

# CYCLIC OLEFIN COPOLYMER/EXFOLIATED GRAPHITE NANOPLATELETS NANOCOMPOSITES FOAMED THROUGH SUPERCRITICAL CARBON DIOXIDE

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## Abstract

In this work novel cyclic olefin copolymer (COC) nanocomposites filled with exfoliated graphite nanoplatelets (xGnP) and foamed through supercritical carbon dioxide were prepared and characterized. The density of the prepared foams was noticeably lower than that of the bulk materials, especially at high foaming pressures (i.e. 150 bar). An increment in the foaming pressure led to an enhancement of the cell diameter, while nanofiller addition reduced the cell diameter and increase the cell density. Tensile tests performed both on bulk and foamed materials highlighted an increment in the elastic modulus and in the creep resistance with the xGnP loading content, while the stress and the elongation at break were decreased.

Electrical resistivity measurements showed how the percolation threshold for the electrical conductivity was found to be around 10% and 15% of xGnP loading amount, both for bulk and foamed samples. Increasing the foaming pressure, the electrical resistivity increased as well. Considerable surface heating upon voltage application was detected for highly loaded bulk nanocomposites, while a limited heating with a voltage of 220 V was detected for foamed materials.

## 1. Introduction

Polymeric foams are lightweight materials extensively applied in automotive, aerospace, construction and in packaging sectors. The significant reduction in the weight of structural parts can lead to substantial fuel savings in transports with obvious economic and environmental advantages [1]. Porous plastics are commonly produced with processing routes like physical blowing by low boiling hydrocarbons or their halogenated derivatives, and their usage represents a critical environmental problem because of the noticeable emission of toxic compounds and of polluted waste water production [2]. Therefore, various research groups have considered the usage of supercritical fluids (SFCs) as a path to produce polymer foams [3]. The physical properties of SCFs are generally described as intermediate among gases and fluids. In fact, they manifest a density close to that of the liquids, a viscosity similar to that of the gases and a greater diffusion coefficient compared to liquids [4]. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, thus allowing a fine tuning of their properties. Among supercritical fluids, carbon dioxide is the most utilized, because of its easy processability, cheapness, non-toxicity and non-flammability [5].

Particular interest has been devoted in the last years to cycloolefin copolymers (COCs) [6], which are amorphous thermoplastics obtained by the copolymerization of norbornene and ethylene. COCs are suitable for the production of transparent moldings (optical data storage, lenses, and sensors),

packaging of drugs, medical and diagnostic devices, food containers, etc. On the other hand, it is well known that the incorporation of nanofillers at low concentrations (5–10 wt%) into a polymer matrix can significantly improve its mechanical properties, dimensional stability, thermal degradation and chemical resistance and also gas and solvents impermeability [7]. In the last years, particular attention has been devoted in the open literature to nanocomposite systems filled with carbonaceous plate like nanofillers, such as exfoliated graphite nanoplatelets (xGnP). Due to the honeycomb arrangement of the carbon atoms in the crystal lattice, xGnP shows exceptional properties in terms of stiffness and strength and therefore it can be used to improve the mechanical properties of a wide range of polymeric materials [8]. Moreover, xGnP has been successfully used to improve barrier properties as well as electrical properties of polymeric materials at low percolation threshold. In the open scientific literature it is possible to find some works on the preparation and physical properties of polymer nanocomposites foamed through supercritical carbon dioxide (scCO<sub>2</sub>) [9] but, quite surprisingly, only marginal attention has been devoted to xGnP based nanocomposites foamed through supercritical carbon dioxide [10]. To the best of our knowledge, no papers dealing with the physical properties of COC/exfoliated graphite nanoplatelets foamed through scCO<sub>2</sub> have been published.

On the basis of these considerations, the objective of the present work is to prepare and characterize COC/xGnP nanocomposites at various filler concentrations and to foam them through scCO<sub>2</sub>. A general comparison between bulk and foamed samples will be then carried out, in order to evaluate the real effectiveness of xGnP nanoparticles in improving the mechanical and electrical properties of the foams.

## 2. Experimental Part

### 2.1. Materials

Polymer chips of a cycloolefin copolymer (COC) Topas 8007 (melt flow index at 2.16 kg, 190 °C = 2.17 g/10min, density = 1020 g/dm<sup>3</sup>) were supplied by Ticona (Florence, Kentucky, USA). Exfoliated graphite nanoplatelets xGnP-M-5, with a specific surface area of 120 m<sup>2</sup>/g, a mean diameter of 5 μm and a thickness of 6–8 nm, were provided by XG Sciences Inc. (East Lansing, Michigan, USA). Both materials were used as received.

### 2.2 Samples preparation

For as concerns bulk materials preparation, the filler was melt compounded with COC in a Thermo Haake internal mixer at 190 °C at a rotor speed of 90 rpm. The nanoparticles were added in the hot chamber of the mixer immediately after the complete melting of the COC, in order to prevent nanoparticles agglomeration. The mixing process was set at 15 minutes, enough to promote a complete and homogeneous mixing. The materials were then hot pressed at 0.2 kPa for 10 minutes at a temperature of 190 °C in a Carver press in order to produce 0.8 mm thick square sheets. Each sample was denoted indicating the matrix, the nanofiller type and its weight concentration. For instance, COC-xGnP-1 denotes the nanocomposite bulk sample with a xGnP content of 1 wt%.

Polymer foams were prepared through a supercritical carbon dioxide treatment by using specific equipment available at the BIOtech Center of the University of Trento. The equipment was composed by a CO<sub>2</sub> tank, a cryostat, a pump and a reaction chamber. Foamed samples were prepared starting from bulk rectangular specimens 0.5 cm width and 2 cm long. Pure COC copolymer and COC/xGnP bulk nanocomposites with different filler percentage were placed within high-pressure reaction vessel (BR-300, Berghof Products + Instruments, Eningen, Germany), consisting of a stainless steel vessel with an internal polytetrafluoroethylene (PTFE) liner. The PTFE cylinder with a capacity of 700 ml had a diameter of 60 mm and an height of 250 mm. A cryostatic bath set at -9 °C (Model M408-BC, MPM Instruments s.r.l., Bernareggio, MB, Italy) was used for the cooling of the CO<sub>2</sub> lines and pump

head. Once the system had been sealed, liquid CO<sub>2</sub> was pumped into the reactor and pressurized till the supercritical conditions at desired working pressure was reached through a high-performance liquid chromatography (HPLC) pump. In this study, neat COC copolymer and composite samples were exposed to scCO<sub>2</sub> at five different pressures (90, 110, 130 and 150 bar) for 30 min. Temperature was set constant at 95 °C (i.e. 15 °C higher than COC glass transition temperature). Foaming was obtained upon fast depressurization from supercritical to ambient conditions. Foamed samples were designated indicating the matrix, the filler type, the filler content and the foaming pressure. As an example, COC-xGnP-5\_e90 indicates nanocomposite foams with a filler amount of 5 wt%, expanded with depressurization from 90 bar.

## 2.3 Experimental techniques

Density measurements were carried out by a displacement method in acetone (density at 20 °C of 0.792 g/cm<sup>3</sup>) by using a Gibertini E42 hydrostatic balance. The distribution of the cell size was measured through a Heerbrugg Wild M3Z optical microscope, and a statistical analysis was then performed to determine the mean cell diameter and the relative standard deviation values. The microstructural features of the cell walls were observed through a Carl Zeiss AG Supra 40 FESEM microscope, operating at an acceleration voltage of 5 kV. Before the observations, samples were cryofractured in liquid nitrogen. A TEM microscope Tecnai G2 Spirit Twin FEI operating at an accelerating voltage of 120 kV was used to investigate the silica dispersion within the polymeric matrix of both bulk and foamed materials in bright field (BF) imaging mode.

Quasi-static tensile tests to evaluate the mechanical properties of the bulk samples were performed through an Instron 4502 tensile testing machine. Elastic modulus was evaluated at 1 mm/min, by using a resistance extensometer having a gage length of 12.5 mm, while tensile tests at break were carried out without the extensometer at a crosshead speed of 5 mm/min. Mechanical properties of the foamed samples were evaluated at 1 mm/min in compression mode on square specimens with a lateral dimension of about 10 mm and a height of about 3 mm. All the tests were performed at ambient temperature and at least five specimens were tested for each composition. Creep tests were carried out through a DMA Q800 machine (TA Instruments, USA) at a testing temperature of 30 °C for 60 minutes under a constant stress of 10% of the ultimate tensile strength of the neat matrix. Rectangular specimens 5 mm wide and 1 mm thick with a gage length of 10 mm were used to test both bulk samples and the polymer foams.

The evaluation of the electrical resistivity of the produced materials was performed by using a Keithley model 6517A multimeter, supplied by Keithley Instrument, Inc. (Cleveland, USA), in a four point collinear probe configuration. Both bulk and foamed materials at 150 bar were tested. The applied voltage was taken constant for all the specimens at a value of 10 V. In order to evaluate the surface heating through by the Joules effect upon voltage application, an IR thermographic camera Ti9 Thermal Imagers FLUKE<sup>®</sup> was used. The evolution of the surface temperature was recorded as a function of time.

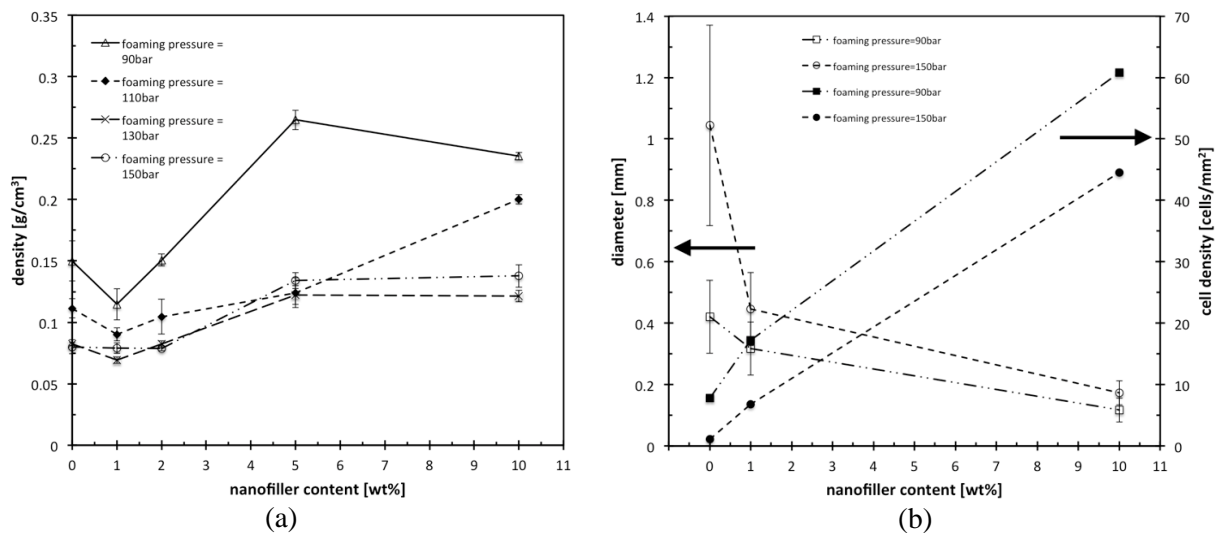
## 3. Results and Discussion

### 3.1. Morphological features

In Fig. 1a the foams density as a function of the nanofiller content is represented. A systematic density increase with the nanofiller amount can be observed over the whole range of applied pressures. Considering the density variation due to nanofiller addition in bulk samples (from 1.01 g/cm<sup>3</sup> of neat COC to 1.05 g/cm<sup>3</sup> of the COC-xGnP-10 nanocomposite), it is clear that the density increase in the nanocomposite foams cannot be simply explained by the higher density of xGnP with respect to COC, but also by a morphological change within the foam microstructure (i.e. cell density and cell size). In

fact, as the foaming pressure increases, a density reduction can be observed for all the compositions. This could be due to the fact that at elevated pressures, the diffusion of the scCO<sub>2</sub> within the matrix is favoured and the foaming process is more efficient.

To fully understand the density increment of the foams and the real contribution played by xGnP addition on the morphology of the prepared cellular solids, FESEM analysis was carried out. All foams present closed cell morphology with a narrow statistical distribution of the cell size around an average value (not reported here for the sake of brevity). A quantitative evaluation of the cell size distribution was performed by using ImageJ software. Average cell diameter and cell density (cells/mm<sup>2</sup>) as a function of the nanofiller content for foams expanded at 90 and 150 bar are reported in Fig. 1b. The nanofiller introduction hinders the cell growth during the expansion process, thus reducing the cell diameter both at 90 and 150 bar. At the same time, it promotes cell nucleation, increasing the cell density. It is therefore reasonable to assume that xGnP can enhance the matrix viscosity above the glass transition temperature, thus hindering the expansion process. Moreover, when scCO<sub>2</sub> pressure increases, the cell size increases while the cell density decreases. Therefore, it can be hypothesized that at higher pressure cell growth is favoured over cell nucleation.

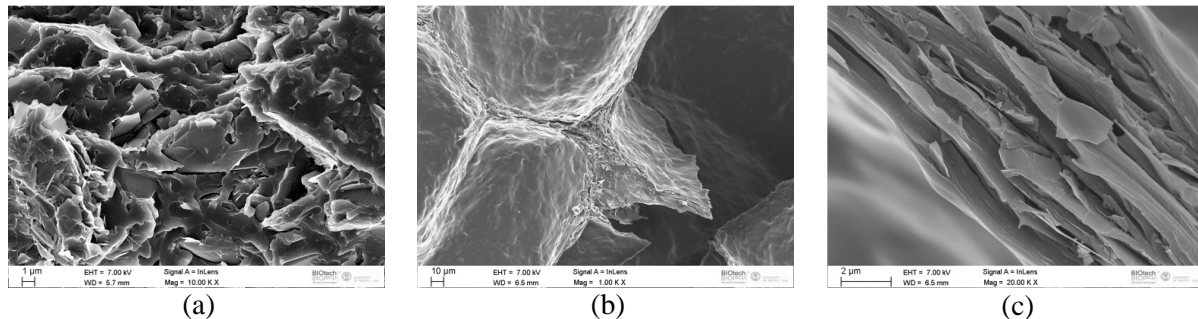


**Figure 1.** Morphological features of the prepared foams. (a) Foams density as a function of the nanofiller content for different foaming pressures. (b) Cell diameter (open symbols) and cell density (full symbols) as a function of the nanofiller content for nanocomposite foams expanded at 90 bar and at 150 bar.

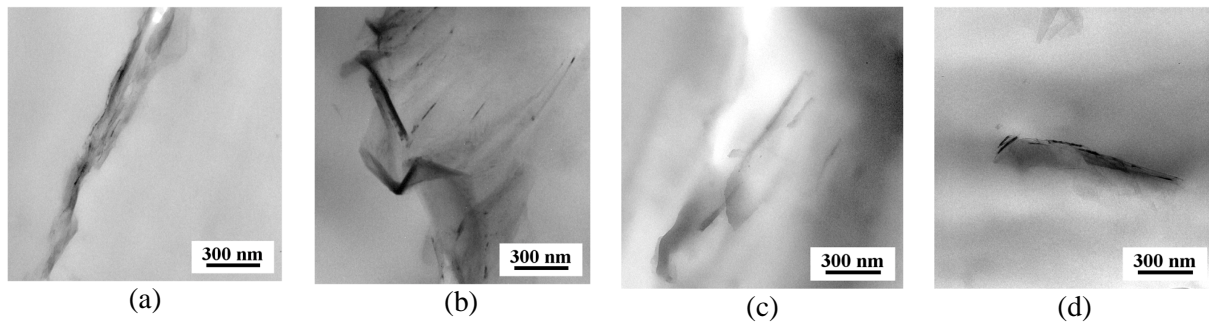
A more detailed analysis at higher magnification levels was performed with FESEM equipment (see Fig. 2(a-c)). It is possible to observe that xGnP nanoplatelets are randomly oriented within the matrix, with the presence of agglomerates of stacked lamellae. Moreover, the fracture surface is irregular and jagged (Fig. 2a). In the foamed materials, an alignment of xGnP nanoplatelets along the cell walls can be noticed, and this effect is more pronounced at higher foaming pressures, where thinner cell walls can be detected (Fig. 2(b-c)). It is possible that under the selected foaming conditions the xGnP exfoliation process and alignment along the cell wall was promoted.

In order to perform a deeper investigation of the dispersion level of xGnP in both bulk and foamed samples, TEM analysis was carried out. In Fig. 3(a-d), TEM micrographs of bulk and foamed samples are reported. In Fig. 3a it is clear that bulk samples at low filler amounts are characterized by stacks of xGnP lamellae with a lateral dimension of less than 50 nm and a length of about 1 μm. As already seen in other nanocomposite systems, an increase of the filler loading promotes a strong aggregation of the

nanoplatelets [11]. It is interesting to observe that the foaming process leads to an improved exfoliation of xGnP nanoplatelets, thus reducing the agglomeration of the xGnP stacks. The same effect can be detected at higher filler loadings.



**Figure 2.** FESEM micrographs of the cryofractured surfaces of the samples: (a) COC-xGnP-10, (b) and (c) COC-xGnP-10\_e150 at different magnifications.



**Figure 3.** TEM micrographs of the bulk and foamed samples. (a) COC-xGnP-1, (b) COC-xGnP-10, (c) COC-xGnP-1\_e150 and (d) COC-xGnP-10\_e150.

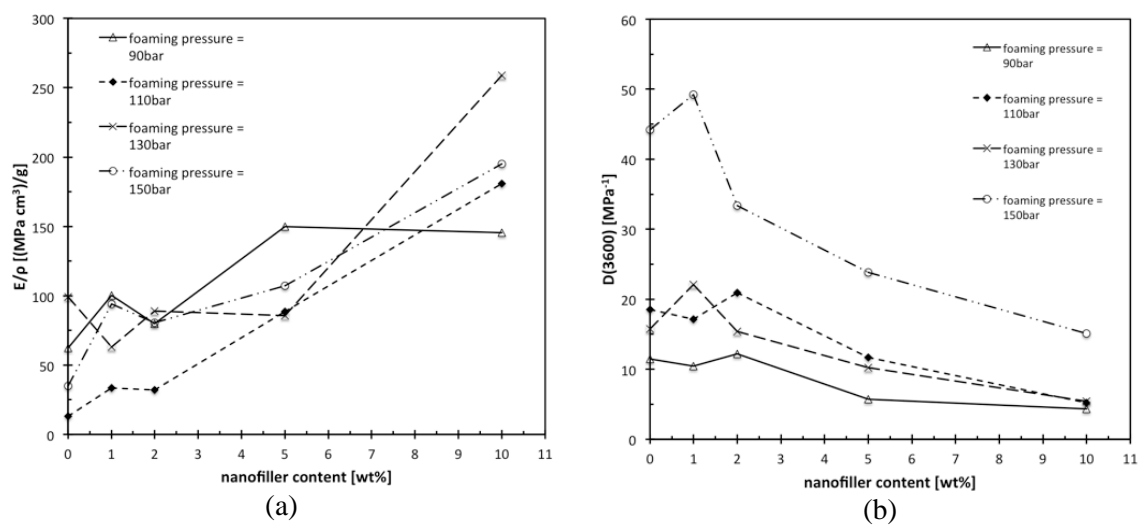
### 3.2. Mechanical behaviour

The effect of the nanofiller loading on the quasi-static tensile properties of the bulk samples was investigated. As frequently observed in nanofilled samples, the xGnP introduction leads to a noticeable increase of the elastic modulus (from 2.17 GPa of neat COC up to 3.36 GPa of COC-xGnP-10 sample). As a drawback, the presence of the nanofiller causes an embrittlement of the bulk samples, revealed by the decrease of both the stress at break ( $\sigma_b$ ) (from 59.4 MPa of neat COC up to 37.7 MPa of COC-xGnP-10 sample) and of the strain at break ( $\epsilon_b$ ) (from 5.75 % of neat COC up to 3.22 % of COC-xGnP-10 sample) as the xGnP content increases. Most likely the nanofiller aggregation observed at higher filler loadings plays a negative effect on the ultimate properties of the resulting materials.

The effect of xGnP introduction on the mechanical behaviour of the prepared foams under compression has been also investigated. A quantitative evaluation of the elastic properties of the foams as a function of the nanofiller loading is reported in Fig. 4a, where the trends of the specific modulus (i.e. the ratio between the elastic modulus and density) are represented. It is interesting to observe how the nanofiller introduction leads to a remarkable increase of the elastic modulus of the foams, over the whole range of applied foaming pressures. It is worthwhile to observe that the increase of the elastic modulus displayed by the nanofilled foams is noticeably higher than that of the corresponding bulk materials. It is therefore clear that the enhancement of the foams stiffness is partially due to a change in the foams density, but the greater contribution is due to the xGnP addition. As already observed in

the previous paragraph, the occurrence of xGnP exfoliation and orientation given by the foaming pressure can increase the mechanical properties of the matrix itself.

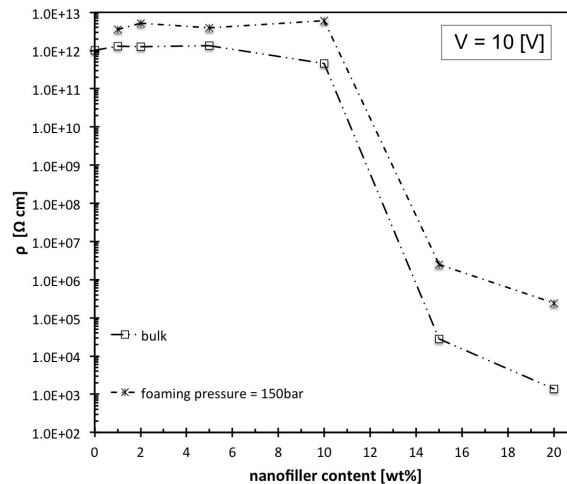
In order to confirm the positive effect played by xGnP nanoplatelets on the mechanical behaviour of bulk and foamed nanocomposites, creep tests were performed. It was found that the stabilizing effect due to nanofiller introduction in the bulk materials leads to an interesting decrease of the creep compliance with respect to the neat COC. For instance, with a nanofiller amount of 10 wt%, the creep compliance at 3600 s is reduced of about 45% with respect of the neat COC. This effect is even more pronounced for foamed materials. Fig. 4b shows the creep compliance values at 3600 s of nanocomposite samples foamed at different pressures. In accordance with elastic modulus results, it can be concluded that the creep stability increases due to nanofiller introduction along the whole range of applied pressures. Even in this case, the observed stabilizing effect is partly due to a change in the foam density, and a key role is played by xGnP exfoliation and orientation effects.



**Figure 4.** (a) Normalized elastic modulus over density ( $E/\rho$ ) of the foamed samples. (b) Creep compliance at 3600 s as a function of the nanofiller content for nanocomposite foams at different foaming pressures.

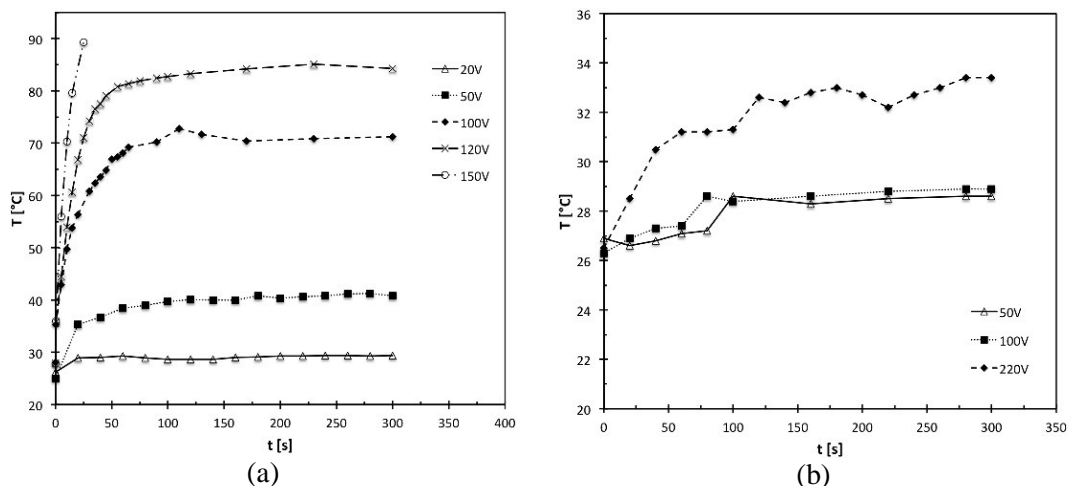
### 3.3. Electrical properties

Considering the possible application of these nanocomposites as electroactive packaging materials it is now important to evaluate their electrical behaviour. In Fig. 5 the electrical resistivity values against the nanofiller content for bulk materials and nanocomposite foams are reported. A strong decrease of the electrical resistivity can be detected for nanofiller amounts higher than 10 wt%, both for the bulk and for the foamed materials. In particular, with a nanofiller loading of 20 wt%, an electrical resistivity of  $1.37 \times 10^3$  and  $2.44 \times 10^5 \Omega \cdot \text{cm}$  can be obtained for bulk and foamed materials at 150 bar respectively. It should be noted that the electrical resistivity of the foamed materials at 150 bar is systematically higher than the corresponding bulk samples. This fact can be due to the porous structure of the foam. In these conditions the effective cross area of the tested samples is strongly reduced. It has also to be taken into account the effect of the foaming process on the microstructural features of the materials. In fact, the formation of a percolative network due to the contact between the nanoplatelets is hindered by the matrix foaming, especially at elevated pressures, when the nanofiller alignment is more pronounced.



**Figure 5.** Electrical resistivity on neat COC and relative nanocomposites for bulk and foamed materials at a pressure of 150 bar (applied voltage equal to 10 V ).

It is now important to evaluate the surface heating capability of the prepared materials upon voltage application (i.e. through Joule effect). In Fig. 6(a-b) the evolution of the surface temperature of COC-xGnP-20 and COC-xGnP-20 e150 samples at different applied voltages are respectively reported. From Fig. 6a it is evident that an appreciable heating can be obtained for relative low voltages. In fact, with an applied voltage of 50 V the surface temperature is 40 °C after 70 seconds, while at 120 V a temperature greater than 80 °C can be reached in the same time. For a voltages lower that 150 V, a stabilization of the surface temperature can be detected, even after 300 s. This means that the sample reaches a thermal equilibrium, because the heat flow produced through the Joule effect is equal to the dissipated power. Even in the case of foamed materials (Fig. 6b), an homogeneous distribution of the surface temperature within the sample can be observed, but a very limited temperature increase can be obtained with an applied voltage of 220 V (7 °C increase after 200 seconds). This result can be explained considering the higher electrical resistivity value reported obtained for the foamed materials.



**Figure 6.** Evaluation of the surface temperature with time of (a) COC-xGnP-20 and (b) COC-xGnP-20 e150 samples at different applied voltages.

#### 4. Conclusions

Cycloolefin copolymer/exfoliated graphite nanoplatelets (xGnP) composites were prepared at different filler amounts through a melt compounding process. The resulting materials were foamed through a supercritical carbon dioxide based process by varying the foaming pressure. It was observed how the xGnP introduction systematically increased both bulk and foam density, while elevated foaming pressures promoted a consistent density reduction. Microstructural analysis on the resulting foams highlighted a progressive increase of the mean cell size with the foaming pressure, accompanied by an evident exfoliation and orientation of the nanoplatelets along the cell walls direction. These microstructural effects were responsible for an important improvement of the mechanical properties of the foams, with a progressive enhancement of the elastic properties with xGnP amount, and also the creep stability was noticeably improved.

Nanofiller introduction leads to an important volume resistivity decrease of bulk materials up to  $10^3$   $\Omega$ .cm for xGnP loading higher than 10 wt%. The foamed materials showed a systematic increase of the volume resistivity with respect to the corresponding bulk samples. Evaluation of the surface temperature upon voltage application demonstrated how it is possible to obtain a rapid heating of the bulk samples at relatively low voltage levels, while the lower conductivity of the foams leads to a limited surface temperature increase.

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