

Microcellular foams from high performance miscible blends based on PEEK and PEI

Livia Cafiero^{1,2,3}, Salvatore Iannace^{3,4}, Luigi Sorrentino^{1,3}

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

ABSTRACT

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 0.9 and 2.3 μm , was obtained and nucleated bubbles up to 10^{12} cells cm^{-3} were detected. Higher CO_2 uptake allowed a decrease of the foam density at each foaming temperature (down to 0.13 g cm^{-3}), while a complex relationship between foaming temperature and cellular morphology (in terms of nucleated cells and mean cell size) emerged.

Keywords: Foams; Supercritical carbon dioxide; Blends; High Performance Thermoplastics

Introduction

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 **insulation** 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. Raw thermoplastic matrices are a promising choice since they have several advantages: a potential infinite shelf life, thus cutting the low temperature storage costs typical of thermoset resins or pre-impregnated fibres, increased impact resistance, higher damage tolerance and interlaminar toughness due to the presence of the amorphous phase that can retard the crack propagation and accommodate larger deformations [1].

In this framework, high performance thermoplastic polymers like Poly(ether ether ketone) – PEEK or Poly(ether imide) – PEI are gaining ever more interest. PEEK is a semicrystalline engineering thermoplastics, with good chemical stability, thanks to the presence of aromatic groups along the macromolecular backbone, and excellent thermal and mechanical properties [2]. Its good adhesion to glass and carbon fibers allows to prepare high performance thermoplastic fiber reinforced laminated composites [3]. Furthermore, the high service temperatures, due to its glass transition temperature (T_g) equal to 144°C and its peak melting temperature (T_m) equal to 343°C, make PEEK suitable for applications at temperatures **in excess of** 120 °C [4].

Due to the challenging processing conditions of PEEK, a lot of efforts are made to **ease** its processing requirements. Blending is a very compelling approach to create new materials whose properties exploit the best of all constituent phases and gives the possibility to have a synergetic effect. Blend performances depend on the properties of the constitutive components, the composition, the morphology and the mutual interactions of the phases [5]. Among the different pairs of high performance thermoplastics, blending of PEEK with PEI has been widely investigated in the past, since PEEK/PEI blends can form miscible blends in the solid state in a very wide composition range [3, 6, 7]. PEI is an amorphous thermoplastic polymer that shows a high glass transition temperature ($T_g = 217^\circ\text{C}$), great mechanical performances [8, 6], good electrical properties [6], and a good chemical stability, even if lower than PEEK because of the lack of crystalline phase [3]. The high glass transition temperature of PEI and the even higher melt

temperature of PEEK, coupled with their excellent mechanical properties, make their blends very interesting for high demanding applications, such as in the aeronautics industry in order to replace thermosetting matrices.

Available studies on PEEK/PEI blends report on their **quiescent** crystallization kinetics [3, 6, 9, 10], dynamic mechanical behaviour [3, 6], and blend morphology [4, 11]. The blend morphology depends on the PEI monomer conformation and on the degree of crystallinity of the PEEK phase. In particular, a partial phase separation occurs during the crystallization of PEEK and the actual composition of the amorphous phase, formed by PEI and not crystallized PEEK, is richer in PEI as reported by Crevecoeur et al [3] and Lee et al [9]. In fact PEI is segregated during the crystallization process of PEEK and variations of the blend morphology are detected. Moreover, a rigid amorphous fraction (RAF) of PEEK, which doesn't mix with PEI, is present when the **degree of crystallinity is sufficiently high. This RAF is immobilized by the formed crystals and** doesn't contribute to the glass transition temperature lowering [9, 12, 13]. In this case, the glass transition temperature of the blend is dependent on the local rather than the overall composition of the amorphous phase and can shift from 144 °C towards 210 °C quicker than expected [3, 9]. This phenomenon can consequently affect the foaming process of the blend.

Few works report on the foaming of such high performance **blends** [14, 15, 16]. In general, polymer blending has been exploited in foams to increase the strain hardening and other rheological properties of the host polymer [17, 18], to use the available interfaces in immiscible blends for heterogeneous cell nucleation [19, 20], to adjust the open/closed cell content [21, 22], to control the absorption of the foaming agent [23, 24] and to tailor the mechanical strength [25, 26]. Literature about PEEK/PEI foams is very poor, and it is essentially based on **some results obtained by Nemoto et al.** [27]. **They obtained high density** foams starting from PEEK/para-diamine PEI (immiscible) and PEEK/meta-diamine PEI (miscible) blends at two compositions (**60/40 and 40/60 percent by weight**). It was observed that the PEEK/p-PEI blend shows unique sea-island morphology, in which the PEI forms the strip-pattern disperse domain. The size and the location of bubbles were highly controlled in the p-PEI disperse domain. **Cells growth occurred** between the PEEK crystalline layers and **were characterized by a nanometric size**. PEEK/meta-diamine PEI miscible blends were foamed and used as a reference cellular structure, **since they showed a microsized cellular morphology**.

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.

Experimental

PEEK (Vitrex 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). The blends were prepared by means of a fast extrusion process performed at temperatures between 190 °C and 380 °C and cut in pellet form. Such pellets (as well as neat polymers) were then processed in an injection moulding machine, operating at temperatures ranging from 300 °C and 380 °C (180 °C to 280 °C for neat PEI), to produce plates 60 mm x 40 mm x 2 mm in size. The injection moulding process was set in order to keep the crystallinity in samples as low as possible. The mould temperature was set according to each blend composition by using the lowest value that allowed the complete filling of the mould internal volume.

All samples were vacuum dried at 120 °C for 24 h before thermal and dynamic mechanical analyses and gas absorption experiments. 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 (referred to as “pristine samples”) and selected DSC traces have been reported. The glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and crystallization enthalpy (ΔH_c) were evaluated from DSC heating scans performed from room temperature to 380 °C at a heating rate of 100 °C/min on pristine samples (Table 1). Such high heating rate was used to maximize the signal to noise ratio and get sharper thermal transitions. In particular, it allowed an easier and more accurate evaluation of the glass transition temperature. The relative crystallinity (X_c) been evaluated as the ratio between ΔH_c and ΔH_m^0 , where ΔH_m^0 is the crystallization enthalpy of the perfect PEEK crystal (130 J/g) [3]. 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. The annealing temperature was specific of each composition. It was evaluated from preliminary DSC heating scans performed on pristine samples and was the peak temperature of the cold crystallization temperature range.

Solubilized samples, intended to be characterized with the DMA and to be foamed, were solubilized in a high pressure vessel operated at 8.0 MPa or 12.0 MPa. 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 for foaming were cut from the injection moulded plates and were 10 mm x 10 mm x 0.5 mm in size. Their thickness was reduced from 2 mm to 0.5 mm by symmetric milling with respect to the middle plane. The thickness reduction was

needed to keep the duration of sorption experiments within 72 hours. Samples were foamed immediately after the evaluation of the blowing agent uptake. The solid state foaming technique was used and samples were immersed in a bath containing silicon oil set at the desired foaming temperature (ranging from 135 °C to 265 °C). The time interval from the pressure release in the high pressure vessel to the foaming process was less than five (5) minutes, in order to minimize the gas escape from samples before DMA characterization or foaming. Foamed samples always completed the expansion process within 10 s from the immersion and were quenched in cold water to stabilize the cellular structure just after that time. 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 on pristine and solubilized samples by means of a dynamic mechanical analyser – DMA (Tritec 2000 from Triton, Grantham, United Kingdom) using the three-point bending configuration set 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. All samples for DMA characterizations were cut from the plates. Their size was 30 mm x 9.0 mm x 1.0 mm and the support span was set equal to 21 mm. The samples thickness for DMA characterizations was reduced from 2 mm to 1.0 mm by symmetric milling with respect to the middle plane, in order to have a support span ratio higher than 20.

Transmission electron microscopy (TEM) analysis was performed by using a TECNAI G12 Spirit-Twin with a LaB6 source (FEI; Eindhoven, The Netherlands). Samples for TEM analysis have been obtained from injection moulded plates by cutting 70 nm thick layers with an LKB ultramicrotome (LKB, Stockholm, Sweden).

Scanning electron microscopy (SEM) analysis was performed on cryogenic fractured surfaces of foams by using a Quanta 200 FEG (FEI, The Netherlands). All surfaces were gold-coated before the observation to render the specimen surface conductive. 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:

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

with

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

where V_f is the void fraction of the foam, ρ_s and ρ_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).

Results and discussion

Thermal and morphological analysis of blends

PEEK/PEI blends showed complete miscibility in the amorphous state, as proved by the DSC analysis performed on **pristine (Figure 1A) and annealed (Figure 1B) 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, 8, 9]:

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

where w_1 and w_2 represent the weight fractions of each blend constituent, and T_g , T_{g1} and T_{g2} 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 red marks** in Figure 2. 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, 6, 7]. The trend of experimental data was consistent with the T_g value calculated with the Fox equation (solid line in Figure 2).

Since the presence of crystals can influence the foaming process, the extent of crystallinity and the morphology of crystals 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 crystallinity, since the capability of PEEK to develop a crystalline phase, and its formation rate, is reduced by the presence of PEI [3, 9]. 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].

The morphology of **annealed blends** has been analysed by means of TEM, and micrographs are shown in Figure 3. PEEK crystalline spherulites within PEI matrix can be clearly detected, such as in PEEK 20/PEI 80 and PEEK 30/PEI 70 blends. The similarity of spherulities in all compositions, coupled with the limited variation of the melting temperature in blends suggest similarly developed crystalline phases among all compositions. Hence, a limited dependence of both crystal morphology and degree of order of PEEK crystals on the composition can be hypothesized. This suggest that PEI and amorphous PEEK can generally separate from PEEK crystals without being segregated

between lamellas [3]. The crystallization of PEEK induced by the annealing process enriched the amorphous phase with PEI. An abrupt shift towards the T_g of PEI was detected in samples with PEEK content from 20 to 50 wt% (blue square marks in Figure 2), differently from the expected values in the same conditions calculated with the Fox equation (dashed line in Figure 2). The same behaviour was detected by Crevecoeur and Groeninckx in [3], who characterized PEEK/PEI blends by DMA. The authors found that blends with PEEK content equal or lower than 50 wt % showed a higher than expected T_g after annealing as a result of the formation of a RAF phase in the proximity of PEEK crystals that does not participate in the glass transition due to the immobilization by crystallites [9, 11].

Carbon dioxide solubilization and T_g depression in blends

In order to choose the solubilization duration for PEEK/PEI blends, a preliminary study was performed at 50 °C and 80 bar to evaluate the sorption kinetics of carbon dioxide in all compositions (Figure 4A). All blends reached a plateau after a sorption time interval of 240 hours. For experimental needs a shorter sorption time was needed and a 72 hours duration was selected. The difference in CO₂ uptake between the latter time interval and 240 hours was in the range between 0.1 % and 0.34 % by weight. Figure 4B reports the CO₂ uptake in samples exposed to a solubilization pressure of 80 and 120 bar after 72 hours. As already reported in literature, CO₂ solubility increases with both PEI content and solubilization pressure [27].

The CO₂ uptake affects the elasticity of the blend and reduces the glass transition temperature [28]. The T_g depression has an important role on 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. It has been calculated as the temperature gap between the storage modulus drop in not solubilized and solubilized samples, evaluated at the same storage modulus value (selected in the range between 200 and 600 MPa and after the storage modulus drop). Selected storage modulus plots are reported in Figure 4A-B to show how the storage modulus changed after the CO₂ uptake, while Table 2 reports the glass transition temperature reduction for all compositions. The plasticization effect was very strong and dependent on the PEI content [27].

Foaming of blends

Foamed samples have been prepared by quickly increasing their temperature in an oil bath at the desired temperature. The formation of the cellular structure is fostered by the temperature increase through the simultaneous occurrence of a) a drastic thermodynamic instability that induce the

separation of gaseous and polymeric phases and b) the softening of the polymeric matrix that allows the growth of cells. Foaming temperatures were selected in order to be higher than the actual glass transition temperature of the blend after solubilization, and accidentally laid in a range between the glass transition temperatures of neat dry polymers (160, 180, 200 and 213 °C).

The densities of foamed samples solubilized at 80 bar and 120 bar are reported in Figure 6A and 6B, 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% (except that for foams obtained at 160 °C, as explained in the following). 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.

To better understand the role of both crystallinity and crystallization rates in PEEK on the foam density, a thermal analysis was conducted on foamed samples expanded at 180 °C and 200 °C, and results were compared to unfoamed samples (Figure 7). It is evident that the degree of crystallinity strongly increased during the foaming process in comparison to its starting value in unfoamed samples (“Pristine matrix” marks in Figure 7), in particular after the foaming process conducted at 200 °C. It is worth to note that unlike all other blends, PEEK 50/PEI 50 developed a very limited crystallinity during foaming at 180 °C, and showed the smallest increase after foaming at 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 (rigid amorphous fraction, RAF), immobilized between PEEK crystallites [11]. The presence of such RAF could slow down the crystallization rate and allow the further expansion of cells [3]. **The crystallization behaviour of PEEK/PEI blends during foaming isn't completely clear. Even if the crystallization kinetics has been already investigated in the past, the foaming process adds some complications. In fact, the cell growth induces an elongational viscous flow in cell walls. Unlike in quiescent crystallization the formation of a crystalline phase is fostered during the foaming process even if its duration is very short, i.e. not more than 10 seconds. A marked increase of the crystallinity in all samples has been detected even if the blend was initially (almost) amorphous. The PEEK 50/PEI 50 composition showed to be the less sensitive**

blend to this phenomenon but, also due to the small amount of crystals already developed in the PEEK phase before foaming, a significant degree of crystallinity ranging from 8 to 18 % was measured at the end of the expansion.

SEM micrographs of samples foamed at 200 °C and solubilized at 80 bar and 120 bar are shown in Figure 8 and Figure 9, respectively, to exemplify the cellular morphology developed by PEEK/PEI blends. A regular and homogeneous closed cell morphology was detected in all foams, independently of the blend composition, except that in neat PEEK samples where the formation of a cellular structure was hindered by the presence of more the 28 wt% of crystalline domains. The cellular morphology is generally characterized by very small cells, and the qualitative cell size distribution is very narrow. This can be due to the coupling of two effects: the presence of crystals (acting as heterogeneous nucleation sites) and the very fast raising of the blend glass transition temperature during the escaping of CO₂ from the polymer, that helps in quenching the cellular structure. It is worth noting that the use of a higher solubilization pressure did not result in a significant improvement of the cellular morphology. In particular, the nucleation process was not enhanced.

In order to better understand the role of the crystallization rate on the foam density, selected compositions (PEEK 30/PEI 70, PEEK 50/PEI 50, PEEK 70/PEI 30) were foamed at temperatures below 160°C (namely 135, 140, 145, 150 °C) to limit the crystallization rate during the foaming process, and above 213 °C (namely 245, 255, 265 °C) to additionally lower the polymer viscosity.

Density measurements are reported in Figure 10. It's evident that at foaming temperatures equal or lower than 160 °C the lowest foam density was showed by samples containing higher amounts of PEEK (PEEK 70/PEI 30). This is an indirect evidence that the lowering of the molecular mobility delays the formation of crystals and allows to exploit the lower glass transition temperature of the blend with higher PEEK content to consistently reduce the foam density with respect to higher PEI containing samples. On the contrary, at high foaming temperatures (well above the glass transition temperature of PEI) the minimum in density was still showed by PEEK 50/PEI 50 foams. High temperatures increase both the mobility of macromolecules and the diffusivity of carbon dioxide (i.e. gas escaping) through the polymer, in turn promoting the increase of the crystallization rate when a high degree of crystallinity is already present (high PEEK containing samples). The density of PEEK 30/PEI 70 samples increased because the very high diffusivity of CO₂ through the polymeric phase reduced the amount of gas available for foaming with respect to 200 and 213 °C. This very fast diffusivity of carbon dioxide at high foaming temperatures, coupled with the fast raise of the glass transition temperature, was also confirmed by the presence of unfoamed skins in

PEEK 30/PEI 70 samples (Figure 11).

Evaluation of morphological parameters

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 Figure 12 morphological parameters evaluated from samples foamed at $T_f=200$ °C are shown for both solubilization pressures. When the solubilization pressure is equal to 80 bar the number of nucleated cells ranged between $9.47 \cdot 10^{10}$ and $1.84 \cdot 10^{12}$ cells/cm³ 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 CO₂ 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 1.3 μm and 2.3 μm.

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 Figure 13. Nucleated cells showed a growing trend with the foaming temperature up to 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/cm³ is combined with a sub-micrometric mean cell size equal to 0.9 μm.

Conclusions

High performance thermoplastic foams, with density down to 0.13 g/cm³ (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 CO₂ uptake can be controlled by means of the sorption pressure and is dependent on the relative amount of the blend constituents. A higher CO₂ 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 10¹² cells/cm³) 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.

It has also been demonstrated that one of the main controlling parameters for the density reduction of high performance polymeric blends is the crystallization rate of the semicrystalline species. In fact, PEEK 50/PEI 50 foams, always characterized by the lowest developed crystallinity after all foaming tests, showed the best results in terms of density and morphological parameters.

Acknowledgements

This study has been carried out with financial support from MIUR Ministry (Italy) within the TECOP project (PON02_00029_3206010). Authors would like to thank Mr Fabio Docimo for its contribution to the preparation of all tested samples. Authors would also to thank Dr Michele Iannone and Dr Floriana Esposito from Alenia Aermacchi SpA (Italy) for their helpful contribution in the analysis of the blend properties.

References

1. Simeoli, G., Acierno, D., Meola, C., Sorrentino, L., Iannace, S. and Russo, P. *Compos. Part B Eng.* 62, 88 (2014).
2. Zhou, B., Ji, X., Sheng, Y., Wang, L. and Jiang, Z. *European Polymer Journal* 40, 2357–2363 (2004).
3. Crevecoeur, G. and Groeninckx, G. *Macromolecules* 24, 1190-1195 (1991).
4. Hudson, S. D., Davis, D. D. and Lovinger, A. J. *Macromolecules* 25, 1759-1765 (1992).
5. Utracki, L.A. *Polymer blends handbook* Vol.1, Kluwer Academic Publishers (2003).
6. Frigione, M., Naddeo, C. and Acierno, D. *Polymer Engineering and Science* Vol. 36,16 (1996).
7. Ramani, R. and Alam, S. *Thermochimica Acta* 511, 179-188 (2010).

8. Goodwin, A. A. and Simon, G. P. *Polymer* Vol. 37, 6, 991-995 (1996).
9. Lee, H. S. and Kim, W. N. *Polymer* Vol. 38, 11, 2657-2663 (1997).
10. Morales, A.R. and Bretas, R. E. S. *European Polymer Journal* 32, 3, 349-363 (1996).
11. Jonas, A. M. and Ivanov, D. A. *Macromolecules* 31, 5352-5362 (1998).
12. Jonas, A and Legras, R. *Macromolecules* 26, 813-824 (1993).
13. Aurilia, M., Sorrentino, L. and Iannace, S. *European Polymer Journal* 48, 26–40 (2012).
14. Sorrentino, L., Aurilia, M., Cafiero, L. and Iannace S. *Journal of Applied Polymer Science* 122, 3701–3711 (2011).
15. Sorrentino, L., Aurilia, M., Cafiero, L., Cioffi S. and Iannace S. *Journal of Cellular Plastics* 48(4), 355–368 (2012).
16. Sorrentino, L., Cafiero, L. and Iannace S. *Polym.Eng. Sci.* (2015).
17. Dhavalikar, R., Yamaguchi, M. and Xanthos, M. *J. Polym. Sci. Part A Polym. Chem.* 41, 958 (2003).
18. Reichelt, N., Stadlbauer, M., Folland, R., Park, C. B. and Wang, J. *Cell. Polym.* 22, 315 (2003).
19. Ramesh, N. S., Rasmussen, D.H. and Campbell, G.A. *Polym.Eng. Sci.* 34, 1685 (1994).
20. Ramesh, N. S., Rasmussen, D.H. and Campbell, G.A. *Polym.Eng. Sci.* 34, 1698 (1994).
21. Krause, B., Diekmann, K., van der Vegt, N. F. A. and Wessling, M. *Macromolecules* 35, 1738 (2002).
22. Krause, B., Koops, G.H., N.F.A., van der Vegt, N. F. A., Wessling, M., Wubbenhorst, M. and van Turnhout, J. *Adv. Mater.* 14, 1041 (2002).
23. Bouma, R. H. B., Nauta, W.J., Arnauts, J.E.F., van Den Boomgaard, T., Steuten, J.M. and Strathmann, H. *J. Appl. Polym. Sci.* 65, 2679 (1997).
24. Wang, J., Xingguo, C., Mingjun, Y. and Jiasong, H. *Polymer* 42, 8265 (2001).
25. Liu, L. C., Chuang, C. K. and Tsiang, R. C. C. *J. Polym. Res.* 11, 149 (2004).
26. Rodriguez-Perez, M. A., Duijsens, A. and De Saja, J. A. *J. Appl. Polym. Sci.* 68, 1237 (1998).
27. Nemoto, T., Takagi J. and Ohshima, M. *Polymer Engineering and Science* Vol.50, 12, 2408-2416 (2010).
28. Krause, B., Sijbesma, H. J. P., Munuklu, P., van der Vegt, N. F. A. and Wessling, M. *Macromolecules* 34, 8792-8801 (2001).

Figure Captions

- Figure 1. DSC traces from tests performed at 100 °C/min: A) Pristine samples; B) Annealed samples.
- Figure 2. Glass transition temperatures of pristine and annealed samples, and theoretical glass transition temperature trends from the Fox equation.
- Figure 3. Different magnifications of spherulites in TEM micrographs of blends after the annealing treatment: A) e B) PEEK 20/PEI 80 blend, C) e D) PEEK 30/PEI 70 blend.
- Figure 4. Results from sorption experiments: A) CO₂ uptake in PEEK/PEI blends for different solubilization times; B) CO₂ uptake in PEEK/PEI blends after 72 h of gas sorption at different solubilization pressures (80 and 120 bar).
- Figure 5. Evaluation of the T_g reduction after the CO₂ sorption process (solubilization performed at 80 bar for 72 hours) in the high pressure vessel: A) PEEK 20/PEI 80, B) PEEK 50/PEI 50.
- Figure 6. 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.
- Figure 7. A) DSC traces from the heating scan of selected foamed samples and B) Degree of crystallinity of PEEK/PEI blends in pristine and foamed samples, processed at 180 and 200 °C, as a function of the PEEK content.
- Figure 8. 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.
- Figure 9. Morphology of foams (foaming conditions: P_{sol}=120 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.
- Figure 10. Density of samples (solubilization pressure P_{sol}= 80 bar) foamed at different temperatures, as a function of the PEEK content.
- Figure 11. SEM micrograph of PEEK 30/PEI 70 foam, T_f= 265 °C.
- Figure 12. Morphological parameters (Mean size and Nucleated cells) from PEEK/PEI foams foamed at 200 °C: A) solubilization performed at P_{sol}= 80 bar B) solubilization performed at P_{sol}=120 bar.

Figure 13. Morphological parameters (Mean size and Nucleated cells) from PEEK 50/PEI 50 foams, as a function of the foaming temperature.

Tables

Sample	PEEK (wt%)	PEI (wt%)	Annealing Temperature (°C)	T _g (°C)	T _c (°C)	T _m (°C)	X _c (wt %)
Neat PEI	0	100		218.32	0	0	0
PEEK20/PEI80	20	80	294.0	198.45	286.81	334.47	2.44
PEEK30/PEI70	30	70	274.0	195.48	272.37	334.64	5.21
PEEK50/PEI50	50	50	236.0	170.94	236.38	339.59	5.15
PEEK70/PEI30	70	30	211.0	163.37	211.56	342.01	8.42
PEEK80/PEI20	80	20	199.0	149.83	195.02	339.45	13.45
Neat PEEK	100	0	171.0	144.10	171.32	345.12	28.23

Table 1. Blend composition (weight percent), annealing temperature, glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) and crystallization degree after normalization for the PEEK content (X_c) of neat polymers and PEEK/PEI blends from pristine samples.

Blend	T_g of the Plasticized Sample [°C]	T_g Reduction [°C]
Neat PEI	108.3	- 110
PEEK 20	120.8	- 80
PEEK 50	117.5	- 60
PEEK 70	114.5	- 50
Neat PEEK	92.2	- 50

Table 2. Glass transition depression after gas sorption at $P_{sol}=80$ bar in selected PEEK/PEI blend.