COMPOSITE FOAMS WITH ANISOTROPIC STRUCTURAL AND FUNCTIONAL PROPERTIES

Luigi Sorrentino[1,], Marco D'Auria[1,2], Roberto Pantani[3] and Daniele Davino[1,2]*

[1]Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche, Portici, Italy
[2]Dipartimento di Ingegneria, Università degli Studi del Sannio, Benevento, Italy
[3]Dipartimento di Ingegneria Industriale, Università di Salerno, Fisciano (SA), Italy
[*]Email: luigi.sorrentino@cnr.it

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Abstract
Composite lightweight materials based on a polymeric matrix with embedded magnetic micro-particles were developed. The application of a magnetic field (MF) during the foaming of samples tailored the assembling of magnetic particles along the MF lines, forming reinforcing chain-like structures in the foamed polymer. The presence of aligned micro-particles imparted peculiar anisotropic structural and functional responses. In fact, such foams showed higher compressive performances (in terms of Young's modulus and compressive strength) along the alignment direction with respect to randomly reinforced foams. The proper variation of the processing parameters during foaming allowed to change the constitutive stress-strain compressive relationship. Samples with aligned particles exhibited improved performances with particle volume content, in accordance with the increase of linear aggregates length and thickness. On the contrary, the mechanical response of randomly dispersed particle foams was almost independent on the volume content. The effect of the the application of a MF after foaming was investigated. A magneto-elastic behaviour was showed by all systems but the presence of aligned particles strongly increased the mechanical response. A magnetostrictive or magnetostrengthning effects were exhibited in dependence of the compressive strain applied to foams with aligned particles.

1. 1. Introduction

Cellular materials are widely used in applications like packaging, shock absorbing, cushioning, thermal and acoustic insulation. They are also used in the energy and transport industries as lightweight structural materials (most notably as the core material in structurally-efficient sandwich panels), where lightweight and high-stiffness to weight ratio are required. In some applications the mechanical performance and the integrity of the structural morphology can be critical. Each application typically require a specific mechanical response obtained with a specific polymeric formulation, density, or production technology. In addition, several parameters should be considered to design a customized foam for specific application, such as elastic modulus, yield point, and length of stress plateau.
The mechanical properties of cellular materials are highly dependent upon the cellular morphology in service conditions, as well as the bulk properties of the polymer the foam is made of, both of which may be influenced by the presence of reinforcing additives. The relative density (defined as the ratio between foam density and bulk polymer density) is a key parameter and both stiffness and yield depend on it according to a power law (the lower the density the lower the properties). Also cell shape affects the structural response. Both in synthetic and natural cellular materials the cell shape tend to be elongated in the direction of foaming (also referred to as the foam rise direction) when a mould is used. The elongated cell shape is usually a defect since it develops without or with a poor control in

the mould, where geometrical constraints hinder the cells to grow with a spherical shape. Hence, even if some degree of anisotropy can be induced by all conventional foaming processes, isotropic mechanical performances are a standard in foams.
Mechanical properties of foams are strongly related to the expansion ratio (defined as the ratio between foam density and bulk polymer density) and to the cell morphology. Conventional methods used to improve the mechanical response of foams fall within two main categories: a) the increase of the elastic properties of the matrix, by incorporating a reinforcing filler such as particles or fibers in the polymeric matrix and b) the insertion of structural reinforcements after the foaming process. Numerous studies have reported improvements in the mechanical properties of polymer foams reinforced with short fibres, particles, or nano-particles. This approach implies that isotropic materials with moderate increase of structural properties are obtained when low filler content is added. Conversely, a lot of difficulties are experienced during the foaming process when high filler content is used and low expansion ratios are obtained with a poor control of the cellular morphology, because of the filler interference during the cellular morphology development. In approaches based on the insertion of rigid reinforcements, metallic pins or stitch bonds are the most used methods, in particular in sandwich applications. These methods are mechanically effective but needs a complex and long post-processing step, in turn rising costs, and can damage the integrity of the foam layer during the pins' insertion.
When a mechanical response is required in a preferential direction, the isotropic dispersion of reinforcing particles is not the most efficient way to exploit the filler reinforcement. In this regard, materials with an aligned reinforcement have shown a strong increase of the mechanical response (in the alignment direction) with respect to systems with randomly dispersed one [1]. Borrowing such approach to increase the mechanical response and combining with the application of a MF, such as experienced in MR fluids [2] and MREs [3], Sorrentino et al. have produced reinforced foams based on a PU matrix by assembling and aligning magnetic particles during the foaming process under a low MF (about 0.1 T) [4]. These foams showed relevant increments of both Young's modulus and tensile strength (up to 1500% with respect to unaligned particle filled configurations). Furthermore, the same materials show a potential “active” behaviour due to mechanical relaxations induced by a MF [5],[6]. In this work, a time dependent MF was used to change the mechanical response of the foam during the foaming process through the proper alignment of embedded particles in order to change the entire compressive behaviour from small to large deformations (higher than 50%).

2. Experimental

2.1. Materials

A polyether polyol (Elastoflex W 5105/172, density equal to 1.03 cm^{-3}), provided with all chemical agents (water, catalysts and surfactants) for the foaming reactions, and a 4,4'-Methylene diphenyl diisocyanate (ISO 135/111, density equal to 1.20 g cm^{-3} and NCO content of 29.5%), both supplied by BASF Poliuretani Italia (Italy), were used as polyurethane foam. Carbonyl iron powder (CIP) (grade SQ-R, mean size 10 µm, particle surface treated to avoid particle corrosion and supplied by BASF SE, Germany) were used as reinforcing particles in this work.

2.2. Foams preparation

The criterion of constant matrix mass was used for the preparation of the foams: the reinforement content was calculated with respect to the mass of the polymer, which was the same for all systems. Iron based micro-particles, in composite foams, were dispersed into the polyalcohol in a flask and stirred for 5 minutes at 2000 RPM by means of a homogenizer to assure their even dispersion; then diisocyanate was added to the filled polyalcohol and intimately mixed for 10 seconds before being poured in a 120 mm x 120 mm x 20 mm (length x width x thickness) aluminium mould. The samples were left in the mould at room temperature for 20 minutes in order to complete the curing process.
The spatial distribution of particles was manipulated during the foaming process by means of an external magnetic field that aligned the particles along magnetic field lines. A custom made

electromagnet was used, powered by a laboratory power supply EA-PS 8065-10DT (EA-Elektro-Automatik GmbH & Co. KG, Germany) in order to generate a magnetic field during the foaming process. A first investigation was carried out to study the influence of the particle content on the mechanical response: five percentages by weight (from 5 wt% to 25 wt%) were prepared. For samples with aligned particles the value of the magnetic field ranged between 24 and 275 kA/m. A further study was conducted in order to investigate how the time profile of the magnetic field affected the spatial particle distribution fixing the particle content equal to 25 wt%. The amplitude, the switch-on and switch-off times of the magnetic field were changed.
Samples are coded specifying the type of process (RP for reinforced foams foamed without the application of the magnetic field, AP for reinforced foams foamed under MF), particle content by weight (if absent the amount is 25 wt%), the strength of magnetic field (in kA/m), the switch on and switch off times (in minutes). For instance, “AP15_189 OFF 10” refers to a sample reinforced with 15 wt% of particles, produced using a magnetic field with a strength equal to 189 kA/m applied just after the mixture was poured in the mould (time 0) and switching it off after 10 minutes.

2.3. Characterization of foams

The morphology of the samples was investigated by using an optical (PlanApo MZ16, from Leica MicroSystems, Germany) microscope. Samples density, calculated as the ratio of mass and geometric volume, was evaluated on parallelepipeds 50 mm x 20 mm x 20 mm in size (length x width x thickness), cut from the core of foamed slabs to reduce boundary effects related to the morphological inhomogeneity of the cellular structure near the mould walls.
The compressive response was evaluated on specimens 50 mm x 20 mm x 20 mm in size (length x width x thickness) by means of a universal testing machine (model 4304 from SANS – China, now MTS – USA) equipped with a 5kN load cell and operated at a cross-head speed of 10 mm min^{-1}. The testing direction was coincident with the foaming direction and, when applicable, with the alignment direction (in AP foams), because the mechanical performance are maximized in this direction. Three samples for each configuration were tested, and the average values and standard deviations were calculated.
An experimental setup was specifically designed and custom made to apply the magnetic field on specimens during the magneto-mechanical characterization. Firstly a pre-strain was applied (5.0, 10.0, 20.0 and 30.0% of sample height, starting from contact position stated as 0.0% strain). Then, a uniform MF was applied along the direction where the chain-like structures were aligned: it was demonstrated that the magneto-elastic response is more significant in this configuration. A time delay of 20 minutes was awaited to stabilize the mechanical response of the foamed sample before applying the time-variable MF (in step, sine, or triangle waveforms) and the changes in stress were recorded. The MF amplitude and frequency were set to 120 kA/m and 0.05 Hz, respectively. Sample dimensions were 50 mm x 20 mm x 20 mm (length x width x thickness).

3. Results and Discussion

3.1. Foam preparation and morphology

The analysis with the optical microscope operated at a magnification of 5x showed an open cell morphology in all samples. The addition of micro-particles in RP and AP samples did not result in alterations of the cellular morphology with respect to the unfilled foam. It is remarkable that the application of the MF successfully allowed to form chain-like structures along the direction of MF lines during the foaming process without affecting the development of the foam morphology in terms of porosity, cell shape and mean cell size (Figure 1).

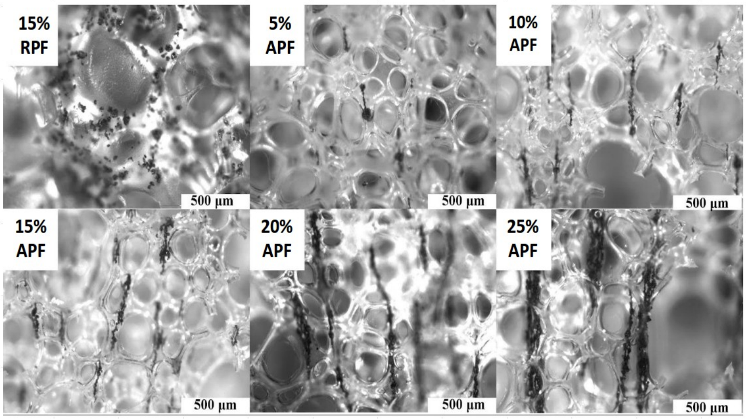

Figure 1 Optical micrographs of: (A) RP15, (B) AP05, (C) AP10, (D) AP15, (E) AP20 e (F) AP25.

Foams produced without the application of the MF exhibited a random distribution of the filler in the polymeric matrix while aligned particles were clearly visible when MF was applied during the foaming process. It is worth noting that the length of the chain-like structures was in direct proportion with the particle content and MF strength during foaming. Foams produced without the application of the MF exhibited a random distribution of the filler in the polymeric matrix while aligned particles were clearly visible when MF was applied during the foaming process. The unreinforced sample (UF) sample exhibited a density of 0.095 kg/dm^3, the lowest value among all samples. The density was higher in reinforced foams, with a maximum of 0.127 kg/dm^3 for AP20, but porosity, evaluated as the complement to 1 of the actual volume filled by solid phase, was around 91% for all samples (Table 1.).

Table 1. Composition, measured density, evaluated porosity and chain-like structures length, elastic modulus in compression, yield stress and yield strain values of all systems.

Sample	Particles content (%) by weight	Particles content (%) by volume	Density (kg dm^{-3})	Porosity (%)	Chains Length (μm)	E (kPa)	σ_y (kPa)	ε_y (mm mm^{-1})
UF	0	0	0.095 ± 0.007	91.3 ± 0.7	------	114 ± 4.7	9.2 ± 0.04	9.3 ± 0.24
RP05	5	0.69	0.103 ± 0.003	91.0 ± 0.2	------	117 ± 4.3	9.7 ± 0.05	9.6 ± 0.26
RP10	10	1.83	0.101 ± 0.012	91.5 ± 1.0	------	119 ± 4.5	9.4 ± 0.09	10.1 ± 0.33
RP15	15	2.05	0.118 ± 0.009	90.5 ± 0.7	------	203 ± 9.3	14.3 ± 0.07	8.4 ± 0.25
RP20	20	2.72	0.126 ± 0.009	90.2 ± 0.7	------	179 ± 8.7	13.0 ± 0.09	10.6 ± 0.35
RP25	25	3.37	0.124 ± 0.012	90.7 ± 0.9	------	207 ± 19.3	14.3 ± 0.14	8.5 ± 0.42
AP05	5	0.69	0.102 ± 0.008	91.1 ± 0.7	231 ± 81.3	386 ± 39.9	26.8 ± 0.31	7.1 ± 0.53
AP10	10	1.38	0.100 ± 0.011	91.6 ± 0.9	227 ± 78.9	392 ± 27.2	26.8 ± 0.10	7.5 ± 0.27
AP15	15	2.05	0.111 ± 0.008	91.1 ± 0.6	372 ± 159.7	941 ± 50.0	39.4 ± 0.03	4.7 ± 0.19
AP20	20	2.72	0.127 ± 0.014	90.1 ± 1.1	455 ± 217.9	1549 ± 194.3	63.8 ± 0.07	4.3 ± 0.29
AP25	25	3.37	0.123 ± 0.008	90.7 ± 0.6	885 ± 611.7	1048 ± 282.5	43.2 ± 0.11	4.5 ± 0.47

3.2. Mechanical Characterization

The mechanical characterization showed that AP samples have a high structural anisotropy, mostly because of the widespread presence of aligned aggregates along the vertical struts. The compressive response along the foaming direction is summarized in Table 1. Reinforced foams showed an improved compressive response compared to UF sample. On the other hand, the presence of chain-like structures imparted a significant increase of the elastic modulus in the MF direction on equal weight content. The mechanical performance increased with particle volume content in accordance with the the mechanics of composite materials that predicts an increase of the composite stiffness with the particle content. In addition, in AP samples the formation of long particles aggregates acts as short fibers and is much more effective in reinforcing the composite [4]. These results demonstrate that it is possible to strongly increase the mechanical response of foams by properly aggregating low amounts of spherical particles without affecting the cellular morphology of the hosting foam.

By changing the MF signal during foaming, the mechanical behaviour in compression was strongly affeced. In particular, the stronger the MF the higher the mechanical response (Figure 2). Furthermore, changing the swith-on and switch-off times allowed to tailor the height of the foam plateau and the compressive modulus (Figure 3).

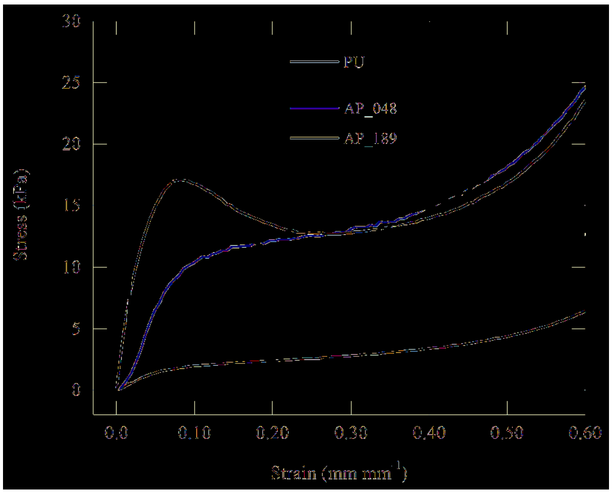

Figure 2 Effect of the MF strength during foaming on the compressive response of foams.

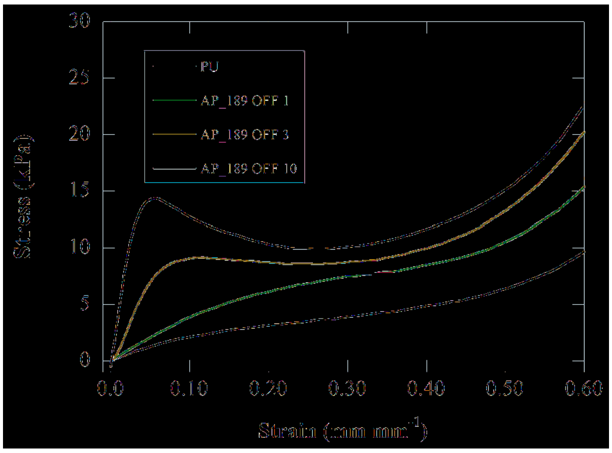

Figure 3 Effect of the MF swtich-off time during foaming on the compressive response of foams.

3.3. Magneto-elastic behavior

The magneto-elastic characterization of foams was aimed at evidencing a smart behavior. A uniform MF was applied to the pre-strained foams and changes in force were measured. Both strain and MF were applied along the foaming direction, that was also coincident with the alignment direction in AP samples. The magneto-elastic behavior resulted to be dependent on the pre-strain level, on the MF strength, on the amount and on the spatial distribution of particles. In particular, below the yield strain a magnetostrictive behaviour was detected and the application of MF reduced the stress (Figure 4) in both RP and AP systems (AP to higher extent). At pre-strain higher than the yield strain the stress variation was positive in AP samples (Figure 5), resulting in a reinforcing effect instead of a magnetostrictive one. A representative case is reported in Figure 5. Before MF application, the stress was steady and was due to the applied pre-strain. After the application of the MF, the stress started to follow the MF field. The stress variation was always negative for the RP20 foam, and a lower peak was reached in occurrence of each minimum and maximum of the MF signal. Conversely, a positive stress variation was detected after the MF application in AP20 sample and a minimum occurred at each minimum or maximum of the MF signal. This means that a reinforcing effect was present, instead of a magnetostrictive one. This is an indirect evidence of the variation of the material stiffness (Young's modulus reduction), corresponding to a micro-deformation applied to the cellular structure. Moreover, this is the correspondent of the so called ΔE-effect of magnetostrictive materials [6].

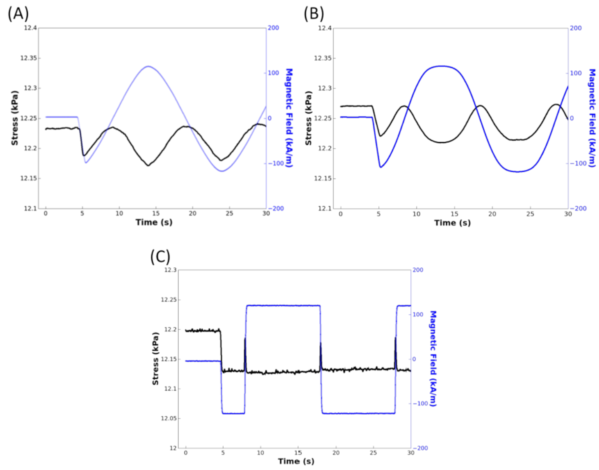

Figure 4 Typical effect of different magnetic field waveform (blue curves) on the stress variation (black curves) at 5.0% pre-strain for samples AP05 sample: (A) triangle waveform; (B) sine waveform; (C) square waveform.

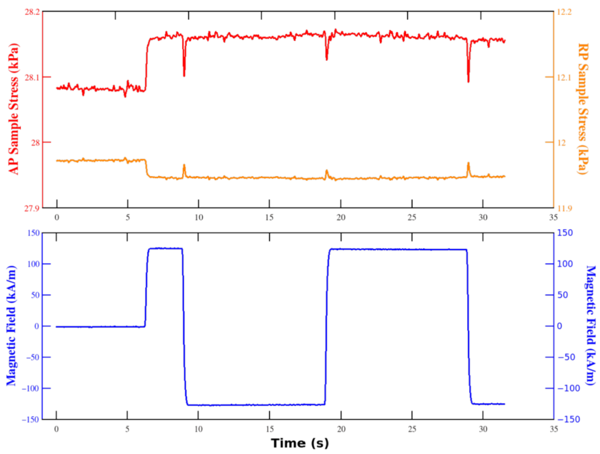

Figure 5 Effect of magnetic field on the stress variation at 10.0% pre-strain for RP20 (orange, top plot, lower curve) and AP20 samples (red, top plot, upper curve), under a square waveform MF (blue, step curve).

4. Conclusions

The aim of this work was to show how the performance of lightweight magneto-elastic materials with a low density can be improved in compression with respect to conventional foams by assembling spherical microparticles through the use of a magnetic field. Iron micro-particles were dispersed in polyurethane foams and their spatial distribution was managed by using a magnetic field during the production of foams. Magnetic particles rearranged in chain-like structures aligned along the magnetic field lines and such structures were consolidated after the polymer cure, as evidenced by microscope analysis. The assembling of particles was tailored to change the constitutive stress-strain relationship by managing the magnetic field time profile.

Prepared foams showed a magneto-elastic behaviour. A clear dependence of the mechanical response was detected, even with a magnetic field of moderate intensity. Samples with random particle distribution showed a negative variation of the compressive stress (magnetostriction), indicating that samples have undergone a micro-contraction in the direction of the magnetic field. For systems with chain-like structures, such response was more pronounced. In foams with aligned particles the application of the magnetic field at pre-strains higher then the yield strain induced a strengthening effect (positive variation of the measured stress) in proportion to the MF strength, as a result of the tendency of chain-like aggregates to align along the magnetic field lines and to reduce the buckling.

5. Acknowledgments

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