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Macromolecular modifications of poly(etherketoneketone) (PEKK) copolymer at the melting state

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A B S T R A C T

Macromolecular modifications of poly(etherketoneketone) (PEKK) copolymer prepared from diphenyl ether (DPE), terephthalic acid (T) and isophthalic acid (I) with a T/I ratio of 60/40 have been investigated above its melting temperature by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and rheological measurements to assess the evolution of PEKK matrix during composite consolidation step. We mainly focused in this study on anaerobic conditions, i.e. degradation under nitrogen or in lack of oxygen. During exposure, thermal degradation leads to an increase of weight average molar mass M_w and viscosity which is typical to crosslinking/branching mechanism as already observed for PEEK in the literature. However, thanks to GPC measurements, it appears that a chain scission mechanism occurs in the same time related to a constant number average molar mass M_n . Crosslinking kinetics are identified at several temperatures between 320 and 400 °C with rheological measurements from a kinetic scheme governing the crosslinking mechanism. At last, the influence of the crosslinking process on PEKK crystallization is investigated. The final crystallinity and crystallization kinetics decrease with crosslinking due to branching of macromolecular chains.

Keywords:

PEKK

Thermal degradation

Crosslinking

Crystallization

PACS:

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1. Introduction

Poly(ether-ketone-ketone) (PEKK) high performance thermoplastics are currently studied with a great interest by the aeronautic industry as matrix for carbon fiber reinforced structural parts. In fact, PEKK composites can be consolidated out of autoclave and they have lower processing temperatures than PEEK composites. The final mechanical performances of composite parts are closely linked to their processing. In fact, depending on the thermal processing cycle, the matrix properties as well as the interaction between the matrix and the carbon fibres are modified. PEKK composites are consolidated at high temperature (around 360 °C) to obtain a viscosity decrease of the matrix in order to evacuate all porosities under pressure. During this step, PEKK matrices can evolve due to chemical transformation of the macromolecular chains. This modification could alter the matrices properties and consequently the final mechanical properties of the composite parts [1,2].

It has been reported by different authors [3–13] that PEEK undergoes macromolecular modifications and mass losses at high temperature (around 400 °C) in both nitrogen and air in an early stage. These macromolecular modifications are attributed to crosslinking mechanisms. This mechanism under nitrogen atmosphere is presented in Fig. 1 [11]. It is initiated by scissions of macromolecular chains located in the carbonyl and ether bonds (Step 1), creating radicals which miss hydrogen molecules (Step 2). Day et al. suggested in a first article [4] that first scissions occurs at the carbonyl functional groups. In a second article [5] as for Tsai et al. [14], they assumed that chain scissions begin at the ether linkages. Other authors [3,8,14] made the assumption that they begin at the same time since activation energies of bond dissociations for ether and carbonyl linkages are very close. Radicals can then rearrange by removing hydrogen molecules from aromatics cycles forming phenyl radicals (P^\bullet) (Step 3), which can rearrange with an adjacent radical to produce crosslinks (Step 4). Another possibility for phenyl radical is to rearrange by internal combination, to produce dibenzofuran or fluorenone derivatives:

As a result, the crosslinking increases viscosity of the matrix [1,9,10] which can involve bad impregnation of the carbon fibers

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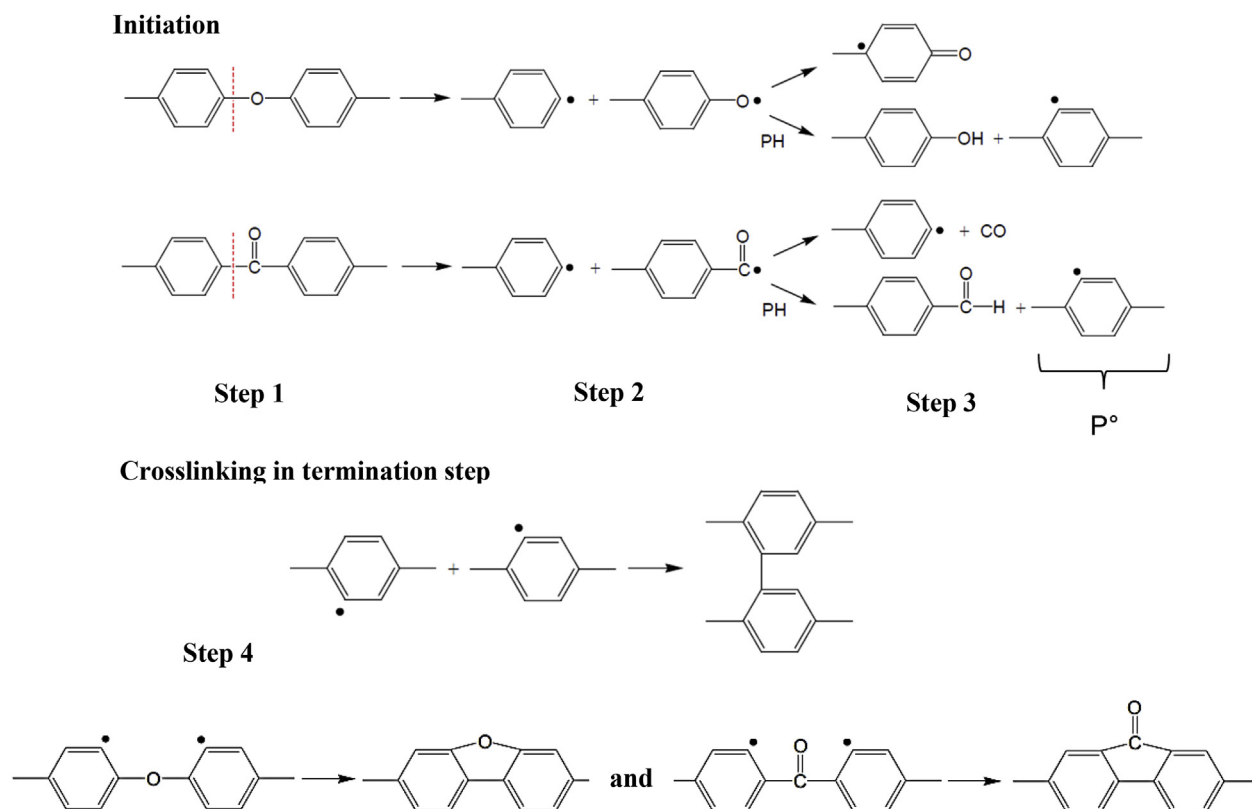


Fig. 1. Crosslinking mechanism steps of PEKK [11].

during processing and thus impact the final health and performance of composite parts. It has also been reported in the literature that after exposure at high temperature, crosslinking decreases the crystallization kinetics and the final crystallinity [1,2,6,15,16] and thus the final mechanical properties of the composite parts [1,2].

The objective of this paper is to assess the macromolecular modifications of PEKK above its melting temperature and identify their origins. We will mainly focus on crosslinking process and assess the kinetic associated to this process as a function of temperature of exposure. A second objective is quantified these macromolecular modifications and model their apparition kinetics.

2. Experimental

2.1. Materials

PEKK used in this study was provided by Arkema referenced as PEKK 6002. It was prepared from diphenyl ether (DPE), terephthalic acid (T) with para phenyl links and isophthalic acid (I) with meta phenyl links with a T/I ratio of 60/40 (Fig. 2). PEKK 6002 has a weight- and number average molar mass (M_w and M_n) of about $68\,800\text{ g}\cdot\text{mol}^{-1}$ and $29\,800\text{ g}\cdot\text{mol}^{-1}$ respectively. PEKK samples were supplied amorphous with no crystalline traces measured by DSC and WAXS. The glass transition and melting temperatures were respectively measured about 155°C and 305°C by DSC with a heating stage of $10^\circ\text{C}/\text{min}$.

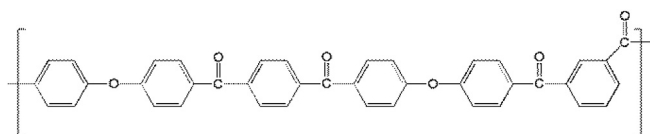


Fig. 2. Chemical structure of PEKK copolymers.

2.2. Exposure conditions

Two ways were chosen to perform thermal degradation on PEKK samples. The first one were performed in situ in rheometer or in DSC under nitrogen, see more details in §2.4 and §2.5. The second way was used to prepare thermally degraded samples for GPC measurements. For this purpose, thin samples were taken from the core of 2 mm thick samples exposed at 400°C in air. Knowing oxidation is confined at the surface of thick samples due to diffusion limited oxidation, oxidized surface was removed from the core of thick samples. Since oxidation products appear in the oxidized surface layer, it was checked out by FTIR measurements (spectra were not shown here) that no oxidation products were detected in the samples after the oxidized surface layer removal.

2.3. Gel permeation chromatography (GPC)

GPC measurements were performed by Arkema Company on a Waters Alliance 2695 device with a Waters 2414 RID detector. Samples preparation and experimental conditions are confidential.

2.4. Differential scanning calorimetry (DSC)

Isothermal crystallization analyses were carried out in a TA Instruments Q2000 on PEKK 6002 amorphous granules of about 7–8 mg previously heated at 400°C under nitrogen during 1 h, 2 h, 3 h and 4 h. Specimens were first heated at $10^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to 360°C during 5 min. This temperature is above PEKK equilibrium melting temperatures [17] to erase the thermal history and obtain a fully amorphous polymer. Specimens were then cooled at $40^\circ\text{C}\cdot\text{min}^{-1}$ to 230°C during 240 min and finally cooled at $40^\circ\text{C}\cdot\text{min}^{-1}$ to room temperature. This cooling rate was high enough to make sure that the polymer does not crystallize

before exposure and the exposure time was long enough to allow the polymer to fully crystallize. Finally, a heat scan at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $400\text{ }^{\circ}\text{C}$ was carried out to measure the glass transition, the melting temperature and the melting enthalpy induced by the crystallization cycle. The glass transition temperature was measured as the inflexion point.

2.5. Rheological measurements

Rheological properties of PEKK 6002 were measured with an Anton Paar MCR 502 rheometer under nitrogen for isothermal temperatures conditions. PEKK 6002 amorphous granules previously dried at $120\text{ }^{\circ}\text{C}$ during 48 h were first introduced between 25 mm diameter aluminum parallel plates at the testing temperature and then crushed by the plates separated by a 1 mm gap. The melted polymer between plates was then deburred. After this step, the polymer was thermally stabilized at the testing temperature before the beginning of the test. This procedure was done as rapidly as possible to neglect the possible modification of the polymer before the analysis. Sinusoidal deformation mode was used with a strain amplitude of 1% to remain in the viscoelastic linear domain and a frequency of 1 rad s^{-1} to carry out tests in the Newtonian domain to ensure that the viscosity only depends on the exposure time and temperature.

3. Results

3.1. Gel permeation chromatography (GPC) analysis

Gel permeation chromatography measurements were carried out on PEKK samples exposed at $400\text{ }^{\circ}\text{C}$ for duration between 5 and 240 min (see Fig. 3). Less than 5% of insoluble were measured for all exposure times. It can be noticed a slight appearance of short chains ($3000 < M < 20\,000\text{ g mol}^{-1}$) after 60 min of exposure, the major changes witnessed in Fig. 3 is the broadening of the molar mass distribution towards higher molar masses. However, the peak position remains almost constant during the exposure at $400\text{ }^{\circ}\text{C}$. At last, a slight shoulder can be observed at $4 \times 10^5\text{ g mol}^{-1}$ after 240 min corresponding to high degrees of conversion for the thermal degradation.

Fig. 4 shows the evolution of the weight and number average molar mass (M_w and M_n) and the polydispersity index (I_p) as a function of the exposure time. As reported for PEEK by Jonas et al.

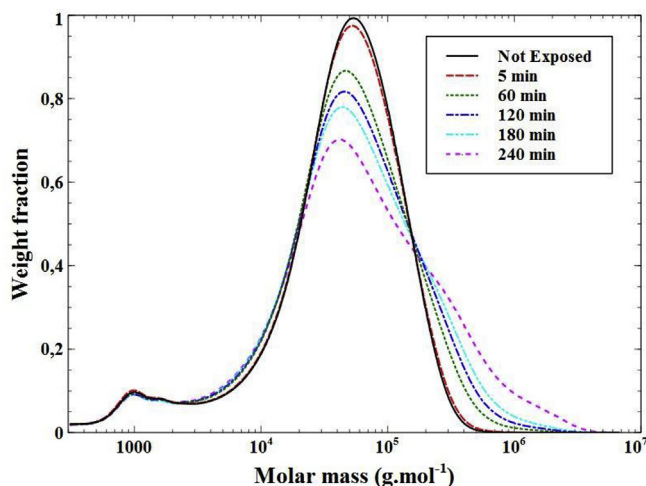


Fig. 3. Molar mass distributions (normalized weight fraction) of neat PEKK 6002 exposed at $400\text{ }^{\circ}\text{C}$.

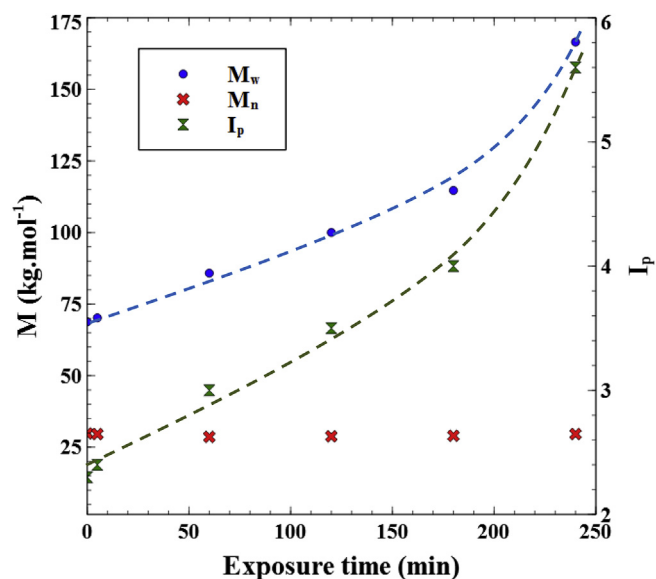


Fig. 4. Evolution of M_w , M_n and I_p as a function of the exposure time at $400\text{ }^{\circ}\text{C}$ of neat PEKK 6002.

[6], it can be observed an increase of M_w and I_p with the exposure time according to the molar mass distribution changes. These increases are undoubtedly associated to a crosslink process corresponding to the reactions between thermal degradation induced radicals as shown in Fig. 1 step 4. For an exposure time of 30 min at $400\text{ }^{\circ}\text{C}$ under air an increase for M_w of about 7% was measured for PEEK by Jonas et al. compared to 13% for PEKK here. However, the fact that M_n remains constant which is also the same observation than for PEEK by Jonas et al. could imply necessarily a chain scission process in a same time. The fact that the crosslinking and the chain scission processes are synchronised indicate for us that both processes have the same source in terms of radical formation. In other words, radicals coming from the chain scission mechanism (steps 1 to 3 Fig. 1) contribute the crosslinking mechanism (step 4 Fig. 1). As a result, the macromolecular changes have to take into account not only a crosslinking process but also a chain scission mechanism which is in our knowledge the first time mentioned in the literature for PAEK polymers. This point will be discussed later.

3.2. Thermal analysis

The impact of crosslinking on thermal properties and crystallization behavior have been studied by different authors and was shown to decrease crystallization kinetic and final crystallinity and increase glass transition [2,6,15,16]. In fact, crosslinking reduces the chain mobility and chain folding occurring during crystallization process. Crystallization peaks of PEKK 6002 crystallized from the melt at $230\text{ }^{\circ}\text{C}$ measured by DSC after different exposure times at $400\text{ }^{\circ}\text{C}$ are presented in Fig. 5. It can be noticed that the crystallization peak decreases with the exposure time at $400\text{ }^{\circ}\text{C}$. As reported in a previous article [18], the integration of crystallization peak was made difficult due to the truncation of the crystallization peak beginning. Due to this truncation instead of studying the crystallization half time $t_{1/2}$ to assess the impact of exposure time on crystallization kinetics which could lead to strong degree of inaccuracy, the evolution of the minimum peak time (t_{cpeak}) as a function of the exposure time were measured in Fig. 6. It can be observed an increase of the minimum peak time which shows that crystallization kinetics decreases with crosslinking which is consistent with the PEEK literature [6,15].

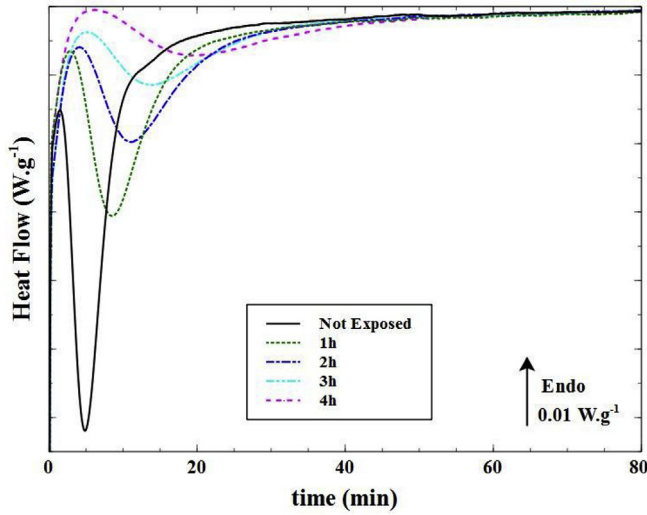


Fig. 5. Isothermal DSC thermograms of neat PEKK 6002 crystallized at 230 °C from the melt after different exposure times at 400 °C under nitrogen.

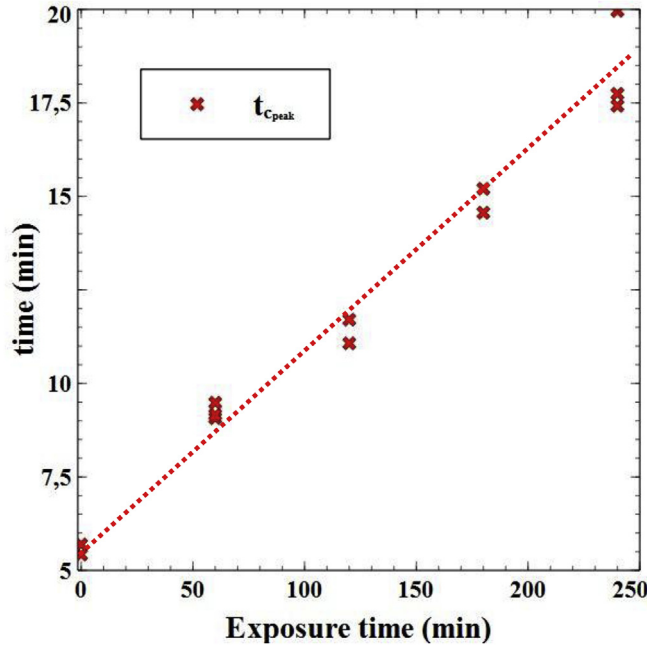


Fig. 6. Crystallization minimum peak time t_{cpeak} vs exposure time at 400 °C under nitrogen of neat PEKK 6002.

The evolution of the melting enthalpy and glass transition after crystallization are presented in Fig. 7. The melting enthalpy decreases with the exposure time up to a value of about 25 J g^{-1} after 4 h exposure at 400 °C whereas T_g increases with the exposure time of about 5 °C. Similar behavior was reported for PEEK [6,15,16] and was attributed to crosslinking decreasing macromolecular mobility. Consequently, even if we have seen that chain scission mechanism occurs in the same time, it seems that crystallization kinetics and final crystallinity are mainly governed by the crosslinking process.

3.3. Rheological analysis

Isothermal rheological measurements for exposure temperatures above T_m were carried out to investigate the evolution of

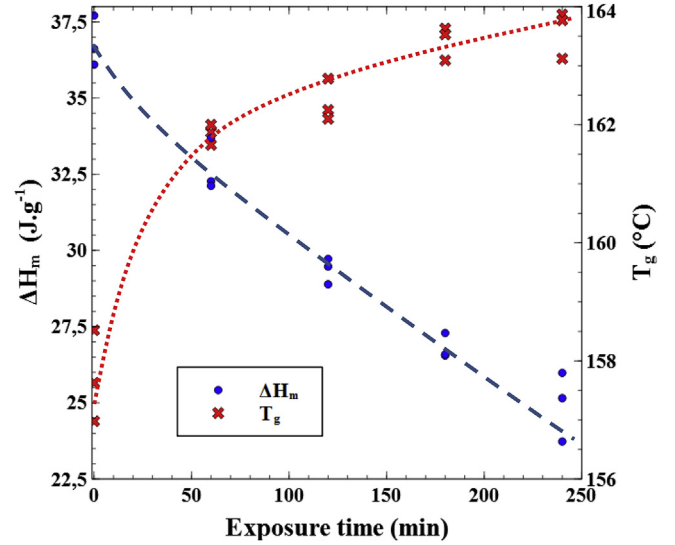


Fig. 7. Melting enthalpy ΔH_m and glass transition temperature T_g vs time of neat PEKK 6002 exposed at 400 °C under nitrogen during different times and crystallized at 230 °C.

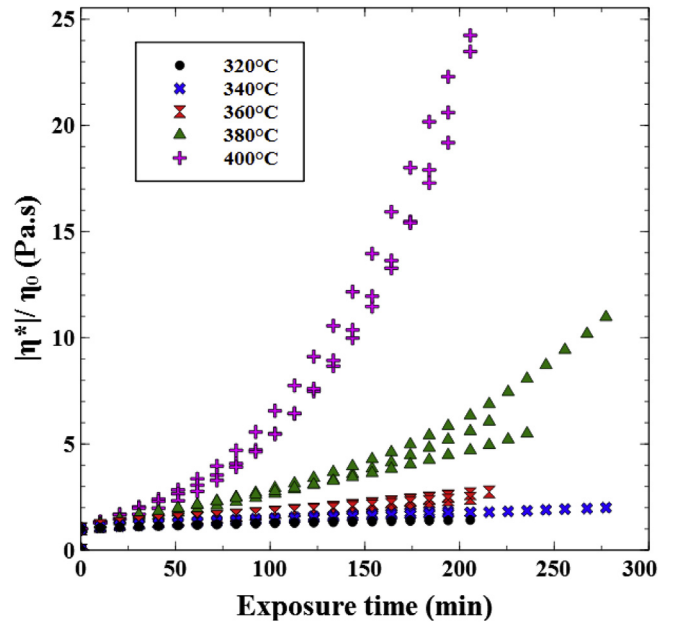


Fig. 8. Modulus of the complex viscosity divided by the Newtonian viscosity vs exposure time of neat PEKK 6002 for different isothermal tests under nitrogen.

PEKK 6002 viscosity at high processing temperatures. Fig. 8 shows the evolution of the normalized viscosity for a given temperature under nitrogen atmosphere as a function of time for different temperatures measured with a strain rate of 1% and a frequency sweep of 1 rad s^{-1} . Let us recall here that the strain rate and frequency sweep values have chosen to ensure that the measured viscosity corresponds to a Newtonian viscosity. However, it is expected that the viscosity measured loses its Newtonian character at high degrees of conversion of the degradation. For exposure temperatures between 320 °C and 360 °C, the viscosity slightly increases with the exposure time whereas above 360 °C, the viscosity strongly increases with the exposure time with an onset of 130 min at 380 °C and 60 min at 400 °C. This phenomenon is the same as observed for PEEK in the literature [1,9,10] and is consistent

with the formation of crosslinking for PEKK heated at high exposure temperatures.

4. Discussion

4.1. Crosslinking and chain scission assessment

According to all experimental results, macromolecular architecture is strongly affected by the thermal degradation. First of all, we propose to compare the results obtained by the different ways in terms of chain scission and crosslinking number occurring during the degradation.

In a first approach, the evolution of the number of crosslinking and scission events x and s (mol.kg^{-1}) with the exposure time can be assessed from the number and weight average molar mass (M_n and M_w) according to the Saito's approach [19,20]:

$$s - x = \frac{1}{M_n} - \frac{1}{M_{n0}} \quad (1)$$

$$\frac{s}{2} - 2x = \frac{1}{M_w} - \frac{1}{M_{w0}} \quad (2)$$

with $M_{n0} = 29.8 \text{ kg mol}^{-1}$ and $M_{w0} = 68.8 \text{ kg mol}^{-1}$. Knowing crosslink mechanism leads necessarily to branched macromolecules, the main hypothesis here is to assume that the macromolecules can be considered statistically as linear macromolecules for the degrees of conversion understudied here. This strong hypothesis is supported by the fact that less than 5% of insolubles were measured for all exposure times.

By solving the equations system (1) and (2) with GPC measurements, the evolution of x and s as a function of the exposure time at 400°C were calculated. Results are presented in Fig. 9. It can be observed a quasi linear increase of x and s and a strong correlation between them which is consistent with the degradation mechanism scheme shown in Fig. 1. If the quasi linear behavior is a characteristic of thermal degradation (see the kinetic aspects

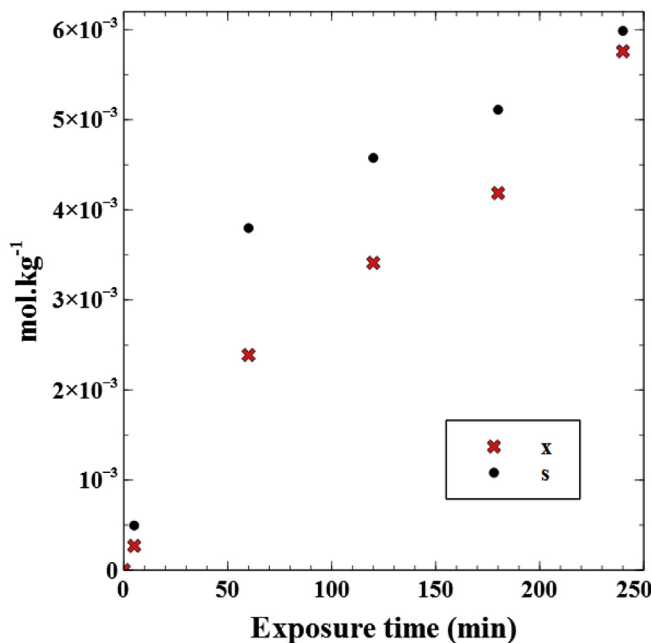


Fig. 9. Number of crosslinking and chain scission events x and s vs exposure time at 400°C under air of neat PEKK 6002.

below), the fact that s and x are strongly correlated comes from the constant M_n values. Although the same experimental results were found for PEEK indicating constant M_n and increasing of M_w and I_p increase by Jonas et al. [6], it is noteworthy that the Saito approach allows us to assess the appearance of chain scission in parallel to crosslinking mechanism.

The evolution of the number of crosslinking events can also be assessed from the rheological measurements. It is well known the complex viscosity measured in Fig. 8 can be related to the weight average molar mass at a temperature T according the following relationship:

$$|\eta^*| = K M_w^{3.4} \quad (3)$$

where K is a constant depending on the temperature. As it was shown from GPC measurements, the number average molar mass is quasi-constant and consequently $s \approx x$. With this assumption, from Eq. (2), the number of crosslinking events x can be expressed by:

$$x = -\frac{2}{3} \left(\frac{1}{M_w} - \frac{1}{M_{w0}} \right) \quad (4)$$

Consequently, from Eqs. (3) and (4), the number of crosslinking events can be expressed as a function of the modulus of the complex viscosity by:

$$x = \frac{2}{3 M_{w0}} \left[1 - \left(\frac{\eta_0}{|\eta^*|} \right)^{\frac{1}{3.4}} \right] \quad (5)$$

where $M_{w0} = 68.8 \text{ kg mol}^{-1}$ and η_0 the viscosity Newtonian which depends on the exposure temperature. The evolution of x as a function of time calculated with Eq. (5) is plotted in Fig. 10. As expected, it can be observed an increase of x with the exposure time with highest values at 400°C . We can witness that the crosslinking process doesn't exhibit a significant induction period: the crosslinking rate is maximum at the beginning of the exposure which is characteristic of thermal degradation where the initiation step controls the kinetic (see kinetic part §4.2).

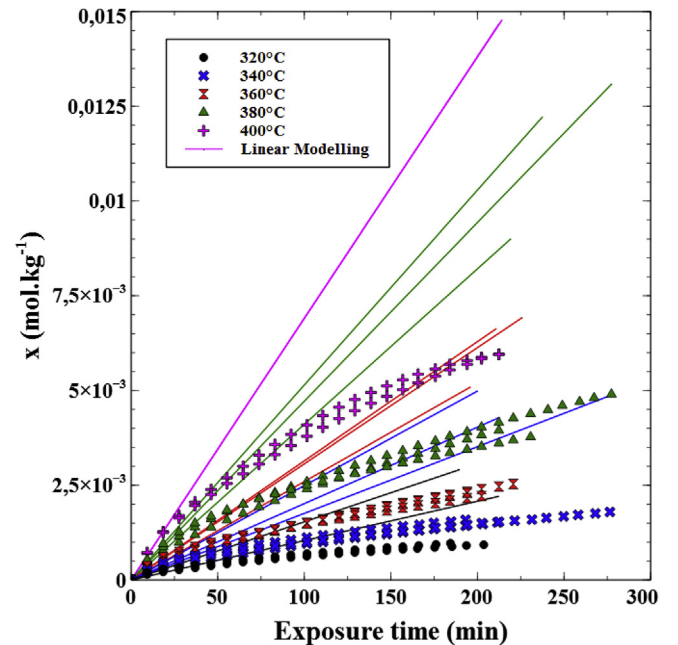


Fig. 10. Number of crosslinking events x vs exposure time of neat PEKK 6002 for different temperatures under nitrogen with the linear modelling.

Fig. 11 shows the comparison of the values of the number of crosslinking events x of PEKK 6002 exposed at 400 °C determined by rheological (viscosity) and GPC (M_n , M_w) measurements. Interestingly, a good correlation between both methods is put in evidence especially at low degrees of conversion. At high degree of conversion, the values of x assessed by GPC appear to be slightly lower than for those assessed by the rheological measurements for values higher than $3 \cdot 10^{-3} \text{ mol kg}^{-1}$ in our case. This discrepancy can be attributed logically to the overestimation of the crosslink number by the rheological measurements or by its underestimation by GPC measurements. On the one hand, the overestimation from a rheological data can be associated to the polydispersity increase associated to the polymer branching. Indeed, for a given molar mass, a branched polymer shows a higher viscosity compare to a linear one. In other words, the scaling law in Eq. (5) has to be modified. On the other hand, some crosslinks can be trapped in the insoluble fraction leading to reduce artificially the M_w increase measured by GPC during the degradation. As a result, the observed correlation shows that the proposed assessment of x and s is valid at low degrees of conversion although this first approach includes some strong hypotheses.

The last way to assess x and s in the literature [21] is to follow the evolution of the number crosslinking events x with the glass transition temperature T_g thanks to the Fox Flory law [22]:

$$T_g = T_{g\infty} - \frac{k_{FF}}{M_n} \quad (6)$$

where $T_{g\infty}$ is the theoretical glass transition of a linear polymer with an infinite molar mass and $k_{FF} = 203.6 \text{ K kg mol}^{-1}$ is the constant of Fox Flory determined for PEEK. The difference of T_g before and after exposure can be expressed by:

$$T_g - T_{g0} = -k_{FF} \left(\frac{1}{M_n} - \frac{1}{M_{n0}} \right) \quad (7)$$

where T_{g0} is the glass transition at the initial time. From Eq. (1), Eq. (7) can thus be written:

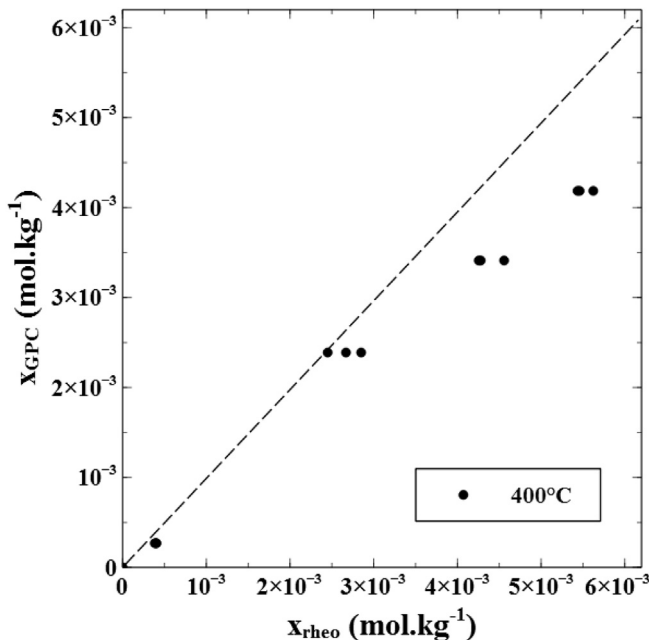


Fig. 11. Comparison of the number of crosslinking events x of PEKK 6002 exposed at 400 °C determined by rheological measurements and GPC measurements.

$$T_g - T_{g0} = -k_{FF}(s - x) \quad (8)$$

However, according to our GPC measurements where M_n remains constant, the T_g predicted by Eq. (8) should be constant which is not consistent regarding Fig. 7. Thus, in our case the Fox Flory law cannot be used to assess the evolution of the number crosslinking events. The main cause could be explained by the fact that the Fox Flory law was established for monodisperse polymers such as PS. As a result, the use of the T_g changes during degradation to monitor macromolecular modification is highly questionable.

4.2. Crosslinking kinetic modelling

Attempts were made to model the evolution of the number of crosslinking events as a function of the thermal processing temperature. A mechanistic approach can be carried out to model x depending on the temperature for any exposure time by exploiting the chemical reaction equations leading to crosslinking. As presented previously, the different steps of the crosslinking mechanism under nitrogen atmosphere can be expressed by:



where PH corresponds to the macromolecular chains, P° to phenyl radicals, x to the number of crosslinking events (mol.kg^{-1}) and k_0 , k_3 and k_4 to the reaction rate constants of the initiation, propagation and termination by crosslinking steps respectively. The kinetic scheme of crosslinking mechanism can thus be written:

$$\frac{d[P^\circ]}{dt} = 2k_0[PH] - 2k_4[P^\circ]^2 \quad (12)$$

$$\frac{d[PH]}{dt} = -k_0[PH] \quad (13)$$

$$\frac{dx}{dt} = \gamma_4 k_4 [P^\circ]^2 \quad (14)$$

where $[P^\circ]$, $[PH]$ correspond to the concentration of PEKK monomer and macromolecular chains respectively, k_0 , k_3 and k_4 to the reaction constants and γ_4 is a constant which is between 0 and 1 allowing to take into account the fact that radicals can also rearrange by internal combination.

In first approach, it can be assumed that at low degree of conversion the PH consumption is negligible. Hence, Eq. (12) becomes:

$$\frac{d[P^\circ]}{dt} = 2k_0[PH]_0 - 2k_4[P^\circ]^2 \quad (15)$$

With $[PH]_0$ the initial concentration of PH which depends on the number of potentially sites which can be activated for crosslinking reactions so precisely the sites where macromolecular chains can be broken:

$$[PH]_0 = n_{\text{sits}} \frac{1}{M_{0\text{PEKK}}} d_{\text{PEKK}} \quad (16)$$

Where n_{sits} is the number of sites which can be activated, $M_{0\text{PEKK}} = 300.3 \text{ g mol}^{-1}$ is the molar mass and $d_{\text{PEKK}} = 1.3$ is the density. n_{sits} can take three different values, if chains scissions occurs at the carbonyl functional groups $n_{\text{sits}} = 4$, if chains scissions

occurs at the ether bonds $n_{\text{sits}} = 2$ and finally if we consider that the chain scission occurs randomly at the carbonyl and ether bonds $n_{\text{sits}} = 6$.

By solving Eq. (15), the concentration of alkyl radicals P° can be expressed by:

$$[P^\circ] = [P^\circ]_{\text{stat}} \frac{1 - \exp(-\frac{t}{\tau})}{1 + \exp(-\frac{t}{\tau})} \quad (17)$$

With $[P^\circ]_{\text{stat}}$ the concentration of alkyl radicals at the stationary state equal to:

$$[P^\circ]_{\text{stat}} = \left(\frac{k_0 [PH]_0}{k_4} \right)^{1/2} \quad (18)$$

And the characteristic time to reach the stationary state τ equal to:

$$\tau = \frac{1}{4 (k_0 k_4 [PH]_0)^{1/2}} \quad (19)$$

As alkyl radicals (P°) are highly reactive ($k_4 > 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$), the stationary state for P° is reached at the very beginning of exposure. Thus, at low degree of conversion, it can be written:

$$[P^\circ] = \left(\frac{k_0 [PH]_0}{k_4} \right)^{1/2} \quad (20)$$

Consequently, for low exposure time, by solving Eq. (14), the number of crosslinking events x is equal to:

$$x = \gamma_4 k_0 [PH]_0 t \quad (21)$$

This equation corresponds to a linear equation which passes by 0 with a slope of $\gamma_4 k_0 [PH]_0$ corresponding to the apparent crosslinking kinetics k_{app} . Consequently, straight lines were fitted with the beginning of the number of crosslinking events x curves plotted in Fig. 10 ($t < 20 \text{ min}$) to determine k_{app} depending on the exposure temperature.

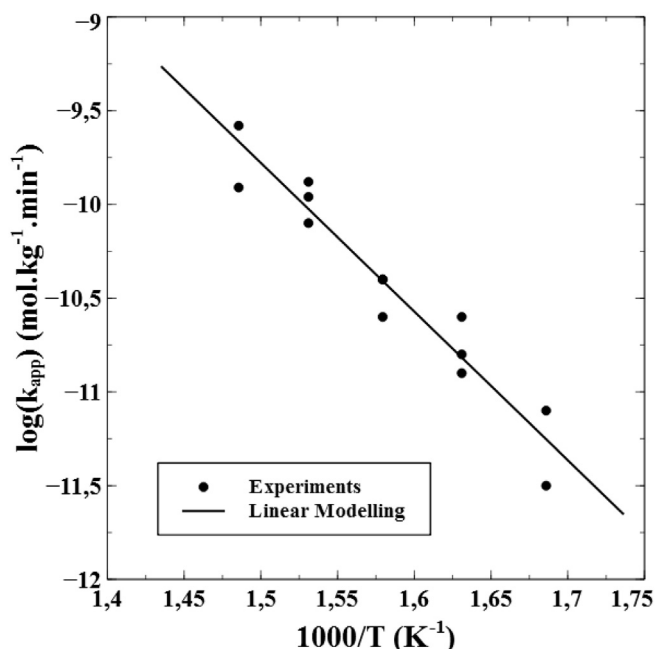


Fig. 12. Arrhenius plot of the apparent crosslinking kinetics of neat PEKK 6002 under nitrogen.

The logarithm of the apparent crosslinking kinetics k_{app} is plotted as a function of the inverse of the exposure temperature in Fig. 12. First, it can be observed k_{app} follows an Arrhenius behavior. The apparent crosslinking activation energy E_{akapp} and $k_{\text{app}0}$ have been determined to be equal to 65.9 kJ mol^{-1} and $8.27 \text{ mol.kg}^{-1} \text{ min}^{-1}$. It's noteworthy that the crosslinking activation energy of PEKK is quite lower than the value reported from mass loss measurements (TGA) in the literature for carbon PEKK close to 210 kJ mol^{-1} [13] and for PEEK between 220 and 320 kJ mol^{-1} over temperatures ranging from 400 to 700°C [3,23,24].

5. Conclusion

From rheological, GPC and DSC measurements, it has been shown that PEKK 6002 matrix is modified above 320°C under nitrogen or lack of oxygen. The witnessed modifications are characterized by an increase of the viscosity, the weight average molar mass M_w and the glass transition temperature T_g . If all these phenomena are typical to a crosslinking/branching mechanisms occurring during exposure, the fact that M_n values remain constant indicates that a chain scission mechanism occurs in the same time. According to Saito's approach based on molar masses changes, it has been established that for each crosslinking event, one chain scission occurs. Based on this result and the viscosity changes as a function of the exposure temperatures, the crosslinking kinetics has been investigated. These mechanisms have been observed to be thermally activated and following an Arrhenius law. From the kinetic scheme of crosslinking mechanism, crosslinking/branching kinetics has been modelled with a linear model for low exposure times ($t < 20 \text{ min}$). Finally, crosslinking occurring at the melting state has been found to decrease crystallinity and crystallization kinetics with the decrease of the crystallization melting enthalpy and the increase of the minimum crystallization peak time.

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