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Influence of thermal history on the mechanical properties of poly(ether ketone ketone) copolymers

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Abstract

Since poly(ether ketone ketone) (PEKK) is a good candidate as a matrix for composite structural parts, the mechanical properties of PEKK copolymers prepared from diphenyl ether, terephthalic acid (T), and isophthalic acid (I) with different T/I ratios were assessed at room temperature and above their glass transition temperature depending on the thermal history during processing. The influence of cooling conditions and macromolecular modifications at high exposure temperatures was investigated. Results show that modulus and yield properties for a given testing temperature follow a master curve driven mainly by crystallinity regardless of the PEKK copolymers. By modifying PEKK during exposures at 400°C, which leads to branching mechanisms before crystallization, it is shown that modified PEKKs follow the master curve, thus confirming the predominant role of crystallinity in small deformation properties. However, for some morphologies, depending on the crystallization conditions such as cold or melt crystallization, a slight deviation is observed from the global master curve.

KEYWORDS

crystallinity, mechanical properties, PEKK

1 | INTRODUCTION

The aeronautics industry is currently making considerable efforts on thermoplastic composites, as they could be consolidated in a one-step process using automated fiber placement machines. Indeed, unlike thermosets, thermoplastic materials do not require crosslinking. This one-step process is known as in situ consolidation. Consolidation can then be accomplished by quickly heating the impregnated reinforcement above the melting temperature of the matrix using a laser diode while applying pressure with a roller, which allows the automated fiber placement machines to ensure adhesion and avoid the formation of air pockets and voids. As no further heating or pressure steps are required after completing fiber placement, this could drastically decrease processing times and costs, and enable the aeronautics industry to reach higher production rates.

Poly(etheretherketone) (PEEK) and poly(ether ketone ketone) (PEKK) thermoplastics, which belong to the poly(aryletherketone) (PAEK) family, are the most appropriate for manufacturing structural parts due to their high mechanical performances. The PEKK matrix has similar mechanical properties but a lower melting temperature than PEEK, which results in a wider process window and makes PEKK a very suitable candidate as a matrix for structural composite parts.

The final mechanical performances of composite parts are strongly linked to the thermal cycle applied during their manufacturing. Since PEKK is consolidated at a high temperature (around 360°C), chemical transformations of the macromolecular chains such as chain scission and crosslinking mechanisms can occur.^[1,2] In addition, after consolidation, the matrix can crystallize with different crystalline ratios and morphologies depending on the

cooling rate.^[3-6] As reported for the other PAEKs, macromolecular modification at high temperatures^[7,8] and crystallization^[9-15] directly impact the mechanical properties of the PEKK matrix^[6] and consequently, the composite. For this reason, these phenomena must be understood and controlled in order to predict and then optimize processing parameters regarding the mechanical performances and processing times of the composite parts.

This article aims to investigate the influence of thermal history on the mechanical properties of PEKK copolymers. We mainly assess the impact of the macromolecular modification of PEKK as well as the crystalline ratio and morphology on the Young modulus and stress at yield at room temperature and 180°C, that is, above PEKKs T_g .

2 | EXPERIMENTAL

2.1 | Materials

The PEKK copolymer is prepared using diphenyl ether (DPE) and terephthalic acid (T; Figure 1A). Terephthalic acid with para phenyl links can be substituted by isophthalic acid (I) with meta phenyl links (Figure 1B). The PEKK copolymers thus comprise two different isomers, namely terephthaloyl (Figure 1A) and isophthaloyl isomers (Figure 1B).

The PEKK copolymers used in this study are provided by Arkema and referenced as PEKK 6002, 7002, and 8002. The ratios of terephthalic acid with para phenyl links and isophthalic acid with meta phenyl links are 60/40, 70/30, and 80/20 for PEKK 6002, 7002, and 8002, respectively (Table 1). The three PEKK grades have an average weight (M_w) and number average molecular mass (M_n) of around 70 and 30 kg mol⁻¹, respectively. Using differential scanning calorimetry (DSC) with a heating rate of 10°C/min, T_g values for PEKK 6002, 7002, and 8002 are close to 160°C, 162°C, and 165°C, respectively and melting temperatures at around 305°C, 332°C, and 358°C, respectively (Table 1). Maximum crystallization enthalpy was measured using DSC for each PEKK by heating them above the equilibrium melting temperatures^[4] at 360°C for PEKK 6002, 380°C for PEKK 7002, and 400°C for PEKK 8002 for 5 minutes and then cooling them to room temperature at a rate of 1°C/min, which is slow enough to allow the polymers to crystallize at their maximum ($X_{C \text{ max}}$) for industrial applications. The crystallinity is then assessed during final heating of 10°C/min by:

$$X_c = \frac{\Delta H_f}{\Delta H_{100\%}} \quad (1)$$

where ΔH_f is the crystallization enthalpy (J g⁻¹) and $\Delta H_{100\%}$ the fully crystallized polymer enthalpy, which was considered the same for PEEK equal to 130 J g⁻¹^[16]

2.2 | Sample preparation

Amorphous plates of 100 x 100 x 2 mm³ provided by Arkema were first dried in an oven at 120°C for 48 hours. PEKK 6002 plates were either crystallized from the melting state (360°C for 5 minutes) at 260°C for different times to obtain different crystallinity ratios (Figure 2A) or from the glassy state at 200°C, 230°C, or 260°C (T_c ; Figure 2B). Only fully crystallized PEKK 8002 and 7002 from the glassy state plates could be obtained due to its very fast crystallization rates (Figure 2B). PEKK 6002 plates were also heated above their melting temperature at 400°C for 1, 2, 3, and 4 hours, and then cooled until 260°C for 4 hours to fully crystallize the polymer.

Steel casing was used during the crystallization to keep the plate flat with the same dimensions. For the crystallizations from the glassy state, plates were put between PTFE films. For the crystallizations from the melt, a more complex environment was carried out due to the problem caused by bubbles appearing on the surface of the plates: the superposition of Thermalimide strips and woven fiber glass of 300 g m⁻² showed a good performance to evacuate these bubbles on the plate surface.

After these crystallization processes, DSC scans using TA Instruments Q2000 from room temperature to 400°C at 5°C min⁻¹ were performed on pieces of about 7 to 8 mg cut from the crystallized plates. According to SAXS measurements, the crystallized plates can be considered as isotropic.

TABLE 1 Thermal properties of PEKK copolymers measured by DSC

Grade	T/I ratio	T_g (°C)	T_m (°C)	$X_{c \text{ max}}$ (%)
PEKK 6002	60/40	160	305	28
PEKK 7002	70/30	162	332	33
PEKK 8002	80/20	165	358	40

Abbreviations: DSC, differential scanning calorimetry; PEKK, poly(ether ketone ketone).

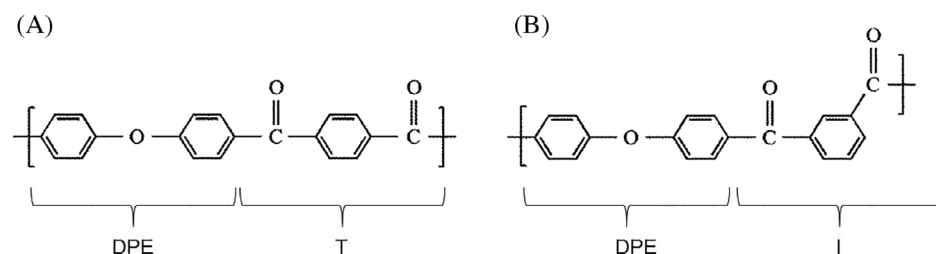


FIGURE 1 Poly(etherketoneketone) (A) terephthaloyl and (B) isophthaloyl isomers

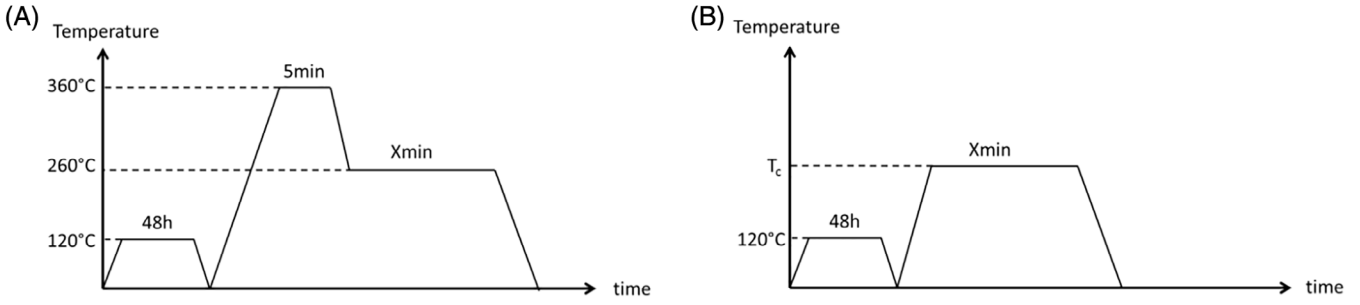


FIGURE 2 Isothermal melt for 6002 (A) and cold (B) crystallization thermal cycles for all poly(ether ketone ketone) plates

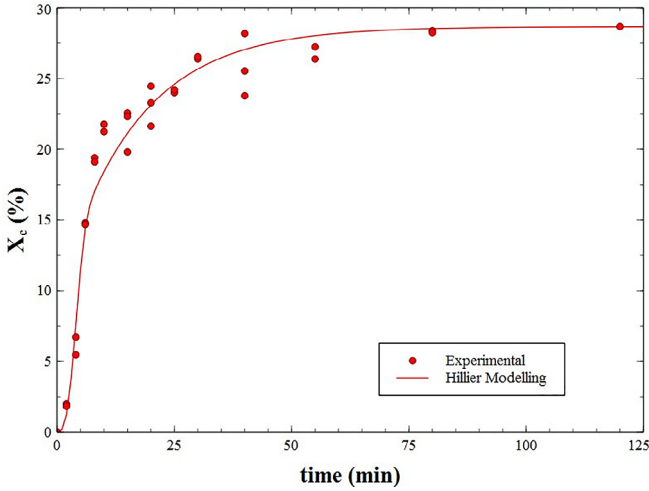


FIGURE 3 Comparison between the crystallinity of PEKK 6002 plates crystallized at 230°C from the glassy state at different times and the Hillier model. PEKK, poly(ether ketone ketone)

2.3 | Tensile tests

Mechanical tests were carried out with a tensile test machine Instron 5966 equipped with a laser extensometer and an oven to conduct tests at high temperature. Tests were performed on normalized 1BA tensile samples (ISO 527) with a length of 75 mm, a width of 5 mm, and a thickness of 2 mm machined from the crystallized plates. Specimens were tested at 23°C and above T_g at 180°C with a testing speed of 1 and 100 mm min⁻¹, that is, 0.033 and 3.3 seconds⁻¹, respectively. At 180°C, the amorphous phase of PEKK is at the rubbery state, and the testing speed must be high enough to measure entanglement network properties and avoid as much as possible the chain flow due to disentanglement. At this temperature, the crystallization kinetics is low enough to assume that the polymer does not crystallize during the test.^[3]

3 | RESULTS AND DISCUSSION

3.1 | Crystallinity measurement of PEKK plates

The crystallinity X_c of PEKK 6002 is plotted in Figure 3 as a function of the crystallization time at 230°C from the glassy state, calculated as:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100\%}} \quad (2)$$

where ΔH_m is the melting enthalpy (J g⁻¹), ΔH_{cc} the cold crystallization enthalpy (J g⁻¹), and $\Delta H_{100\%}$ the fully crystallized polymer enthalpy, which was considered the same for PEKK equal to 130 J g⁻¹.^[16] We compared these experimental results to Hillier's crystallization kinetics model^[17] expressed by^[11]:

$$X_c = X_{c \max} w_1 [1 - \exp(-K_1 t^{n_1})] + w_2 K_2 n_2 \int_0^t [1 - \exp(-K_1 \theta^{n_1})] (t - \theta)^{n_2 - 1} \exp[-K_2 (t - \theta)^{n_2}] d\theta \quad (3)$$

where $X_{c \max}$ is the maximum crystallinity of PEKK 60/40 (Table 1), n_1 and n_2 correspond to the Avrami exponents, K_1 and K_2 to the crystallization rate constants, and w_1 and w_2 to the weight factor for the primary and secondary crystallization, respectively. The Hillier model with parameters identified in a previous article^[3] for isothermal crystallization at 230°C is plotted in Figure 3. A good agreement between the Hillier model and the experimental points is observed, which validates the ability of our modeling to predict crystallinity depending on the crystallization conditions.

3.2 | Influence of crystallinity on PEKK matrix mechanical properties

3.2.1 | Modulus as a function temperature

According to dynamical mechanical analysis (DMA) measurements, storage modulus as a function of the temperature for fully crystallized PEKK 6002, PEKK 7002, and PEKK 8002 is shown in Figure 4. For all, the storage modulus is quasi constant until T_g where it collapses until another plateau. The storage modulus of the first plateau is around 3 GPa and the glass transition was measured around 155°C.

It can be observed that for temperatures below T_g , the storage modulus for the three materials are very close whereas above T_g , it can be noticed a strong difference between them. PEKK 8002 has the highest storage modulus, followed by PEKK 7002 and finally PEKK 6002. This phenomenon is attributed to the fact that they have different maximum crystallinity when they crystallized at 230°C (see Table 1). Indeed, PEKK 8002 crystallized with 40%, PEKK 7002 with 33%, and PEKK 6002 with 28%, which explains that PEKK 8002 has a

higher storage modulus than PEKK 7002, and that PEKK 7002 has a higher storage modulus than PEKK 6002. Above T_g , it is the crystalline phase that gives the mechanical strength to the matrix which explains a more important difference between the storage modulus of three PEKK matrices above T_g . In the following paragraph, tensile tests were carried out at room temperature and at 180°C to investigate more

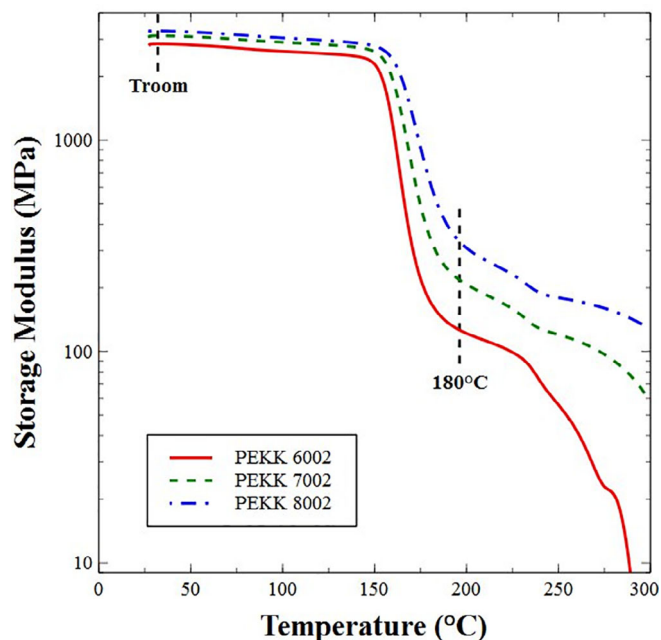
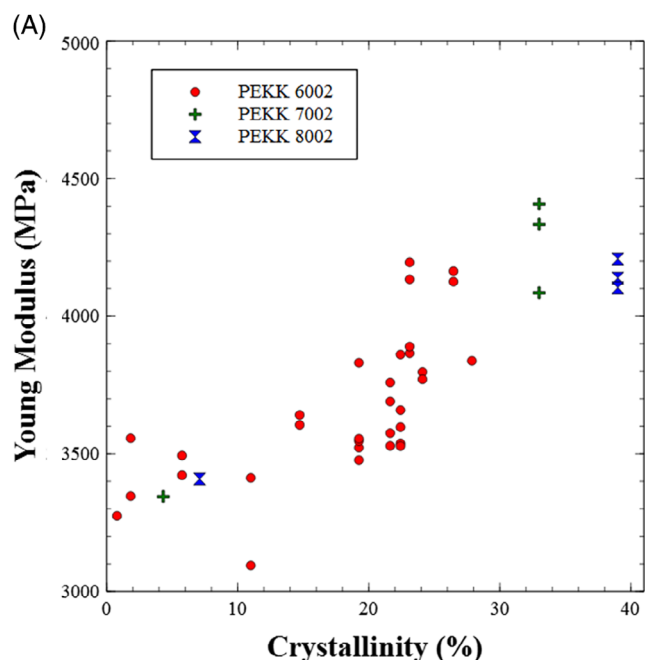


FIGURE 4 Storage modulus vs temperature for fully crystallized PEKK 6002, PEKK 7002, and PEKK 8002. PEKK, poly(ether ketone ketone)



precisely the impact of crystallinity on the mechanical properties below and above T_g .

3.2.2 | Tensile tests at room temperature

The changes in the Young modulus, stress at yield, and strain at break as a function of crystallinity for the tensile tests carried out at room temperature are shown in Figures 5 and 6. Due to the low crystallization rate of PEKK 6002, it is possible to investigate the mechanical properties for a wide range of crystallinity. In a first approach, for an isotropic semicrystalline polymer, we will consider that crystallinity ratio is often the relevant parameter that drives mechanical properties at small deformation (modulus and yield stress).

The Young modulus and stress at yield respectively increase from around 3250 and 88 MPa for amorphous PEKK to 4250 and 120 MPa for fully crystallized PEKK 8002 ($X_c = 40\%$), corresponding to an increase of 30% and 36%. It appears that fully crystallized PEKK 8002 has the highest stress at yield, which could be explained by its higher maximum crystallinity ($X_{cmax} = 40\%$) compared to PEKK 6002 and 7002 (see Table 1). As a result, we can conclude in a first approximation that the variations of modulus and stress at yield for the three studied PEKK are mainly driven by crystallinity level.

The observed increase in the Young modulus and stress at yield with crystallinity is consistent with the literature for PEEK^[9,11,14,18] and other semicrystalline polymers such as poly(ethylene)terephthalates^[13] and poly(lactic acid),^[19] which have their amorphous phase in a glassy state at room temperature. Since the crystalline modulus is between 3.1 GPa for perpendicular and 71 GPa for parallel to the chain axis^[20] and the amorphous modulus is around 3.2 GPa, the data shown here can be used to validate the micromechanics

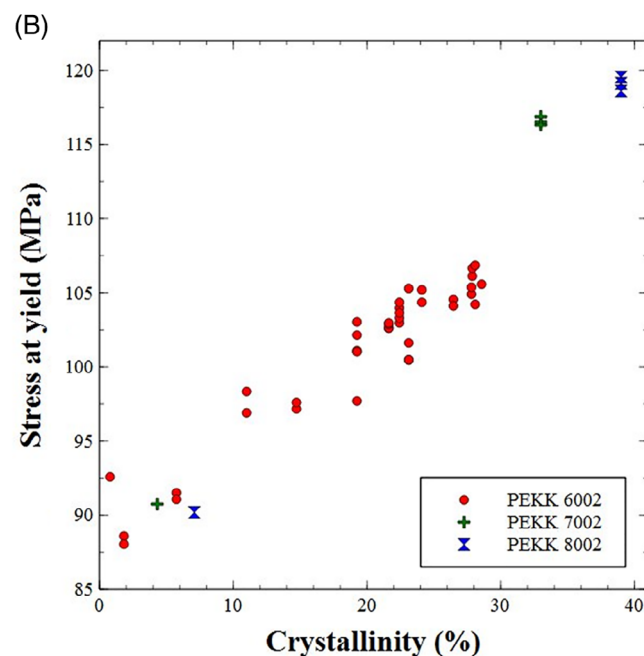


FIGURE 5 Young modulus (A) and stress at yield (B) vs crystallinity at room temperature of neat poly(ether ketone ketone) crystallized at 230°C from the glassy state

models proposed in the literature.^[21] It is noteworthy that these micromechanics models, referred to as composite inclusion models, show a curvature between modulus and crystallinity.

The change of strain at break with crystallinity is quite different from that of the Young modulus and stress at yield. A decline in strain at break can be observed at around 22% of crystallinity, which

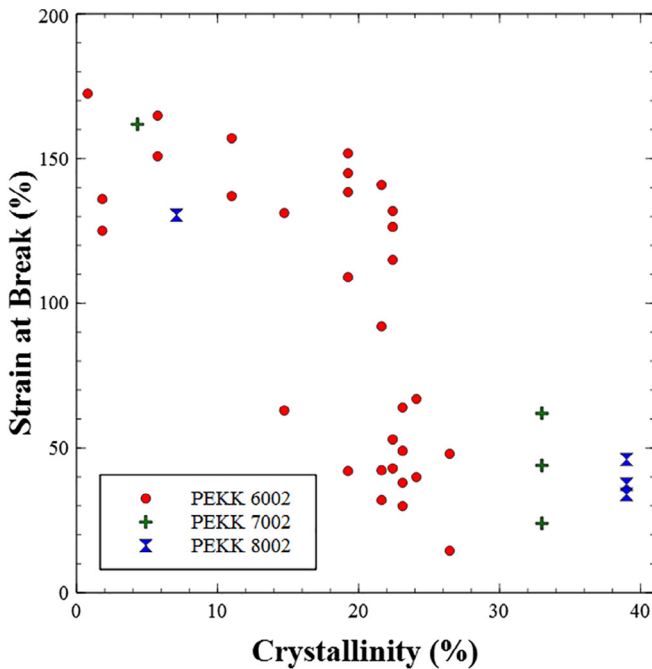
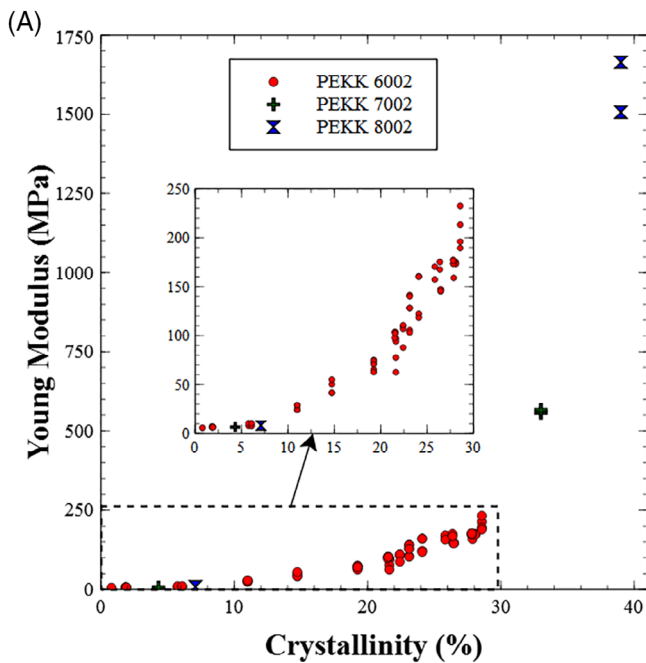


FIGURE 6 Strain at break vs crystallinity at room temperature of neat poly(ether ketone ketone) crystallized at 230°C from the glassy state



decreases from 150% to 40%, leading to less ductile behavior. It is noteworthy that this lower value of 40% ± 10% remains higher than the yield strain, which is close to 10%. As a result, if the elastic mechanical properties of PEKK matrices continuously increase with crystallinity, then the ductile behavior is limited, as crystallinity is higher than 20%.

The ductile behavior of PEKK in the glassy state, regardless of the crystallinity level, can be associated with a low molar mass between entanglements such as polycarbonates.^[22] However, damage mechanisms such as cavitation can be promoted over plastic deformation by increasing crystallinity, thus leading to reduced macroscopic strain at break. It is recognized that the ductile behavior of semicrystalline polymers can be limited not only by crystallinity level, but also by crystalline morphology. For a given crystallinity, some authors suggest that an increase in spherulite size due to a slow cooling process can also lead to embrittle PEEK at room temperature.^[14]

3.2.3 | Tensile tests at 180°C

To verify the crystallinity influence on mechanical properties above T_g , mechanical tests were carried out at 180°C on the same samples, that is, crystallized at 230°C from the glassy state. In Figure 7, the change in the Young modulus and stress at yield as a function of crystallinity for tensile tests at 180°C are presented. First, it can be observed that, as expected, the Young modulus and stress at yield are much lower compared to the test at room temperature, as the amorphous phase is in a rubbery state. Furthermore, it can be witnessed that crystallinity has more influence at 180°C than at room temperature.

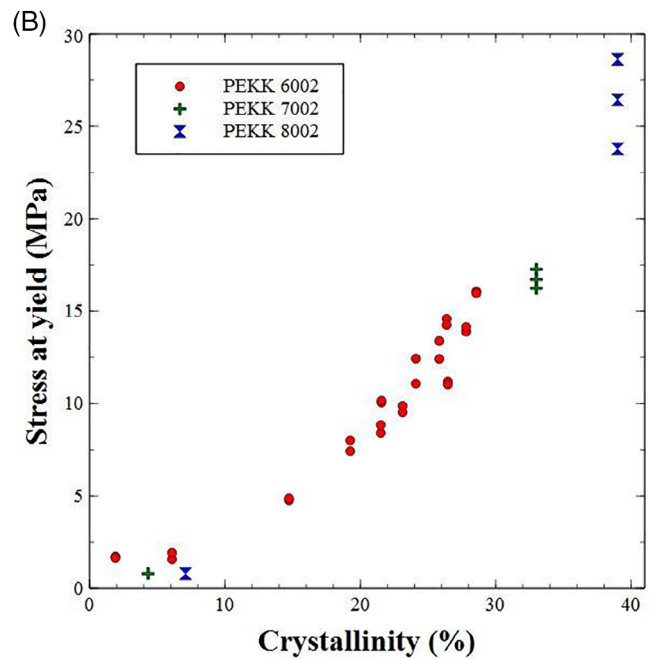


FIGURE 7 Young modulus (A) and stress at yield (B) vs crystallinity at 180°C of neat poly(ether ketone ketone) crystallized at 230°C from the glassy state

A strong increase in the Young modulus and stress at yield is respectively observed from nearly 5 and 0 MPa at the amorphous state until 1650 and 29 MPa for highly crystallized PEKK 8002. At this test temperature, PEKK 8002 clearly has a higher Young modulus and stress at yield than PEKK 7002 and 6002 due to its higher maximum crystallinity. For this temperature test, high strains at break could not be measured due to the maximum tensile test machine displacement, as they were higher than 100%. Finally, regarding ambient temperature, we can conclude that the changes in modulus and stress at yield for the three studied PEKK are mainly driven by crystallinity, with the data set following the same master curve linking crystallinity and modulus/stress at yield.

3.3 | Influence of crystalline morphologies on PEKK 6002 mechanical properties

In this part, the effect of crystallization temperature on mechanical properties was assessed by testing PEKK 6002 specimens crystallized at 200°C, 230°C, and 260°C from the glassy state and at 260°C from the melt. In fact, depending on the crystallization temperature and thermal history prior to crystallization, the crystalline morphologies are not the same. As reported in a previous article,^[1] large spherulites of 16 μm were observed for crystallization at 270°C from the melt, whereas at 200°C from the glassy state, spherulites are too small to be observable by optical microscopy.

To highlight the possible influence of crystallization temperature on the mechanical properties for a given crystallinity level, only results for tensile tests at 180°C are presented. Figure 8 plots the changes in the Young modulus and stress at yield as a function of crystallinity for specimens crystallized in different conditions.

First, it appears that the Young modulus and stress at yield for crystallization at 200°C are higher than for the other crystallization temperatures. Second, the results for crystallization at 230°C and 260°C are similar regarding the Young modulus. This could be due to the fact that for crystallization at 260°C, the polymer begins to crystallize during heating until the crystallization temperature, especially as the polymer passes through crystallization temperatures around 240°C^[1,3]; for this reason, we also investigate crystallization at 260°C from the melt. It can be observed that the Young modulus for crystallization at 260°C from the melt is close to crystallization at 200°C from the glassy state until 20%; it then stabilizes between 110 and 145 MPa. However, crystallization at 260°C from the melt and crystallization from the glassy state lead to similar trends for the stress at yield.

As a result, it could be assumed that the presence of small spherulites (crystallization from the glassy state at temperatures close to T_g , that is, 200°C here) enhances the elastic properties of PEKK matrices compared to large spherulites, that is, crystallizations from the melt at temperatures close to T_m . This is consistent with the findings of Kargin et al.^[23] and Chan et al.,^[7] which showed that high nucleation density and thus small crystallites involve a more homogeneous crystalline structure and thus higher mechanical properties.

3.4 | Impact of macromolecular changes on mechanical properties

In a previous article,^[24] we showed that for high temperature and time exposure, PEKK 6002 undergoes macromolecular modifications due to crosslinking/branching mechanisms that lead to a decrease in the final crystallinity and crystallization kinetics. This is consistent with

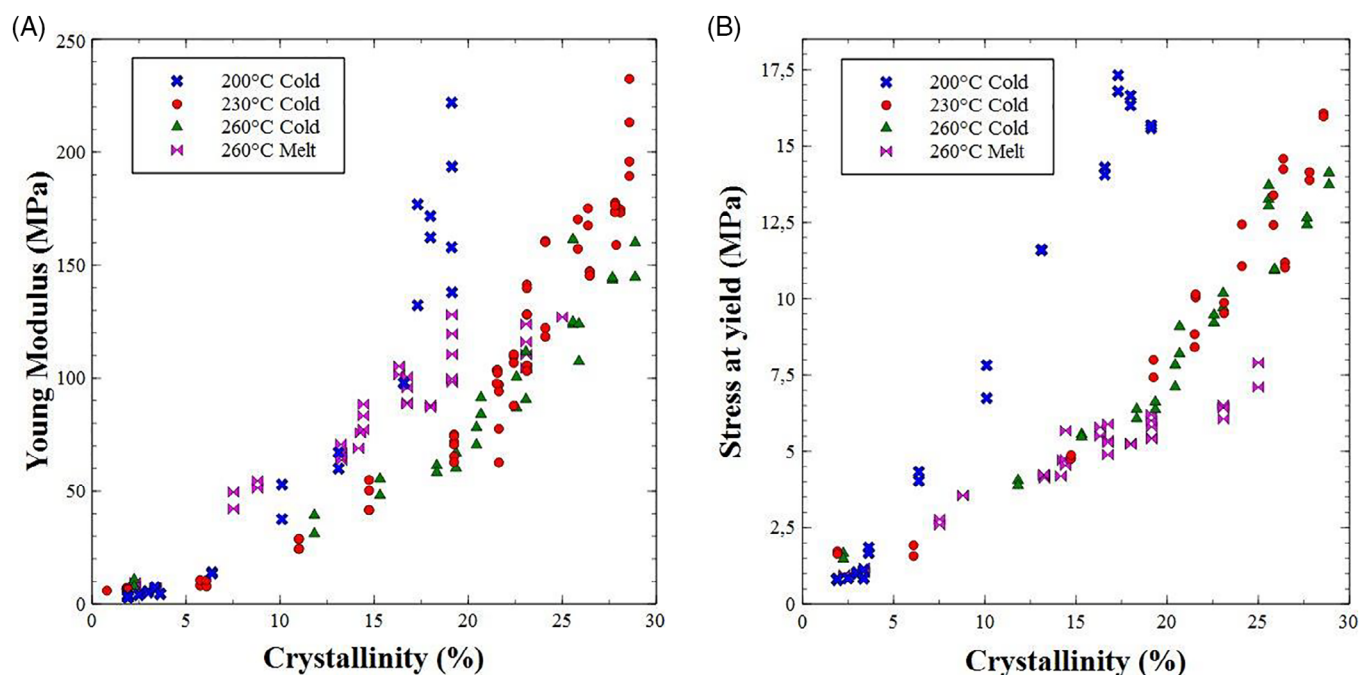


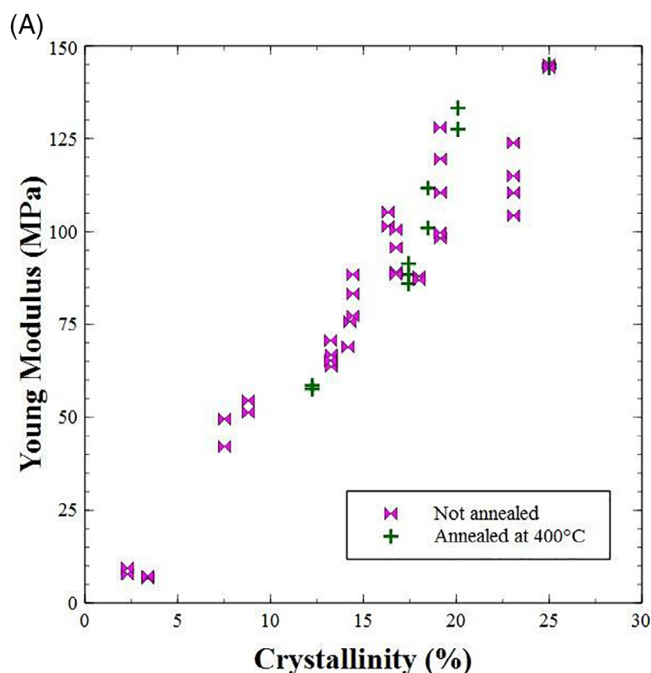
FIGURE 8 Comparison of the evolution of the Young modulus (A) and stress at yield (B) vs crystallinity at 180°C of neat PEKK 6002 depending on the crystallization conditions. PEKK, poly(ether ketone ketone)

TABLE 2 Mechanical properties at 180°C of neat PEKK 6002 crystallized at 260°C from the melting state after exposure at 400°C with the corresponding number of crosslinking events (x)^[23]

Exposure time at 400°C (min)	x (mol kg ⁻¹)	Crystallinity (%)	Young modulus (MPa)	Stress at yield (MPa)
Not annealed	0	25	145	7.5
60	$2.4 \cdot 10^{-3}$	20	130	6.1
120	$3.4 \cdot 10^{-3}$	18	106	4.8
180	$4.2 \cdot 10^{-3}$	17	89	4.7
240	$5.8 \cdot 10^{-3}$	12	58	3.1

Abbreviation: PEKK, poly(ether ketone ketone).

the results of Chan et al^[7,8,25] for PEEK, where crosslinking during heat aging leads to a decrease in crystallization rates. In this part, we assessed the impact of macromolecular modifications at high temperature exposure on PEKK 6002 mechanical properties. Table 2 presents the evolution of the crystallinity, Young modulus, stress at yield, and number of crosslinking events (x) reported in a previous article^[24] as a function of the exposure time at 400°C for PEKK 6002 crystallized at 260°C from the melting state. Only tensile test results at 180°C are presented in Figure 9, as no significant differences were observed at room temperature due to the higher dispersion of measurements and the lower sensitivity of mechanical properties to crystallinity. It can be observed that the Young modulus and stress at yield decrease with the exposure time at 400°C and thus with the number of crosslinking events (x), which was assumed to be mainly attributed to the decrease in crystallinity.



To assess the impact of macromolecular changes on mechanical properties independently of crystallinity, the Young modulus and stress at yield for exposed and nonexposed specimens at 400°C as a function of crystallinity are compared in Figure 8. Regarding the results, there is little difference between the exposed and nonexposed specimens, which shows that macromolecular changes involve lower mechanical properties due to the significant decrease in crystallinity. It thus appears clearly that the branching process modifies the mechanical properties investigated here only by decreasing crystallinity. In other words, the fact that the amorphous phase architecture (linear chains to branched chains) is largely modified does not contribute to the mechanical property changes for a given crystallinity.

4 | CONCLUSION

Tensile properties of PEKKs are investigated as a function of crystallization conditions. It was shown that the Young modulus and stress at yield of PEKKs with different T/l ratios increase with crystallinity, whereas the strain at break is reduced. This behavior is emphasized for testing temperatures above the glass transition, because at these temperatures, the amorphous phase is in rubbery state, and the mechanical properties of the polymer only depend on the crystallinity level.

To highlight an influence of crystalline morphology, several isothermal crystallization conditions have been used: cold crystallization at 200°C, 230°C, and 260°C and melt crystallization at 260°C. It appears that a higher Young modulus and stress at yield were observed for low crystallization temperatures involving small

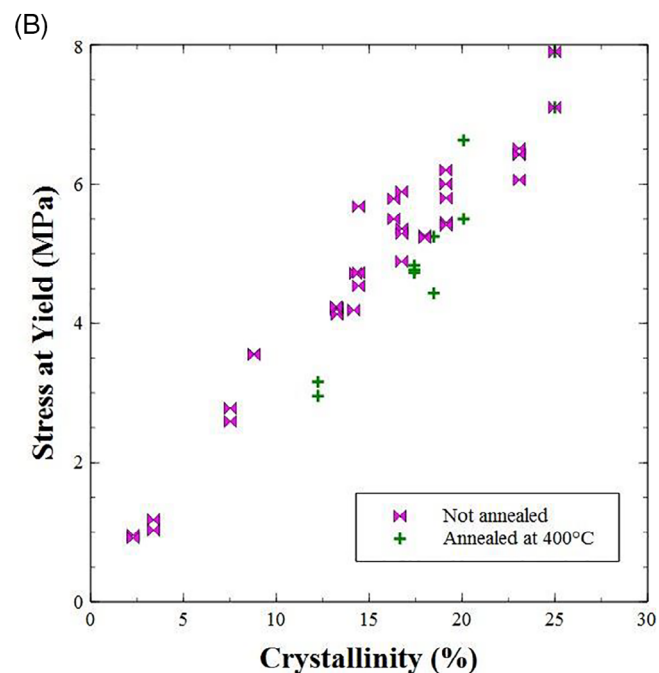


FIGURE 9 Young modulus (A) and stress at yield (B) vs crystallinity at 180°C of annealed and nonannealed PEKK 6002 at 400°C under air and crystallized at 260°C from the melting state. PEKK, poly(ether ketone ketone)

spherulites, which were attributed to a more homogeneous crystalline structure compared to large spherulites.

Finally, it was shown that mechanical properties decrease after high exposure temperatures where thermal degradation can occur. This decrease was assumed to be associated with the decrease in crystallinity, since branching reduces the final crystallinity. As a result, even if the amorphous phase architecture (linear chains to branched chains) is largely modified, the changes in small deformation properties are mainly driven by crystallinity.

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