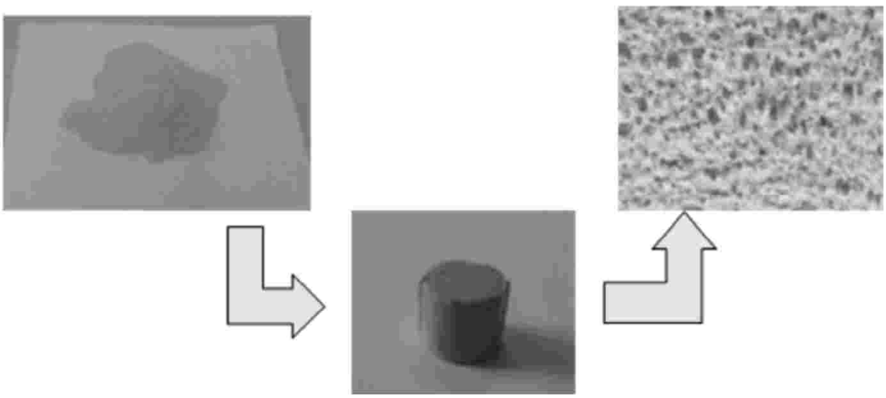


Figure 1: The Foaming Process

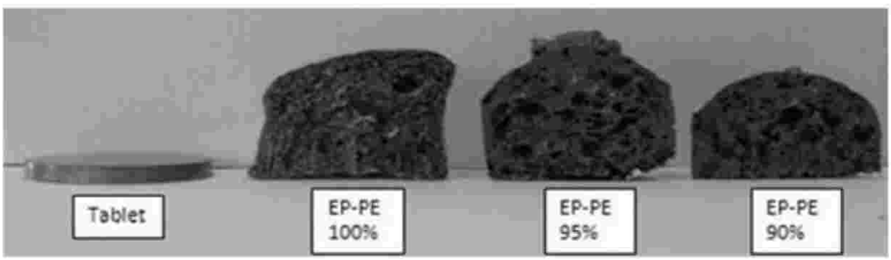


Figure 2: Effect of the Nano-MMT Content on the Foaming Ratio

the medical and sanitary applications, however any other nano-filler could be processed in a solid state foaming process. A hydraulic press was used to compact the tablets. Powder was put in a cylindrical stainless steel mold and pressed up to the pressure of 100 bar. After compaction, the tablets had a diameter of 50 mm and a height of 5 mm. The tablets foamed when inserted in a muffle at high temperature. The foaming process was performed in air, placing the tablets in cylindrical steel molds with an external diameter of 50 mm and a thin wall. In order to avoid the direct contact of the resin tablet with the mold or the muffle, a thin aluminum sheet was used to cover the internal mold wall as well as the base of the mold. The foaming time was fixed at 10 min, whereas the foaming temperature was 250 °C for the epoxy-polyester powder and 320 °C for the epoxy. Higher temperatures or times determined the resin burning whereas at low times or temperatures the resin polymerization was not completed. After foaming, the specimens were cooled in air and extracted from the molds. The foam tip was cut to have a cylindrical shape and the foam density was evaluated. Compression tests were performed using a universal material testing machine (MTS Alliance RT/50) at a test rate of 5 mm/min.

Functionally graded nano-foams (FGMs) may be efficiently produced by solid state foaming. Functionally graded foams are produced by compressing tablets with a distribution of the filler content along the height. Figure 3 shows the sections of two functionally graded nano-foams and one unfilled epoxy foams. Also in this case, the nano-foams were filled by means of MMT. The first step of the foam production process is the mixing of the uncured resin powder with the nano-filler at different weight contents. Subsequently, the powder mixtures are deposed in the steel mold layer by layer for the cold compaction. The first layer presents the higher content of filler and the last one is unfilled. The layering strategy depends on the final application, and is very flexible beacause the mixing process is carried out at room temperature in solid state. Finally, the compacted tablet is already a functionally graded material which will also preserve this characteristic after foaming. The subsequent stage of the foaming process is the heating of the layered tablets. In this case, a further process parameter is present as the tablet may be positioned leaning on the unfilled layer or the maximum filled one. For this reason, in Figure 3, a difference in the filler content distribution is reported.

Both foam on the left and the central one were produced with a nano-filler content ranging from 0 to 4 wt%, but for the foam on the left the unfilled layer was used as the leaning layer during foaming whereas for the foam in the centre of the figure the tablet leaned on the higher filled layer. The correct evaluation of the property gradient is already a difficult task for bulk functionally graded materials, even if it is a key-factor for the design of new materials or processing technologies as well as for the optimization of the existing ones. A new characterization technique is necessary to provide information about the local mechanical performances of the functionally graded nano-foams. A good solution was found with the use of an instrumented macro-indentation test to measure the effect of the local nano-filler content. The foams were cut to extract a slice 10 mm thick. In Figure 3 these slices are shown and the indentation

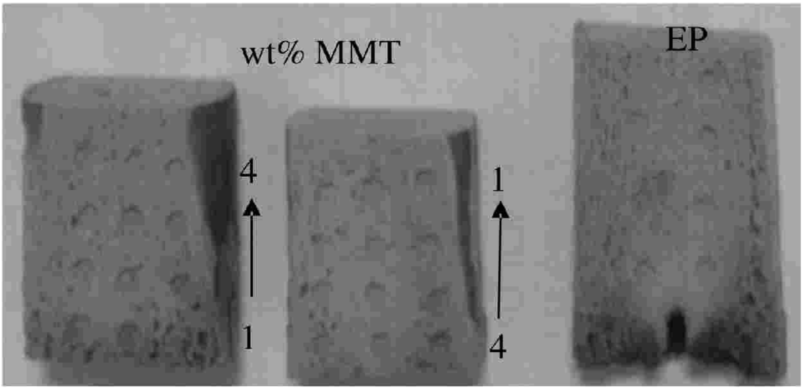


Figure 3: Functionally Graded Nano-foams

marks are visible. More indentations were performed at different heights of the foamed slices. Tests were carried out by means of a material testing machine equipped with a tungsten carbide cylindrical flat indenter, having a tip diameter of 2 mm. The test rate was 5 mm/min, the maximum displacement was 1 mm and the pre-load was 10 N. The pre-load value was optimized to reduce the initial non-linearity of the curve which is due to the absence of a perfect parallelism between sample and indenter surface.

3. RESULTS AND DISCUSSION

The effect of the nano-filler content on the properties of the nano-foams is shown in the next figures. By increasing the MMT content, the foam density (Figure 4) increases as in the case of micro-fillers. Higher densities are measured for epoxy foams due to lower foamability of this resin in comparison with the epoxy-polyester resin. The effect of the filler content on the foam mechanical properties is important: Figure 5 shows the compression curves of the nanocomposites.

From these curves the plateau stress and the maximum strain were extracted, and are reported in Figure 6a and 6b respectively. By increasing the MMT content, an increase of the plateau stress and a decrease of the maximum strain are observed.

An important mechanical property for foam is the toughness which is related to the maximum amount of energy that may be absorbed by the foam during its collapsing. Generally higher plateau stress and ductility lead to a higher toughness, but a high plateau stress is measured in less ductile foams. For this reason, by increas-ing the MMT content, a maximum is expected for the foam toughness. Figure 7 shows that the maximum of the compression toughness for the nano-composite epoxy foam is reached at filler content lower than 10 wt%. Instead, in the epoxy-polyester resin case, the maximum of the compression toughness is expected at higher values of the filler content.

Functionally graded materials (FGMs) are composite materials with a gradual variation in properties which is dependent on a continuous spatial distribution of two or more components along a direction of the product. Functionally graded polymer

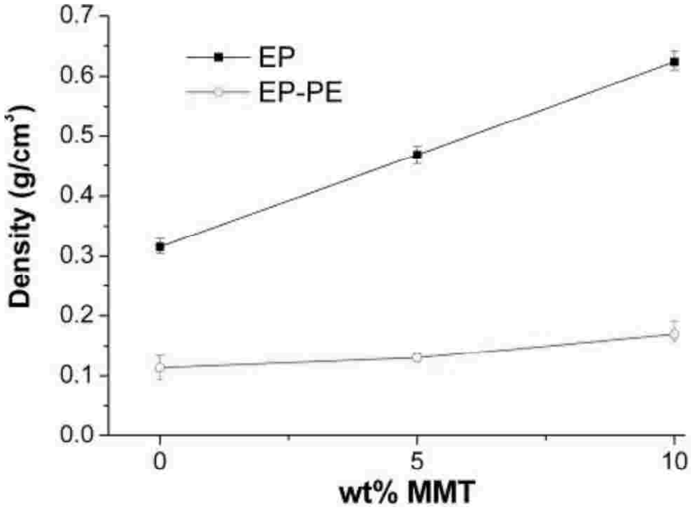


Figure 4: Foam Density

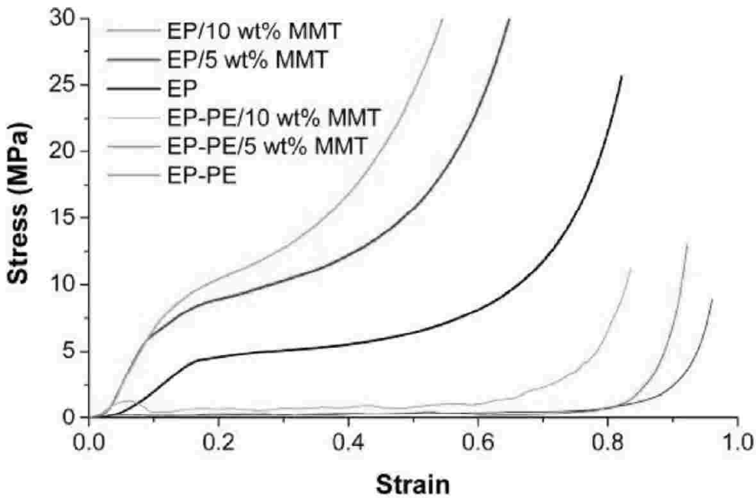
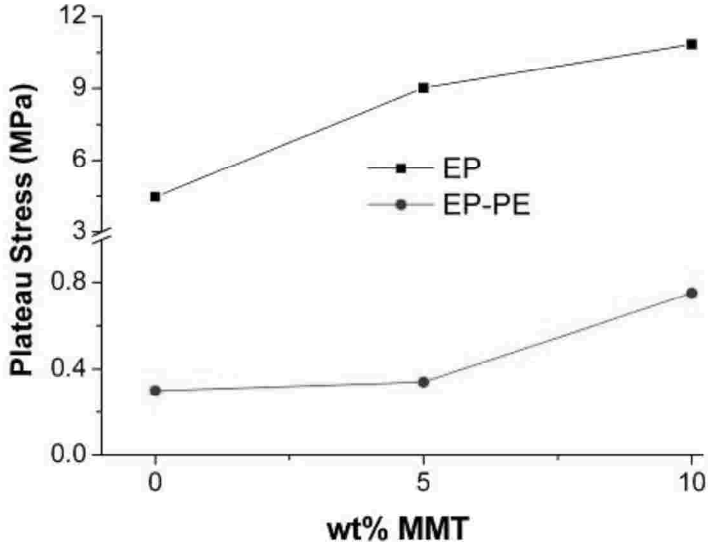


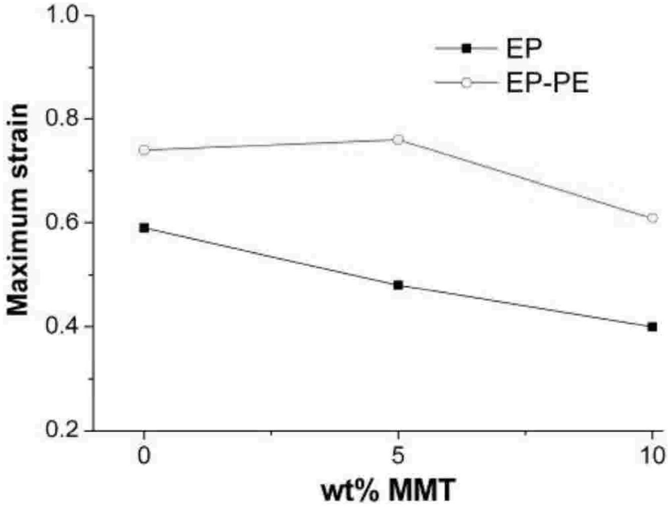
Figure 5: Compression Tests

composites offer excellent mechanical properties and environmental resistance. Several manufacturing processes may be used to produce these composites in dependence of the matrix typology and the expected performances. The combination of a graded material property with a foamed structure is in the forefront of the material processing.

Figure 8 shows some typical indentation curves for MMT filled foams with different filler contents. The indentation curves are very similar to the compression ones apart from the densification stage which is never reached. The first part of the loading stage is almost linear; by increasing the penetration depth, the indentation curve approaches



(a)



(b)

Figure 6: Compression Test Results in Terms of Plateu Stress (a) and Maximum Strain (b)

a plateau which corresponds to a significant material collapsing. The plateau value is directly related to the MMT content; higher nano-clay contents lead to higher mechanical performances.

At the end of the loading stage, after the load removal, the material recovery is basically absent; showing that, during indentation the mechanism of the bubble rupture dominates. In order to have a comparison between the indentation results, the load at the fixed displacement of 1 mm was extracted from the curves. This indentation load

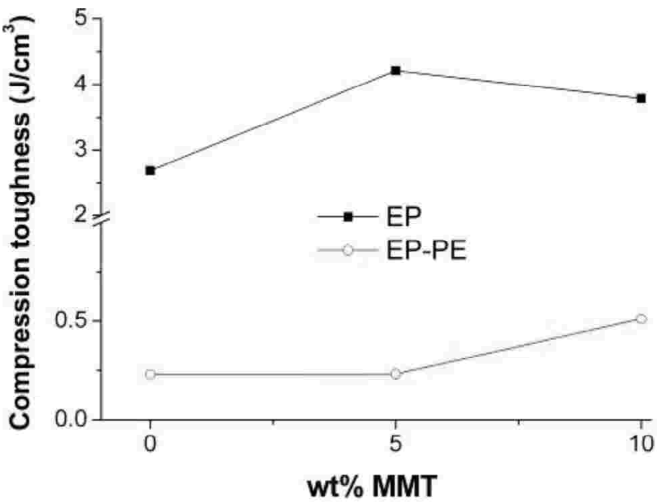


Figure 7: Compression Test Results in Terms of Compression Toughness

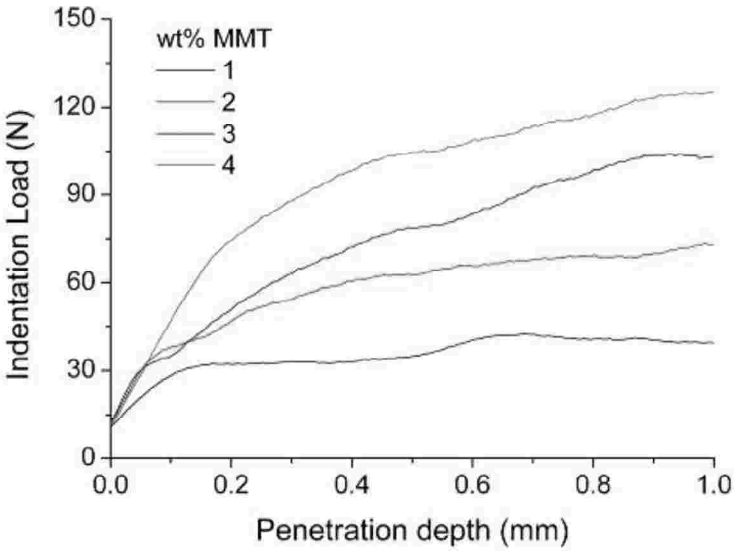
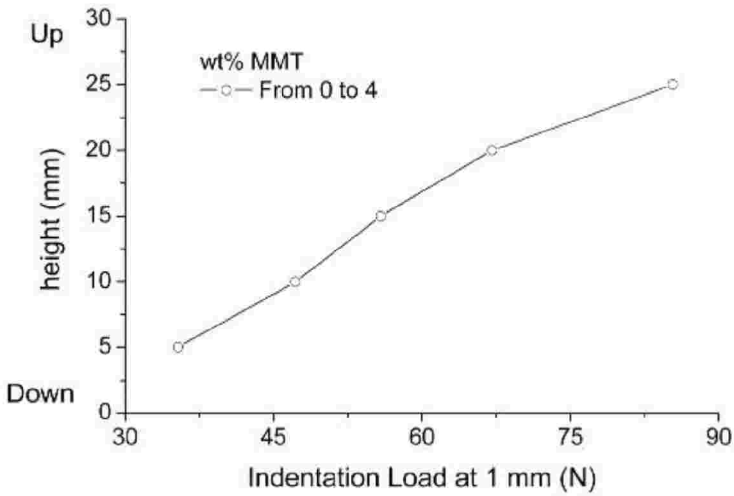
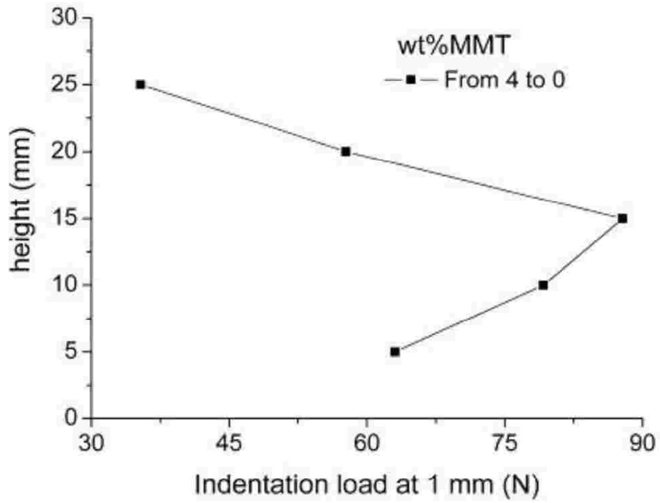


Figure 8: Indentation Tests on Functionally Graded Foams

is reported in Figure 9a and 9b for both functionally graded nano-composite foams of Figure 3. In the ordinate axes the distance from the bottom surface of the foams is reported. In the case of the tablet which was foamed leaning on the unfilled layer, a correct trend is measured. By increasing the distance from the bottom surface, the MMT content increase as well as the indentation load. In the opposite case, a maximum is observed in the middle of the foam where a medium content of nano-filler was expected. Considering that, the final foam density was comparable in the two cases, this difference in the indentation load distribution is particularly important. Evidently,



(a)



(b)

Figure 9: Indentation Test on Functionally Graded Foams: Correlation Between Indentation Load and The Sample Height

in the foaming process under consideration, a higher foaming temperature was reached in the air exposed surface of the tablet. In the case of the tablet leaning on the unfilled layer, this positive effect compensates the negative effect of the resin filling which is generally related to higher foaming ratio. As a result, an almost linear trend of the MMT content was achieved. In the second case, when the tablet leaned on the highly filled layer, the maximum of the foaming temperature was associated with the maximum of the resin content. As a consequence, a lower foaming ratio was obtained in the top of the foam whereas the fillers agglomerated in the bottom.

4. CONCLUSIONS

As a conclusion, solid state foaming is able to produce FGM nano-foams with a strict control of the distribution of mechanical properties. Nano-composite foam can be designed for a specific application by changing the filler content and distribution. Higher filler content leads to a higher toughness but also to a higher density. The proposed technology presents a lot of advantages: the absence of a blowing agent, the low cost of equipments, and the easiness of the application. In the reported results commercial powders were used and they showed an optimal behavior. In the future, appropriate formulations could lead to better results. Many industrial applications can take advantages from this technology. Structural applications seem to be the most interesting, as panels and structural sandwiches can be easily fabricated. In order to produce a sandwich panel with a metal skin and a foamed core, sheet metals may be placed in the mold before foaming. Figure 10 shows a sandwich with a metal skin made of aluminum alloy (1 mm thick), and a thick foamed epoxy core. The total thickness of the panel is 27 mm and the size is 80×80 mm^2.

Furthermore macro-indentation tests are able to evaluate the complex distribution of mechanical properties in the functionally graded nano-composite foam. Mechanical tests on bulk samples did not allow the same result. In fact, compression tests were performed on functionally graded bulk samples, and on foamed samples in which the nano-filler was homogenously distributed. By comparing functionally graded and homogenous samples with the same average filler content, similar results were obtained in terms of plateau stress and compression toughness.

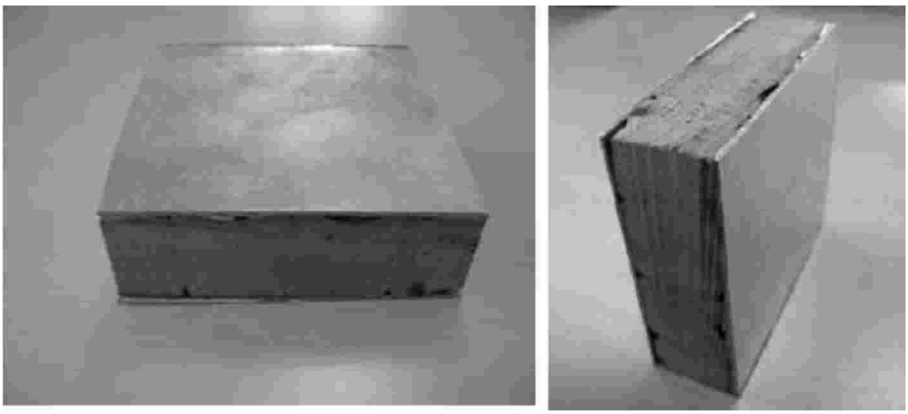


Figure 10: Structural Panel with a Foamed Core

References

[1] El-Hadek M. A., Tippur H. V. Simulation of Porosity by Microballoon Dispersion in Epoxy and Urethane: Mechanical Measurements and Models. *Journal of Materials Science* 2002; 37:1649-1660.

[2] Stefani P. M., Tejeira Barchi A., Sabugal J., Vazquez A. Characterization of Epoxy Foams. *Journal of Applied Polymer Science* 2003; 90:2992–2996

[3] Lee S. T., Ramesh N. S. Polymeric Foams: Mechanisms and Materials. IEEE Electrical Insulation Magazine.

[4] Murray N. G. D., Schuh C. A., Dunand D. C. Solid-state Foaming of Titanium by Hydrogen-induced Internal Stress Superplasticity. *Scripta Materialia* 2003; 49:879-883.

[5] Yang C. C., Nakae H. Foaming Characteristics Control During Production of Aluminum Alloy Foam. *Journal of Alloys and Compounds* 2000; 313:188-191.

[6] Guglielmotti A., Quadrini F., Squeo E. A. Composite Foam by Solid State Foaming. *The 1st International Conference on Polymer Processing Engineering* 2007.