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Dynamic rheological behavior of poly(ether ketone ketone) from solid state to melt state

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ABSTRACT: High performance thermoplastic poly(ether ketone ketone) (PEKK) polymers with various meta phenyl links ratio were investigated by dynamical mechanical analysis. Analyses were carried out in a wide range of temperature from solid state (torsion rectangular mode) to the melt state (torsion parallel plates mode) as function of thermal history and environmental conditions. In the solid state, this study was focused on the secondary relaxations in the vitreous state. A complementary investigation conducted with different poly(aryl ether ketones) allowed us to propose a molecular interpretation of PEKK sub-vitreous relaxations. In the molten state, storage modulus (G'), loss modulus (G''), storage viscosity (η'), and loss viscosity (η'') were studied to determine zero shear-rate viscosity (η_0) and thermal activation energy E_a . Master curves were built and the shift factor a_T was determined. Thermal activation energies were extracted from an Arrhenius model on the shift factor temperature's dependency. Finally, E_a and η_0 were determined thanks to the dynamic viscosity fit with Cross model and Cole–Cole representation. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, *135*, 46456.

KEYWORDS: mechanical properties; rheology; structure–property relationships; thermoplastics; viscosity and viscoelasticity

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INTRODUCTION

The interest in poly(aryl ether ketones) (PAEKs) as matrices for high performance composites has been increasing in the last years due to attractive mechanical properties, weight savings, and environmental resistance.¹ Among PAEKs, poly(ether ketone ketone) (PEKK) received specific interest with modulated macroscopic properties coming from a chemical structure containing different para/meta phenyl isomers (T/I ratio). The influence of the T/I ratio on physical structure of PEKK was extensively studied. Hsiao *et al.*^{2,3} reported the evolution of melting and crystallization behavior of PEKK upon the influence in meta links content. We recently published a combined study by differential scanning calorimetry and dynamic mechanical analysis (DMA) in the solid state of PEKK with different thermal history and T/I ratio (80/20, 70/30, 60/40).⁴ In the vitreous state, very few works concern sub-glass relaxations of PEKK. Contrarily, PEEK is probably the most widely studied PAEK. Its molecular mobility has been extensively studied by mechanical and dielectric techniques. Sasuga and Hagiwara observed by DMA a broad relaxation mode near -80°C : it was associated to oscillations of phenyl groups.⁵ David and Etienne⁶ studied a wide mode in the same temperature range as result of two different contributions. At low temperature, the β_1

contribution (-110°C) was associated with the mobility of phenyl groups around their axes; at higher temperature (-33°C) the β_2 contribution was associated with an inter chain mobility. Mourgues-Martin presented complementary data obtained by a dielectric approach.⁷ Indeed, thermally stimulated current technique revealed the bimodal behavior of the low temperature relaxation mode, the so-called γ mode, in the same temperature range. The lower temperature contribution at -90°C was associated with the local mobility of phenyl groups in the amorphous crystallizable phase, meanwhile the higher temperature contribution at -40°C was associated to local mobility of non-crystallizable amorphous sequences. In comparison, as far as we know, no dynamic mechanical analyses have been performed for PEKK: sub-glass relaxations have only been reported by dielectric methods^{8,9} where γ and β relaxations were observed in the low temperature range, between -135 and -50°C . Consequently, a part of this work is dedicated to this specific point.

Few studies were devoted to high performance thermoplastics in the molten state; Chen *et al.*¹⁰ investigated the evolution of viscosity and shear modulus for blend PEEK and liquid PEAK. Lamethe¹¹ reported the effect of the temperature on PEEK viscosity for structural sticking applications while Guehenec *et al.*¹² considered PEEK filled with carbon nanotubes to study

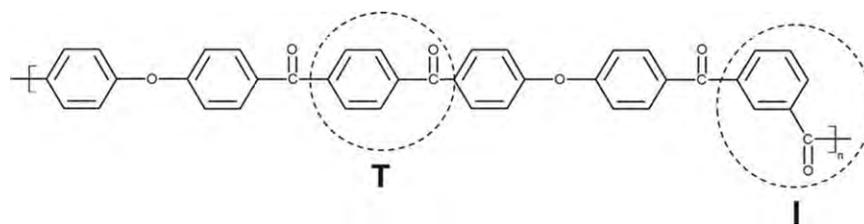


Figure 1. Molecular structure of PEKK with para and meta links.

the nanocomposite viscosity. Considering the specificity of PAEKs in the molten state, it sounds relevant to use as reference the behavior of molten technical polymers, with more flexible chains. An extensive literature concerns the flow behavior of such polymers. Yasuda *et al.*¹³ investigated the effect of polymer structure and molecular weight on viscosity of linear and branched polystyrene. Collins and Metzger¹⁴ show the influence of molecular weight on the activation energy for poly(vinyl chloride). Various configurations of melt polymer rheology have been explored: semi-hyperbolic die channel system (Collier *et al.*¹⁵), cone-plate¹³, and plate-plate configuration.^{10–12,16} In this work, a parallel plate configuration is proposed. Master curves have already been built for technical polymers; for example Yin and Ferry¹⁷ have investigated rheological behaviors of poly(ethyl butyl methacrylate) with various chain lengths and molecular weights. The shift factor a_T could be determined by shifting the complex modulus along shear-rate axis (horizontal axis). In order to describe a_T temperature dependency, El Sawi *et al.*¹⁸ and Ferry¹⁶ used Williams-Landel-Ferry (WLF) phenomenological equation. Arrhenius equation was extensively used for technical thermoplastics^{14,18,19} and for PEEK.^{10–12} Consequently, a_T function was fitted with Arrhenius model for PEKK and activation energies were extracted for various T/I ratios.

Shear viscosity was classically followed to extract zero shear-rate viscosity. Polymers viscosity behavior tends to a constant value for low shear-rate.²⁰ Several models were used to determine η_0 : Carreau-Yasuda model was used to fit dynamic viscosity of technical thermoplastic like low-density polyethylene,²¹ high-density polyethylene,²² or particles filled polymer.^{11,16,23} Cross model has been already used for PEEK.^{11,12} As PEEK and PEKK are chemically similar, Cross model has been chosen. The dependence of η_0 with temperature allows us to determine E_a . Cassagnau *et al.*²⁴ used Cole-Cole representation to fit shear viscosity and to extract E_a . It will be interesting to confront activation energy values obtained thanks to Cross model, Cole-Cole representation, and shift factor behavior. E_a is an important data for processing thermoplastic, with high thermal activation energy the behavior of the polymer will rapidly evolve to a more liquid-like state.

To the best of our knowledge, a rheological analysis from the solid state to the molten state for PEKK with different T/I ratio, is original. Such a set of data is of interest for improving the processing conditions of PEKK. This manuscript proposes a study in an extended temperature range of its dynamic behavior as a function of physical structure and hydration. A specific attention has been paid to shear viscosity and the related

activation parameters that might allow us to predict the rheological behavior.

EXPERIMENTAL

Materials

PEKK KEPSTAN 7003 and PEKK KEPSTAN 6003 (Figure 1) were supplied by Arkema, France in powder form (20 μm).

These two grades have similar chemical structure but they differ by their T/I ratio. For PEKK KEPSTAN 7003 and 6003 the T/I ratios are 70/30 and 60/40, respectively.

Methods

DMA in the Solid State. Sub-vitreous relaxations of PEKK were studied using an ARES strain controlled rheometer from Thermal Analysis Instruments in the rectangular torsion mode. For dynamic analysis, sinusoidal strain γ^* is imposed with a constant angular frequency ω . Viscoelasticity of polymers leads to a phase lag between strain and stress σ^* which allows us to define in the linear domain the complex shear dynamic mechanical modulus. Storage and loss moduli, G' and G'' , were recorded as a function of temperature. Measurements were achieved in a temperature range from -130 to 270°C , with a scanning rate of 3°C min^{-1} . The angular frequency ω was 1 rad s^{-1} and the strain γ was 0.1%. Test samples have parallelepipedic shape with 40 mm in length, 10 mm width, and a thickness of 500 μm . Semi-crystalline samples were obtained by annealing amorphous samples at 240°C in an oven for 5, 10, 30, and 60 min.

DMA in the Molten State. The shear flow behavior of the PEKK with different T/I ratio was measured in the parallel plate configuration with the same rheometer as described previously. Samples were elaborated from powders in a hot press above

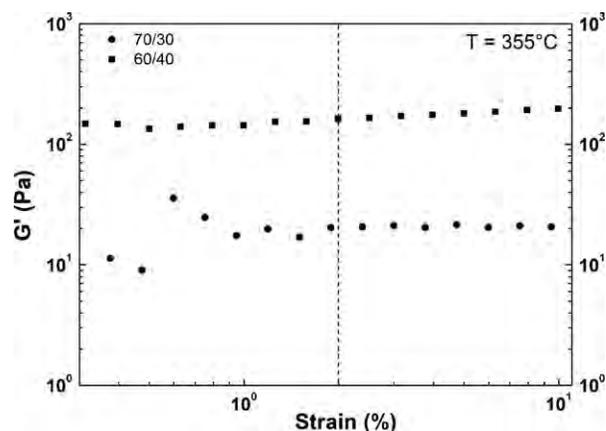


Figure 2. Shear flow modulus function of strain for PEKK 60/40 and PEKK 70/30 at 355°C .

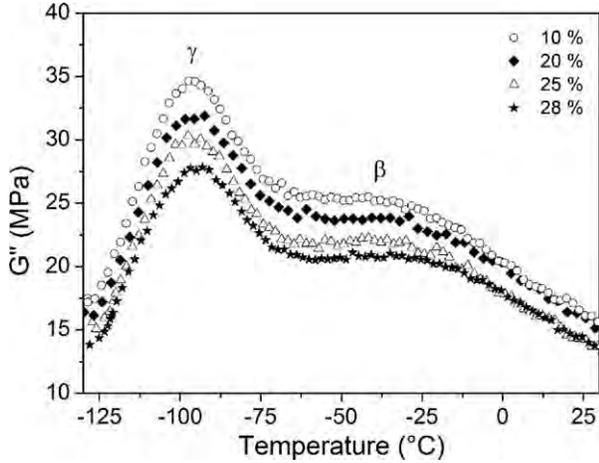


Figure 3. G'' versus temperature at 1 rad s^{-1} for PEKK 60/40 for different % crystallinity.

350°C for 10 min and then pressed at 0.3 MPa to obtain 1.5 μm thickness pellets with 25 mm in diameter. Preliminary studies were done to determine steady shear state for PEKK measuring shear modulus in strain rate sweep (Figure 2). Strain ranged from 0.1% to 10% with an angular frequency of 1 rad s^{-1} . Analyses were carried out for the isotherm 355°C .

For low strain, the signal for PEKK 70/30 showed disturbance due to the sensitivity limit of mechanical sensors. The higher value of viscosity for PEKK 70/30 could explain these disturbances. According to the preliminary study, the strain rate for both PEKK will be chosen at 2%. The steady shear modulus and viscosity were measured at a shear rate from 10 to 350 rad s^{-1} . For PEKK 60/40, the shear flow was studied at temperature ranging from 326 to 345°C and from 355 to 367°C for PEKK 70/30.

Analysis of the Rheological Behavior by the Cross Model. The non-Newtonian behavior of the viscosity $\eta(\omega)$ of PEKK was described by the Cross model according to the following equation [eq. (1)]:

$$\eta(\omega) = \frac{\eta_0}{1 + (\tau_c \omega)^n} \quad (1)$$

where η_0 refers to the asymptotic value at very low shear-rate (or zero shear viscosity), n is the power law exponent characteristics of the deviation from a Newtonian behavior and τ_c is a time characteristic of the slope discontinuity.²⁵

Cole–Cole Representation. In the Cole–Cole representation, the imaginary part of the viscosity $\eta''(\omega)$ is plotted as function of the real part $\eta'(\omega)$ of the complex viscosity $\eta^*(\omega)$. Data was fitted with a half-circle equation [eq. (2)] and zero shear viscosity was found at the intersection of the circle with the real viscosity axis.^{11,26}

$$\eta_0 = x_c + \sqrt{R^2 - y_c^2} \quad (2)$$

where η_0 refers to the zero shear viscosity, x_c and y_c are the graphical coordinates of the center of the circle and R is the radius.

RESULTS AND DISCUSSION

The first part of this section is devoted to the mechanical properties of PEKK in the solid state, the second part concerns the rheological behavior in the molten state.

Mechanical Properties in the Solid State

Influence of Thermal History on Sub- T_g Relaxations. Various samples of PEKK 60/40 were annealed at 240°C for 5, 10, 30, and 60 min after a fast cooling from the melt state. The evolution of G'' in the low temperature region for those samples is reported in Figure 3.

In this region, the two G'' maxima observed correspond to secondary relaxations here called γ and β , located at $T_\gamma = -96 \pm 1^\circ\text{C}$ and $T_\beta = -33 \pm 1^\circ\text{C}$, respectively. Different crystallinity ratio was achieved, varying from 10% to 28% for annealing times ranging from 5 to 60 min. Before analyses, samples were equilibrated for a couple of hours at room temperature to reaching the same equilibrium state before the analysis. The amplitude of the sub-glass relaxations decreases when the crystallinity increases, i.e., when the amorphous phase decreases. This molecular mobility of the γ and β relaxations has been associated to amorphous sequences. Comparison between amorphous and semicrystalline PEKK was reported by Sauer *et al.*⁸ by Thermo-Stimulated Current technique. A γ mode was observed at -135°C and a β mode at -70°C : Both relaxations have been also associated to the amorphous phase. These results are consistent with our data.

Influence of Moisture. The influence of hydration has also been considered for crystalline PEKK. The evolution of G'' in the low temperature region for samples equilibrated in environments with different humidity rate is presented in Figure 4. The dried samples were dehydrated directly in the DMA oven. Some samples were soaked in water for 7 days. The maximum content of absorbed water was determined at 1.2% in weight. Samples equilibrated in laboratory conditions ($25^\circ\text{C}/\text{R.H. } 55\%$) for 2–24 h do not undergo a specific procedure.

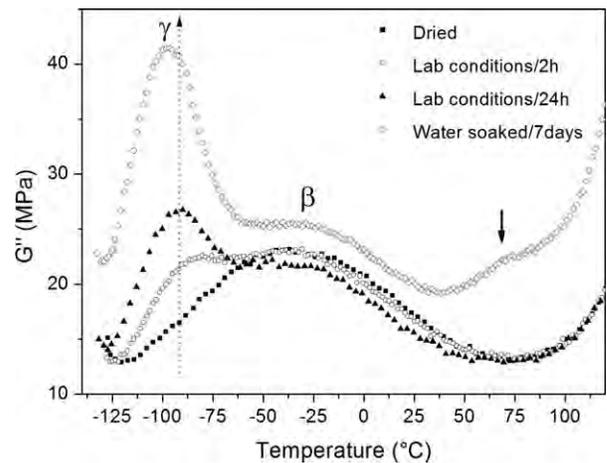


Figure 4. G'' versus temperature at 1 rad s^{-1} for annealed PEKK 60/40 samples, with $\chi = 25\%$, equilibrated in different humidity content environments.

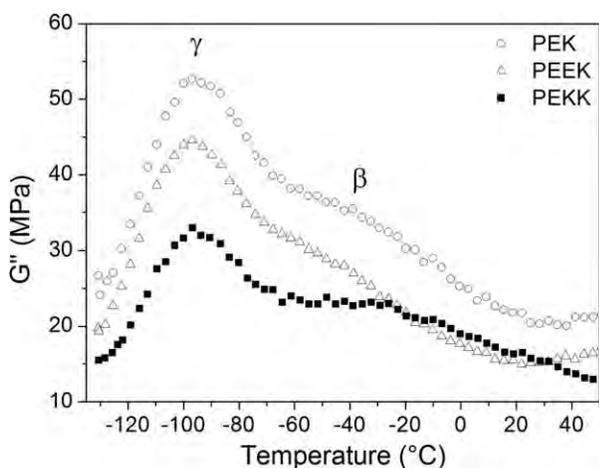


Figure 5. Loss modulus versus temperature at 1 rad s^{-1} for PEK, PEEK, and PEKK equilibrated in laboratory conditions.

For dried samples, only one maxima of G'' is observed, corresponding to the β mode. γ relaxation disappeared while β mode broadens in a wide range of temperature from -120 to 70°C . With the increasing humidity content in samples, the γ mode amplitude increases, first as a shoulder of the β mode and then as a well-defined relaxation. Nevertheless, the temperature maxima decreases with water content. No specific evolution was observed for β relaxation. Goodwin and Hay⁹ already observed a sub-glass relaxation in PEKK near to -50°C and its sensitivity to absorbed moisture: an amplitude and temperature decrease was reported with absorbed moisture. It is consistent with our results. This last behavior has already been reported for PEEK. Bas *et al.*²⁷ reported a β relaxation at -80°C assigned to the mobility of polar entities that interact with absorbed water.

In addition, when PEKK was soaked in water, a supplementary mechanical phenomenon pointed by an arrow appeared near to 75°C . Its origin must be related with a water desorption manifestation.

Low Temperature Molecular Mobility in PAEKs. In order to move further with our interpretation of the molecular origin of the sub-glass transitions, a complementary study has been conducted. Sub-vitreous relaxations were followed for three members of the PAEKs family, PEEK (EK301400 Goodfellow), poly(ether ketone) (PEK) (EK351100, Goodfellow), and PEKK 60/40. In the low temperature range, the loss modulus behavior for these polymers that were all equilibrated at laboratory conditions are presented in Figure 5.

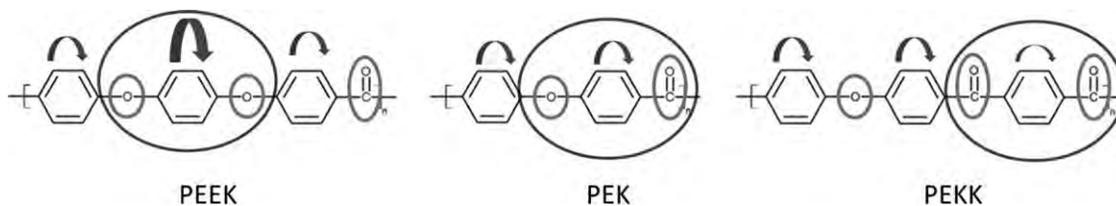


Figure 6. Chemical structure of PEEK, PEK, and PEKK.

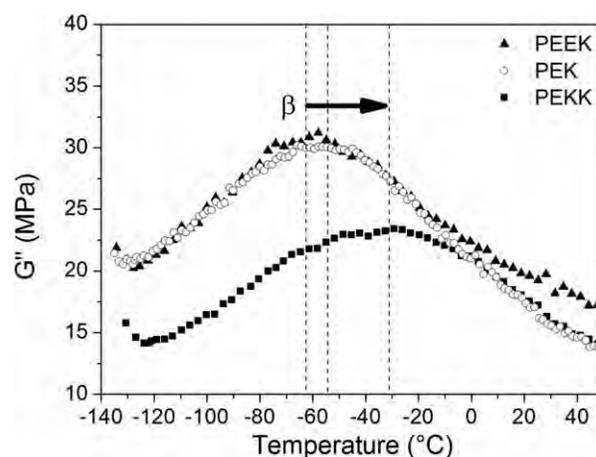


Figure 7. Loss modulus versus temperature at 1 rad s^{-1} for PEK, PEEK, and PEKK in the dehydrated state.

For samples equilibrated in laboratory conditions along several hours, the G'' behavior is quite similar. The γ and β relaxations are observed for the three polymers in the same temperature range at $T_\gamma \sim -96^\circ\text{C}$ and $T_\beta \sim -33^\circ\text{C}$ for PEKK, -35°C for PEK, and -40°C for PEEK. The fact that PAEK polymers are a similar chemical structure explains the weak difference between thermograms (Figure 6).

Figure 7 shows the evolution of G'' for the three polymers dehydrated above 100°C . As it was previously observed, γ relaxations disappear when the sample is dried also for PEK and PEEK. Only the β relaxation is still observable in the same temperature range. However, a shift toward higher temperatures of β relaxation is observed for PEK and PEKK compared to PEEK: $T_\beta = -33^\circ\text{C}$ for PEKK, $T_\beta = -55^\circ\text{C}$ for PEK, and $T_\beta = -63^\circ\text{C}$ for PEEK.

These results confirm that the molecular origin of these two relaxations is very close for these three polymers, since the evolutions are similar and temperature manifestations are very close.

Regarding the γ relaxation and considering previous results,²⁷ this relaxation has been associated with entities which can interact with water, like a polar entity. Based on our results, we can assume that γ relaxation can be associated with the interaction between ketone and absorbed water.

Since ketone linkages are more rigid than ether linkages,^{28,29} the oscillations of a phenyl ring have to be easier between two ether linkages or between ether-ketone linkages than between two ketone-ketone groups. Since the proportion of ketone groups are 33% for PEEK, 50% in PEK, and 66% in PEKK, the shift

Table I. T_α Values versus Crystallinity Ratio

Crystallinity ratio χ_c (%)	T_α (°C)
10	153.5
20	153.5
25	155
27.5	157.5

observed toward higher temperatures up to 30 °C can be related to an easier mobility of phenyl groups. Considering interpretations in literature and based on our results, we can confirm that β relaxation is related to the mobility of phenyl groups around their axis.

Molecular Mobility at the Viscoelastic Transition. The viscoelastic transition of PEKK has been extensively studied by DMA in a previous paper.⁴ A specific attention has been paid to the influence of crystallinity and T/I ratio in the T_α region. We recall in this part data necessary for the following. The analysis of G'' shows a broadening of the α mode with increasing crystallinity ratio. This result was associated with a reduced mobility of the liquid amorphous phase. However, no particular evolution was observed for T_α values. Table I reports T_α values for different crystallinity ratio.

Regarding the effect of the T/I ratio on the viscoelastic behavior of PEKK, few evolutions were observed: T_α showed little increase (154 °C for $T/I = 60/40$, 157 °C for $T/I = 70/30$, and 161 °C for $T/I = 80/20$) with increasing T/I ratio.⁴ This result was related to the increase of mobility with increasing meta links proportion.³

Rheological Behavior in the Molten State

Master Curves. Figure 8 shows the shear modulus as a function of shear-rate for several isotherms above the melting. As expected, loss modulus and storage modulus increase with the shear-rate. The storage modulus is lower than the loss modulus for low shear-rate, which is usual for melt polymers. Moreover, both storage and loss moduli show a temperature dependence.

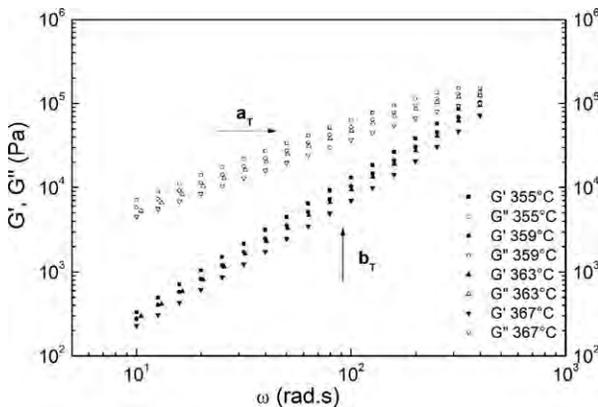


Figure 8. Frequency sweep of storage modulus and loss modulus for four isotherms (355, 359, 363, and 367 °C) of PEKK 70/30.

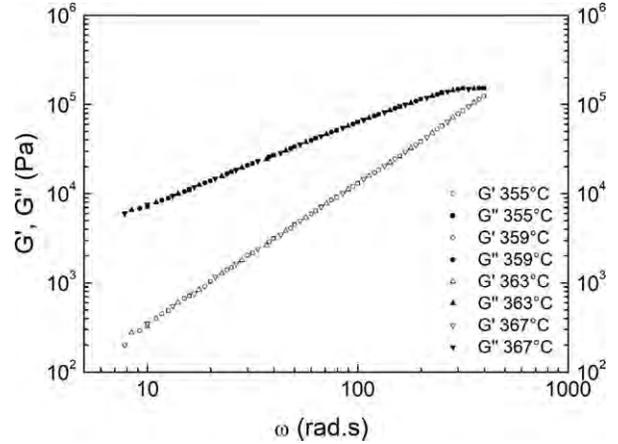


Figure 9. Master curve of storage modulus and loss modulus for the reference temperature $T_{ref} = 355$ °C for PEKK 70/30.

Master curves were built for a reference temperature $T_{ref} = 355$ °C (Figure 9) by shifting isotherms along horizontal and vertical axis.

The activation energy E_a is deduced from the horizontal shift factor a_T [eq. (3)].

$$a_T = A \times \exp\left(\frac{E_a}{R} \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (3)$$

Figure 10 reports the plot of a_T as a function of temperature for the reference temperature T_{Ref} . For the PEKK 70/30, the activation energy $E_a = 156$ kJ mol⁻¹ is obtained from the Arrhenius plot.

The configurations of PEKK characterized by the T/I ratio have an influence on E_a : indeed, PEKK 60/40 has an activation energy $E_a = 136$ kJ mol⁻¹. The configurational defects might perfectly explain this decrease. It is interesting to note here that the activation energy of PEEK is 90 kJ mol⁻¹ according to the following references.^{11,12} This value is lower than the PEKK one. This difference is explained by the wider percentage of ether groups.

For polymers containing phenyl groups, the activation energy remains of the same order of magnitude i.e., for polycarbonate

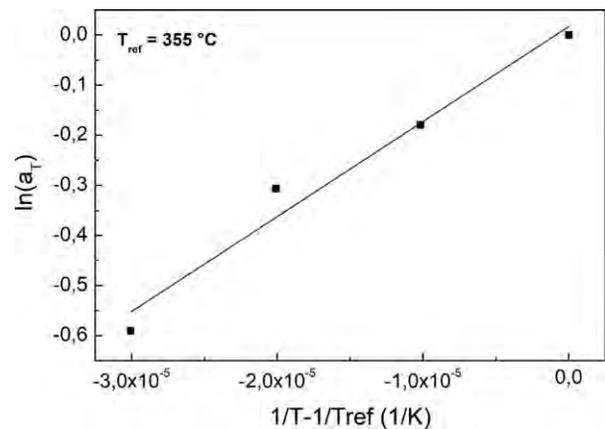


Figure 10. Arrhenius diagram of the shift factor of G' for PEKK 70/30.

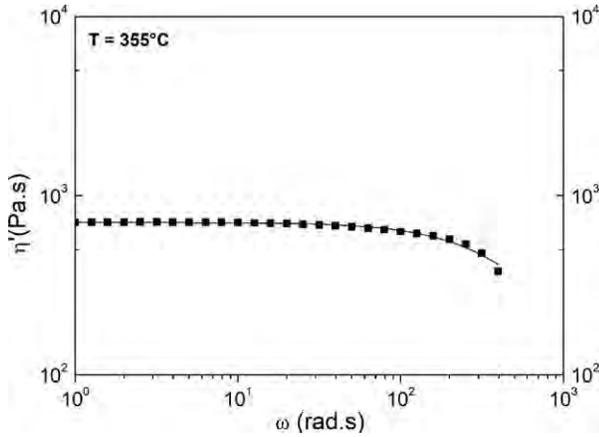


Figure 11. Isothermal variation of viscosity versus frequency for PEKK 70/30: The solid line corresponds to the fit with Cross model.

$E_a = 85 \text{ kJ mol}^{-1}$.²⁰ Contrarily, for polymers with flexible chains, like polyethylene, polybutadiene, and polyesters,²⁰ low values of E_a (about 25 kJ mol^{-1}) are reported.

Analysis by the Cross Model. For isotherms above melting, shear viscosity behavior was plotted as a function of shear rate from 1 to 400 rad s^{-1} (Figure 11). From 10^2 rad s^{-1} , the observed viscosity decreases: This is consistent with a rheofluidifying behavior which is classical for linear polymers.^{10,18} For low shear rate at 355 °C, the constant value corresponding to the zero shear-rate viscosity η_0 is 710 Pa s.

From the Cross model, the exponent parameter is $n = 0.97$ close to 1 which is characteristic of a Newtonian fluid; the characteristic time is $\tau_c = 0.009 \text{ s}$.¹³

The zero-shear viscosity was plotted versus reciprocal temperature (Figure 12). It allows to determine the activation energy E_a according to the Arrhenius equation [eq. (4)].

$$\ln \eta_0 = \ln A + \frac{E_a}{RT} \quad (4)$$

Activation energy determined from the Cross model for PEKK 70/30 is 153 kJ mol^{-1} . This value is consistent with the one obtained from the master curve approach (155 kJ mol^{-1}). The same analysis, with the Cross model was applied on PEKK 60/40: an activation energy of 131 kJ mol^{-1} (136 kJ mol^{-1} with

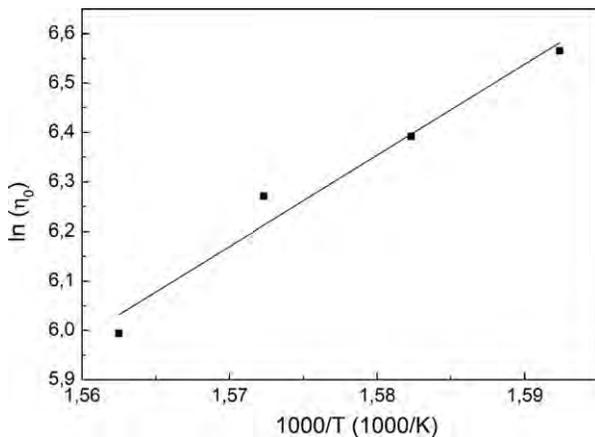


Figure 12. Activation diagram for the zero shear rate viscosity η_0 .

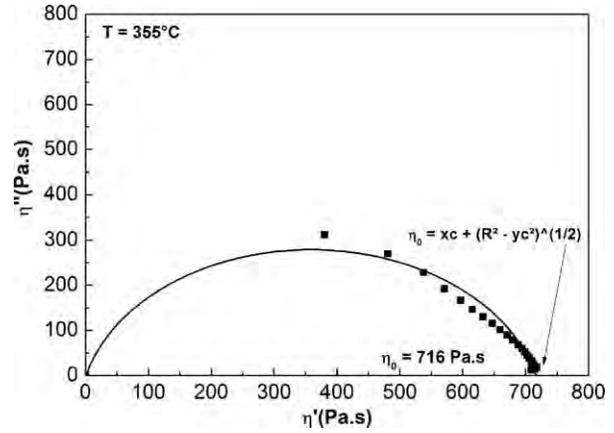


Figure 13. Cole-Cole plot for viscosity on isothermal sweep frequency for PEKK 70/30.

the master curve approach) is obtained. Both approaches are perfectly consistent. With Cross model, we directly link energy and viscosity. Thus, we can calculate the zero-shear rate for any temperature above melting, which corresponds to the apparent viscosity of the polymer.

Cole-Cole Representation. Figure 13 shows the imaginary part of viscosity versus its real part. For a rheofluidifying fluid this curve is commonly an arc of circle.^{12,13,25} Values of zero shear-rate viscosity were obtained from the arc of circle fit. The intersection of the horizontal axis and the curve correspond to the zero shear-rate viscosity.

The zero shear viscosity obtained from Cole-Cole plot at 355 °C was 716 Pa s. Zero-shear viscosity was plotted versus reciprocal temperature on an Arrhenius diagram to determine activation energy (Figure 14).

Activation energy obtained from the Cole-Cole plot for the PEKK 70/30 is 155 kJ mol^{-1} . The experimental value deduced from the analysis with the Cross model of PEKK 60/40 is in the same range: i.e., 134 kJ mol^{-1} . Even if the determination from the Cole-Cole plot is less accurate than the value deduced from the master curve, the difference is weak and confirms previous results.

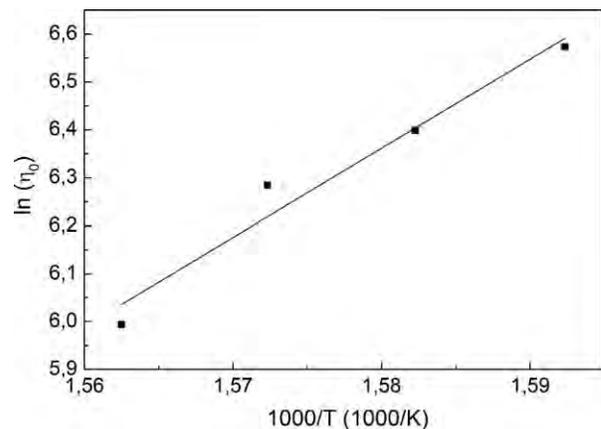


Figure 14. Arrhenius diagram of the zero shear rate viscosity η_0 determined from the Cole-Cole plot.

CONCLUSIONS

Rheological properties of PEKK were studied in a large range of temperature. In the solid state, at low temperature, two sub-glass relaxations were identified: γ at -96°C and β at -33°C . The influence of moisture was highlighted for γ relaxation, not only for PEKK but also for PEK and PEEK. γ relaxation was associated with the interaction between ketone entities and water molecules. Based on comparison between different PAEEKs at the dried state, β relaxation was associated with the mobility of phenyl groups around their axis. PEKK is a semicrystalline polymer, and its crystallinity can be conducted by varying processing conditions. However, it was shown how sub-glass relaxations are uninfluenced by crystallinity. Moreover, the effect of the T/I ratio on sub-glass relaxations had already been discussed. The influence of crystallinity ratio and T/I ratio is more evident in the viscoelastic transition region, as it was already shown.

In the molten state, master curves were built using G' and G'' isotherms. It is interesting to note that those data are consistent with the ones deduced from Cole–Cole diagram. For PEKK 70/30 and 60/40, the shift factor a_T has an activation energy of 156 and 136 kJ mol^{-1} , respectively. The decrease of the activation energy upon the decrease of the T/I ratio is explained by a higher concentration in configurational defects. It is also interesting to note that for PEEK, the activation energy is lower than for PEKK. The flexibility of the ether group also perfectly explains this evolution.

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