# MICROCELLULAR FOAMS FROM HIGH PERFORMANCE PEEK/PEI MISCIBLE BLENDS

Luigi Sorrentino[1,3], Livia Cafiero[1,2,3], Salvatore Iannace[3,4]

[1] Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche, Piazzale E. Fermi 1, 80055 Portici (NA) – Italy
[2] Università di Napoli, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Piazzale V. Tecchio 80, 80125 Napoli – Italy
[3] IMAST S.c.a.r.l. Distretto Tecnologico sull'Ingegneria dei Materiali Compositi e Polimerici e Strutture, Piazza Bovio 22, 80122 Napoli – Italy
[4] Istituto per lo Studio delle Macromolecole , Consiglio Nazionale delle Ricerche, Via Alfonso Corti 12, 20133 Milano – Italy
Corresponding author: luigi.sorrentino@cnr.it

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## Abstract

The growing need for reducing weight in high performance applications such as in automotive, transport and aeronautic industries is leading to wider use of foams in composite structures, i.e. in sandwich structures, and in applications where low thermal and electric conductivity, or acoustic isolation are required. Furthermore, the awareness of the need to reduce the environmental impact of composites production is pushing towards the use of more lightweight structures, sustainable processes and recyclable raw materials. The foamability of miscible blends based on semicrystalline Poly(ether ether ketone) – PEEK and amorphous Poly(ether imide) – PEI have been investigated for their potential outstanding mechanical, thermal and chemical-physical specific properties with the aim to produce high performance foams with a microcellular or sub-microcellular morphology and low density. Foams have been obtained by using supercritical carbon dioxide as blowing agent and were prepared by means of the solid state foaming technique, which uses a fast temperature increase to induce bubbles nucleation and growth in samples previously solubilized with the blowing agent. The role of blend composition, solubilization pressure, and crystallinity on density and morphological parameters of the resulting foams has been investigated. A closed cell microcellular morphology, with average cell size between 1 and 2.5 μm, was obtained and nucleated up to $10^{12}$ cells per cubic centimeter were detected. Higher $CO_2$ uptake allowed a decrease of the foam density at each foaming temperature (down to 0.2 g/cm$^3$), while a complex relationship between foaming temperature and cellular morphology (in terms of cells density and cell size) was evidenced. In this work the foamability of miscible blends based on PEEK and PEI has been investigated with the aim to find the proper conditions to develop low density microcellular foams for high performance lightweight applications.

## 1. Introduction

Blending thermoplastic polymers can be a convenient method to create new materials combining the best properties of both components, with the possibility of having a synergistic effect without increasing the cost or chemically modifications. Blends performance depends on the components, their concentration and morphology [1]. In this work blends based high performance semicrystalline (PEEK)/amorphous (PEI) polymers have been analyzed, to understand how the blend thermal and gas sorption behaviours affected the foaming properties.

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Poly(ether ether ketone) (PEEK) is a semicrystalline engineering thermoplastic polymer, with very good chemical stability, thanks to the aromatic structure, and excellent thermal and mechanical properties. The high service temperatures (due to its $T_g$ = 145°C and $T_m$ = 345°C) make PEEK suitable for structural applications [2]. It's also used as matrix for thermoplastic composites because of it's good adhesion to glass and carbon fibers [3]. Poly(ether imide) (PEI) is an amorphous thermoplastic polymer, characterized by a high glass transition temperature ($T_g$ = 220°C), good electrical and mechanical performances [4, 5], and a high (for an amorphous polymer) chemical stability [3]. The blending of PEEK and PEI polymers has been considered by many scientists since it is an interesting route to combine the excellent and complementary properties of both polymers, and to achieve thermoplastic matrix material for high performance composites [5]. This goal can be reached thanks to the miscibility of opportune PEI polymers with PEEK, in the amorphous state, at all compositions [3, 5, 6]. The high glass transition temperature of PEI and the high melt temperature of PEEK make blends of such polymers very useful for aereonautical structural applications. In fact, in this application field many studies are aimed at finding a thermoplastic replacement to thermosetting resins to cope with high service temperatures and environmental resistance.

In order to get lightweight structures, foams based on PEEK/PEI blends are very promising but few works report on the foaming process of blends based on high performance polymers. In particular, those focused on PEEK/PEI foams [7]. This work reports on investigations on the foamability of a wide range of PEEK/PEI compositions and on the understanding of their capability to be foamed at low densities.

## 2. Experimental

PEEK (Victrex 450G) and PEI (Ultem 1000) were supplied by Victrex ltd (United Kingdom) and SABIC Innovative Plastics (Saudi Arabia), respectively. PEEK/PEI blend samples were supplied by Alenia Aermacchi SpA (Italy), in plates 60 mm x 40 mm x 2 mm in size.

Thermal properties have been evaluated with a differential scanning calorimeter (Q1000 DSC from TA Instruments, New Castle, DE – USA) on samples cut from injection moulded plates (pristine samples). $T_g$, $T_m$, $T_c$ and $\Delta H_c$ were evaluated from DSC heating scans from room temperature to 380 °C at a heating rate of 100 °C/min on pristine samples (Table 1). An annealing process was also performed for 10 minutes at a temperature dependent on the blend composition (reported in Table 1) to prepare annealed samples. They were used to measure the glass transition temperature after maximizing the degree of crystallinity of the PEEK phase.

Solubilized samples, intended to be characterized with the DMA and to be foamed, were solubilized in a high pressure vessel operated at 80 bar or 120 bar. The solubilization process was performed at a temperature of 50°C for 72 h. The physical blowing agent for foaming was carbon dioxide (purity 99.9%; supplied by Rivoira, (Italy). Samples were foamed immediately after the evaluation of the blowing agent uptake by using solid state foaming technique by immersion in a bath containing silicon oil set at the desired foaming temperature (ranging from 135 °C to 265 °C). The foam density has been measured by using the water displacement method according to ASTM D792.

DSC scans were also performed on foamed samples to evaluate the foaming process on the degree of crystallinity of PEEK.

Dynamic mechanical tests were carried out to estimate the glass transition temperature depression operated by the carbon dioxide on pristine and solubilized samples. A dynamic mechanical analyser – DMA (Tritec 2000 from Triton, Grantham, United Kingdom) was used and all tests were performed by means of the three-point bending configuration according to ASTM D 5023. The investigated temperature range was from 30 to 350°C, and the heating rate and oscillation frequency were 3°C/min and 1 Hz, respectively. Scanning electron microscopy (SEM) analysis was performed on cryogenic fractured surfaces of foams by using a Quanta 200 FEG (FEI, The Nederlands). The morphological parameters of cellular structures have been evaluated from SEM micrographs. In particular, the mean cell diameter was calculated as the average between at least 50 measures, whereas nucleated cells ($N_0$) was calculated with the following formula:

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$$N_0=\left(\frac{n}{A}\right)^{\frac{3}{2}}\cdot\frac{1}{1-V_f}$$

with

$$V_f=1-\frac{\rho_f}{\rho_s}$$

where $V_f$ is the void fraction of the foam, $\rho_s$ and $\rho_f$ are the bulk polymer and foam densities respectively (in g/cm$^3$), n is the number of cells in the SEM micrograph, and A is the area of the micrograph (in cm$^2$).

## 3. Results and discussion

PEEK/PEI blends showed complete miscibility in the amorphous state, as proved by the DSC analysis performed on pristine and annealed samples. A single $T_g$ has been detected in all composition. The dependence of $T_g$ on the composition for a miscible binary blend of amorphous polymers can be described by the Fox equation [3, 4, 8]:

$$\frac{1}{T_g}=\frac{w_1}{T_{g1}}+\frac{w_2}{T_{g2}}$$

where $w_1$ and $w_2$ represent the weight fractions of each blend constituent, and $T_g$, $Tg_1$ and $Tg_2$ are the glass transition temperatures of the blend and the two polymers, respectively. The glass transition temperatures measured on pristine samples are represented with circular blue marks in Fig 1. They range from $T_g$ = 144 °C (the lowest value) in neat PEEK to $T_g$ = 218°C in neat PEI (highest value) in an almost linear trend [3, 5, 6]. The trend of experimental data was consistent with the $T_g$ value calculated with the Fox equation (dashed blue line in Fig. 1).

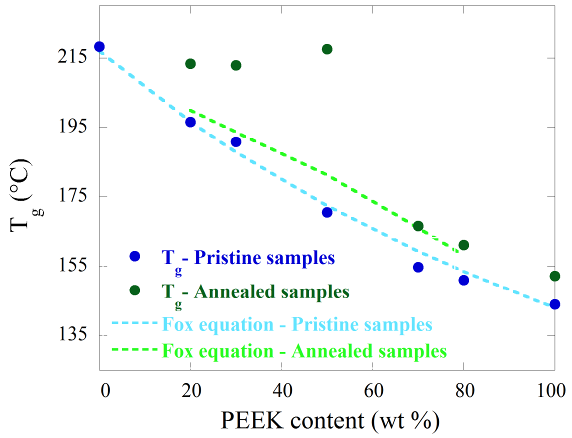

**Figure 1.** Glass transition temperatures of pristine and annealed samples, and theoretical glass transition temperature trends from the Fox equation.

Since the presence of crystals can influence the foaming process, the extent of crystallinity has been evaluated after an annealing treatment. The degree of crystallinity, normalized by the actual PEEK content, has been reported in Table 1. Samples with higher PEEK content showed higher cristallinity, since the capability of PEEK to develop a crystalline phase, and its formation rate, is reduced by the presence of PEI [3, 8]. Table 1 also shows that, unlike the glass transition temperature, the melting temperature of blends was only slightly affected by the addition of PEI. This is due to the fact that the lamella thickness in PEEK crystals, that affect the melting point of crystallites, is almost independent of the blend composition [3].

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The crystallization of PEEK induced by the annealing process enriched the amorphous phase with PEI. A strong shift towards the $T_g$ of PEI was detected in samples with PEEK content from 20 to 50 wt% (green circular marks in Fig. 1), differently from the expected values in the same conditions calculated with the Fox equation (dashed green line in Fig. 1), in accordance with previous foundings [3, 8, 9].

**Table 1.** Blend composition (weight percent), annealing temperature, glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), crystallization degree after normalization for the PEEK content ($X_c$) of neat polymers and PEEK/PEI blends from pristine samples; crystallization degree after normalization ($X_{c\ Foamed}$) from foamed samples.

| Sample | PEEK (wt%) | PEI (wt%) | Annealing Temperature (°C) | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $X_c$ (wt %) | $X_{c\ Foamed}$ 180°C (wt%) | $X_{c\ Foamed}$ 200°C (wt%) |
|---|---|---|---|---|---|---|---|---|---|
| Neat PEI | 0 | 100 |  | 218.32 | 0 | 0 | 0 | 0 | 0 |
| PEEK20/PEI80 | 20 | 80 | 294.0 | 198.45 | 286.81 | 334.47 | 2.44 | 17.92 | 28.96 |
| PEEK30/PEI70 | 30 | 70 | 274.0 | 195.48 | 272.37 | 334.64 | 5.21 | 14.92 | 23.59 |
| PEEK50/PEI50 | 50 | 50 | 236.0 | 170.94 | 236.38 | 339.59 | 5.15 | 7.12 | 17.65 |
| PEEK70/PEI30 | 70 | 30 | 211.0 | 163.37 | 211.56 | 342.01 | 8.42 | 26.31 | 36.90 |
| PEEK80/PEI20 | 80 | 20 | 199.0 | 149.83 | 195.02 | 339.45 | 13.45 | 18.83 | 39.10 |
| Neat PEEK | 100 | 0 | 171.0 | 144.10 | 171.32 | 345.12 | 28.23 | 31.06 | 31.55 |

Figure 2A reports the $CO_2$ uptake in samples exposed to a solubilization pressure of 80 and 120 bar after 72 hours. As already reported in literature, $CO_2$ solubility increases with both PEI content and solubilization pressure [7]. The $CO_2$ uptake affects the elasticity of the blend and reduces the glass transition temperature [10]. The $T_g$ depression plays an important role for the choice of the foaming temperatures to reach low foam densities and dynamic mechanical tests, according to ASTM D5023, were performed on solubilized samples (solubilization conditions: 80 bar, 50 °C, 72 hours) to estimate the extent of the $T_g$ reduction. A selected storage modulus plots is reported in Fig. 2B to show how the storage modulus changed after the $CO_2$ uptake; the glass transition temperature reduction ranged from 50°C for the neat PEEK to 110°C for the neat PEI. The plasticization effect was very strong and dependent on the PEI content [7, 11].

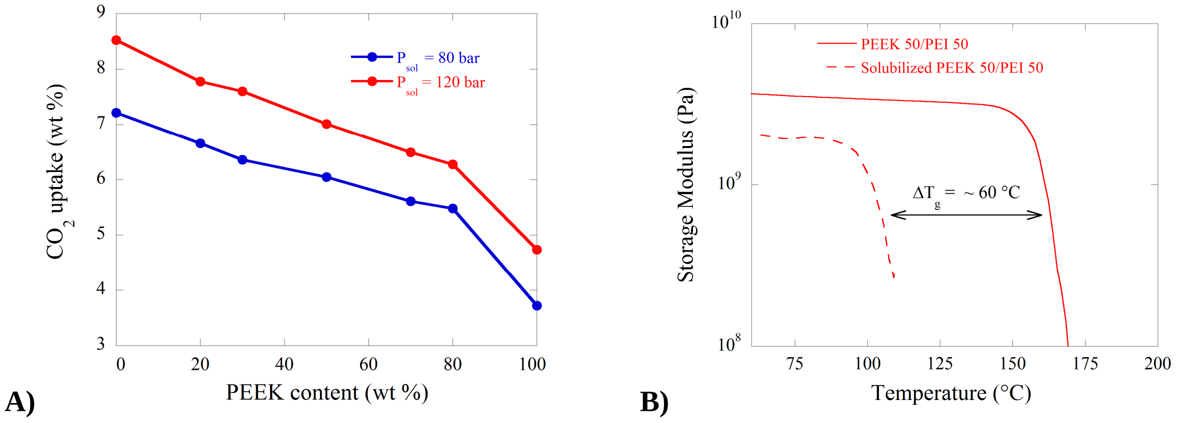

**Figure 2.** A) $CO_2$ uptake in PEEK/PEI blends after 72 h of gas sorption at different solubilization pressures (80 and 120 bar); B) Evaluation of the $T_g$ reduction after the $CO_2$ sorption process (solubilization performed at 80 bar for 72 hours) for PEEK 50/PEI 50 blend.

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Foamed samples have been prepared by increasing their temperature in an oil bath at the desired temperature. Foaming temperatures were selected in order to be higher than the actual glass transition temperature of the blend after solubilization (160, 180, 200 and 213 °C).
The densities of foamed samples solubilized at 80 bar and 120 bar are reported in Fig. 3A and 3B, respectively. Density decreased with the increase of the foaming temperature up to 200 °C. Only a small density reduction was detected at 213 °C with respect to 200 °C. Foams obtained from samples solubilized at 120 bar showed lower densities with respect to 80 bar at all foaming temperatures due to the higher blowing agent uptake. The density trend with respect to the blend composition was the same for both solubilization pressures. The foam density decreased with the increase of PEEK content, showing a minimum centred at 50 wt%. At higher PEEK content the high amount of crystalline phase present in non solubilized samples hindered a significant decrease of the foam density, although the blends were characterized by a lower glass transition temperature.

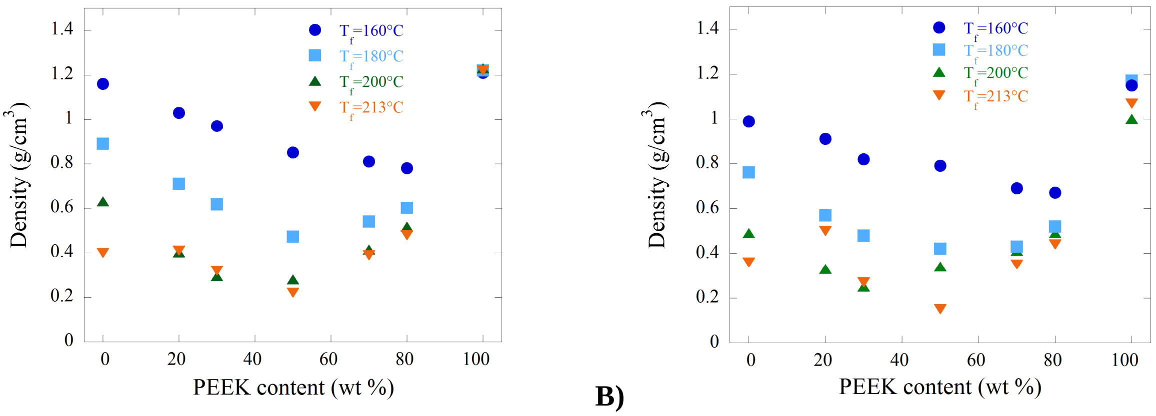

**Figure 3.** Density of samples foamed at different temperatures, as a function of PEEK content: A) solubilization performed at $P_{sol}$= 80 bar; B) solubilization performed at $P_{sol}$=120 bar.

A thermal analysis was conducted on foamed samples expanded at 180 °C and 200 °C (Table 1). The degree of crystallinity strongly increased during the foaming process, in particular after the foaming process conducted at 200 °C. PEEK 50/PEI 50 showed the smallest increase of crystallinity after foaming at both 180 °C and 200 °C. This peculiar behaviour could be the main reason why a minimum in foam density is centred on this composition and it can be probably addressed to a) a slower crystallization rate occurring during the foaming process and b) the presence of portions of amorphous PEEK that remain rigid also above the glass transition temperature (RAF), immobilized between PEEK crystallites [8, 9]. The presence of such RAF could slow down the crystallization rate and allow the further expansion of cells [11].
Selected SEM micrographs of samples foamed at 200 °C and solubilized at 80 bar are shown in Fig. 4 to exemplify the cellular morphology developed in PEEK/PEI foams. The morphology behaviour is the same for both solubilization pressure. A regular and homogeneous closed cell morphology was detected in all foams, independently of the blend composition. In neat PEEK samples the formation of a cellular structure was hindered by the presence of more the 28 wt% of crystalline domains. The cellular morphology has a narrow cell size distribution and is generally characterized by very small cells. This can be due to a) the presence of crystals (acting as heterogeneous nucleation sites) and b) the very fast raising of the blend glass transition temperature during the escaping of $CO_2$ from the polymer, that helps in quenching the cellular structure. The use of a higher solubilization pressure did not enhanced the nucleation process.

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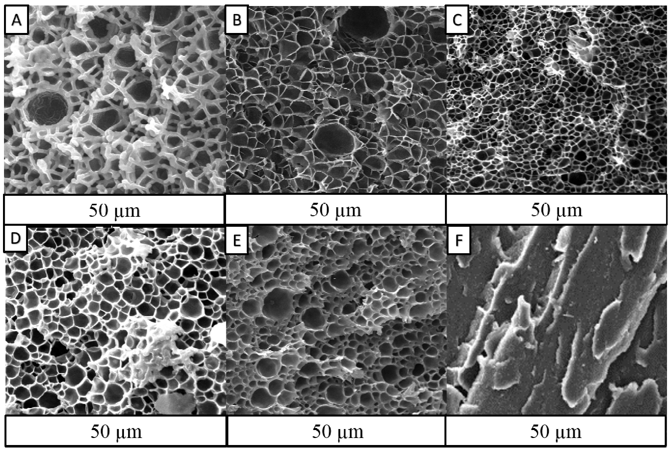

**Figure 4.** Morphology of foams (foaming conditions: $P_{sol}$=80 bar, $T_f$ = 200 °C): A) Neat PEI, B) PEEK 30/PEI 70, C) PEEK 50/PEI 50, D) PEEK 70/PEI 30, E) PEEK 80/PEI 20, F) Neat PEEK.

A closed microcellular morphology was obtained for all compositions and in all foaming conditions. The trend of both nucleated cells and mean cell size with respect to the composition was generally consistent at all temperatures. In Fig. 5A are shown morphological parameters evaluated from samples foamed at $T_f$ = 200 °C ($P_{sol}$ = 80 bar). The number of nucleated cells ranged between $9.47 \cdot 10^{10}$ and $1.84 \cdot 10^{12}$ cells/cm$^3$ and showed a maximum in the PEEK 50/PEI 50 composition, which also showed the lowest foam density. The mean cell size showed an opposite trend with respect to nucleated cells, and a minimum was detected in the PEEK 50/PEI 50 blend. Foams from samples solubilized at 120 bar showed the same trend for nucleated cells and mean cell size, but the higher $CO_2$ uptake didn't quantitatively nor qualitatively enhanced the cell nucleation. The mean cell size was almost the same for both solubilization pressures and ranged between 0.9 μm and 2.3 μm.

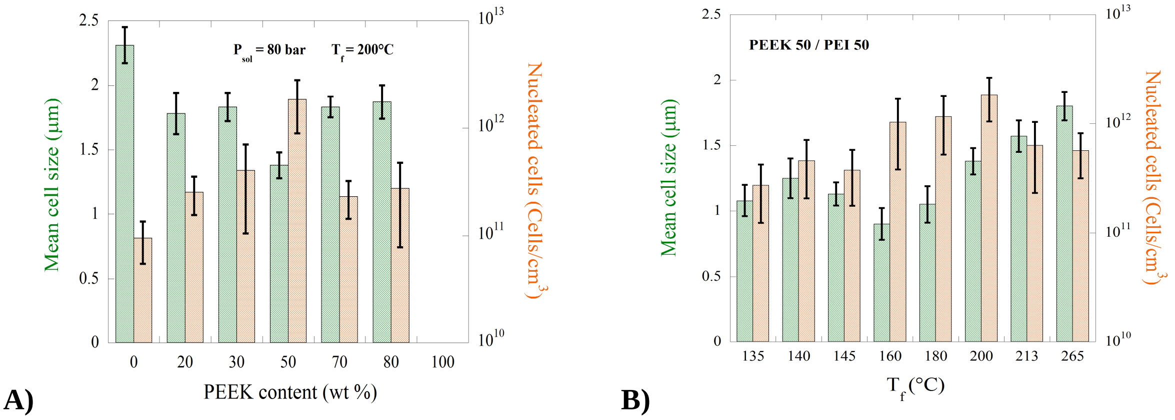

**Figure 5.** Morphological parameters (Mean size and Nucleated cells) A) PEEK/PEI foams foamed at 200 °C and $P_{sol}$= 80 bar; B) PEEK 50/PEI 50 foams, as a function of the foaming temperature.

PEEK 50/PEI 50 resulted to be the composition that gave the best morphological parameters at each solubilization pressure. Interestingly this system also showed the lowest foam densities in quite all processing conditions. The range of foaming temperatures of PEEK 50/PEI 50 composition has been extended at temperatures below 160 °C and above 213 °C and the morphological parameters have been reported in Fig. 5B. Nucleated cells showed a growing trend with the foaming temperature up to

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200 °C and then a reduction took place. Mean cell size showed a more complex trend. In fact, after a first increase between 135 °C and 140 °C, it decreased and a minimum was detected at 160 °C. At temperatures above 160 °C a monotonic increase of the mean cell size was measured. PEEK 50/PEI 50 foamed at $T_f$=160 °C showed very interesting morphological parameters, since a cell density equal to $1.03 \cdot 10^{12}$ cells/$cm^3$ is combined with a sub-micrometric mean cell size equal to 0.9 μm.

## 4. Conclusions

High performance thermoplastic foams, with density down to 0.13 g/$cm^3$ (PEEK 50/PEI 50 sample, $P_{sol}$ = 120 bar), were prepared from miscible blends based on semicrystalline (PEEK)/amorphous (PEI) polymers by using supercritical carbon dioxide as blowing agent. Low density foams were successfully prepared using the solid state foaming technique, which uses a fast temperature increase to induce bubbles nucleation and growth in samples previously solubilized with the blowing agent.

The $CO_2$ uptake can be controlled by means of the sorption pressure and is dependent on the relative amount of the blend constituents. A higher $CO_2$ uptake allowed a decrease of the foam density at each foaming temperature, while a complex relationship between foaming temperature and cellular morphology (in terms of nucleated cells and mean cell size) was detected.

SEM analysis showed that a closed cell microcellular morphology, with average cell size ranging between 0.9 and 2.3 μm, was obtained for all blend compositions and for the whole foaming temperature range. The best composition resulted to be PEEK 50/PEI 50 that in all foaming conditions exhibited the best morphological parameters. In particular, it allowed to combine low density, micrometric cell size (1.2 μm) and very high nucleated cells (higher than $10^{12}$ cells/$cm^3$) when foamed at 200°C, while it showed medium density, sub-micrometric mean cell size and still very high nucleated cells when foamed at 160 °C.

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