

CYCLOOLEFIN COPOLYMER NANOCOMPOSITES EXPANDED THROUGH SUPERCRITICAL CARBON DIOXIDE

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Abstract

A cycloolefin copolymer (COC) matrix was melt compounded with different amounts of fumed silica nanoparticles, and the resulting materials were foamed through a supercritical carbon dioxide treatment. The density values of the foamed materials decreases as the foaming pressure increases. FESEM micrographs on the foams highlighted an evident deformation of the filler aggregates along the cell wall direction. Quasi-static tensile tests and creep tests on bulk and foamed materials evidenced a positive effect played by nanosilica in improving the stiffness, the strength and the creep stability of the polymer matrix. Interestingly, nanosilica introduction determined a systematic enhancement of the properties of the foams over the whole range of applied foaming pressure, proportionally to the nanofiller amount.

1. Introduction

Polymeric foams are utilized in a wide variety of applications, but their synthesis and manufacturing requires enormous quantities of organic and halogenated solvents. It was estimated that about fifteen billion of kilograms of these solvents are worldwide produced every year, and their application represents a critical ecological problem, because of the noticeable emission of toxic compounds and of polluted waste water production [1]. Therefore, in the last years the utilization of non toxic solvents and of eco-friendly manufacturing processes has become a key issue. Recently, many research groups have proposed different solutions for these problems, and among them the application of supercritical fluids seems to be the most promising and convincing way. In fact, polymer matrix foaming with supercritical fluids allows to avoid organic solvents and presents several advantages from a chemical, physical and toxicological point of view. The use of supercritical fluids is not limited to the experimental field, but it can be successfully applied also on industrial scale. Among supercritical fluids, carbon dioxide is the most utilized, because of its easy processability, its cheapness, its non toxicity and non flammability [2].

In the last years, thermoplastic polymers synthesized through metallocene-based catalysts have attracted the attention of many researchers and producers [3]. Particular interest has been devoted to cycloolefin copolymers (COCs) [4], which are amorphous thermoplastics obtained by copolymerization of norbornene and ethylene. COCs are characterized by remarkable properties in terms of stiffness, high chemical resistance, good moisture barrier properties,

low moisture absorption, and low density. Therefore, COCs are suitable for the production of transparent moldings (optical data storage, lenses, and sensors), packaging of drugs, medical and diagnostic devices, food containers, and so on. Considering that the glass-transition temperature (T_g) of COCs can be tailored by varying the percentage of norbornene [5], various COC grades suitable for specific applications are available on the market. Also polyolefin/COC blends, especially polypropylene/COC blends and polyethylene/COC blends, are very interesting materials from a scientific and industrial point of view [6, 7].

Polymer matrix nanocomposites have been studied in recent years as innovative materials. In fact, the incorporation of nanofillers at low concentrations (5–10 wt %) into a polymer matrix can significantly improve its mechanical properties, its dimensional stability, its thermal degradation and chemical resistance and also gas and solvents impermeability [8]. The typical drawbacks (i.e. embrittlement, loss of transparency, loss of lightness) associated with the use of traditional inorganic microfillers can be generally avoided [9]. Quite surprisingly, less attention has been devoted in the open literature to nanocomposite systems filled with isodimensional nanofillers, such as fumed silica nanoparticles. Fumed silica nanoparticles are industrially produced in a wide range of specific surface area (ranging from 50 to 400 m²/g) and with a variety of surface treatments from hydrophilic to hydrophobic. Due to the elevated specific surface area, this nanofiller self-aggregates when dispersed in polymer matrices, forming an interconnected network of interacting particles. It has been recently demonstrated by our group that the mechanical properties of thermoplastic matrices can be remarkably improved by the introduction of this kind of nanoparticles [10].

On the basis of these considerations, the objective of the present work is to prepare and characterize COC/silica nanocomposites at various filler concentrations, to be then foamed through a supercritical carbon dioxide process. A general comparison between bulk and foamed samples will be then carried out, in order to evaluate the real effectiveness of fumed silica nanoparticles in improving the thermo-mechanical properties of the foams. Moreover, a detailed analysis of the influence of the foaming processing parameters on the physical properties of the resulting foams was performed.

2. Materials and methods

Polymeric chips of a cycloolefin copolymer (COC) Topas[®] 8007 (MFI at 2.16kg, 190 °C = 2.17 g/10 min, density = 1020 g/dm³) were supplied by Ticona (Florence, Kentucky). Untreated fumed silica nanoparticles Aerosil[®] A200 (A200), having a specific surface area of 200 m²/g and a mean primary particle size of 12 nm, were provided by Evonik (Frankfurt, Germany). Bulk samples were prepared through a melt compounding process by using a Thermo Haake Rheomix 600p at a temperature of 190 °C, a rotor speed of 90 rpm and a mixing time of 15 minutes. The resulting materials were then hot pressed in a Carver laboratory press at the same temperature, in order to obtain square sheets of composite samples having a thickness of 0.8 mm and a width of 10 cm. In this way, neat COC matrix and nanocomposite samples with volume fractions of 1,3 and 5 vol% were prepared.

Polymer foams were prepared through a supercritical carbon dioxide treatment by using a specific equipment available at the Center for Biomedical Technologies of the University of Trento. Bulk samples were cutted from the sheets and inserted in the reaction chamber whose temperature is gradually increased up to 90 °C. Supercritical CO₂ was purged in the reactor for 30 minutes at different pressures (90, 110, 130, and 150 bar), in order to obtain an uniform diffusion of the supercritical fluid within the polymer matrix. A subsequent de-pressurization

stage was then performed, in order to obtain the foaming of the samples. Finally the temperature was decreased to room temperature. In this way, both neat COC and nanocomposite foams at different nanofiller content were prepared. Bulk samples were denoted indicating the matrix, the nanofiller type and its volume concentration. For instance, COC-A200-1_1 denotes the nanocomposite bulk sample with a silica content of 1 vol%. Foamed samples were designated indicating the matrix, the filler type, the filler content and the foaming pressure. As an example, COC-A200-5_e90 indicates the nanocomposite foam with a filler amount of 5 vol%, expanded at 90 bar.

Density measurements were carried out by using a Gibertini E42 hydrostatic balance through the Archimede principle. The distribution of the cell size was measured through an 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 1.5 kV and at different magnifications. Before the observations, samples were cryofractured in liquid nitrogen.

Thermogravimetric analysis were performed both on bulk and on the foamed samples through a Mettler TG50 machine under an air flow of 150 ml/min. Samples were tested from 50 °C to 700 °C at a heating rate of 10 °C/min. In this way, the temperatures associated to a mass loss of 2 wt% and of 5 wt% and the decomposition temperature (T_d), i.e. the temperature corresponding to the maximum mass loss rate, were determined. Dynamical mechanical analysis (DMTA) were performed both on the bulk samples and on the foams by using a Q800 DMA machine (TA Instruments, USA). Rectangular samples 5 mm wide and 1 mm thick were tested at a frequency of 1 Hz (gage length of 10 mm) in a temperature interval between 20 °C and 120 °C at a heating rate of 3 °C/min. In this way, it was possible to determine the temperature dependence of the dynamic moduli (E' and E'') and of the loss tangent.

Quasi-static tensile test were performed through an Instron 4502 tensile testing machine, equipped with a load cell of 1 kN. Bulk samples were tested by using ISO 527 1BA samples, with a gage length of 30 mm. Elastic modulus was evaluated at 1 mm/min, by using an electrical 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. Tensile properties at break of foamed samples were determined at 5 mm/min by using rectangular samples with a gage length of 1.5 mm. All the tests were performed at ambient temperature, and at least five specimens were tested for each sample. Creep tests were carried out by a Q800 DMA machine (TA Instruments, USA), setting a testing temperature of 30 °C and a creep time of 60 minutes, applying a constant stress equal to the 10% of the ultimate tensile strength of the neat matrix. Rectangular samples 5 mm wide and 1 mm thick with a gage length of 10 mm were utilized to test both the bulk samples and the polymer foams. In this way, the time dependence of the creep compliance, equal to the ratio between the deformation of the samples and the creep stress, was determined.

3. Results and Discussion

It is well known that the physical properties of polymeric foams are directly related to their microstructural properties. Therefore, density measurements and microscopical analysis were conducted. In Figure 1a the density of the neat COC and of the relative nanocomposites as a function of the foaming pressure is represented, while in Figure 1b the mean cell size values are collected. It can be noticed that unfilled materials foamed at 90 bar present a density reduction of about 73% with respect to the corresponding bulk materials, and the density drop is even more pronounced at higher foaming pressures. A systematic increase of the foam

density was detected for the nanofilled samples, because of the higher density of fumed silica with respect to the neat COC. Correspondingly, cell size slightly increases with the applied pressure, regardless to the nanofiller amount. However, considering standard deviation values associated to these measurements, it can be concluded that the variation of the cell diameter with the applied pressure is practically negligible.

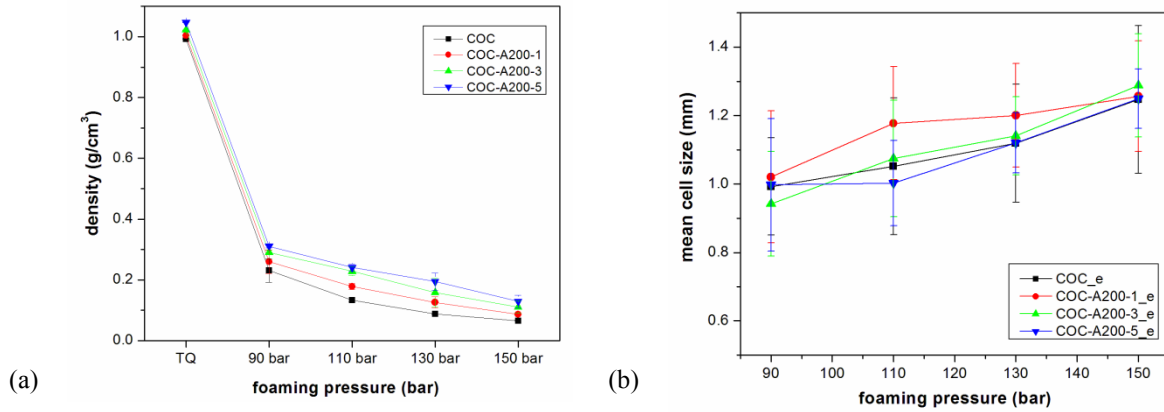


Figure 1. Density (a) and mean cell size (b) of the neat COC and relative nanocomposites as a function of the foaming pressure.

In Figure 2a FESEM micrograph of the cryofractured section of the COC-A200-5 bulk sample is represented. It can be seen the presence of silica aggregates with irregular shape uniformly dispersed within the matrix, with a mean size of around 100 nm. Interestingly, the presence of some voids around the nanoparticles indicates a non perfect interfacial adhesion between the polymer matrix and silica aggregates. This microstructural feature can profoundly affect the mechanical properties of bulk nanocomposites. It could be also interesting to observe the cryofractured section of the cell wall of the foamed samples (Figure 2b). The micrographs of the foams highlight an evident deformation of the aggregates along the cell walls direction. This microstructural feature is probably responsible of the noticeable improvements of the mechanical performances detected for the nanocomposite foams.

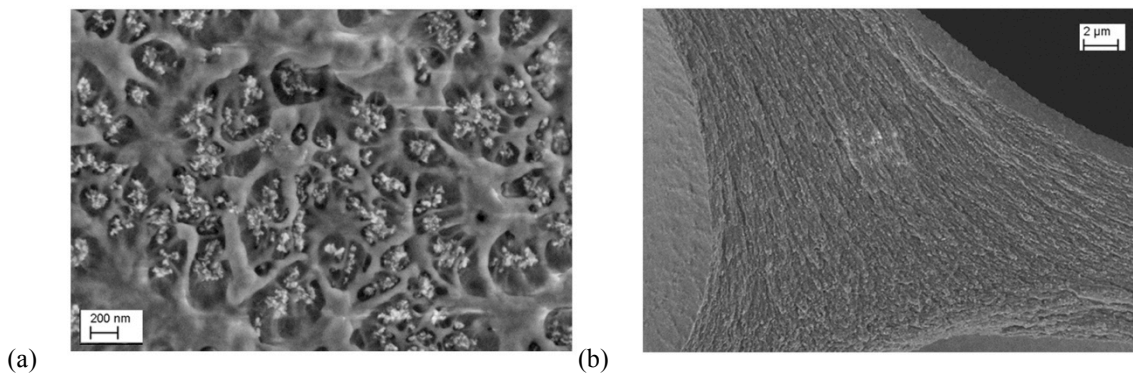


Figure 2. FESEM micrograph of (a) COC-A200-5 sample and of (b) the cell wall of the COC-A200-3_e150 sample.

Thermogravimetric analysis was carried out in order to evaluate the thermal stability of both bulk and foamed materials. From Figure 3 it is evident that an increase of the foaming pressure leads to a decrease of the decomposition temperature T_d (i.e. the temperature associated to the maximum mass loss rate), probably because of the corresponding reduction

of the foam density. Interestingly, from Figure 3 it can be observed how silica introduction can positively affect the thermo-oxidative stability of the foamed materials over the whole range of foaming pressures, with a systematic increase of the decomposition temperature (T_d) with the nanofiller amount.

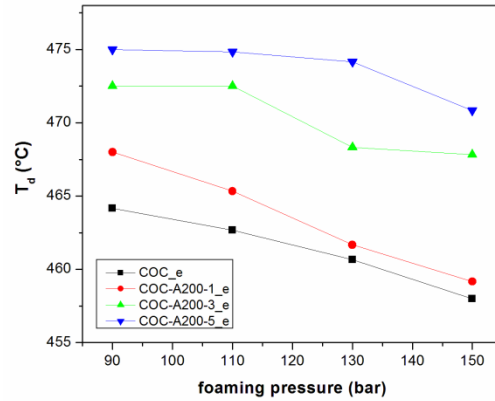


Figure 3. Decomposition temperature (T_d) from thermogravimetric tests on neat COC and relative nanocomposites at different foaming pressure.

Dynamical mechanical analysis was also carried out in order to evaluate the viscoelastic properties of both bulk and foamed materials. While glass transition temperature (T_g) seems to be practically unaffected by nanofiller introduction and/or by the foaming process, from Figure 4a an increase of the storage modulus with the nanofiller amount can be detected for bulk nanofilled bulk samples. In Figure 4b the storage modulus (E') of neat COC and nanocomposite foams as a function of the foaming pressure is represented. It is interesting to note that E' decreases with the applied pressure, because of the more intense foaming, but nanosilica introduction leads to a consistent increase of the storage modulus at all the applied foaming pressures.

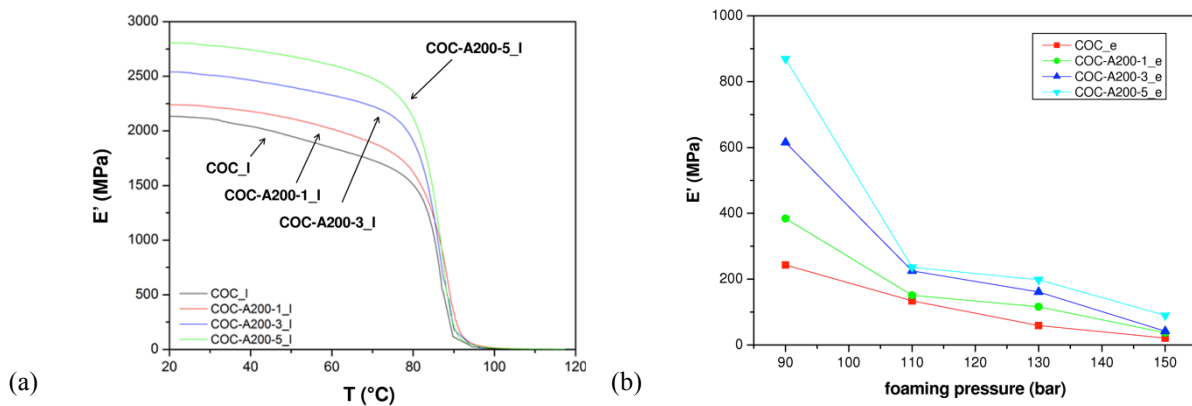


Figure 4. (a) Storage modulus (E') of neat COC and relative bulk nanocomposite foams and (b) storage modulus at ambient temperature of neat and nanofilled composites as a function of the foaming pressure.

As reported in our previous publications on COC based nanocomposites [11], quasi-static tensile tests on bulk materials confirmed the positive effect played by nanosilica in improving both the stiffness and the fracture toughness of the polymer matrix. In Figure 5a and Figure 5b the tensile properties of the nanocomposite foams at different foaming pressures are reported. As expected, an increase of the foaming pressure leads to a decrease of both the stiffness (E) and of the tensile strength (UTS), because of the decrease of the cell density.

Interestingly, nanosilica introduction determines a systematic enhancement of the elastic properties of the samples over the whole range of applied foaming pressure, proportionally to the nanofiller amount, and also the tensile strength was remarkably increased. For instance, applying a pressure of 90 bar, elastic modulus of 5 vol% filled nanocomposite is about 3.5 times higher than that of the unfilled foam at the same pressure, and a similar relative enhancement can be detected for the tensile strength. These effects are probably related to the peculiar microstructural properties of nanofilled foams (i.e. to the alignment of silica aggregates along the cell wall direction).

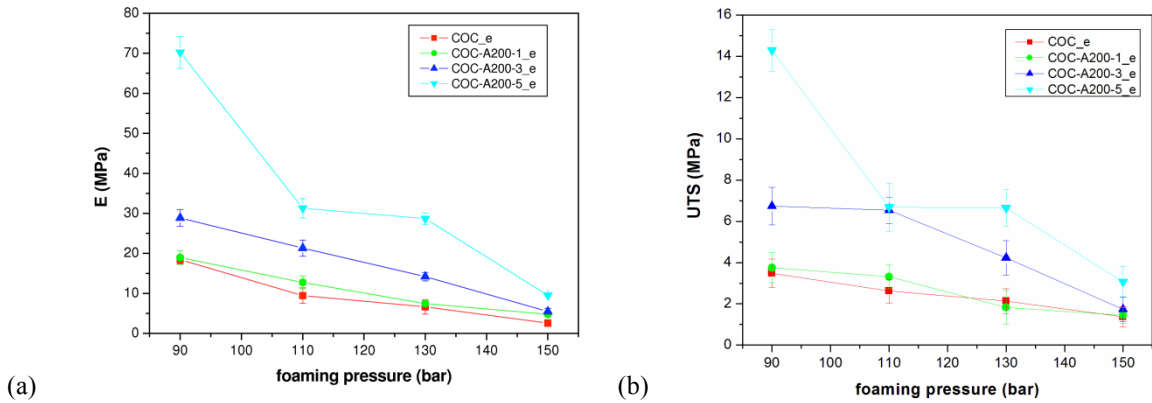


Figure 5. Quasi-static tensile tests on neat COC and relative nanocomposite foams. (a) Elastic modulus and (b) ultimate tensile strength as a function of the foaming pressure.

In order to confirm the positive effect played by silica nanoparticles on the mechanical behaviour of bulk and foamed nanocomposites, creep tests were performed. From Figure 6a it can be observed how the stabilizing effect due to nanofiller introduction leads to an interesting decrease of the creep compliance with respect to the neat COC. This effect is even more pronounced for foamed materials. In Figure 6b creep compliance at 3600 s of neat COC and relative nanocomposite foams as a function of the foaming pressure is reported. It can be seen that the increase of the creep stability due to nanofiller introduction is more evident at elevated creep times and at elevated filler amounts.

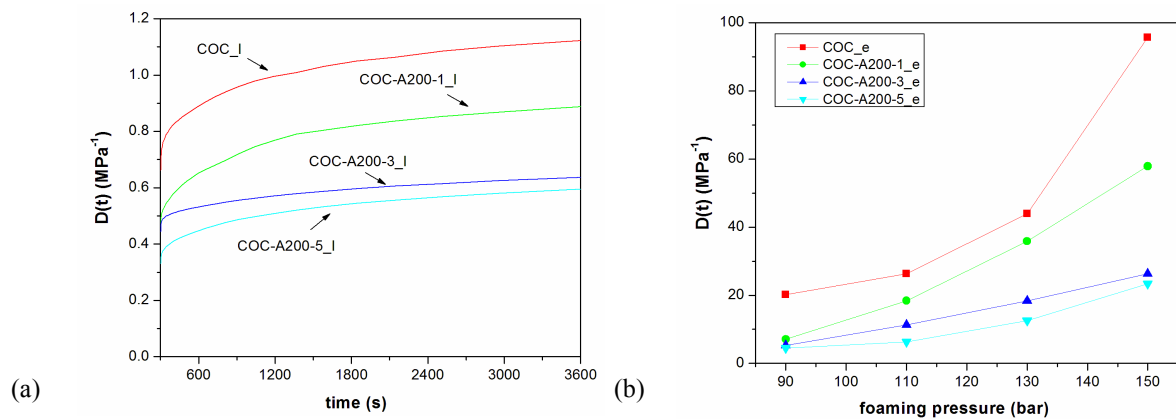


Figure 6. (a) Creep compliance curves of neat COC and relative nanocomposites in bulk form. (b) Creep compliance at 3600 s of neat COC and relative nanocomposite foams as a function of the foaming pressure.

4. Conclusions

Cycloolefin copolymer/fumed silica nanocomposites were prepared at different filler amounts through melt compounding, and the resulting materials were foamed through a supercritical carbon dioxide based process at different foaming pressures. A consistent density reduction with respect of the corresponding bulk materials, especially at elevated foaming pressures, was detected. Microstructural analysis on the foams highlighted an evident deformation of the silica aggregates along the cell walls direction. This microstructural feature is probably responsible of the positive effect played by nanosilica in improving the stiffness, the fracture toughness and the creep stability of the COC matrix. Concluding, foaming process of COC nanocomposites through supercritical carbon dioxide could represent an effective way to prepare low density polymeric foams characterized by a higher thermo-mechanical stability with respect to the corresponding unfilled materials.

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