Deformation and Thermoelastic Behavior of Poly(aryl ether ketones)

A. Tregub,*,†,‡,§ J. Karger-Kocsis,‡ K. Könnecke,|| and H. J. Zimmermann||

Department of Experimental Physics, University of Ulm, Albert-Einstein-Allee-11, D-89079 Ulm, Germany, Institute for Composite Materials Ltd., University of Kaiserslautern, P.O. Box 3049, D-67653 Kaiserslautern, Germany, and Hoechst AG, P.O. Box 80 03 20, 65926 Frankfurt, Germany

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ABSTRACT: The double-melting behavior of poly(aryl ether ketones) (PAEKs) was detected by differential scanning calorimetry (DSC) experiments. The samples tested were poly(ether ether ketone) (PEEK) and poly(ether ketone (PEK), which have been crystallized from the glassy state at different crystallization temperatures T_c. The size and location of the lower peaks on DSC traces were affected by T_c, provided that $T_c > T_g$. An influence of T_c on the mechanical behavior of stretched PEEK and PEK (uniaxial deformation mode at 200 °C) was also observed. The perfection of crystalline structure was thought to be a reason for this influence. Thermoelastic experiments at room temperature, comprising simultaneous measurements of the mechanical work and of the concomitant heat, were performed on semicrystalline PAEKS. This study uses the sensitive thermoelastic technique to examine PAEK thermoelastic properties as a function of the relative abundance of ketone groups on different PAEKs. The effect of PAEK microstructure on thermoelasticity at room temperature was insignificant. This was attributed to the dominant contribution of the immobile amorphous phase on thermoelastic properties.

Introduction

In recent years much research has been devoted to exploring the potential advantages of thermoplastic matrices for composite materials. One such matrix class—poly(aryl ether ketone) (PAEK)—shows exceptional properties due to its semicrystalline character and the molecular rigidity of its repeating units. PAEK materials, isothermally crystallized from the melt or annealed from the glass, reveal double-melting endothermic behavior.[1−4] Two melting peaks are observed, one about 20 °C above the crystallization temperature and a larger one at higher (melting) temperature. This behavior has variously been explained as resulting from (1) kinetics of melting/recrystallization processes during a DSC scan[5−7] and (2) the influence of secondary crystalline structure.[11] In particular, the existence of the morphology-dependent rigid amorphous fraction (RAF) in the amorphous phase of semicrystalline polymers was discussed by Wunderlich and co-workers.[2,12,13]

It was found that the lower melting peaks for poly(ether ether ketone) (PEEK) and poly(ether ether ketone ketone) (PEEKK) are observed over a wide range of heating rates,[12] and the temperatures at which they are observed are dependent on the temperature and rate of isothermal crystallization.[17] The location of the main peak is independent of the conditions of crystallization. These observations contradict the kinetic hypothesis.[5−7]

Experiments aimed at proving the existence of secondary structure were performed using PEEK specimens obtained from different thermal treatments.[5−11,14−16] However, the secondary structure was only observed directly in experiments using thin PEEK films after specific thermal treatments.[15,16] Dielectric relaxation experiments[9] showed two amorphous phases for thermally treated PEEK specimens. In turn, this may prove the possible role of rigid amorphous fractions.

The influence of thermal treatment on the mechanical properties[14,16,22,23] and structure[21] of PAEKs was reported earlier. The mechanical tests were carried out at ambient temperatures in these studies. It is believed that the mechanical tests at elevated temperatures may be more sensitive to PAEK microstructure.

PAEKs, such as PEEK and PEK, have similar crystal structures but differ in ketone content. It is known that the ketone moiety displays more rigid behavior than the ether moiety.[21] Thus, mechanical properties may be different for PAEKs with different ketone content after the same thermal treatment. It was shown earlier[20] that thermoelastic experiments at ambient temperature were sensitive to different thermal treatments of PEEK. It was thought that these experiments might also be sensitive to the influence of ketone content on the mechanical behavior of PAEKs.

The objective of the present study was to relate the bulk mechanical behavior of PAEKs to their microstructure. PAEK samples of various microstructures were available as a result of (i) different thermal treatment and (ii) choice of PAEKs with different ketone content. In particular, we aimed to relate the mechanical properties of PAEKs to the existence of RAF.

Experimental Section

Poly(ether ether ketone) (PEEK) by the name of "Victrex 380 G" was supplied by ICI. Poly(ether ketone) and (PEK) is a product of Raychem Inc. and has the trade name "Stilan I". The materials have similar molecular weights of about 30 000. The thermal treatment consisted of melting for 5 min at 400 (PEEK) or 420 °C (PEK), followed by quenching in ice water and isothermal crystallization for 1 h at different temperatures in the range 160−300 °C. This procedure resulted in different degrees of crystallinity of the specimens. Samples of PEEK and PEK with dimensions of 20 × 2 × (0.15−0.25) mm were cut from these films and tested in the uniaxial stretching deformation mode in the stretching device "Zwick 1425", fitted with a thermochamber. The measurements were performed at ambient and at elevated (200 °C) temperatures with a

* To whom correspondence should be sent.
† University of Ulm.
‡ University of Kaiserslautern.
§ Present address: Department of Chemistry, University of Tennessee, 453 Buehler Hall, Knoxville, TN 37996-1600.
|| Hoechst AG.
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constant rate of stretching (1 mm/min) in both elastic and plastic deformation ranges.

Those PEEK and PEK samples which had been crystallized at 200–220 °C and had X_c values of 25–30% were used for thermoelastic measurements. The dimensions of the specimens were 25 × 2 × (0.3–0.5) mm. Thermoelasticity was measured using a Tian-Calvet type stretching calorimeter.[18–20] The PAEK specimens were fixed in the clamps of the stretching device, placed in the measuring cell, and maintained at room temperature to complete thermal equilibration. The specimens were then deformed uniaxially in the step-by-step deformation mode at a constant cross-head speed of 0.1 mm/min. Corresponding to each deformation step the values of mechanical work and heat were normalized to the total final deformation volume of the stretched specimen. Young's moduli and linear thermal expansion coefficients of PAEKs were determined by fitting the calculated curves to the experimental points. The accuracy of the measurements was estimated to be 2%.

The resultant degree of crystallinity of PAEKs was determined by differential scanning calorimetry (DSC), using a Perkin-Elmer calorimeter equilibrated at 10 °C and purged with dry nitrogen. The scanning rate was set at 20 °C/min. The calorimeter has been calibrated at different heating rates with indium and lead using standard procedures. For each measurement a freshly prepared sample of PEEK/PEK was taken to prevent misleading results due to decomposition. The samples were melted at 400 (PEEK) and 420 °C (PEK) and held there for 5 min in order to remove all residues of crystallinity. It is known[4,17] that for the crystallization and melting peaks three characteristic temperatures are usually considered: the onset, the peak, and the end of crystallization/melting. The observed peak temperatures were considered to be crystallization/melting temperatures. In those cases where the peaks did not overlap, melting enthalpies of lower and main peaks were measured separately and summed. Otherwise, the total heat of fusion was measured. Degree of crystallinity w was calculated as ratio:

$$w = \Delta H_f/\Delta H_{fc} \quad (1)$$

where ΔH_f is the measured heat of fusion of the semicrystalline specimen and ΔH_{fc} is the heat of fusion of the perfect (full crystalline) crystal.[24]

As perfect PAEK crystals are not available, ΔH_{fc} is evaluated by extrapolation of ΔH_f values, measured for semicrystalline polymers of different X_c.[24] This procedure was performed for PEEK[3,21,25] and PEK.[21] Both WAXS and DSC measurements were employed. The heats of fusion of the completely crystalline polymers were found to be nearly the same (130 J g^{-1}) for both PEEK and PEK.[3,21,25] The value ΔH_{fc} = 130 J g^{-1} was used in w calculations.

Results and Discussion

DSC traces for PEEK and PEK crystallized from the glassy state revealed the typical double-melting behavior.[12,17] The lower melting peaks were observed at temperatures exceeding those of crystallization (Figure 1). Increasing the crystallization temperature (T_c) caused a shift of the lower peak to the higher temperature region. At T_c = 260–300 °C this peak turned into a shoulder on the main melting peak (Figure 1). The resultant degree of crystallinity X_c is presented in Figure 2 as a function of T_c. A sharp transition from a low to a high degree of crystallinity occurred around T_c = 150 °C, which coincides with the glass transition temperatures T_g of the tested PAEKs. Different crystallization temperatures in the range of 160–300 °C did not affect the resultant degree of crystallinity. These results are similar to those for PEEK.[22] The residual crystallinity of about 7% was observed even for quenched-from-the-melt samples, which coincides with the data[22,26] for PEEK.

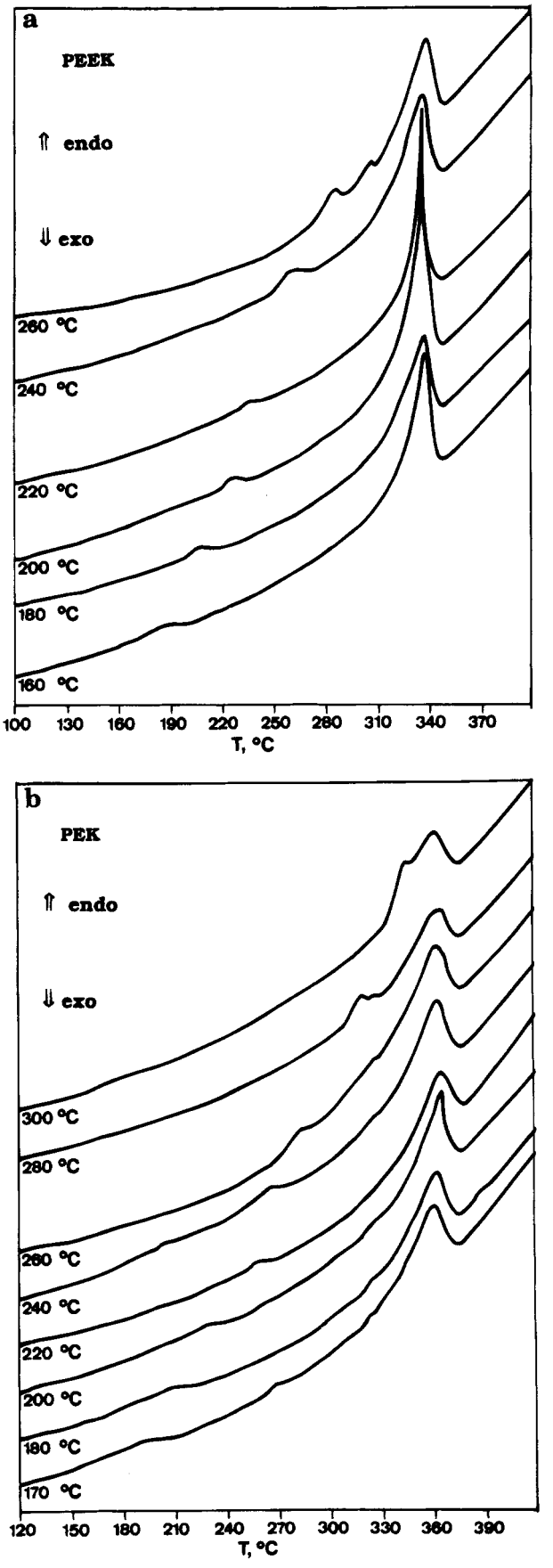

Figure 1. Differential scanning calorimetry traces of PAEKs which had been quenched and crystallized at different crystallization temperatures T_c. (a) PEEK: 1, 2, 3, 4, 5, 6 – T_c = 160, 180, 200, 220, 240, and 260 °C, respectively. (b) PEK: 1, 2, 3, 4, 5, 6, 7, 8 – T_c = 170, 180, 200, 220, 240, 260, 280, and 300 °C, respectively.

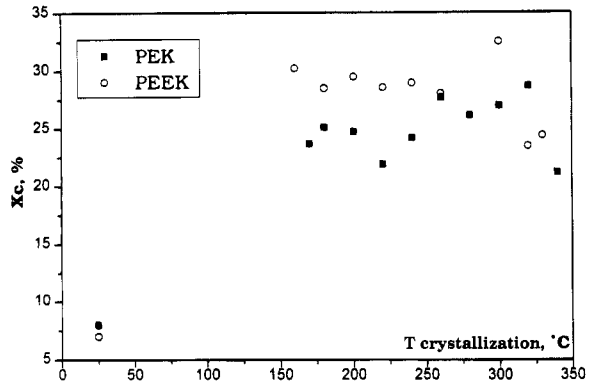

Figure 2. Degree of crystallinity as a function of isothermal crystallization temperature for PEEK and PEK.

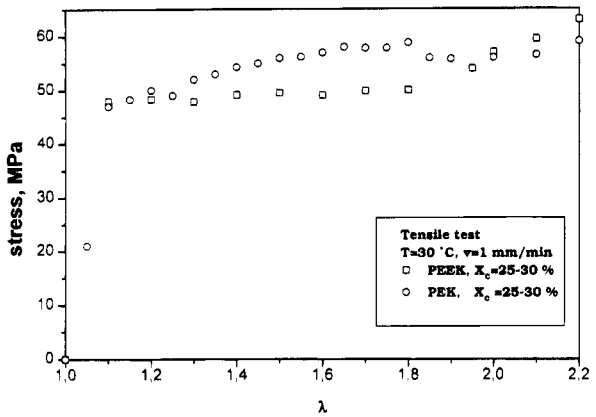

Figure 3. Stress–elongation dependencies of semicrystalline PEEK and PEK at room temperature.

Thermoelastic and tensile tests at room temperature were carried out with semicrystalline PEEK and PEK. They contain 33 and 50% of ketone groups, respectively. Consequently, an effect of different microstructure[21] on their bulk mechanical properties might be expected.

Mechanical experiments at room temperature showed no essential difference (Figure 3) between semicrystalline PEEK and PEK, regardless of the crystallization temperature T_c ($T_c > T_g$). It was thought that a more sensitive technique had to be applied.

It is known that the heat effects of uniaxial stretching of semicrystalline polymers in the elastic deformation range may be about 2–5 times higher than those of mechanical work.[18,20] Therefore, different heat effects might be expected for PAEKs even below the T_g, where no significant difference was found for the mechanical effects (Figure 3).

Thermoelastic behavior was characterized by the deformation dependence of specific mechanical work, W/V (Figure 4a, points), and heat, Q/V (Figure 4b, points). For mechanical work and heat in the elastic deformation range the thermoelasticity of polymer glass was described fairly well by parabolic (Figure 4a, lines) and linear (Figure 4b, lines) functions, respectively. It was in good agreement with the equations expressing the "classical" theory of thermoelasticity of solids:[18]

$$W/V = (E/2)(\lambda - 1)^2 \quad (2a)$$

$$(Q/V)_{p,T} = E\alpha_L T(\lambda - 1) \quad (2b)$$

where V is the final deformation volume of the sample, E is Young's modulus, α_L the is linear thermal expansion coefficient, p is the pressure, $T = 30$ °C, and λ is the elongation.

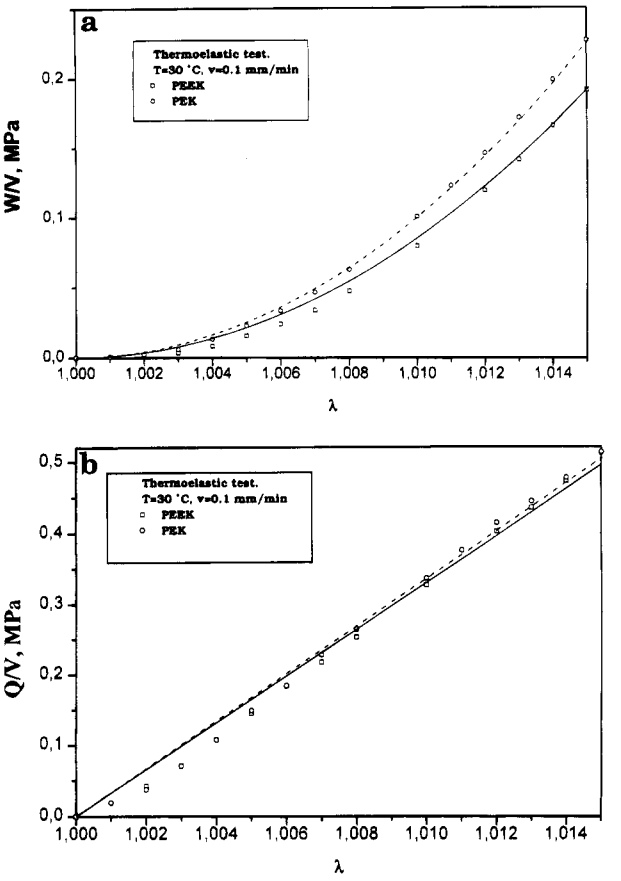

Figure 4. Specific mechanical work (a) and the specific heat (b) as a function of elongation for semicrystalline PEEK and PEK: points, experimental values; solid and dashed curves, calculations for PEEK and PEK, respectively.

The limits of the elastic deformation range (λ_{el}) were determined from the deformation dependencies of both mechanical work and heat as 1.015. Beyond λ_{el} the deviation of experimental points from the predicted parabolic (eq 2a) and linear (eq 2b) functions was observed. Calculations of E and α_L were carried out in the deformation range $\lambda < \lambda_{el}$. Moduli E were equal to 1.75 and 2.0 GPa for PEEK and PEK, respectively. Thermal coefficients α_L determined for PEEK and PEK were equal to 55×10^{-6} and 56×10^{-6}, respectively. The calculated material constants for PEEK were in reasonable agreement with the literature data.[20,25]

The difference between thermoelastic properties in the elastic deformation range of the tested PAEKs was negligible (Figure 4a,b). Thus, similar to mechanical tests, thermoelastic experiments at ambient temperature were insensitive to PAEK ketone content.

The relative invariance of thermoelastic and mechanical measurements to different PAEK structures can be explained by the dominant contribution of the amorphous phase to thermoelasticity and elastic–plastic behavior of semicrystalline polymers at room temperature.

The tensile tests for PEEK and PEK were carried out at 200 °C. It was suspected that the previously discussed RAF would become active at the temperatures above T_g. Consequently, its contribution to PAEK mechanical properties might be significant at elevated temperatures.

Mechanical properties of PAEKs, which had been crystallized at different T_c, were compared in elastic and

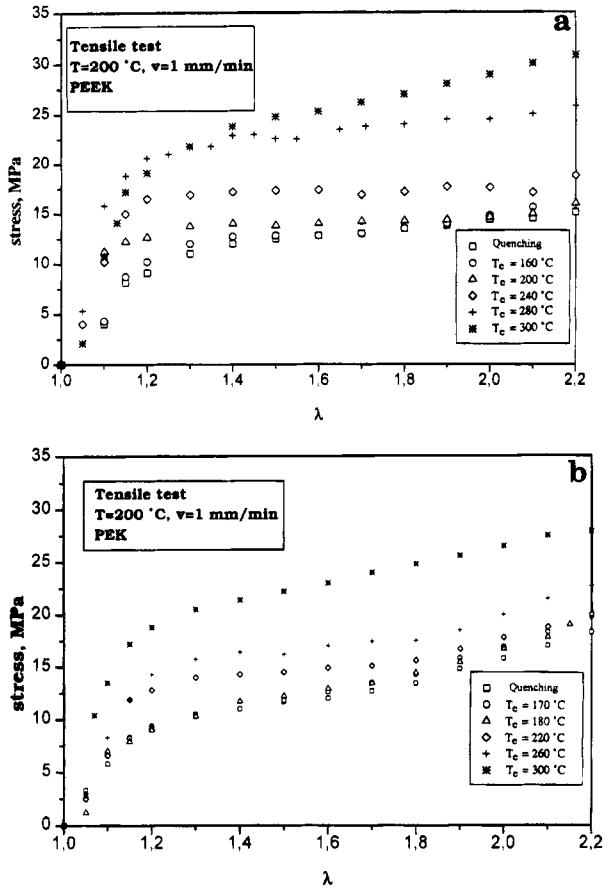

Figure 5. Stress–elongation dependencies of PEEK (a) and PEK (b), crystallized at different crystallization temperatures T_c and tested at 200 °C.

plastic deformation ranges. For both PEEK (Figure 5a) and PEK (Figure 5b) higher tensile stress values (plastic deformation) were observed for higher T_c, when $T_c > T_g$, while Young's moduli (elastic deformation) of the tested PAEKs were similar. Crystallization at temperatures slightly above T_g (160–180 °C) did not substantially affect mechanical properties of amorphous (T_c = 30 °C) PAEKs. Also, the difference between mechanical properties of samples of PEEK and PEK which had been crystallized at about the same T_c was negligible (Figure 5a,b).

As the total crystallinities of the tested samples were about the same (Figure 2), one cannot assign the different tensile stress values of these samples to contributions of X_c. This difference might be assigned to the perfection of the crystals, which had been crystallized at higher T_c. The altering of the structure of PAEKs with the same X_c, but crystallized at different T_c, has been observed elsewhere.[21] It is worth noting that this difference was manifested only for those samples, which were tested at 200 °C.

The expected contribution of a metastable RAF, which could "unfreeze" at 200 °C, might be essential in the elastic deformation range.[24] It is known that the amount of RAF decreases with increasing T_c.[12,24] Thus, more perfect structure forms with decreasing T_c. It is therefore expected that the toughness of PAEKs in the elastic deformation range should increase with decreasing T_c. However, the observed moduli of PAEKs, which had been crystallized at different T_c, were similar. These results might be explained by the dominant contribution of the immobile amorphous phase in the elastic deformation range.

One can conclude that the sensitivity of these conventional mechanical tests, even at $T > T_c$, was insufficient to detect the influence (if any) of RAF on the bulk mechanical properties. We expect, however, that more sensitive thermoelastic measurements, carried out at $T > T_g$, may clarify RAF influence on the mechanical behavior of PAEKs.

Conclusions

Tensile stresses of PEEK and PEK, which had been crystallized from the glass at $T_c > T_g$ and which were tested at 200 °C, increase with increasing T_c. The perfection of crystalline structure was thought to be a reason for this effect.

The moduli of those PAEKs, which had been crystallized and tested under the conditions described above, are similar. Also, the differences in mechanical and thermoelastic properties (tested at room temperature) of semicrystalline PAEK samples with different ketone content are negligible. We conclude that the contribution of the immobile amorphous phase to these properties is dominant.

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