

Tailoring the morphology in partially and fully miscible mixtures of PEEK and PEI

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ABSTRACT

Over the last three decades, the vast body of work related to the control of the morphology of multiphase polymers has concentrated on systems that are inherently immiscible. On the other hand, detailed morphological studies of phase separation in miscible blends have been limited by the highly unstable nature of the structures generated as a function of time and temperature. In this work, we present one basic polymer system, with a slight variation in chemical structure, that allows for a high level of morphological tailoring and control in the miscible to partially miscible region. Two close isomeric forms of polyetherimides (PEI) yield fundamentally different types of morphologies in polyetheretherketone (PEEK)/PEI melt-processed multiphase systems: a partially miscible, phase-separated microstructure for the barely studied PEEK/*para*-PEI (*p*-PEI) system, and the typically reported fully miscible PEEK/*meta*-PEI system (*m*-PEI). The PEEK/*p*-PEI system displays sub- μm , matrix/dispersed phase or co-continuous types of morphologies, with the latter quickly coarsening over tens of μm in length scale under quiescent annealing conditions due to the PEEK/*p*-PEI interfacial tension, which was measured by the breaking thread method at 0.14 mN/m, one of the lowest values ever reported for a polymer pair. On the other hand, for the PEEK/*m*-PEI system, controlling the thermal annealing temperature promotes PEEK recrystallization and the formation of a nanostructured PEI-rich phase. Considering both types of blends, it is then possible to control the morphological length scale of PEEK and PEI domains over nearly 4 orders of magnitude, from ≈ 5 nm to over 15 μm . This is the smallest domain size ever reported for co-continuous systems. The selective extraction of the PEI phase then results in porous PEEK monoliths with full pore interconnectivity, with an average pore size spanning the same considerable range – without any interfacial modifier or block copolymer.

1. Introduction

Polyetheretherketone (PEEK) is a high-performance semi-crystalline polymer well known for its superior thermal and mechanical properties, high solvent resistance, and hence for its use in demanding environments and fields of applications such as biomedical implants or parts in the aeronautics sector. Polyetherimide (PEI) is also a high-performance polymer displaying a significantly higher glass transition temperature and lower costs than PEEK. However, its amorphous character results in lower chemical resistance and mechanical properties. PEI can also be added to PEEK via melt-processing to improve both its processability and thermal properties, while at the same time maintaining high solvent resistance and mechanical properties, with lower material costs.

The miscibility of PEEK/*meta*-polyetherimide (*m*-PEI) systems in their amorphous (melt) state has been confirmed by many authors using differential scanning calorimetry (DSC) [1–9] or dynamic mechanical analysis (DMA) [1,7,8,10] by the observation of a single glass transition temperature (T_g) following the additivity rule – a relatively rare feature in melt-processed polymer blends. Dielectric spectroscopy has also been used to confirm the miscibility of these polymers [5,11]. When analyzed

via infrared spectroscopy, the miscibility of this system has been explained, in part, by a specific interaction between the electron-rich ether functional groups in the PEEK repeating unit, and the electron-deficient imide ring in the *m*-PEI backbone [12], resulting in an interaction parameter (χ_{12}) ranging from -0.058 to -0.196 , promoting miscibility [13]. However, phase separation occurs when PEEK crystallizes – either from the melt state during cooling, or via cold crystallization – and provokes the expulsion and segregation of *m*-PEI. The crystallization of PEEK in this binary system is highly dependent on its molecular weight and the conditions applied, i.e., temperature, isothermal or dynamic crystallization from the melt or solid state, blend composition, blending technique, etc. The segregation of PEI has been reported, by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM), to occur between PEEK crystalline lamellae, fibrils, and/or spherulites – respectively designated as interlamellar, interfibrillar, and interspherulitic segregation, as illustrated in Scheme S1 [1,2,5,14]. The characteristic length scale of the resulting PEI-rich domains increases accordingly to the segregation mode, from a few nm to ≈ 1 μm [2]. As a result, the morphology is quite fine, even without the addition of an interfacial compatibilizing agent such as a block

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Table 1
PEEK and PEI main properties.

	Density ρ Room T (g/cm ³) ^a	M _w (g/mol)	Melt viscosity at 400 °C (Pa s) ^a	MFI at 337 °C (g) ^a	Torque at plateau (N·m) ^c	T _g (°C) ^d
PEEK	1.30	5.97×10^4 ^a	90	–	0.77	147
<i>m</i> -PEI	1.27	4.75×10^4 ^b	–	17.8	1.48	216
<i>p</i> -PEI	1.28	–	–	4.2	3.80	225
<i>p</i> -PEI 2	1.28	–	–	11	–	226

^a Provided by the supplier.

^b Measured by GPC in chloroform at 35 °C.

^c In internal mixer at 370 °C and 50 rpm.

^d Measured by DSC.

copolymer.

High-performance PEEK-based microporous membranes successfully capitalized on the finely tuned crystallization-induced phase separation process in PEEK/*m*-PEI blends [15–21] – a quite unique feature in melt-processed polymer blends. Ding and Bikson [17] were the first to report the use of a novel composite solvent (80 vol% 1-methyl-2-pyrrolidinone (NMP), 10 vol% ethanolamine, 10 vol% water) able to remove all of the *m*-PEI present in PEEK/*m*-PEI blends, via PEI depolymerization. Even interlamellar *m*-PEI could be removed, resulting in a very low average pore size of 11 nm. This range of pore sizes (10–40 nm) was further confirmed by several authors using the same composite solvent, at various blend compositions and crystallization temperatures [18,19]. To the best of our knowledge, there is however no systematic analysis on how blend composition and post-processing thermal treatment impact the resulting morphology, thermal and mechanical properties of bulk PEEK/*m*-PEI blends, and the resulting porosity once the PEI is extracted.

On the other hand, Nemoto et al. [22] reported relatively recently a novel binary system composed of PEEK and *para*-PEI (with a covalent link in *para* position instead of *meta* on its aromatic imide ring, see Supporting Information Scheme S2), which they qualified as immiscible in part because of the development of a phase-separated microstructure. DMA analysis revealed two peaks in the loss tangent curve, which the authors associated with immiscibility. However, the two peaks were shifted from the characteristic curves of the pure components (an increase of 10 °C for the PEEK-related T_g, and a decrease of 15 °C for the *p*-PEI-related T_g), suggesting a certain affinity between the two polymers – a feature that was not linked to potential partial miscibility by the authors however. TEM observations also revealed a fine sub-μm phase-separated microstructure quite reminiscent of immiscible polymer pairs displaying a very low interfacial tension. However, no additional data or work could be found in the literature on this particular system, and no attempts were made to extract the PEI phase to obtain porous PEEK materials, and to control the morphology by post-processing heat treatments, such as quiescent annealing.

It remains unclear for now why *p*-PEI behaves fundamentally differently when blended with PEEK, compared to *m*-PEI. In addition, the effects of blend composition and thermal treatment, both during and after melt processing, on the resulting microstructure, thermal and mechanical properties, are only partly understood in PEEK/*m*-PEI blends and remain mostly unknown for PEEK/*p*-PEI blends.

p-PEI offers a significant yet unexplored potential to generate entirely new morphological structures when melt-processed with PEEK, while preserving the fundamental characteristics of a PEEK/PEI system. The main objective of this work is to understand the impacts of composition and post-processing thermal treatment (both T and time) on the morphology, the thermal properties including the glass transition temperature, and the resulting mechanical properties of melt-processed blends of PEEK with either *meta*-PEI or *para*-PEI. Finally, this work assesses the possibility of preparing porous PEEK materials over an extended porosity range, from a few nm in average pore size to tens of μm, by controlling the morphology via composition and post-processing thermal treatments, followed by the selective extraction of both *m*-PEI and *p*-PEI.

2. Materials and methods

2.1. Materials

Polyetheretherketone (PEEK) 90G under pellet form was obtained from Victrex. Polyetherimides (pellet form) Ultem 1010 (*meta*-PEI or *m*-PEI), Ultem CRS 5001 (*para*-PEI or *p*-PEI) and Ultem CRS 5011 (*p*-PEI 2) were obtained from SABIC, the last two being sold as copolymers of PEI. Note that *p*-PEI was used for most of this work except for the breaking thread experiments (section 2.9) for which *p*-PEI 2 was used. The *para*-diamine composition of Ultem CRS 5001 was first reported by Nemoto et al. [22] and then by l'Abée et al. [23]. Table 1 summarizes some of their main properties.

2.2. Blend preparation

PEEK/*m*-PEI and PEEK/*p*-PEI binary blends were prepared over the full composition range. Prior to melt blending, all polymers were dried for 24 h under vacuum at 100 °C. In a typical mixing experiment, the materials were fed to a micro-compounder (DSM Xplore, mixing volume = 5 cc), with temperature and screw speed preset at 370 °C and 50 rpm, respectively. Based on previous experiments, once all the polymer pellets were added to the micro extruder, the mixing time was set at 6 min in recirculation mode. After blending completion, a ≈30 cm long filament was extruded and either quenched in an icy water bath or allowed to cool at room temperature (these samples are respectively designated as Q and N).

2.3. Quiescent annealing

Before a typical quiescent annealing experiment, ≈1 cm long pieces of quenched binary blend filaments were dried 24 h under vacuum at 100 °C. The pieces were then wrapped up in aluminum foil initially coated with a boron nitride-based releasing agent (Momentive, United States). Annealing was performed with a Carver high-temperature hydraulic press at temperatures ranging from 190 °C to 380 °C. Annealing protocols, specifically aiming at either increasing the crystallinity of PEEK and/or investigating the resulting nano- and microstructure due to phase separation in the PEEK/*m*-PEI binary blends, were performed for 5 min at different temperatures all inferior to the melting T of PEEK (345 °C). The samples were next cooled down in air until they reached room T, and are denoted as R (temperature value) °C. As for quiescent annealing protocols aiming at measuring the level of coarsening in PEEK/*p*-PEI binary blends, they were performed for different durations at 380 °C, over the melting T of PEEK. In this case, the samples were directly quenched in an icy water bath right after annealing to freeze in the morphology.

2.4. Thermal analysis

The neat polymers and their binary blends were analyzed by differential scanning calorimetry (DSC, TA instruments Q2000). The protocol consisted of two heat/isotherm/cool cycles: (1) heating from 50 °C to

380 °C at 10 °C/min, an isotherm of 5 min at 380 °C, cooling to 50 °C at 10 °C/min; (2) heating again to 380 °C at 10 °C/min, an isotherm of 1 min at 380 °C, and finally cooling to 50 °C at 10 °C/min. Glass transition temperatures (T_g) were measured as the inflection points of the baseline during the first and second heating ramps. The crystallinity χ based on the mass of the blend sample was calculated with Equation (1):

$$\chi = \frac{(\Delta H_m - \Delta H_{cc})}{\Delta H_f} \quad \text{Equation 1}$$

where ΔH_m is the specific melting enthalpy, ΔH_{cc} is the specific enthalpy of cold-crystallization upon heating, and ΔH_f is the theoretical heat of fusion of 100 % crystalline PEEK, taken as 130 J/g [24]. Alternatively, PEEK crystallinity based only on the PEEK mass present in each blend, χ_{PEEK} , was obtained from Equation (2):

$$\chi_{PEEK} = \frac{(\Delta H_m - \Delta H_{cc})}{\Delta H_f \times \omega_{PEEK}} \quad \text{Equation 2}$$

where ω_{PEEK} is the mass fraction of PEEK in the blend.

From the DSC analysis and based on Marin and Favis [25] work on partially miscible polymer systems, the compositions ω_i of the two separate $PEEK_{rich}$ and $p-PEI_{rich}$ domains can be calculated (Equations 3-4). The $PEEK_{rich}$ phase is designated as ' and the $p-PEI_{rich}$ phase as ". PEEK is designated as 1 and $p-PEI$ as 2:

$$\omega'_2 = \frac{T_{g2}(T_{g1} - T_{g'})}{T_{g'}(T_{g1} - T_{g2})} \quad \text{Equation 3}$$

$$\omega''_1 = \frac{T_{g1}(T_{g2} - T_{g'})}{T_{g'}(T_{g2} - T_{g1})} \quad \text{Equation 4}$$

where ω'_1 is the PEEK weight fraction in the $PEEK_{rich}$ phase, ω'_2 is the $p-PEI$ weight fraction in the $PEEK_{rich}$ phase, ω''_1 is the PEEK weight fraction in the $p-PEI_{rich}$ phase, ω''_2 is the $p-PEI$ weight fraction in the $p-PEI_{rich}$ phase, T_{g1} is the glass transition temperature of pure PEEK, T_{g2} is the glass transition temperature of pure $p-PEI$, $T_{g'}$ is the glass transition temperature of the $PEEK_{rich}$ phase and $T_{g''}$ is the glass transition temperature of the $p-PEI_{rich}$ phase.

Furthermore, Equations 5 and 6 have been adapted from the previously cited work by subtracting the proportion of crystallized PEEK, providing corrected global weight fractions of both $PEEK_{rich}$ and $p-PEI_{rich}$ domains:

$$\omega' = \frac{\omega_2 - \omega'_2(1 - \chi)}{\omega'_2 - \omega'_2} \quad \text{Equation 5}$$

$$\omega'' = \frac{\omega_2 - \omega'_2(1 - \chi)}{\omega'_2 - \omega'_2} \quad \text{Equation 6}$$

where χ is the level of PEEK crystallinity from Equation (1). ω' is the $PEEK_{rich}$ phase weight fraction in the blend, ω'' is the $p-PEI_{rich}$ phase weight fraction in the blend, ω_1 is the PEEK weight fraction in the blend and ω_2 is the $p-PEI$ weight fraction in the blend. It is assumed that the PEEK crystalline domains are pure and therefore are not considered in the partial miscibility phenomenon.

2.5. Gravimetric analysis

The continuity of the PEI in the blends was measured by gravimetric analysis, by extracting the PEI with a selective solvent. Typically, three ≈ 1 cm long pieces of blend filaments (≈ 100 mg total) were dried 24 h under vacuum at 100 °C and then weighed. The samples were subsequently deposited in a composite solvent (80 vol% 1-methyl-2-pyrrolidone, 10 vol% ethanolamine, 10 vol% deionized water) at 120 °C for 1 h [17]. The samples were then cleaned with ultrasounds three times for 1 min, first while immersed in their extraction solvent (1 min), then in 95 % ethanol (1 min), and finally in deionized water (1 min). The

samples were then dried again for 24 h under vacuum at 100 °C and weighed. For the most delicate samples (generally when the PEI volume fraction > 50 vol%), ultrasounds were not used during the cleaning process, which was instead repeated two times. Post-drying was also replaced with a 3-days freeze-drying step.

The continuity of the PEI was next calculated using Equation (7):

$$PEI \text{ continuity (\%)} = \frac{m_i - m_f}{m_i} \times \frac{m_{blend}}{m_{PEI \text{ in blend}}} \times 100 \quad \text{Equation 7}$$

where m_i is the mass of the sample before extraction, m_f is the mass after extraction, m_{blend} is the mass of the original blend, and $m_{PEI \text{ in blend}}$ is the mass of PEI in the original blend. It was noticed that PEEK absorbed some solvent during the extraction procedure, corresponding to ≈ 1 wt% for recrystallized PEEK, and 3.3 wt% for amorphous PEEK. Hence, a minor correction of sample mass loss was applied depending on the crystallinity and amount of PEEK in the samples.

2.6. Morphological analysis

Scanning electron microscopy (SEM, HITACHI Regulus 8220) was used to characterize the microstructure of the binary blends. Sample surface was prepared at room temperature using a Leica RM2165 microtome equipped with a glass knife. The observed surfaces were always at the center of the cross-sections of the filaments to limit the impact of the skin effect. The PEI phase was selectively extracted following the previous protocol (see Section 2.5) to improve contrast during observation. Finally, the samples were covered with ≈ 8 nm of carbon with a Leica EM ACE600 instrument, and observed at a 2 kV accelerating voltage and a 10 μ A current.

ImageJ 1.53 was used for image analysis to directly measure the diameter of the dispersed phase droplets, whereas the interfacial perimeter was measured for co-continuous phases. For co-continuous morphologies, the specific interfacial area S was calculated with Equation (8) [26]:

$$S = \frac{P}{A} \quad \text{Equation 8}$$

where P is the interfacial perimeter and A the total area of the micrograph. Finally, the average strut thickness d (or domain size) of the PEI co-continuous phases was calculated with Equation (9):

$$d = \frac{4 \times \Phi}{S} \quad \text{Equation 9}$$

where Φ is the PEI volume fraction in the blend. For dispersed phase morphologies, an average of the maximum and minimum Ferret diameters for at least 200 particles was calculated.

2.7. Gas sorption

For gas sorption analysis, binary blends samples (a total of ≈ 400 mg) were first subjected to the solvent extraction protocol to obtain porous PEEK samples (see Section 2.5). The samples were then dried and degassed for 24 h under vacuum at 100 °C and weighed. The measurements of adsorbed nitrogen inside the porous PEEK samples were performed with a TriStar 3000 gas sorption apparatus (Micromeritics), which allows the calculation of the specific surface area, the distribution in pore width, pore area, and pore volume.

2.8. Rheological measurements

Disks of PEEK and PEI (25 mm in diameter and 2 mm thick) were obtained by pressing dried pellets at 380 °C and 300 °C, respectively, using a Carver high-temperature hydraulic press. Amplitude, time, and frequency sweeps were performed at 375 °C under a nitrogen blanket to limit degradation on an MCR 302 rheometer (Anton Paar), equipped

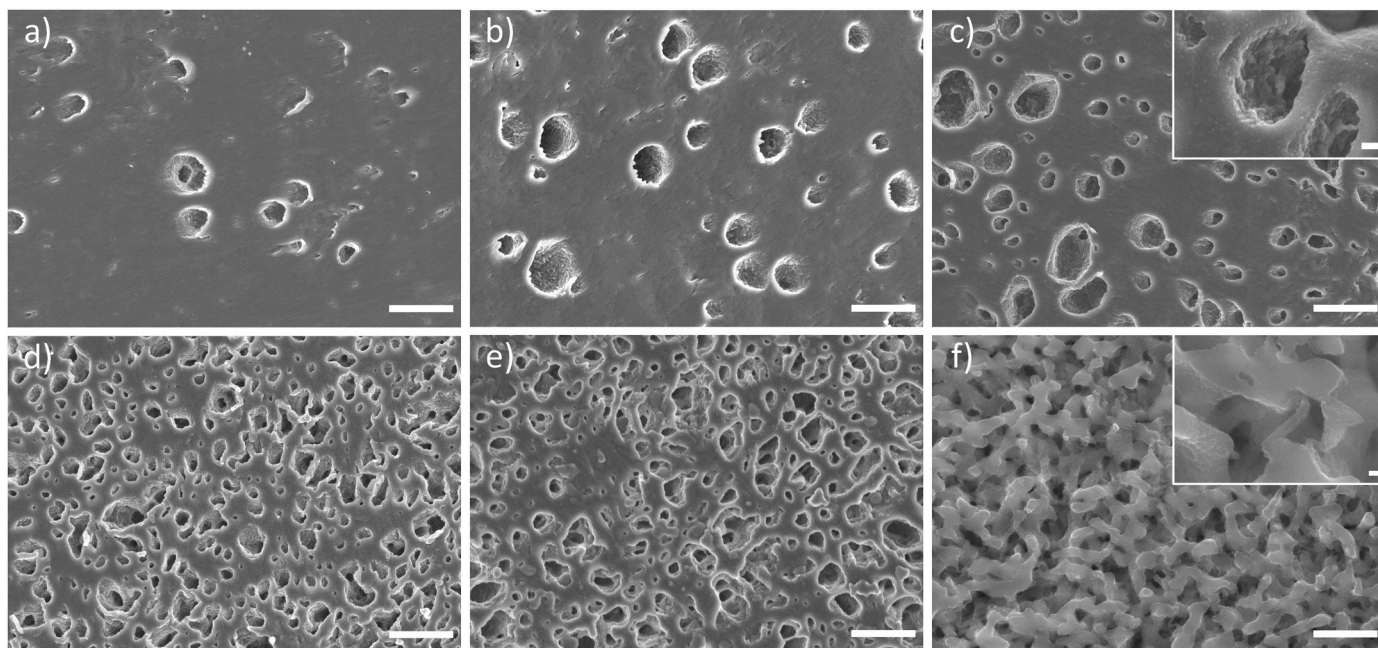


Fig. 1. Microstructure of PEEK/*p*-PEI N blends as revealed after the selective extraction of *p*-PEI. Compositions in vol%: a) 90/10; b) 80/20; c) 70/30; d) 60/40; e) 50/50; f) 40/60. White scale bars represent 1 μm for main magnification and 100 nm for the close-up inset micrographs.

with a CTD 450 oven and a 25 mm diameter parallel plate geometry. The validity of the Cox-Merz rule was assumed for all tested polymers [27–29]. Zero-shear rate viscosity values were obtained by performing at least three frequency-sweep tests at $\gamma_0 = 5\%$ and by extrapolating the Newtonian plateau value with a Carreau-Yasuda model.

2.9. Breaking thread method

Filaments of PEEK, with diameters ranging from 20 to 40 μm , were drawn by hand from pellets molten on a hot plate. Films of *p*-PEI_2 (Ultem CRS 5011) were pressed at 380 $^{\circ}\text{C}$ to perform the experiment, since *p*-PEI (Ultem CRS 5001) was too viscous to achieve acceptable experimental times. Typically, a 2 cm-long PEEK thread was sandwiched in between two 1 cm $\times$ 2 cm films of *p*-PEI, which was then placed on a microscope glass slide with a glass cover. The whole setup was inserted inside a Mettler FP-82HT hot stage controlled by a Mettler FP-90 Central Processor. Observations of the samples were carried out at 375 $^{\circ}\text{C}$ on a Nikon optical microscope. Digitalized images from the microscope were captured with a computer equipped with a Coreco Oculus image analysis system driven by the Visilog 4.1.3 image analysis software. From these acquired images, ImageJ 1.53 was used to measure the diameters and the wavelength of the observed distortions in relation to time.

According to theory, the interfacial tension (γ) can be calculated from Equations 10 and 11:

$$\gamma = \frac{q\eta_m D_0}{\Omega(p, \lambda)} \quad \text{Equation 10}$$

$$q = \frac{\ln\left(\frac{\alpha(t)}{\alpha_0}\right)}{t} \quad \text{Equation 11}$$

$$\text{where } \frac{\alpha(t)}{\alpha_0} = \frac{D_{\max}(t) - D_{\min}(t)}{D_{\max}(t_0) - D_{\min}(t_0)}$$

with q the growth rate of the distortions (α), η_m the zero-shear viscosity of the polymer films used in the experiment (see Section 2.8), D_0 the initial thread diameter, $\Omega(p, \lambda)$ is a reported function in Chappellear's 1964 article [30], α_0 the distortion amplitude at the beginning of the measurements, $\alpha(t)$ the distortion amplitude at time t , $D_{\max}$ is the maximum thread diameter during deformation, $D_{\min}$ is the minimum

thread diameter during deformation. The average of three maximum and two minimum successive diameters were used in the calculations of the distortion for a total of 6 performed experiments.

2.10. Tensile mechanical properties

The tensile mechanical properties were evaluated on a 3365 universal testing system (Instron) at a speed of 50 mm/min. Since the different compositions were not produced in sufficient quantity to manufacture tensile dogbone specimens to follow the ASTM D638 standard, 3 cm long pieces of the filaments cooled in ambient air during extrusion were used to perform the tensile tests. For each composition, at least 5 specimens were evaluated and their mechanical properties were averaged. To evaluate the impact of PEEK crystallinity on the mechanical properties, each composition was also mechanically tested after a thermal treatment of 30 min at 200 $^{\circ}\text{C}$, which was performed to increase PEEK crystallinity to its maximum without deforming the specimens.

3. Results and discussion

Fig. 1 shows the morphology of melt-processed PEEK/*p*-PEI blends cooled at room temperature (N) after exiting the micro-compounder, for compositions ranging from 90/10 vol% to 40/60 vol%, after the selective extraction of *p*-PEI (note that no obvious difference was observed for blends quenched in ice-cold water). The PEEK/*p*-PEI system displays the microstructure of a classical immiscible blend with two distinct phases clearly observable – quite different from the fully miscible PEEK/*m*-PEI system typically reported in the literature and presented below as a point of comparison [1–9]. There is an increase in the visual connectivity of the *p*-PEI phase when its volume fraction in the blend increases. From 60/40 vol% to 40/60 vol% (Fig. 1d–f), the *p*-PEI phase appears continuous. Since PEEK is the major component in Fig. 1 d) and e), the two compositions display similar features. Close-up micrographs reveal a rather rough texture at the interface, which could be the result of solvent-induced crystallization of PEEK at high temperature (based on [19] and confirmed by DSC analysis of PEEK/*m*-PEI performed before and after extraction). The *p*-PEI dispersed phase shows a constant size of

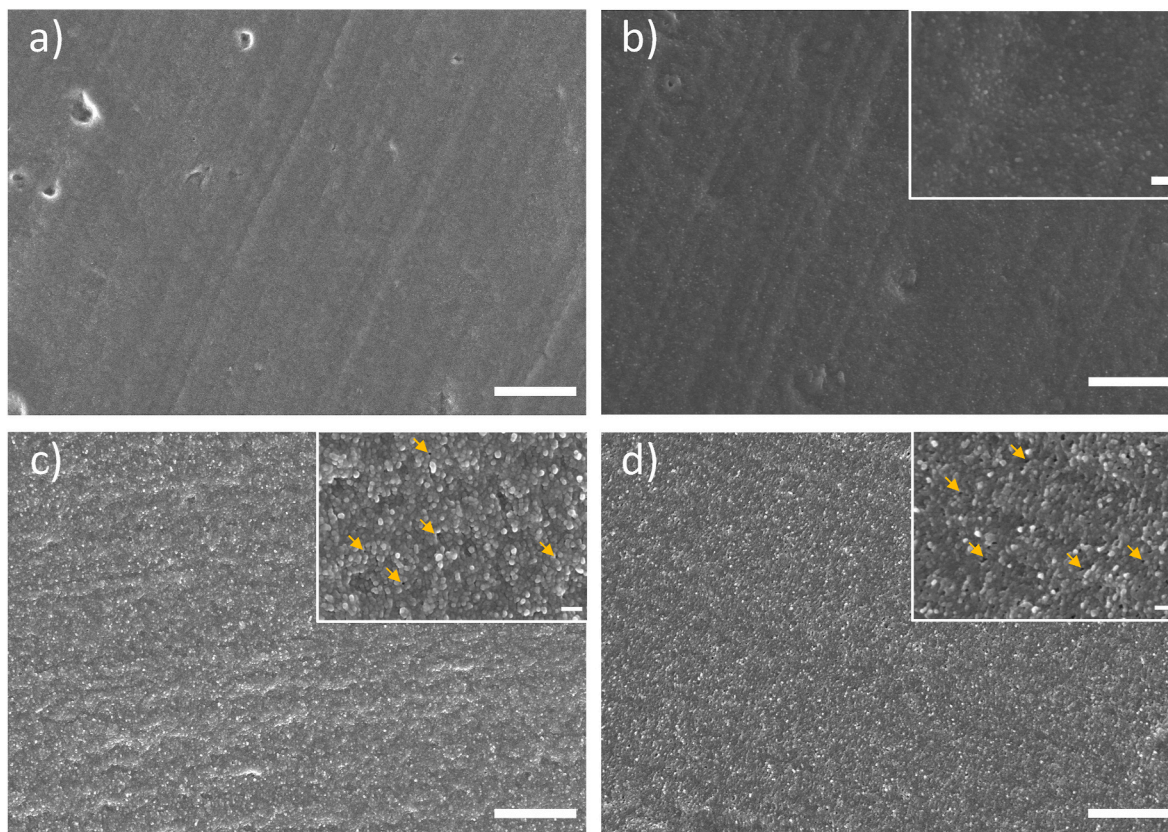


Fig. 2. Microstructure of PEEK/*m*-PEI blends quenched in cold water at the exit of the micro-compounder, as revealed after the selective extraction of *m*-PEI. Compositions in vol%: a) 70/30; b) 50/50; c) 40/60; d) 30/70. White scale bars represent 1 μm for main magnification and 100 nm for the close-up inset micrographs. Yellow arrows indicate mesopores resulting from the extraction of *m*-PEI. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

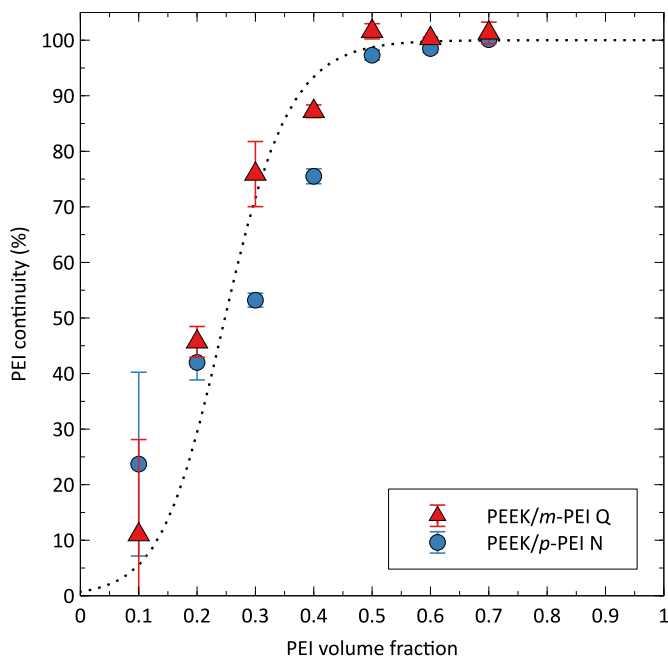


Fig. 3. PEEK/(*m*- or *p*-)PEI co-continuous morphology development curves based on gravimetric results by solvent extraction. The dotted line is a guide for the eye.

approximately 300 nm independently of the blend composition, which is quite fine compared to what is usually observed for fully immiscible polymer blends. Regarding PEEK domains, based on the 40/60 vol% composition (Fig. 1f), the domain size is closer to 150 nm. To the authors' knowledge, this is the first time that such porous PEEK monoliths are obtained from binary melt-processed blends.

In comparison, Fig. 2 presents the morphology of melt-processed PEEK/*m*-PEI blends quenched in an icy water bath after exiting the micro-compounder, for compositions ranging from 70/30 vol% to 30/70 vol%, and after the selective extraction of the *m*-PEI material. For all compositions, the samples appear homogeneous with no distinctive features or evolution of the apparent microstructure, which is consistent with the full miscibility reported for this binary pair over the years [1–9]. Closer inspection reveals small pores of 7–8 nm in diameter for the 40/60 vol% blend, and 8–15 nm for the 30/70 vol% compositions, as higher magnifications illustrate (Fig. 2c and d).

The scale of the nano/microstructure is then completely dependent on the type of PEI melt-blended with PEEK: a sub- μm morphology is obtained with *p*-PEI, whereas *m*-PEI gives rise to a nanoscale/molecular scale structure. Note that nodules of PEEK of 15–30 nm in size are also visible on the surface, which is again the result of solvent-induced PEEK crystallization, where the nodules are composed of crystalline and amorphous PEEK (Huang et al. [19] reported 6.3 nm from XRD, and Olley et al. [31] reported 15.9 nm from etching). However, the characteristic length scale of the nano/microstructure is not impacted by the extraction procedure.

Fig. 3 quantifies the development of the co-continuous morphology for the two systems, by measuring the amount of extracted PEI, as a function of composition. The percolation threshold is quite low for both systems, as low as 10 vol% of PEI, whereas full co-continuity is reached

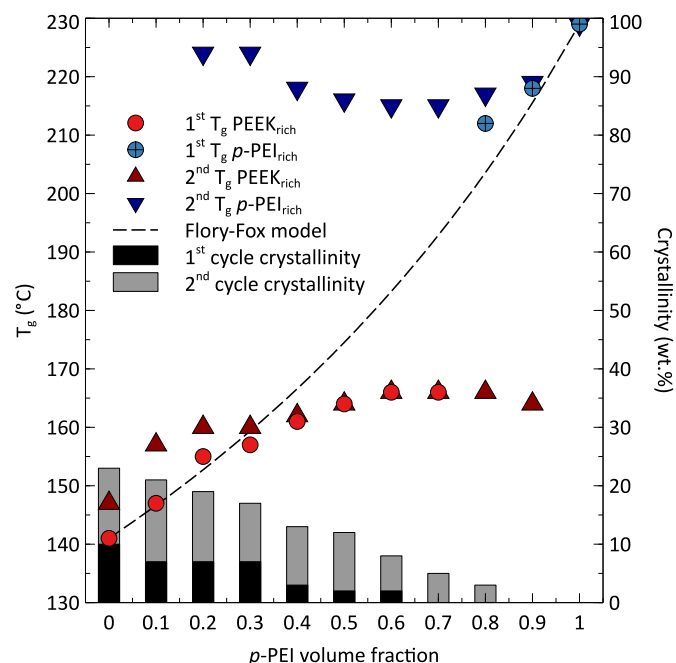


Fig. 4. Glass transition temperatures and total material crystallinity for the 1st and 2nd DSC cycles as a function of *p*-PEI volume fraction for PEEK/*p*-PEI quenched system.

at about 50 vol% in both cases. Both *m*-PEI and *p*-PEI already form highly continuous networks at 30 vol% (see Fig. 1c–f for *p*-PEI, and Fig. 2 for *m*-PEI). Over 70 vol% of PEI, the samples either collapsed (for *m*-PEI as the PEEK network was too tenuous) or lost their integrity, indicating the formation of a dispersed PEEK phase in a *p*-PEI matrix (phase inversion).

Due to the miscibility of *m*-PEI in PEEK, the PEEK monoliths obtained after *m*-PEI solvent extraction display one of the finest continuous porosity reported in the literature – without any interfacial modifier or block copolymer [17]. Whereas *m*-PEI forms a continuous network at the molecular level in the blend or forms a network during the extraction process due to local PEEK recrystallization remains unclear at this point.

For *p*-PEI, such a low value of the percolation threshold, combined with its sub- μ m microstructure, again points to a partially miscible system displaying a low interfacial tension [25,32]. The capacity to extract PEI at such fine scales comes from the solvent composition, which depolymerizes the PEIs and allows a more efficient and complete extraction.

Fig. 4 presents the glass transition temperatures and total material crystallinity for PEEK/*p*-PEI blends initially quenched in cold water (results of the 1st DSC cycle) and after a second run (2nd DSC cycle) - see also Supporting Information Figure S1 for the complete thermograms. First, both 1st and 2nd heating cycles show composition-dependent T_g 's, confirming a certain level of interaction between PEEK and *p*-PEI. However, these T_g 's present a strong deviation from the Fox equation for fully miscible blends (dotted curve): they are shifted compared to the values of the pure components and form two distinct sets with one closer to the T_g of pure PEEK (141 °C or 147 °C), and the second closer to the value of pure *p*-PEI (229 °C) which, combined with the fine sub- μ m morphology (Fig. 1), confirm partial miscibility for this pair. This behavior is also reported for a few other polymer pairs, such as poly (methyl methacrylate) and polycarbonate [25,33]. As a result, two phases of mixed compositions are formed: a PEEK rich (denoted PEEK_{rich}) and a *p*-PEI rich (denoted *p*-PEI_{rich}) phases.

For the 1st heating cycle, the T_g of the PEEK_{rich} phase gradually increases with the composition in *p*-PEI, due to the increased composition of *p*-PEI in the PEEK_{rich} phase – until it could not be detected over

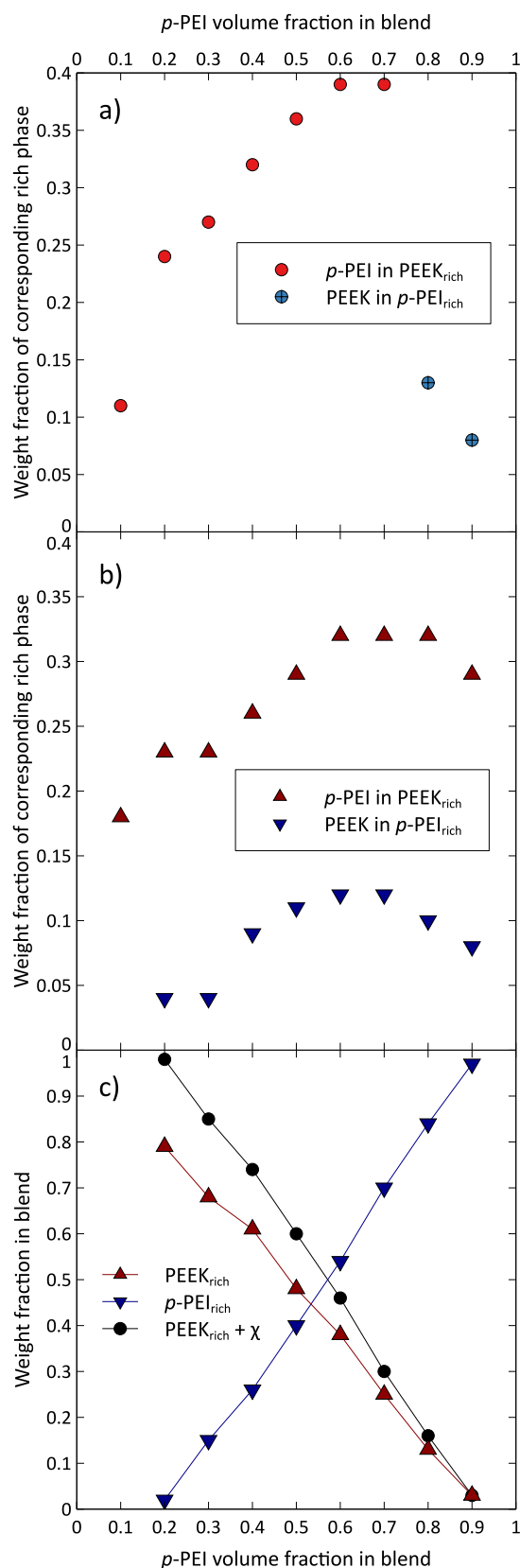


Fig. 5. Weight fraction compositions of the PEEK_{rich} and *p*-PEI_{rich} phases calculated from a) T_g 's from the 1st DSC heating cycle; b) T_g 's from the 2nd DSC heating cycle. c) Weight fractions of the PEEK_{rich} and *p*-PEI_{rich} phases in the total blend, with or without the addition of PEEK crystallinity, calculated from the 2nd DSC heating cycle melting peak and rich phases compositions.

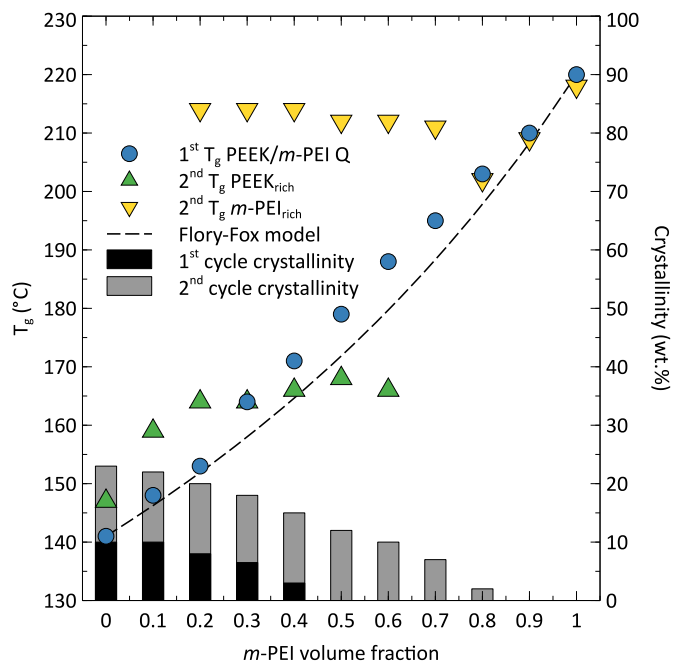


Fig. 6. Glass transition temperatures and total material crystallinity for 1st and 2nd DSC cycles as a function of *m*-PEI volume fraction for PEEK/*m*-PEI quenched system.

70 % of *p*-PEI. For the *p*-PEI_{rich} phase, the *T_g* decreases as PEEK is added to the blend, as expected. Note however that the *T_g* of the *p*-PEI_{rich} phase could not be measured during the 1st heating cycle, from 10 vol% to 70 vol% *p*-PEI, because of the PEEK cold-crystallization exothermic peak

masking the *p*-PEI_{rich} *T_g* on the DSC thermograms.

Two *T_g*'s can also be observed during the 2nd heating cycle, one associated with PEEK_{rich} domains around 160 °C, and the other related to *p*-PEI_{rich} domains around 217 °C. We also note the higher crystallinity of PEEK after the 1st cycle, and the increased range of measurable *T_g*'s (especially for the *p*-PEI_{rich} phase). Subtle differences also appear compared to the 1st heating cycle: (1) the *T_g* of pure PEEK increases due to recrystallization, as reported in other publications [1,34], whereas it remains constant for pure *p*-PEI (an amorphous polymer); (2) the PEEK_{rich} *T_g*'s slightly increase for *p*-PEI compositions between 10 % and 40 vol%, then stabilizes; (3) the *p*-PEI_{rich} *T_g*'s also slightly increase, for the two compositions that could be analyzed (10 % and 20 % PEEK); (4) the *T_g* of the *p*-PEI_{rich} phase also reaches a minimum around 60 %–70 % *p*-PEI overall, and increases again as the composition in PEEK increases. Finally, note that PEEK crystallinity and recrystallization become negligible over 80 % *p*-PEI. A PEEK-rich dispersed phase is also detected at a content as low as 10 vol%, indicating a phase-separated morphology. However, selectively extracting the PEEK phase to observe the morphology was impossible due to the lack of a selective solvent.

These differences between the 1st and 2nd cycles are mainly due to PEEK recrystallization and *p*-PEI expulsion from the PEEK crystalline domains. For the PEEK_{rich} domains at high overall PEEK content, the *T_g* increases both due to PEEK recrystallization, as mentioned earlier, and enrichment of the amorphous PEEK domains with the expelled *p*-PEI. Over 40 % of *p*-PEI, the *T_g*'s of the 1st and 2nd cycles become practically identical, suggesting that both crystallization of PEEK and expulsion of *p*-PEI are less important compared to the effect of the already initially present *p*-PEI in the PEEK-rich phase. For the *p*-PEI_{rich} domains, the differences in *T_g* between the 1st and 2nd cycles are more difficult to interpret since the data for the 1st cycle are only available at 80 % and 90 % *p*-PEI.

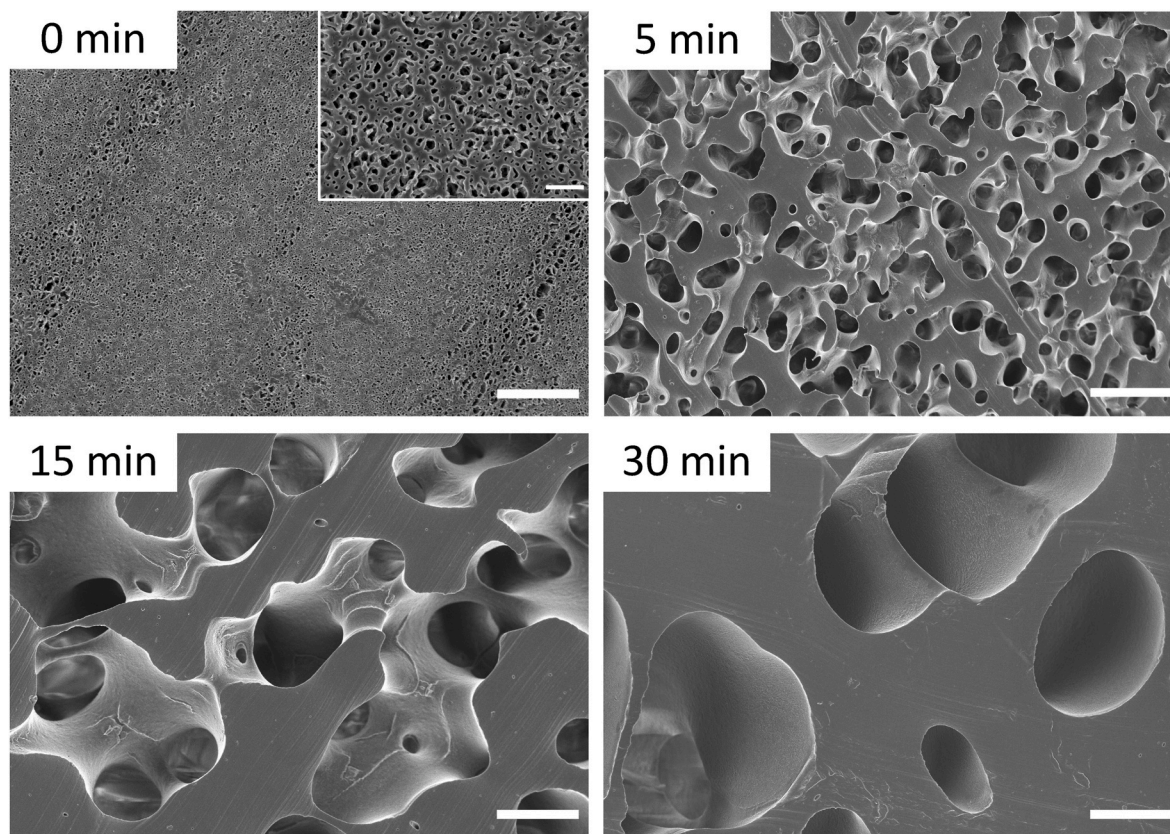


Fig. 7. Microstructure of PEEK/*p*-PEI 50/50 blend, initially quenched, for different times spent under quiescent annealing at 380 °C. White scale bars represent 10 μm for main magnification and 1 μm for the close-up inset micrograph.

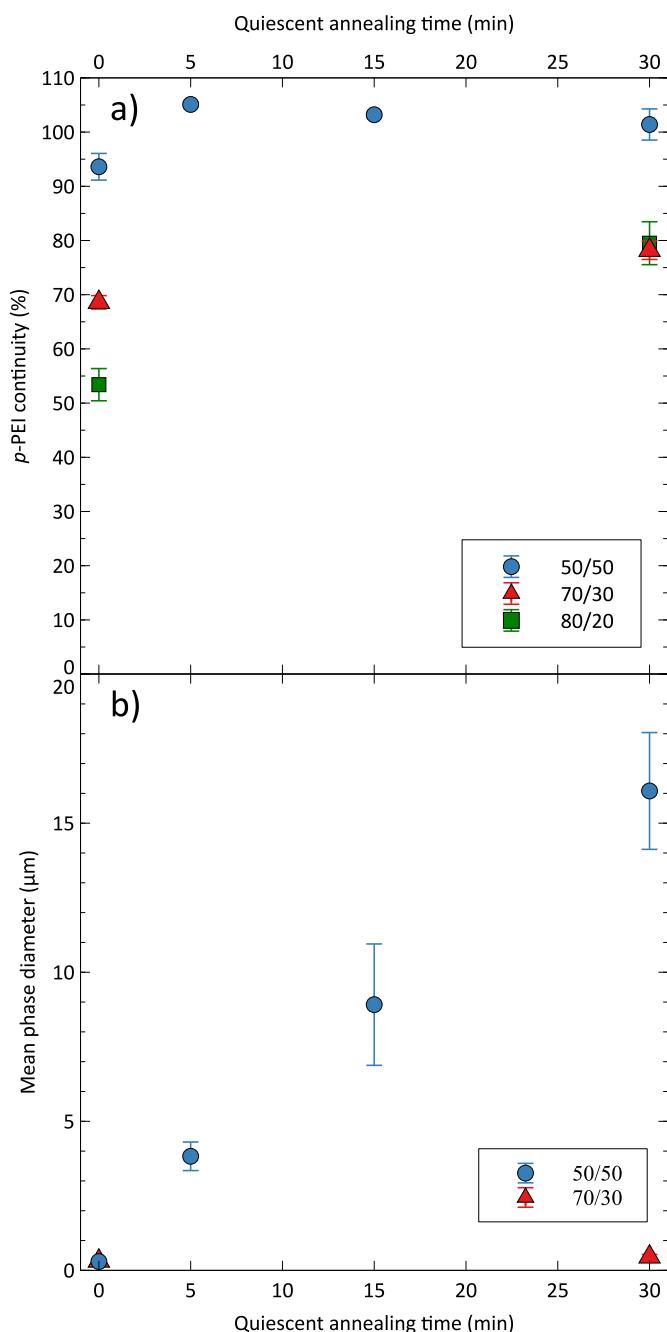


Fig. 8. a) *p*-PEI continuity and b) its average phase diameter, as a function of quiescent annealing time, at 380 °C for three PEEK/*p*-PEI compositions initially quenched.

Fig. 5a and b presents the compositions of the PEEK_{rich} and *p*-PEI_{rich} phases, as a function of the overall *p*-PEI composition. These compositions were calculated based on the Tg's measured by DSC, following Equations (3) and (4) presented in Section 2.4. Since in the first heating cycle of DSC measurements (Fig. 4), the Tg of the *p*-PEI_{rich} phase is only measurable for 10 % and 20 % of *p*-PEI, determining the PEEK weight fraction in this phase is limited to these two compositions. The results show that there is always more *p*-PEI dispersed in the PEEK_{rich} phase than PEEK dispersed in the *p*-PEI_{rich} phase. For both phases, the minor component's composition reaches a maximum between 60 % and 70 % of *p*-PEI in the blend. Note also that between 10 % and 70 % of *p*-PEI, the increase and maximum weight fraction of *p*-PEI in the PEEK_{rich} phase is more pronounced for the first DSC heating cycle compared to the second

heating cycle. This arises from the larger differences between the blends' Tg's and Tg of pure PEEK in the first heating cycle, compared to the second heating cycle. Indeed, during the second heating cycle, PEEK has recrystallized, increasing its Tg, which in turn decreases the calculated amount of *p*-PEI in the PEEK_{rich} phase (Equations (3) and (4)).

Fig. 5c presents the weight fractions of the PEEK_{rich} and *p*-PEI_{rich} phases in the blends. These results were obtained from Equations (5) and (6) presented in Section 2.4, which subtract the amount of crystallized PEEK from the PEEK_{rich} and *p*-PEI_{rich} phases. A third curve is thus added where the PEEK's crystallinity is fully attributed to the PEEK_{rich} domain, since the PEEK composition in the *p*-PEI_{rich} phase is always inferior to 15 wt% (≈15 vol%), and because PEEK does not recrystallize in *p*-PEI at such compositions (see Fig. 4). From the results, it can be observed that above 55 vol% of *p*-PEI in the blend, the PEEK_{rich} domain becomes the minor one, which is corroborated by the SEM observations made in Fig. 1f and the fact that at higher *p*-PEI volume fractions it is impossible to obtain a porous PEEK monolith via extraction. Values lacking at 10 vol% *p*-PEI is due to the difficulty in measuring the Tg of the *p*-PEI_{rich} phase at this composition.

An apparent discrepancy is also observed at low *p*-PEI compositions (≤20 vol%), suggesting the absence of a *p*-PEI_{rich} phase, and nearly full blend miscibility. This is indeed not the case, as the SEM micrographs of Fig. 1 show. Further analysis of Equations (3) and (4), based on the Flory-Fox equation predicting the Tg of miscible homopolymers, and Equations (5) and (6), are probably required in this case and will be addressed in a future work.

In Fig. 6, the Tg's and total crystallinity for PEEK/*m*-PEI quenched blends are presented (see Supporting Information Figure S2 for the thermograms). On the 1st cycle, only one Tg is observed for all compositions, and it nearly follows the Fox equation (with a slight positive deviation), which confirms that PEEK/*m*-PEI systems are miscible in the melt state over the full composition spectrum. This agrees with previously published works [1–9]. The initial crystallinity is also relatively low (with a maximum of 10 % for pure PEEK), and the blends are fully amorphous above 40 vol% of *m*-PEI, which differs from the PEEK/*p*-PEI system presented in Fig. 4 which shows crystallinity up to 60 vol% of *p*-PEI.

During the 2nd cycle, two sets of Tg's are observed. They are also shifted compared to the pure components: up for the PEEK_{rich} phase and down for *m*-PEI_{rich} phase, compared respectively to pure PEEK and *m*-PEI, with each phase containing minor amounts of *m*-PEI and PEEK, respectively. This phase separation is the result of PEEK crystallization, as demonstrated previously [1,2,5] and as observed also for the PEEK/*p*-PEI system. This crystallization creates interlamellar regions rich in PEEK but containing a small amount of *m*-PEI, responsible for the lower Tg, and interfibrillar/interspherulitic regions rich in *m*-PEI but containing small amounts of PEEK, responsible for the higher Tg (Scheme S1) [35]. The Tg's reach plateau values between 20 vol% and 70 vol% of *m*-PEI. No *m*-PEI_{rich} Tg is observed at 10 vol% of *m*-PEI either because it is too faint to be detected or because all of the *m*-PEI is present in the PEEK_{rich} phase and only contributes to the PEEK_{rich} Tg (similar observation for the PEEK_{rich} Tg above 70 vol% of *m*-PEI).

The Tg of the *m*-PEI_{rich} phase decreases between 70 vol% and 80 vol% of *m*-PEI, and increases again at 90 vol%. Two potential contributions are that PEEK does not crystallize sufficiently anymore, remaining mainly amorphous and enriching the *m*-PEI_{rich} phase, lowering its Tg. However, as the *m*-PEI content keeps increasing, the PEEK content decreases and the *m*-PEI_{rich} Tg increases towards the value of pure *m*-PEI, explaining the minima observed at 80 vol% *m*-PEI.

Fig. 7 shows the coarsening of the co-continuous PEEK/*p*-PEI 50/50 vol% blend microstructure, as a function of quiescent annealing time at 380 °C (blend initially quenched). Even if the system is partially miscible, it significantly coarsens, from sub-μm to over 15 μm domains after 30 min of annealing time. The rate of coarsening appears surprisingly fast considering the expected low interfacial tension, which is the coarsening driving force. Furthermore, Fig. 8 confirms that the

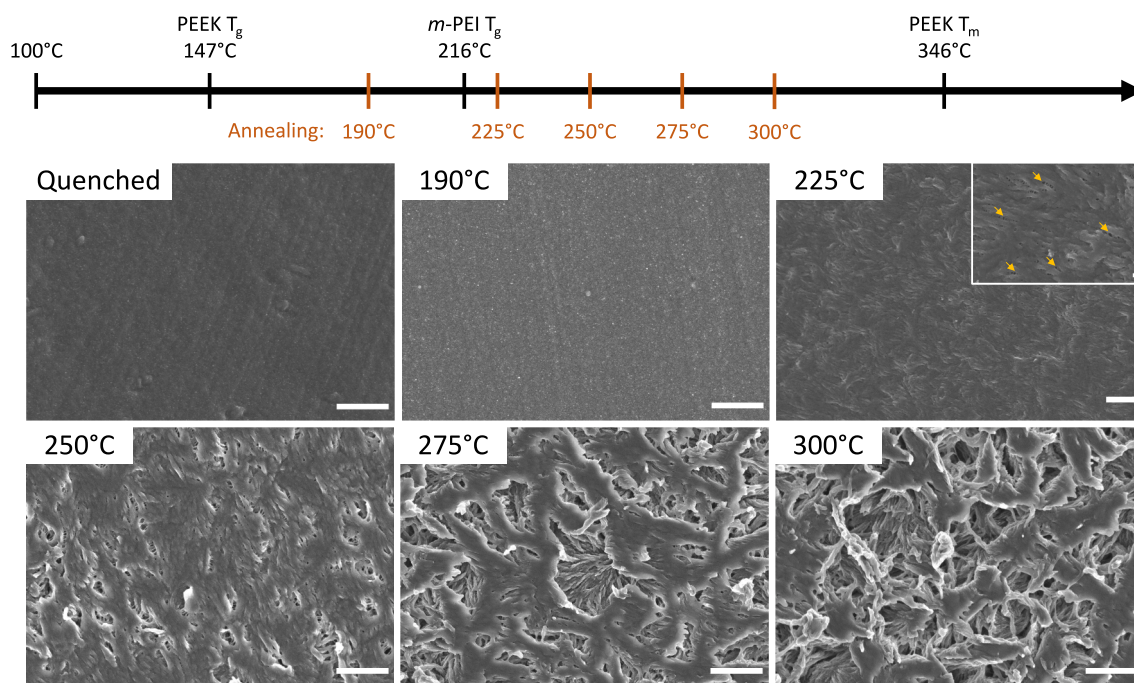


Fig. 9. Microstructure of PEEK/*m*-PEI 50/50 blend as a function of annealing temperature, compared to the initially quenched blend at the exit of the micro-compounder. White scale bars represent 1 μm for main magnification and 100 nm for the close-up micrograph. Yellow arrows indicate mesopores. Note that the *m*-PEI was selectively extracted to enhance contrast. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

continuity of the *p*-PEI phase is maintained during the coarsening process for the 50/50 blend and remains quite high (and even increases) for 30 % and 20 % *p*-PEI. To the authors' knowledge, this is the first time that the coarsening process in partially miscible bulk polymer blends has been reported in the literature.

Fig. 8 presents the evolution of *p*-PEI continuity and the average phase diameter as a function of quiescent annealing time, at 380 $^{\circ}\text{C}$, starting from blends initially quenched in cold water. As the results show, the *p*-PEI phase in the 50/50 blend remains fully continuous even after 30 min of annealing time (results slightly higher than 100 % are caused by the removal of PEEK present in the *p*-PEI_{rich} phase during the solvent extraction protocol). The maintained continuity is accompanied by a quasi-linear increase in the *p*-PEI phase diameter, from $0.29 \pm 0.08 \mu\text{m}$ in the quenched state to $16 \pm 2 \mu\text{m}$ after 30 min of annealing time [36,37]. For the 70/30 composition, a slight increase in continuity is observed for the *p*-PEI phase after 30 min of annealing, with the *p*-PEI dispersed phase diameter only increasing marginally from $0.31 \pm 0.06 \mu\text{m}$ to $0.45 \pm 0.08 \mu\text{m}$. Such high continuity results, even at low *p*-PEI contents, could be explained by a certain level of connectivity between the *p*-PEI_{rich} dispersed phase droplets, via the miscible fraction of *p*-PEI present in the PEEK_{rich} matrix phase – indeed, the solvent can extract the *p*-PEI at a molecular level present in the PEEK_{rich} phase, which could link the droplets together in a network. To the best of the authors' knowledge, this is the first time that such porous PEEK monoliths, with precise control over pore size - over an extended range, from 300 nm to 15 μm and more for longer annealing times - and pore interconnectivity, have been reported in the literature.

The breaking thread (BT) method was then employed to measure the PEEK/*p*-PEI interfacial tension (following the procedure explained in Section 2.9) and a value of $0.14 \pm 0.04 \text{ mN/m}$ was obtained for the PEEK/*p*-PEI₂ system. This value is especially low compared to classical immiscible polymer blends but can be expected for the partially miscible behavior of this system. In comparison, Lee and Kim [33] reported a value of 1.02 mN/m for a PC/PMMA system, which is a well-known partially miscible polymer blend. Although the thermal stability of the

p-PEI posed some problems during the BT experiments, complementary experiments demonstrated that the overall impact on the interfacial tension value was relatively minor and did not affect the main conclusions (see Supporting Information, Section 4).

In comparison, Fig. 9 presents the microstructure evolution for the PEEK/*m*-PEI 50/50 composition for five different annealing temperatures (all below the melting T of PEEK), compared to the initially quenched blend at the exit of the micro-compounder: 190 $^{\circ}\text{C}$ (above the T_g of PEEK but below the T_g of *m*-PEI), 225 $^{\circ}\text{C}$ (slightly over the T_g of *m*-PEI), 250 $^{\circ}\text{C}$, 275 $^{\circ}\text{C}$, and 300 $^{\circ}\text{C}$. At 190 $^{\circ}\text{C}$, PEEK can crystallize but chain mobility remains very limited for the *m*-PEI phase – no significant difference is noticed compared to the quenched blends after *m*-PEI extraction. PEEK can only form crystalline lamellae with *m*-PEI trapped in between because of the very limited chain mobility.

Above the T_g of *m*-PEI at 216 $^{\circ}\text{C}$, both PEEK crystallization and increased *m*-PEI molecular chain mobility occur. At 10 $^{\circ}\text{C}$ above the *m*-PEI T_g , e.g. 225 $^{\circ}\text{C}$, differences between the annealed and initially quenched samples start to appear. The PEEK crystalline microstructure is now easier to distinguish and mesopore formation becomes apparent, left by the *m*-PEI extracted from PEEK interfibrillar spaces ($\approx 20 \text{ nm}$, see inset showing a magnified view in Fig. 9 at 225 $^{\circ}\text{C}$) (Mehta et al. [15] and Ding and Bikson [17] observed 11 nm pores after annealing at 250 $^{\circ}\text{C}$). *m*-PEI now has sufficient molecular mobility to move out of PEEK during fibrillae growth.

By increasing the temperature again, both *m*-PEI and PEEK continue to gain in mobility, which promotes the formation of PEEK spherulites and the progressive expulsion of *m*-PEI in the newly formed interspherulitic spaces, increasing the size of *m*-PEI_{rich} domains – this is especially apparent at 275 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$. The shape of the pores changes at this point, from circular mesopores, to larger but still narrow pores, as observed for example in crystallized PVDF templates prepared from miscible polymer systems [38,39]. The characteristic domain sizes of both PEEK_{rich} and *m*-PEI_{rich} phases significantly increase as the annealing temperature increases, from the nm scale, up to the μm scale. This means that the microstructural length scale can be controlled over three

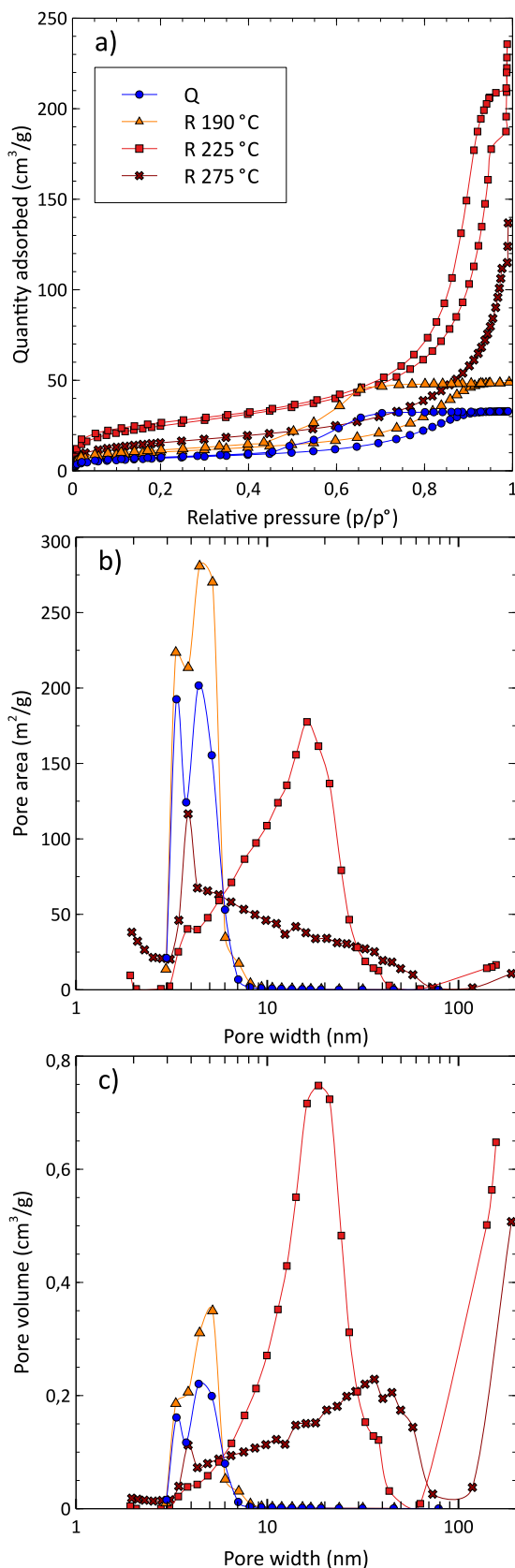


Fig. 10. a) Quantity of adsorbed nitrogen as a function of relative pressure, b) pore area as a function of pore width, and c) pore volume as a function of pore width, obtained from gas sorption experiments on porous PEEK monoliths prepared from PEEK/*m*-PEI 50/50 blend, from the initial quenched state or annealed at different temperatures.

orders of magnitude with simple heat treatments.

These structural features are supported by the DSC data (Fig. 6), which show that PEEK recrystallization drives phase separation and results in the formation of a crystalline PEEK phase, an amorphous interlamellar PEEK_{rich} phase containing *m*-PEI, and an amorphous interfibrillar/interspherulitic *m*-PEI_{rich} phase containing PEEK (probably mostly amorphous also).

Fig. 10 presents the results of gas sorption experiments on porous PEEK monoliths prepared from the PEEK/*m*-PEI 50/50 blend by *m*-PEI extraction, in the quenched state and after annealing at different temperatures. According to IUPAC, the isotherm curves obtained for the quenched sample and the sample annealed at 190 °C (R 190 °C) are of type IV(a), with H1 or H2(a) hysteresis, which corresponds to mesoporous adsorbents. The R 225 °C and R 275 °C samples present composite type IV and type II isotherms, revealing the presence of macropores [40]. These qualitative features are in agreement with the morphological features displayed in Fig. 9.

The pore size distributions - Pore area vs Pore width (Fig. 10b) and Pore volume vs Pore width (Fig. 10c) - were calculated from the desorption isotherm curves using the Barrett, Joyner and Halenda (BJH) method. The results reveal the presence of mesopores of 2–4 nm for the quenched and R 190 °C samples, with similar quantities of adsorbed nitrogen, supporting the similar, homogeneous appearances observed in Fig. 9. The R 225 °C sample shows a higher quantity of adsorbed nitrogen and a wider pore width distribution, centered around 20 nm and extending up to 40–50 nm, and even over 100 nm, in accordance again with SEM observation. The last sample (R 275 °C) adsorbs less nitrogen than R 225 °C. It shows an even broader pore width distribution, with a maximum arising around 3 nm (in Fig. 10b) and another one centered around 35 nm (in Fig. 10c), extending well over 100 nm in both cases – the morphology is now quite open and shows the presence of macropores. However, it was not possible to extend the measurements over 100 nm.

Table 2 summarizes the main results of the gas sorption experiments performed on the PEEK/*m*-PEI 50/50 blend. An estimation of the expected cumulative pore volume, based on the PEEK and *m*-PEI densities at room temperature (see Table 1), gives a value of approx. 0.39 cm³/g, which is close to the result obtained for the R 225 °C sample (0.37 cm³/g). However, the R 275 °C sample presented a lower value of 0.21 cm³/g, which is explained by unaccounted macropores over 100 nm (as Fig. 9 shows).

However, the cumulative pore volume is quite lower for the quenched and R 190 °C samples, compared to the expected calculated value. Apart from pore tortuosity that might restrict nitrogen diffusion, another reason could be the reduction of sample dimensions during drying, i.e. pore collapsing, which was observed after the final drying step in the oven – estimated in between 25 % and 40 % of the total volume for the quenched blend. Such collapsing is thought to come from the capillary forces exerted by the solvent during evaporation in the oven, combined with the more fragile and fine nanostructure of the quenched and R 190 °C blends (compared to the coarser and more solid microstructure of blends annealed at 225 °C and 275 °C). The effect was significantly reduced when using freeze-drying, with only 7 %–13 % of volume reduction. Indeed, after freeze-drying, the cumulative pore volume of the R 190 °C sample increases from 0.08 cm³/g to 0.38 cm³/g, almost matching the theoretical value – with a surface area reaching a maximum of 154 m²/g, amongst the highest values reported for microporous polymer monoliths prepared from melt-processed polymer blend. In comparison, Mehta and Kalika [16] performed mercury porosimetry experiments on similar materials and obtained an equivalent value of 0.28 cm³/g.

Thermal annealing of a PEEK/*m*-PEI 30/70 blend exacerbates the previous morphological features, as Fig. 11 illustrates. After full *m*-PEI extraction and freeze-drying, for example, mesopores of roughly ≈12 nm are already apparent in the quenched sample, as indicated by the yellow arrows in the close-up micrograph. At 10 °C above the T_g of *m*-

Table 2

Gas sorption analysis summary.

	<i>Q</i>	<i>R</i> 190 °C	<i>R</i> 190 °C freeze dried	<i>R</i> 225 °C	<i>R</i> 275 °C
Surface Area BET (m ² /g)	25	38	154	90	57
Surface Area BJH Desorption (m ² /g)	46	69	276	94	61
Cumulative pore volume (cm ³ /g)	0.05	0.08	0.38	0.37	0.21
Average pore width (nm)	4.5	4.4	6.7	15.5	14.1

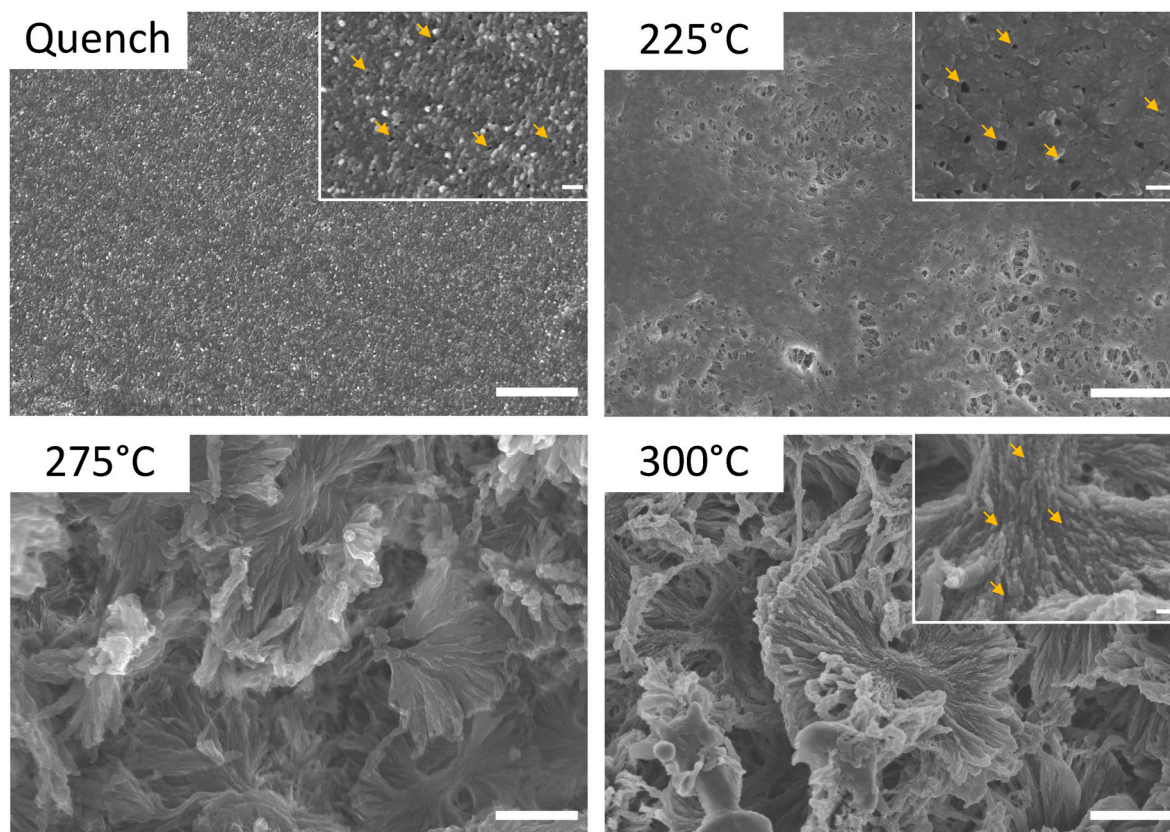


Fig. 11. Microstructure of PEEK/*m*-PEI 30/70 blend as a function of annealing temperature. White scale bars represent 1 μm for main magnification and 100 nm for the close-up inset micrographs. Yellow arrows indicate mesopores. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

PEI, e.g. 225 °C, the mesopores left by extracting the *m*-PEI from PEEK interfibrillar spaces are larger, ≈ 25 nm, following the hypothesis of higher chain mobility (Mehta et al. [15] and Ding and Bikson [17] observed 33 nm pores after annealing at 250 °C). At even higher temperatures (275 °C and 300 °C), both *m*-PEI and PEEK further gain in mobility, which promotes the formation of PEEK spherulites and *m*-PEI rich interspherulitic regions. Since the volume fraction of PEEK is lower at this composition, PEEK possesses a larger available volume for its spherulites to grow without impingement, resulting in a very high porosity after *m*-PEI extraction, large pores, and the formation of “far-falle”-looking PEEK crystalline domains (see also Supporting Information Section 6). Additionally, the *m*-PEI interfibrillar domains are also distinguishable inside the spherulitic microstructure (e.g. close-up micrograph for the 300 °C annealing temperature).

Fig. 12 illustrates some of the mesoporous structures observed in this work, ranging from ≈ 7 nm to ≈ 25 nm, obtained from the PEEK/*m*-PEI system at different compositions or thermal treatments. According to gravimetric analysis, the *m*-PEI originally present was completely removed during solvent extraction. Hence the mesopores are fully continuous throughout the materials. What truly stands out is the range of attainable porosities and average pore size, combined with full pore interconnectivity, and the possibility of independently controlling these

features by simply adjusting blend composition and thermal treatment. It is also quite pertinent to note that the range of porosities and pore architectures reported in this work are quite complementary, for example, to PEEK aerogels and foams prepared by temperature induced phase separation (TIPS) [41,42]. However, the samples decrease in size during the final drying step (although the effect is much less severe when freeze-drying is employed), resulting in a decrease in volume that can be accompanied by either a reduction in pore size and/or pore collapse, thus potentially affecting the continuity. It can also explain why 30 vol% of PEEK apparently occupies so much surface area on the micrographs. Solving this last issue would provide a way to prepare porous PEEK materials over a wide range of porosities and average pore sizes – from nearly 2 to 3 nm to tens of μm .

Fig. 13 summarizes the tensile properties obtained as a function of composition, for the two different systems of PEEK/*m*-PEI (left) and PEEK/*p*-PEI (right), with or without a thermal annealing treatment (30 min at 200 °C). The total crystallinity of the material, the crystallinity based on the PEEK mass present in the blend, Young’s modulus, the tensile strength at yield, and the strain at yield are reported. Note also that the results obtained in this work for the neat polymers are comparable to the data provided by the suppliers.

Apart from the PEEK/*p*-PEI 80/20 composition, all materials present

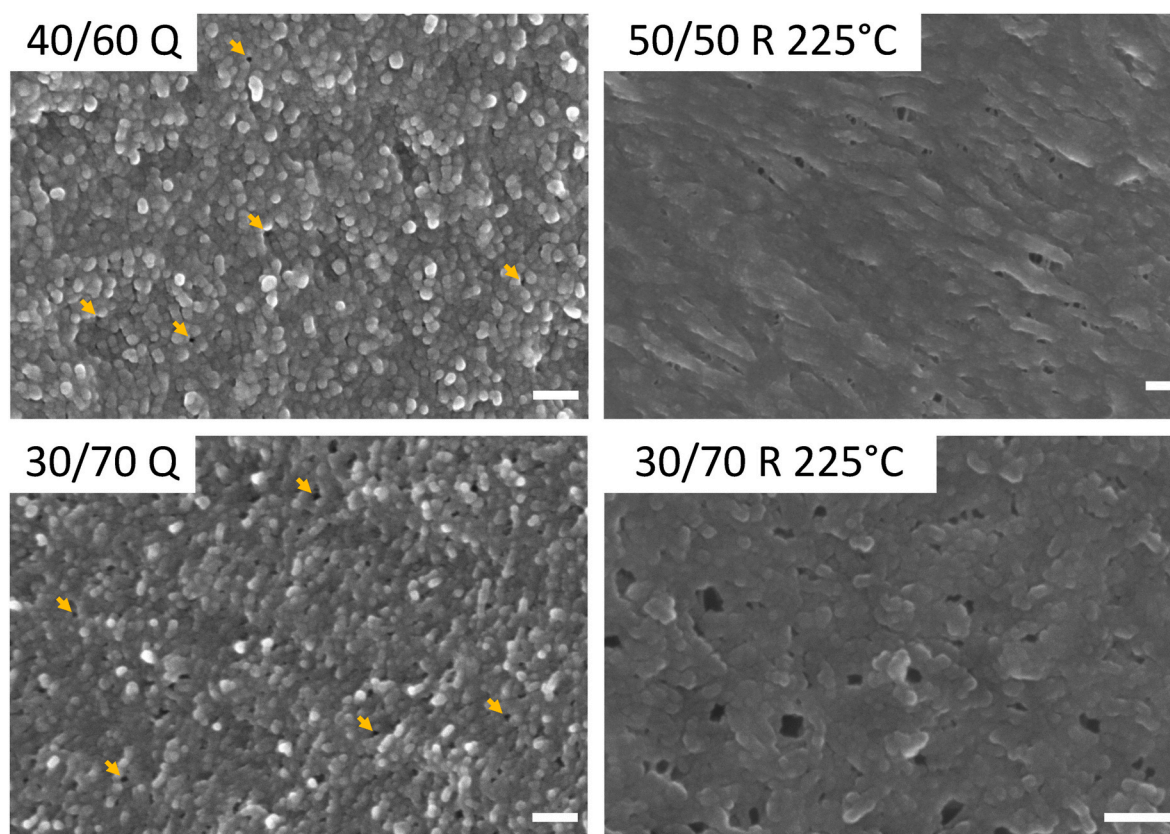


Fig. 12. Mesoporous structures obtained at different compositions and thermal treatments for the PEEK/*m*-PEI system. White scale bars represent 100 nm. Yellow arrows indicate mesopores. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

higher total crystallinity after the annealing step. Since only one specimen for each composition was analyzed by DSC to obtain the crystallinity, it could explain why there is a slight discrepancy for the PEEK/*p*-PEI 80/20. Interestingly, for non-annealed (N) samples, the PEEK/*m*-PEI 80/20, PEEK/*p*-PEI 80/20 and 70/30 compositions all present higher crystallinity, based on the PEEK mass present in the blend, compared to pure PEEK.

All the compositions tested show higher Young's modulus and tensile strength at yield after the annealing step, confirming the relevance of such post-extrusion thermal treatment. Regarding Young's modulus, the highest increases after annealing were observed for the PEEK/*m*-PEI 70/30 and PEEK/*p*-PEI 80/20 blends, with 18 % and 8 % improvement respectively. For the tensile strength at yield, the highest increases reported were 14 % for both the PEEK/*m*-PEI 50/50 and PEEK/*p*-PEI 50/50 compositions.

Comparing pure PEEK with the blends, an increase in Young's modulus of 21 % was observed for the PEEK/*m*-PEI 70/30, and of almost 24 % for the PEEK/*p*-PEI 80/20, after annealing. Regarding the tensile strength at yield, neat PEEK always displays a higher value than the blends. As expected for the two systems, the compositions with the highest moduli in each case also present the lowest tensile strain at yield. Arzak et al. [8] and, Harris and Robeson [43] also evaluated the tensile properties of PEEK/*m*-PEI blends produced by injection molding, with some of the amorphous as-molded blends later annealed at 185 °C and 250 °C, respectively, to increase their crystallinity. While the samples with less than 50 wt% of PEEK showed only marginal improvements in Young's modulus after annealing, annealed PEEK-rich samples possessed the highest stiffness, reaching 3.2 GPa for the 85/15 blend [8] and 3.6 GPa for the 80/20 composition [43]. However, the authors did not report the same positive deviation in Young's modulus observed in this work for the 80/20 and 70/30 compositions compared to pure PEEK. It is worth mentioning that the processing of the tensile samples

and their annealing temperature are different in this work compared to the cited literature which could explain the discrepancies. Regarding ductility, a higher deformation was reported for amorphous samples than for annealed ones.

Another interesting observation is that the type of PEI blended with PEEK doesn't result in significant differences (with a few exceptions) in mechanical properties between PEEK/*m*-PEI and PEEK/*p*-PEI blends. Hence, adding a small amount of PEI to PEEK maintains (and in some cases significantly improves) the material's properties, while at the same time reducing the costs, as PEI is less expensive. PEI is also known to facilitate the processing of PEEK, particularly for 3D printing processes. Future work will aim at characterizing the mechanical properties of porous PEEK monoliths (e.g. in compression) prepared with both types of PEI's, for applications requiring such materials, including PEEK-based scaffolds for bone tissue regeneration, and porous monoliths for heterogeneous catalysis.

By simply changing the position of a linkage in the chemical structure of PEI, we go from a fully miscible system for the PEEK/*m*-PEI pair, to a partially miscible one, displaying a very low interfacial tension of 0.1 mN/m for the PEEK/*p*-PEI system. The resulting blend morphologies right after melt processing (Figs. 1 and 2), and the subsequent morphology control strategies, contrast sharply: (1) for the miscible PEEK/*m*-PEI system, the nm to sub- μ m scale morphology is mainly controlled by the composition, but also by the annealing temperature, with relatively sharp transitions at the polymers' Tg's, over which the significant increases in chain mobility gradually lead to coarser domains, driven by PEEK recrystallization and *m*-PEI expulsion from PEEK-rich domains (Figs. 6, 9, 11 and 12); (2) for the partially miscible PEEK/*p*-PEI system, the sub- μ m to μ m scale morphology is also controlled by composition, but also by annealing over the melting temperature of PEEK, which is much higher than the components Tg's (Figs. 7 and 8b). The resulting coarsening rate is driven by the interfacial tension and

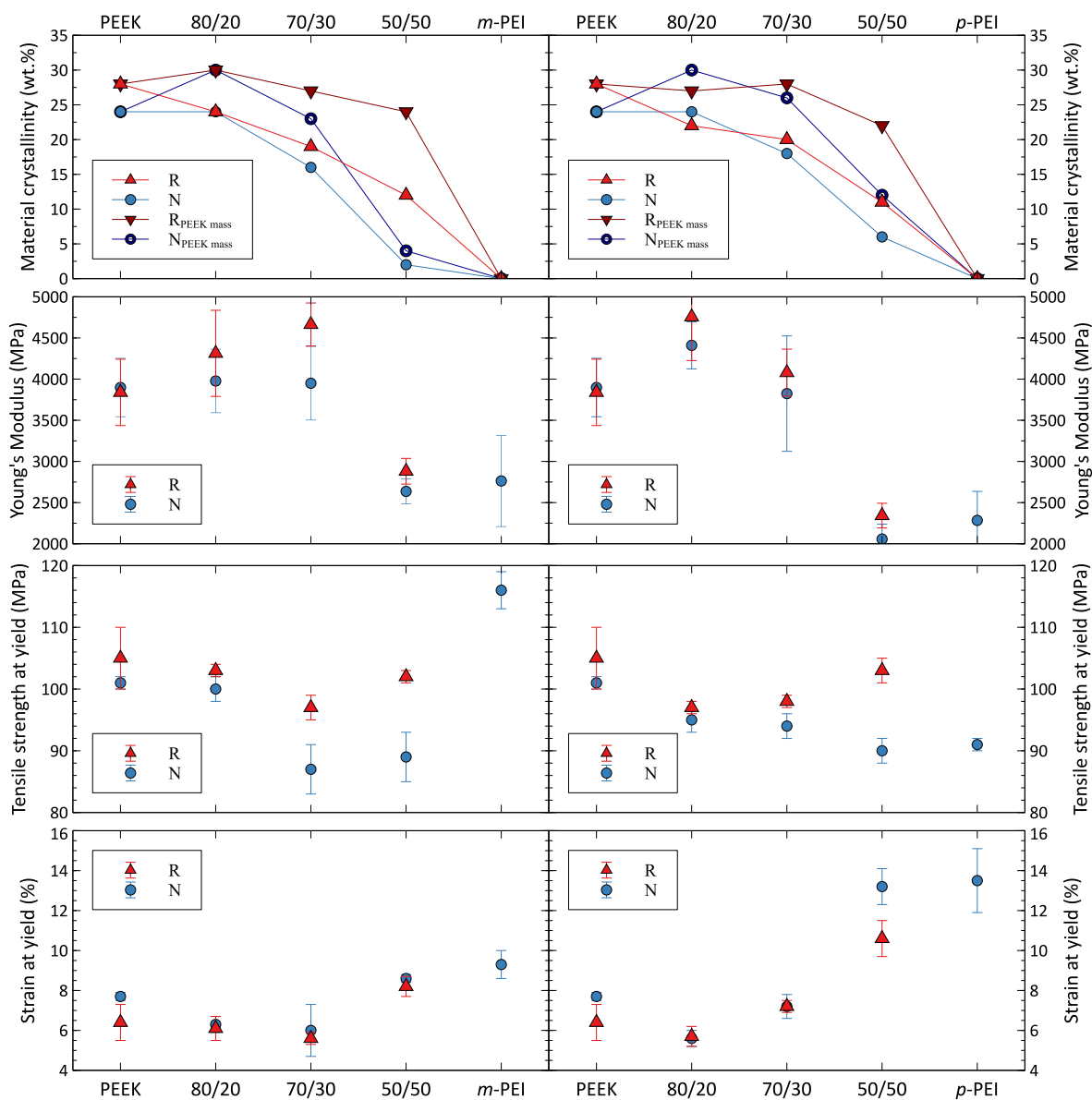


Fig. 13. Tensile properties of both PEEK/*m*-PEI and PEEK/*p*-PEI systems as a function of composition (80/20, 70/30, and 50/50) and thermal treatment (with or without annealing for 30 min at 200 °C, denoted as R and N samples respectively).

modulated by the components' viscosities – a fundamentally different mechanism compared to the PEEK/*m*-PEI system, which does not coarsen since PEEK and *m*-PEI are miscible – there is no interfacial tension; (3) combined together, it is possible to generate morphologies with a characteristic length scale ranging over nearly 4 orders of magnitude, from nearly ≈ 5 nm, to ten's of μm , and which, after the selective removal of the PEI phase, generate porous PEEK monoliths with an average porosity ranging over the same extensive range – probably the widest reported to date in the literature for PEEK monoliths, and polymer monoliths in general. While similar types of intermolecular interactions between PEEK and both PEIs are expected since both PEIs comprise the exact same functional groups, the exact reasons behind these contrasting behaviors are not fundamentally clear. However, *p*-PEI possesses a higher T_g compared to *m*-PEI – nearly 10 °C – suggesting differences in chain flexibility, intra-chains interactions and conformations, leading then to subtle differences in inter-chains interactions with PEEK – sufficient to promote either full miscibility for *m*-PEI, or partial miscibility for *p*-PEI.

Chen et al. [12] have studied the miscibility of the PEEK/*m*-PEI

system by FTIR, and have shown that a specific interaction forms between the electron-rich ether functional groups in PEEK, and the electron-deficient imide rings in the *m*-PEI backbone. Recent work has also shown that the presence of interacting functional groups is not by itself sufficient – the chains must also have sufficient mobility in order for these functional groups to orient properly [44,45]. For example, Heshmati and Favis [44] have shown that a PEO plasticizer located in polylactide (PLA) increases the mobility of the PLA chains (PLA is a relatively stiff polymer), and promotes interfacial interactions between the complementary functional groups of PLA and polyamide11 in that immiscible system. In another work, Bhadane et al. [45] have shown that the addition of a plasticizer to an immiscible blend of brominated poly (isobutylene-*co*-*p*-methylstyrene) and polyamide promotes the formation of a graft copolymer at the interface, by enhancing chain mobility. In the present case, *p*-PEI demonstrates a glass transition temperature almost 10 °C higher than *m*-PEI, a clear indication of lower *p*-PEI chain mobility. Figs. 1 and 2 clearly demonstrate that *p*-PEI possesses a lower level of miscibility compared to *m*-PEI, which could be due to lower chain mobility and, ultimately, differences regarding the

level of specific interactions with PEEK. The investigation and understanding of such subtle changes at the molecular level is beyond the scope of this work, but would constitute an interesting topic for future work.

A number of novel contributions are observed for the PEEK/*m*-PEI blend. The *m*-PEI phase in the miscible PEEK/*m*-PEI system displays a low percolation threshold in-between 10 to 15 % (Fig. 3), with a microstructural characteristic length scale close to molecular dimensions (Figs. 2 and 12) – amongst the finest structures for a co-continuous system reported to date in the literature, and constituting the first investigation related to the development of co-continuity in the limit of a fully miscible binary polymer system. The quiescent annealing temperature impacts the crystallization process of PEEK, the subsequent PEEK/*m*-PEI phase separation process and blend morphology, and ultimately its impact on co-continuity development (Fig. 9, S5 and S6), revealing that co-continuity is indeed maintained, whereas the microstructure length scale gradually increases from a few nm, to a sub- μ m value. Ultimately, it allows the preparation of porous PEEK monoliths when the *m*-PEI is selectively extracted, resulting in some of the finest porous networks, in the nanoscale range, reported to date in the literature when prepared with co-continuous polymer systems, with very high specific surfaces (Fig. 12 and Table 2).

Finally, viscosity doesn't have a significant impact since using the lower viscosity *p*-PEI_2 also yields a phase-separated blend with similar morphological features (Fig. S8). Supposing that *m*-PEI and *p*-PEI are miscible (yet to be verified), this opens the way to explore a unique ternary system where two pairs are fully miscible, and the third pair is only partially miscible - potentially offering the opportunity, for example, to control the miscibility of PEEK with *p*-PEI by the addition of *m*-PEI.

4. Conclusion

This work demonstrates that two close isomeric forms of polyetherimides result in fundamentally different types of morphologies when blended with PEEK: a new partially miscible and phase-separated system for the PEEK/*p*-PEI system, and the typically reported fully miscible PEEK/*m*-PEI system. The PEEK/*p*-PEI system displays sub- μ m, matrix/dispersed phase or co-continuous types of morphologies, with the latter quickly coarsening over tens of μ m in length scale under quiescent annealing conditions due to the PEEK/*p*-PEI interfacial tension, which was measured by the breaking thread method at 0.14 mN/m, a very low value. On the other hand, the PEEK/*m*-PEI system displays full miscibility over the whole composition spectrum. Then, controlling the thermal annealing temperature promotes PEEK recrystallization and the formation of a nanostructured *m*-PEI-rich phase. Taken altogether, it is then possible to control the morphological length scale of both PEEK and PEI domains over nearly 4 orders of magnitude, from $\approx$ 5 nm to over 15 μ m. The selective extraction of the PEI phase then results in porous PEEK monoliths with full pore interconnectivity, with an average pore size spanning the same considerable range, without the addition of interfacial modifiers – a unique feature in the field of binary melt-processed polymer blends. Considering the extensive range of average pore size, from approx. 5 nm to over ten's of microns, this work opens the way to a variety of applications, including PEEK-based porous materials for nanofiltration and separation processes in general, monoliths for heterogeneous catalysis in continuous flow systems, and 3D porous PEEK scaffolds for regenerative medicine applications, for example.

CRediT authorship contribution statement

Arthur Lassus: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Daniel Therriault:** Resources, Funding acquisition, Conceptualization. **Basil D. Favis:** Writing – review & editing, Validation, Supervision, Conceptualization. **Nick Virgilio:** Writing – review & editing, Writing – original

draft, Validation, Supervision, Resources, Methodology, Conceptualization.

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Declaration of competing interest

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2025.128315>.

Data availability

Data will be made available on request.

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