

A comparison of the α -relaxation of amorphous poly(aryl-ether-ether-ketone) (PEEK) probed by dielectric and dynamic mechanical analysis

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A re-examination of the α -relaxation of amorphous PEEK is performed based on dielectric (DEA) and dynamic mechanical (DMA) probes. The skewed arc shapes of the DEA and DMA data presented in Cole–Cole coordinates indicate the necessity to use the Havriliak–Negami (HN) equation to analyse the data. The analysis of isochronal scans measured in a wide frequency range is performed by fitting the HN equation to the complex inverse of the dielectric susceptibility simultaneously with the complex dynamic mechanical modulus. The satisfactory quality of the simultaneous DEA/DMA fit provides strong support to the general scaling character of the α -relaxation and the similarity of the nature of relaxing units examined by both probes. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

Poly(aryl-ether-ether-ketone) [PEEK, poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)] is a semi-crystalline high-performance thermoplastic with a fully para-aromatic backbone arrangement. The combination of high-performance properties of PEEK such as thermal and chemical stability, excellent mechanical properties, high glass transition temperature (T_g) and extremely large temperature interval of crystallization, is outstanding. From the scientific point of view the properties of PEEK have attracted significant attention since its early introduction to researchers¹. Indeed, these properties allow the creation of a great variety of semi-crystalline morphologies and thus pave the way to the study of a wide range of structure/property relationships.

Fully amorphous PEEK is available by quenching the polymer melt from high temperatures. The fully amorphous state of PEEK has been the subject of extensive studies focusing on thermal properties², transport phenomena³, physical ageing⁴, subglass relaxations and glass transition^{5–11}. Motions in amorphous PEEK were examined on a wide frequency range from NMR frequencies¹² down to the rates of structural relaxation within some range below T_g ^{6,13} using various probes, usually dielectric analysis (DEA)^{5,7–15} and dynamic mechanical analysis (DMA)^{5,11,16}. The important features of the glass transition (or α -relaxation) of PEEK (e.g. temperature dependencies of characteristic times^{10,11}, relaxation strength^{7,9} and spectral shape parameters^{6,9,10}) were also determined. Nevertheless, some questions remain open concerning the α -relaxation of pure amorphous PEEK. These questions are:

- (1) The applicability of the time–temperature superposition principle in its simplest form¹⁷. Indications of departure from thermo-rheological simplicity were given by David and Etienne¹¹, based on a series of isothermal DMA frequency sweeps. However, time–temperature superpositions were apparently successfully performed

by other authors^{16,18}. It has been proposed that part of these discrepancies originate from the existence of significant nonlinear time–temperature-dependent effects below T_g , which were interpreted as arising from irreversible microstructural rearrangements from a quasi-stable state^{11,19}.

- (2) The origin of the reported difference between the characteristics of the α -relaxation of pure amorphous PEEK when probed by different techniques. First, the parameters characterizing the shape of the α -relaxation were found to be different by DMA, DEA and differential scanning calorimetry⁶. Second, a recent study by Krishnaswami and Kalika¹⁶ showed a noticeable offset of dynamic mechanical versus dielectric relaxation times obtained for amorphous PEEK samples. The origin of this offset was not much clarified. It is our belief that these differences originate largely from an improper choice of the dynamic variables examined. Indeed, one should not compare directly dielectric permittivity with mechanical modulus, as the first is dependent on the spectrum of retardation times, while the second depends on the relaxation time spectrum^{20,17}. To the best of our knowledge, this difficulty has not been seriously pondered in the context of constructing the overall relaxation pattern of PEEK.

The present work is thus aimed at re-examining the applicability of the time–temperature superposition principle of the α -relaxation of pure amorphous PEEK, and to show that dielectric and dynamic mechanical results are consistent, provided they are appropriately analysed.

Experimental section

Quenched amorphous PEEK sheets (350–500 μm thick) were prepared from dry commercial powder (I.C.I. grade 150 P) as described elsewhere⁵. The guarded dielectric measurements were performed at frequencies between 400 and 100 kHz with a HP4174A bridge. The electrodes were made of evaporated gold. The measuring electrode was

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12 mm in diameter; the guard electrode was a 5 mm-wide ring. The sample was sandwiched between insulated small copper plates to ensure lateral homogeneity of the temperature, which was measured with a thin thermocouple located on the sample outside the measuring electrodes. Prior to measurements, the sample was annealed for 3 h at 100°C. This temperature was selected to be sufficiently high to dry the sample, while being sufficiently low to avoid a large ageing effect. The readings were collected continuously for different frequencies during heating at a constant heating rate of 2.0°C/min from 50 to 162°C, above which a rapid crystallization process occurs. Corrections for ionic conduction were introduced above the glass transition region as follows. Isothermal dielectric data were fitted at high temperatures (above 200°C) to a ω^{-1} relationship in order to extract static conductivity. These conductivities were then plotted as a function of temperature; they could be well represented by an Arrhenius equation in the range 200–270°C. For lower temperatures, the static conductivity was too small to be evaluated experimentally. Values were then computed from the Arrhenius fit. These values were negligible in the temperature range of the α -relaxation of pure amorphous PEEK; consequently, static conductivity can be safely neglected for the present study. The estimated standard errors amount to 0.25% for the real part of the dielectric permittivity and to 0.001 for the imaginary part.

Dynamic mechanical analysis was performed in tension mode with a Rheometrics RSAII on rectangular 5 mm \times 30 mm samples. The temperature was measured with a thermocouple positioned close to the vertically mounted sample. Before the measurements, the quenched specimens were equilibrated slightly above the calorimetric T_g in an attempt to remove the effect of sub- T_g structural relaxation and achieve a good reproducibility of successive isochronal curves. Isochronal experiments were carried out on different samples for selected test frequencies between 3.0 mHz and 10.0 Hz in the temperature interval of 120–149°C. Temperature ramps (1.0°C/min) or temperature steps (equilibrium time of 5 min) were used as heating regimes. The choice of the regime depends upon the test frequencies. Control isochronal scans (1.0 Hz) were performed at the beginning and at the end of each experiment to check the reproducibility and monitor possible changes in sample morphology. No differences could be detected between these two control scans for all experiments. Because different samples were used in this case to obtain the data, inaccuracies in the determination of the shape factor of each sample add to the apparatus errors, resulting in much larger estimated standard errors than for dielectric measurements. For DMA, standard errors were then estimated to amount to 5%.

Nonlinear least-squares curve fitting was performed using the iterative Marquardt–Levenberg algorithm. This included estimation of the values of adjustable parameters in order to minimize the functional:

$$\chi^2 = \sum_{i=1}^N \left[\frac{f(x_i) - y_i}{\sigma_i} \right]^2$$

where $f(x)$ is a fitting function, and σ_i the estimated standard error on measurement y_i . The statistical significance of the obtained parameters and their possible interdependence were analysed with the help of covariance matrices.

Results and discussion

The empirical description of complex dielectric permittivity:

$$\epsilon^* = \epsilon' - i\epsilon''$$

in terms of a generalized form of Debye equation, the Havriliak–Negami (HN) equation²¹, has proved to be of great use in dealing with polymeric materials^{22–25}. Taking into account that the mechanical analogue of ϵ^* is the complex compliance¹⁷:

$$J^* = J' - iJ''$$

we could apply the same type of analysis for the frequency dispersion of J^* (with the retardation spectra being involved in both cases²⁰). However, we will not do that because the largest absolute values of compliances are subject to very large errors in our dynamical mechanical experiments. Instead we will use the complex tensile modulus:

$$E^* = E' + iE''$$

and its dielectric complement: the complex inverse of the dielectric susceptibility,

$$[\epsilon^* - 1]^{-1} = \kappa^* = \kappa' + i\kappa''$$

which are represented in a similar fashion. In this case of relaxation rather than retardation process, HN equation reads²⁶:

$$E^* = E_U - \frac{E_U - E_R}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma} \quad (1)$$

where U and R designate unrelaxed and relaxed values, τ_{HN} is the central relaxation time and α and γ are shape parameters which correspond to symmetric and asymmetric broadening of the distribution function of relaxation times, respectively. The construction of a master curve by simple translation along the ($\log \omega$) axis of isothermal frequency sweep measured at different temperatures is only possible if E_U , E_R , α and γ are independent of temperature. In this case, the only temperature-dependent parameter is τ_{HN} , whose dependence can be represented by a Wimmiams–Landel–Ferry law²⁷. We have plotted our experimental points in the Cole–Cole co-ordinates as shown in *Figure 1*. The dielectric isochronals obtained at different frequencies (*Figure 1a*) show a very good correspondence. Within experimental error, they merge into a single master curve, which implies the validity of the time–temperature superposition principle in its simplest form. The correspondence of dynamic mechanical isochronals is less accurate. This difference can in part be accounted for by larger experimental errors of dynamic moduli as compared with dielectric data. It is worthy to note in this respect that all dielectric measurements were performed on one single sample, whereas different samples had to be used for the DMA measurements. Nevertheless, the DMA Cole–Cole curves all have the same shape; this fact can be verified in double-logarithmic co-ordinates (*Figure 1b*). Systematic deviations from the dynamic mechanical master curve can only be found below the calorimetric glass transition temperature and will be discussed in the sequel.

The bi-logarithmic plot of *Figure 1b* is not usual for mechanical measurements, but is the best representation for a comparison of different isochronals, given the relatively large estimated standard error of the measurements (see

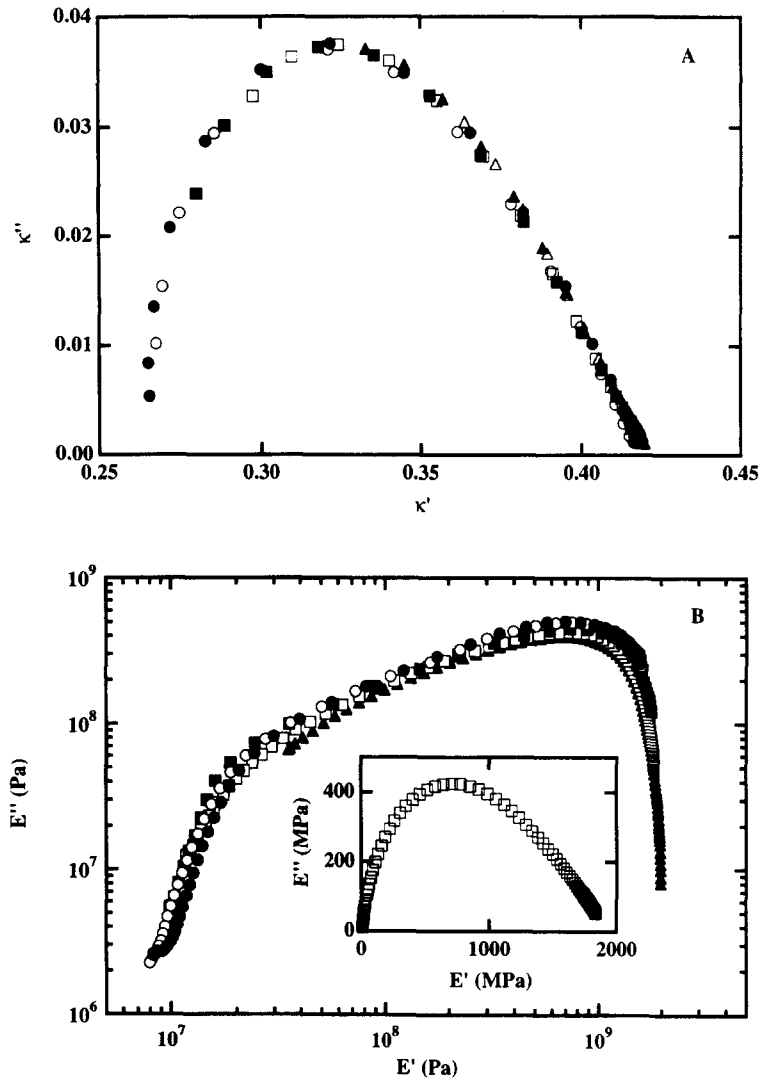


Figure 1 (a) Imaginary part of the inverse of dielectric susceptibility *versus* its real part, for amorphous PEEK in the temperature range of its α -relaxation. Symbols: ●, 400.0 Hz; ○, 1.0 kHz; ■, 4.0 kHz; □, 10.0 kHz; ▲, 40.0 kHz; △, 100.0 kHz. (b) Imaginary part of the dynamic mechanical modulus *versus* its real part, in logarithmic co-ordinates, for amorphous PEEK in the temperature range of its α -relaxation. Symbols: ●, 3.0 mHz; ○, 10 mHz; ■, 100 mHz; □, 1.0 Hz; ▲, 10.0 Hz. Inset: The same data at a frequency of 1.0 Hz, plotted in linear co-ordinates

Experimental Section). A single mechanical isochronal is also displayed in the inset of *Figure 1b* in the usual Cole–Cole representation, to allow direct comparison with the dielectric results. Clearly, dielectric and DMA Cole–Cole plots show a characteristic skewed arc shape, which cannot be described with a Cole–Cole equation and can only be accounted for by a HN equation.

Initially, for the sake of completeness, we introduced slight temperature dependencies in equation (1). The dependencies of $\kappa_R(T)$ and E_R with temperature are known to be described^{28,17} as:

$$\kappa_R = \kappa_U - \kappa_{R0}T^{-1} \quad (2)$$

$$E_R = E_{R0}T \quad (3)$$

where κ_{R0} and E_{R0} are constants and T the temperature in K. Since the temperature dependencies of E_U , α , γ were *a priori* unknown, we simply considered Taylor expansions limited to first order for these dependencies. This is acceptable since the temperature range in which our data have been acquired is limited. Hence we wrote:

$$E_U = E_{U0} + E_{U1}(T - T_0) \quad (4)$$

and similar equations for κ_U , α and γ .

The fits were then performed in two steps. First, equation (1) complemented by equations (2)–(4) were fitted to the DEA and DMA data separately. The results obtained for both sets of data showed much similarity. Therefore in the next stage we performed the fitting at once of all the dielectric and dynamic mechanical data with a single set of parameters for α , γ and τ_{HN} . In order to take into account slight differences in the temperature calibrations of both experiments, we introduced a supplementary fittable parameter representing a relative temperature shift between the temperature scales of DEA and DMA.

Finally, we progressively held to zero the fit parameters expressing the temperature dependence of the HN equation while controlling the evolution of the chi-square and of the covariance matrix. This analysis permitted the gradual exclusion of all the useless parameters from the equations. We found that statistically the same quality of fit could be obtained after having removed the temperature dependencies of α , γ , E_U and κ_U . This final fit is presented in *Figure 2*, while fit parameters so obtained are shown in *Table 1* and *Figure 2*. The obtained HN fit is satisfactory. The estimated standard deviations of the HN parameters displayed in *Table 1* have been estimated from the diagonal elements of the covariance matrix; they are on the order of 1%. The

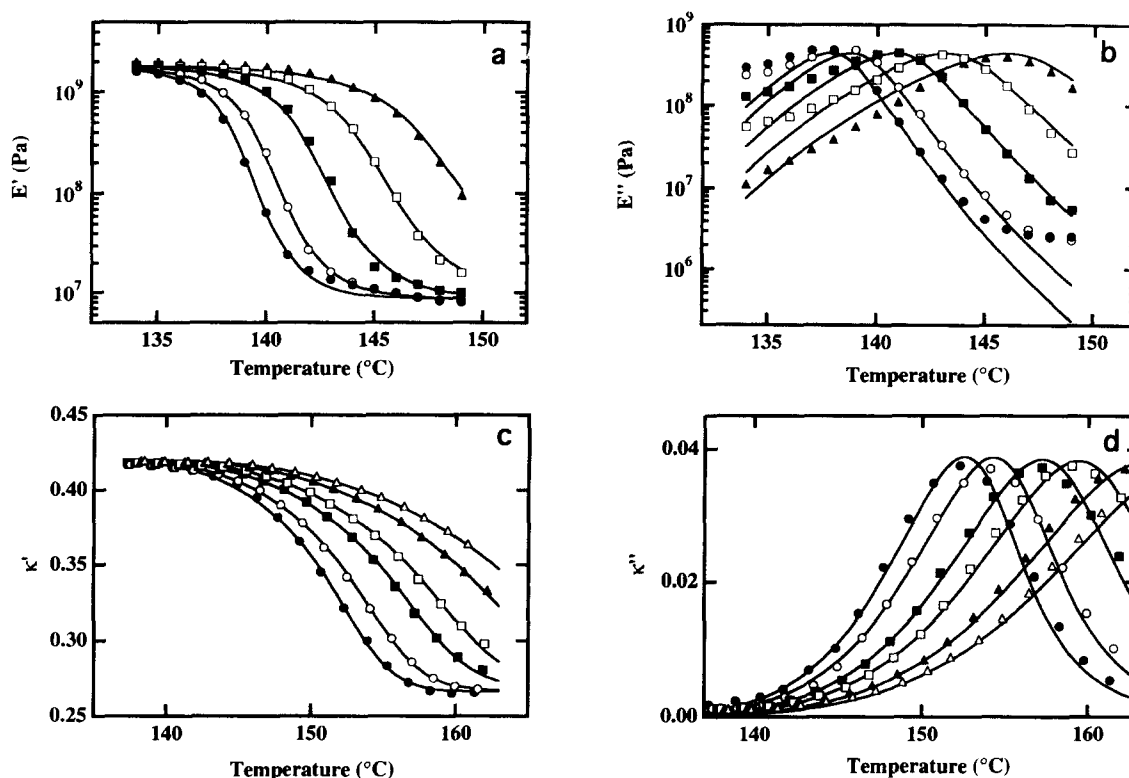


Figure 2 Isochronals corresponding to the dynamic mechanical (a,b) and dielectric (c,d) experiments on pure amorphous PEEK in the temperature range of its α -relaxation. The symbols in (a,b) refer to the following frequencies: ●, 3.0 mHz; ○, 10 mHz; ■, 100 mHz; □, 1.0 Hz; ▲, 10.0 Hz. Designations in (c,d) are similar to those of $\langle \text{FIGR} \rangle > 1 < / \text{FIGR} > a$. Solid lines represent HN fits of the data (see text for more details)

Table 1 Havriliak–Negami parameters obtained from the fit of the HN equation to dielectric and dynamic mechanical data of pure amorphous PEEK

α	0.86
γ	0.36
E_U (GPa)	1.81
κ_U	0.42
E_{R0} (Pa/K)	20.5×10^3
κ_{R0} (K)	67.7
ΔT (K) ^a	0.9

^a Difference between the temperature scales of DEA and DMA measurements

agreement between the readings of thermocouples in both experiments is found to be quite reasonable (0.9°C). The parameters of the WLF equation are determined with less accuracy, due to the limited experimental range. However, the values of central relaxation time computed from this equation at each temperature are probably much more accurate, and are displayed in *Figure 3* in our experimental temperature range. The temperature dependence of relaxation times shows the gradual decrease of the apparent activation energy as predicted by the WLF equation.

Some deviations of dynamic mechanical modulus from the HN model is observed at low temperatures, specifically below the calorimetric T_g of the sample (142°C at 10°C/min). These deviations can be explained as the influence of the structural relaxation alluded to in the Introduction. Indeed, one can expect a significant rate of thermal ageing in this temperature range given the long annealing times at each measurement temperature. The out-of-equilibrium conditions at these temperatures are supported by the large relaxation times ($\tau_{HN} = 10^1 - 10^5$ s) found from the HN fit (*Figure 3*). At higher temperatures the fit is much better except in the highest temperature range where the

small values of E'' are most probably subject to large experimental errors.

The possibility to perform a satisfactory HN fit of both dielectric and dynamic mechanical data provide evidence for a general scaling character of the α -relaxation. Moreover, it shows similarity of the nature of relaxing units examined by both probes given the correct choice of the dynamic properties. The constancy of α with temperature for both probes is different to the findings of Kalika and Krishnaswamy⁹, where a sharp increase of the broadening parameter of their Cole–Cole modified Debye equation was observed (meaning a narrowing of the relaxation with temperature). This is probably due to the inadequacy of the Cole–Cole equation in describing the PEEK α -relaxation. Also, the calculated variation of relaxation strength $\kappa_U - \kappa_R$ with temperature is much smaller than that from the references^{8,9}, probably for the same reason. Note that the correct evaluation of the relaxation strength ($\kappa_U - \kappa_R$) is critical when attempting to evaluate the so-called ‘rigid amorphous fraction’ from DEA data on semi-crystalline PEEK, since this parameter is obtained by the comparison of the relaxation strength of semi-crystalline PEEK with the pure amorphous PEEK.

Conclusions

Re-examination of the scaling behaviour of the α -relaxation of pure amorphous PEEK revealed that:

- (1) DEA and DMA data presented on a Cole–Cole plane show a characteristic skewed arc shape that can be described by the Havriliak–Negami equation.
- (2) A simple time–temperature superposition principle is fully applicable for DEA data (acquired in the 400–100 kHz range). It is also valid for DMA data, provided

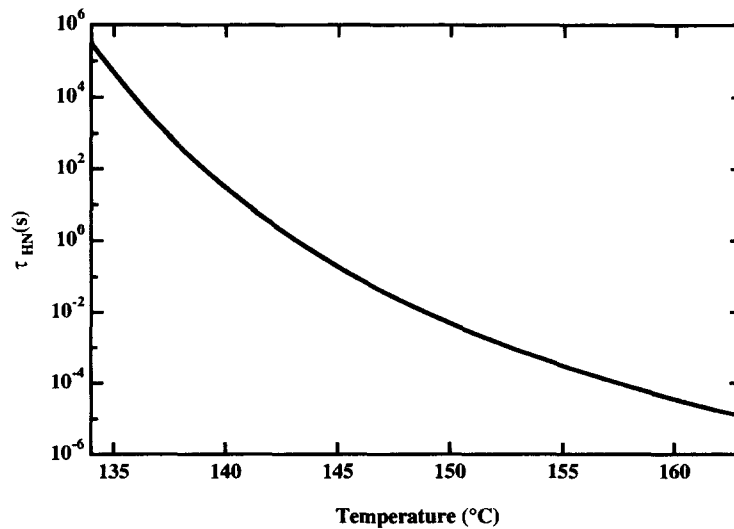


Figure 3 Temperature dependency of the central relaxation time of the α -relaxation of pure amorphous PEEK, as obtained from the HN fit

the limited accuracy of the technique is taken into account.

- (3) Fitting the DEA and DMA data together with one single set of Havriliak–Negami parameters gives satisfactory results provided the proper choice of properties is performed (complex inverse of dielectric susceptibility and dynamic mechanical modulus). This observation provides strong evidence for a general scaling character of the α -relaxation and the similarity of the nature of relaxing units examined by both probes.
- (4) In the probed temperature range, only the thermal dependence of κ_R and E_R have to be taken into account, while temperature-independent α , γ , κ_U and E_U may be safely taken. The origin of the discrepancies between DMA and DEA results reported by others^{6,16} lies either in an improper choice of the properties analysed or in the inadequacy of Cole–Cole equation in representing the α -relaxation of PEEK.

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