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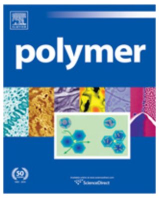

Synthesis, mechanical properties and chemical/solvent resistance of crosslinked poly(aryl-ether–ether–ketones) at high temperatures

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ABSTRACT

A synthetic two-stage procedure was developed for the synthesis of moderately crosslinked polymers based on poly(aryl-ether–ether–ketone) (PEEK). Rigid crosslinks based on aromatic imines were synthetically introduced into PEEK polymer matrix resulting in PEEK materials with various degrees of crosslinking. Two specific crosslinked PEEK polymers (5% and 10% of ketone groups crosslinked) were characterized and studied in detail. Thermomechanical properties, as well as chemical/solvent resistance of these materials at high temperatures (175–280 °C) were investigated and compared to the original PEEK material (Victrex 151G). The introduction of rigid crosslinks was shown to disrupt crystallinity of PEEK very efficiently. Because tensile properties of PEEK depend on its crystallinity, we observed a decrease in properties such as Young's modulus and the ultimate elongation, the extent of which depended on the degree of crosslinking. We also observed an improvement in the elastomeric properties of the crosslinked materials, such as decrease in initial permanent set during high temperature cyclic tensile testing. Mechanical creep behavior at high temperature also improved for crosslinked polymers vs the original commercial Victrex 151G in terms of a reduced irreversible creep component. All crosslinked materials showed excellent resistance to hot oily, acidic and basic environments, as well as excellent thermal stability. Overall, we were able to synthesize “softer” materials that are more rubbery at high temperature than commercial thermoplastic Victrex 151G; these elastomer-like materials showed promising mechanical properties for high temperature applications in hot/corrosive environments.

1. Introduction

Poly(aryl-ether–ether–ketone) (PEEK) is a high performance semicrystalline thermoplastic with wide applications in aerospace, automotive, coating, electrical insulating material and oil fields. Highly crystalline PEEK materials display excellent mechanical, thermal and chemical resistance properties which allow filled or unfilled PEEK to be used in various hostile environments [1,2].

Even though PEEK materials have been shown to perform satisfactorily up to temperatures of 200 °C [3], there are a few current applications that require materials with even higher upper temperature limits. Furthermore, there is a well recognized interest specifically in elastomers for high temperature applications, such as, for example, O-rings and sealants in petrochemical and automotive industries. From the view point of classical polymer theory, elastomers or rubbers (both terms are usually used interchangeably) are amorphous polymers which are well above their glass transition temperature, so that at typical use temperatures considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft ($E = 1$–10 MPa) and deformable. For most applications, especially for high temperature materials, rubbers are vulcanized/crosslinked, thus forming a crosslinked 3D polymer network, in order to prevent creep or “set”. The entropic elasticity of rubbers is derived from the ability of the polymer chains to change their microstructural conformation in order to accommodate large applied stresses. The crosslinks, on the other hand, ensure that the elastomer will return to its original configuration when the stress is removed; they also improve the mechanical integrity of the material overall. Introduction of covalent crosslinks into a semicrystalline PEEK matrix is expected to disrupt the crystallinity of the aromatic polymer chains, and may result in a formation of amorphous and crosslinked polymer that could exhibit rubbery properties at high temperatures. Chemical crosslinking is also the most direct way of increasing the resistance of the polymeric material to swelling by aggressive solvents and mechanical creep. In the present work we investigate the effect of covalent crosslinking on the crystallinity of

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PEEK, and more importantly, the mechanical and chemical resistance properties of the resulting materials at elevated temperatures.

Several procedures for crosslinking PEEK polymer matrix have been reported previously. These methods include – the introduction of biphenylene units into the polymer backbone [4], the addition of xanthenes [5], halogenated alkanes [6], sulfur [7] and the formation of imines with aromatic diamines [8]. The latter of these synthetic procedures is appealing, because it does not involve free-radical chemistry, and allows for an easily controlled and traceable means of introducing rigid, thermally stable aromatic imine crosslinks into the PEEK matrix. In the original synthetic work [8] highly crosslinked PEEK materials were targeted, which consequently were found to be impossible to process or mechanically characterize. Herein, we report a modified procedure for the synthesis of moderately crosslinked PEEK polymers (1–10%), and study their mechanical and chemical/solvent resistance properties at elevated temperatures (175–280 °C).

2. Experimental

2.1. Materials

The PEEK used in this study was grade 151G, supplied by Victrex. The molecular weight M_w for this grade is known to be in a range of 30,000 [9]. 1,4-Phenylene diamine (97%) was purchased from Alfa Aesar and used without purification. Diphenyl sulfone (97%) was purchased from Sigma–Aldrich and used without purification. IRM 903 oil (a current substitute for previously used ASTM 3 standard oil) was purchased from. R.E. Carroll Inc. Silicone rubber, polychloroprene rubber and EPDM rubber samples were provided by Schlumberger Doll Research.

2.2. Characterization methods

Differential scanning calorimetry was performed on a DSC Q 1000 (manufactured by TA Instruments). Heating/cooling scans were conducted at 10 °C/min. X-ray photon spectroscopy data was obtained on a Kratos Axis Ultra with monochromated Al source operating at 150 mW (manufactured by Kratos Analytical of Manchester, England). Elemental microanalysis was conducted by Atlantic Microlab Inc., Norcross, GA. Dynamic mechanical analysis was performed on a DMA Q 800 (manufactured by TA Instruments). Rectangular shaped specimens were cut out and tested at a heating rate of 3 °C/min, in tension mode at 1 Hz frequency and 0.2% strain amplitude. In mechanical creep testing rectangular specimens were maintained under a constant load of 3 MPa at 280 °C for 2 h. After 2 h the load was removed and the sample was allowed to relax for 20 min with the sample strain being monitored. Stress–strain tests and cyclic loading tests were performed on a Zwick Materials Testing Machine equipped with environmental chamber and oven, model Z010 with 500N load cell (manufactured by Zwick/Roell GmbH). Rectangular shaped specimens were cut out and subjected to testing in tension mode at 220 °C with cross-head speed of 45 mm/min. In cyclic loading test the sample was stretched to 20% strain at 220 °C and then returned to zero load at the same cross-head speed (45 mm/min). The sample was subjected to three loading–unloading cycles. Infra red spectra were recorded on a Nexus 870 (manufactured by Nicolet). IR spectra were recorded from KBr pellets under nitrogen. Thermal gravimetric analysis was performed on a TGA Q 50 (manufactured by TA Instruments) using heating rates of 20 °C/min.

2.3. Exposure tests

Pre-weighed rectangular shape specimens of the various polymeric samples were placed in hermetically sealed stainless steel containers (exposure chambers) with various media (IRM 903 oil, pH 4 buffer and pH 9 buffer). The exposure chambers were then placed in an oven, heated to 175 °C and maintained at this temperature for 100 h. After 100 h the exposure chambers were cooled to room temperature and polymer samples were removed. The surfaces of the samples were carefully wiped with paper tissue and samples were weighed again. The weight percent change due to the solvent uptake was calculated for all of the samples. The average of two measurements for each material was reported.

2.4. Synthesis of PEEK with 10% of ketone groups crosslinked (PEEK 10%)

10 g of PEEK (Victrex 151G), 200 g of diphenyl sulfone and 1.45 g of phenylene diamine was placed in a 500 mL three-neck round bottom flask. The flask was placed under continuous nitrogen purge. The mixture was then quickly heated to approximately 300–320 °C with vigorous stirring. When the temperature of the mixture reached 260 °C, the nitrogen purge was discontinued. Because the boiling point of 1,4-phenylene diamine is 267 °C, care had to be taken not to purge the system extensively at temperatures above 260 °C to avoid the loss of the crosslinking agent. As soon as the PEEK material dissolved, the reaction mixture was cooled to 250–260 °C and maintained at this temperature for 3 h with stirring. After every hour of reaction the system was purged with nitrogen for a short period of time (10 min) to rid the system of the water by-product. After 3 h the hot mixture was poured onto a glass dish, forming a solid. That solid was broken into small pieces, ground and placed into a round bottom flask with acetone and stirred overnight. In addition the mixture was sonicated for 1 h to dissolve unreacted phenylene diamine and diphenyl sulfone. Upon completion of the first extraction, the suspension in acetone was filtered on a vacuum filter. This purification procedure was repeated two more times, or to the point where the supernatant acetone solution exhibited no color and IR spectroscopy revealed absence of diphenyl sulfone in the product. After purification the product was dried on a vacuum filter, and then heated in a vacuum oven at 100 °C overnight. The resulting product was recovered quantitatively as greenish or yellowish powder.

2.5. Processing and post-curing

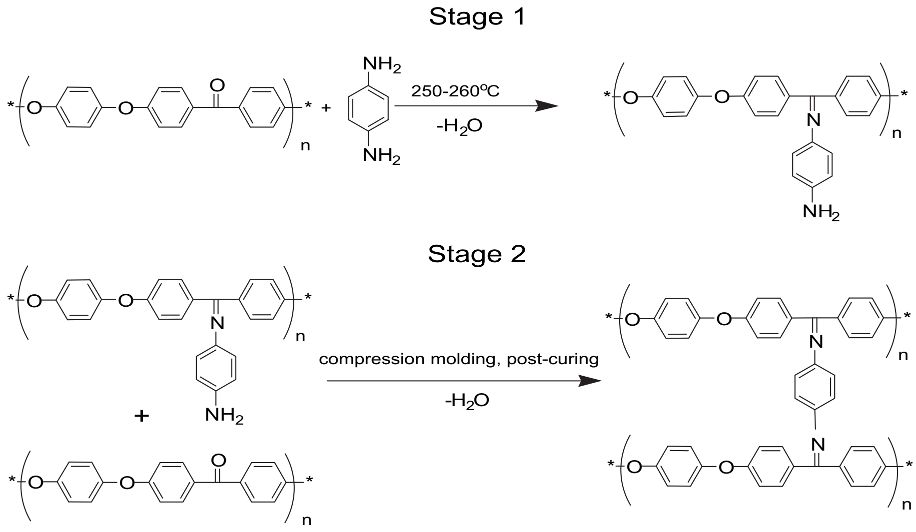
All modified PEEK polymer powders were hot-pressed by Carver 4120 hydraulic press at 343 °C and post-cured at 250 °C for 4 h. This procedure resulted in films approximately 0.3–0.5 mm thick, from which specimens for tensile and exposure testing were cut out.

3. Results and discussion

3.1. Crosslinked PEEK analysis

Employing the chemistry outlined in Scheme 1 we were able to establish a reproducible synthetic protocol to synthesize PEEK materials with various degrees of crosslinking.

The two-stage nature of the crosslinking process employed is crucial to successful generation of the crosslinked polymer. The first stage allows for the introduction of a crosslinking agent, while still keeping the polymer in solution. Otherwise, complete crosslinking at the first stage would render the polymer insoluble in the reaction mixture, resulting in poor reaction control and difficulty in purifying and processing the polymer following reaction. Between the first and the second stages, solvent and excess unreacted crosslinking agents are removed. In the second stage, crosslinking of the polymer is completed in the bulk. It was reported previously for a similar synthetic procedure, that crosslinking did not proceed to



Scheme 1. Stage-wise synthetic protocol employed for crosslinking poly(aryl-ether–ether–ketones). Only a crosslinked part of a polymer matrix in a final product is shown for clarity.

completion in the reaction solution [8]. Indeed, we observed unreacted amino groups in the polymer matrix, as can be seen from the IR spectrum of the product of the reaction (Fig. 1). Peaks characteristic to N–H stretching vibrations around 3400 cm^{-1} were clearly visible after the reaction in solution. The fine structure of these peaks disappeared upon processing and post-curing (Fig. 1). Further evidence of incomplete crosslinking in the first stage (solution reaction) is demonstrated by DSC data of PEEK 10% before and after processing and post-curing (Fig. 2).

First we can see that the processed PEEK 10% does not exhibit any crystal melting peaks upon heating, or upon cooling. It appears to be a completely amorphous fully crosslinked material; the chain folding required for crystallinity is impeded by the presence of the crosslinked network. The unprocessed PEEK 10% exhibits a strong crystalline melting endotherm at 317 °C on the first heating, revealing the presence of a large fraction of crystallites due to incomplete crosslinking. At the end of the first DSC heating scan, the exposure of the sample to high temperatures enables the completion of crosslinking, destroying all crystallinity, and upon subsequent cooling and heating scans of the sample only T_g transitions are visible. All modified PEEK materials discussed here were hot-pressed above their melting points and post-cured at 250 °C, which resulted in the disappearance of free amino groups and complete crosslinking. Once crosslinked, the material cannot be dissolved or reprocessed by hot-pressing effectively. Thermal gravimetric analysis (TGA) shows that all crosslinked PEEK samples are stable up to 500 °C, with no weight loss observable.

Elemental analysis was used as a primary method for determining the extent of crosslinking, by measuring the relative amount of nitrogen present [8] in our products. As revealed by elemental analysis (C, O, N, H ratios) of our post-processed samples, we obtained polymers in which the following percentage of ketone groups was crosslinked: 60% [8], 18%, 10%, and 5%. In this paper we will only focus on the lighter crosslinked PEEKs (Table 1), namely PEEK 10% (10% of ketone groups crosslinked) and PEEK 5% (5% of ketone groups crosslinked), due to our principal interest in observing "rubbery" properties of modified PEEK at high temperatures, as discussed above. It must be mentioned, however, that

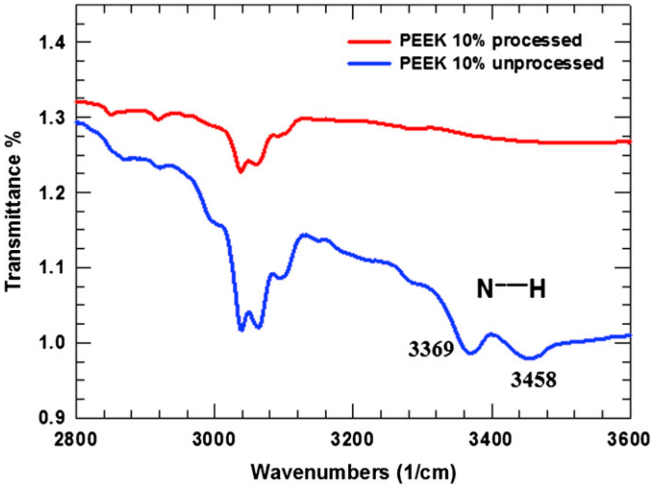


Fig. 1. IR spectrum of PEEK 10% after the solution reaction and after processing/post-curing.

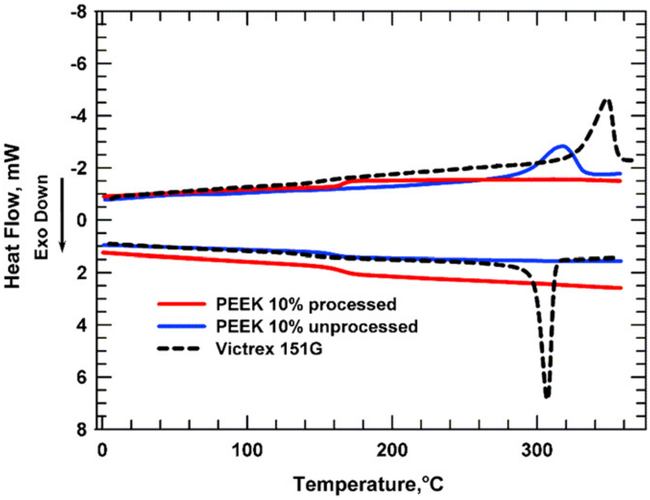


Fig. 2. Differential scanning calorimetry thermograms of PEEK 10% samples. First heating (upper curves) and cooling scans (heating/cooling rate 10 °C/min).

Table 1
Elemental analysis and XPS results for processed PEEK 5% and PEEK 10%. For elemental analysis, the average of two measurements is reported. Error limit is reported to be ±0.3% both for precision and accuracy by Atlantic Microlab.

Element, weight%	PEEK 10%			PEEK 5%		
	EA	XPS	Theory	EA	XPS	Theory
C, %	78.65 ± 0.06	78.74	78.62	79.31 ± 0.007	–	78.88
H, %	4.26 ± 0.01	–	4.19	4.18 ± 0.08	–	4.20
N, %	1.09 ± 0.01	0.66	1.10	0.54 ± 0.06	–	0.55
O, %	15.70 ± 0.07	20.60	16.09	15.95 ± 0.08	–	16.37

elemental analysis provides limited resolution of this system's composition, which becomes apparent for systems in which the nitrogen introduced is exceedingly low. For example, the minimum amount of nitrogen distinguishable by elemental analysis technique employed was 0.3% by weight, whereas in PEEK 5% the amount of nitrogen calculated to be present was 0.54% (Table 1).

To gain additional insight on the composition of our samples XPS (X-ray photon spectroscopy) was performed on a PEEK 10% sample surface. The results are summarized in Table 1 and the corresponding emission curves are provided as supporting information. XPS analysis confirmed the presence of nitrogen on the surface of the polymer, but at a relative amount somewhat lower than previously found by elemental analysis (0.66% by XPS and 1.09% by elemental analysis) (see Supplementary Material). This difference is close to the experimental resolution limit and may arise from the different nature of the two probes: XPS measures the composition of the material on the surface (i.e. top 2–3 nm) and the surface composition may vary from the bulk due to surface segregation of particular groups.

3.2. *Chemical exposure tests*

PEEK 10% samples were tested together with pristine Victrex 151G (uncrosslinked PEEK) and an assortment of commercially available rubbers in various aggressive media at 175 °C for 100 h. (This is a typical screening test for new materials administered by Schlumberger.) In this study we seek to investigate the influence of crosslinking on environmental resistance of PEEK polymer, particularly to oil, as well as acid and base conditions relevant to downhole oil-field applications. The results are summarized in Table 2.

Remarkably, excellent resistance of 10% crosslinked PEEK to various aggressive media is observed at high temperatures. The introduction of a crosslinked matrix does not seem to affect the solvent and chemical resistance of the resulting PEEK polymers when compared to the original Victrex material, and outperforms other rubbers with regard to oil resistance.

3.3. *Dynamic mechanical analysis*

To examine the high temperature mechanical properties of the crosslink modified PEEK, we subjected a series of PEEK polymers (PEEK 10%, PEEK 10% following 100 h exposure to IRM 903 oil, PEEK 5% and Victrex 151G) to dynamic mechanical analysis (DMA). The results are shown in Fig. 3 below.

Table 2
Comparison of exposure tests of 10% crosslinked PEEK samples. An average of two measurements is reported.

Polymer/exposure conditions	IRM 903 oil 100 h @ 175 °C	pH 4 buffer 100 h @ 175 °C	pH 9 buffer 100 h @ 175 °C
Victrex 151G	3.5% Weight gain	–	–
PEEK 10%	3% Weight gain	0% Weight gain	0% Weight gain
Silicone rubber	6% Weight gain	–	–
Neoprene rubber	43% Weight gain	–	–
EPDM rubber	226% Weight gain	–	–

Comparing the DMA data of PEEK 10% vs Victrex 151G we see that the introduction of crosslinks increases the glass transition temperature significantly, as expected [7]. For Victrex 151G the glass transition temperature is $T_g = 142$ °C [9], whereas it is increased to 175 °C for PEEK 10%, as revealed by the shift in the loss modulus or tan δ DMA data (Fig. 3B). Analysis of DSC data (discussed in detail below) supports this shift and gives $T_g \approx 168$ °C. This change manifests itself in a shift of the storage modulus (E') drop for PEEK 10%, compared to Victrex 151G. A significant drop in modulus was exhibited by PEEK 10% at the glass transition, and it also exhibited an extremely broad "rubbery plateau" from 200 °C to 400 °C at small strains. From the value of (E') for PEEK 10% at 200 °C the average molecular weight between the crosslinks of this material was calculated to be 1024 g/mol. Given the molecular weight of the monomer unit being 288 g/mol, the degree of crosslinking was found to be higher by this method than by Elemental analysis or XPS (Table 1). It must be noted that PEEK 10% did not exhibit flow at temperatures within the range of the instrument ($T_{max} = 450$ °C), confirming the presence of a truly crosslinked and thermally stable network. On the contrary, Victrex 151G flowed irreversibly beyond its melting point of $T_m = 340$ °C [9]. The PEEK 5% crosslinked sample exhibited a much higher modulus rubbery plateau than PEEK 10%, which dropped around

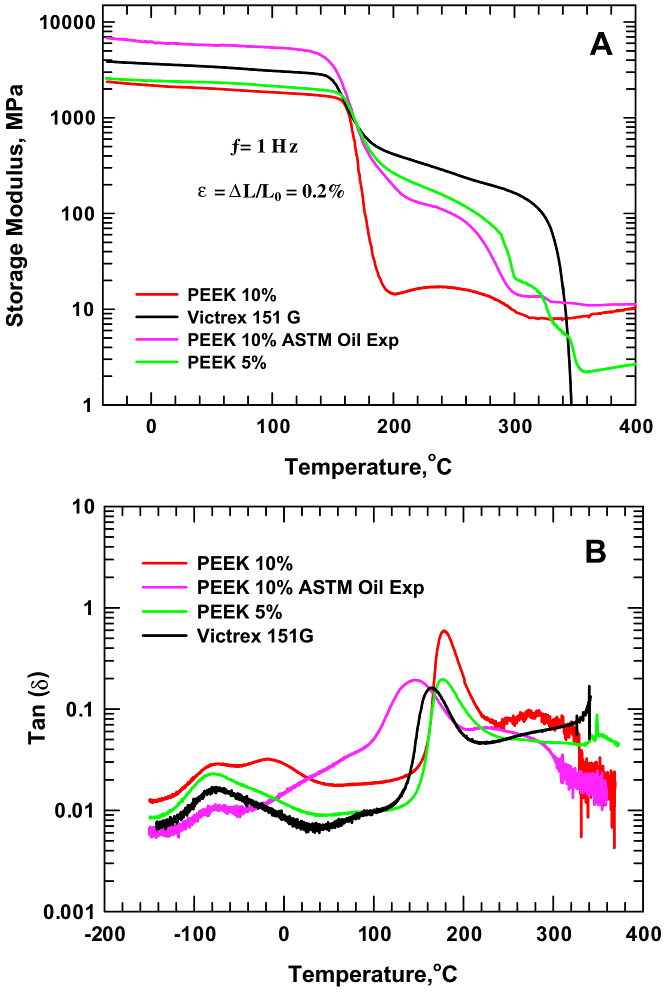


Fig. 3. Storage modulus (A) and tan δ (B) responses of a series of PEEK samples.

300 °C, but did not flow above that point. In a range of 350–400 °C, PEEK 5% exhibits lower modulus plateau than PEEK 10%, which can be attributed to higher degree of crosslinking in the latter. It must be noted here that PEEK 5% storage modulus response exhibits step-wise drop, with 4 distinctive steps observable. This phenomenon will be addressed later in this paper, in DSC results discussion.

An oil-exposed PEEK 10% sample exhibited a surprisingly high modulus that exceeded that of the initial PEEK 10%. The storage modulus of oil-exposed PEEK 10% eventually dropped with high temperature and the two materials became similar. It is well documented in the literature that for semicrystalline materials, solvents such as oil can act as plasticizers for PEEK, decreasing its T_g and at the same time also inducing additional crystallinity, due to increased local segmental mobility [10,11]. Similarly, in our case the effect of absorption of a small amount of oil by PEEK 10% resulted in a small decrease in T_g (165 °C vs 175 °C, as revealed by loss modulus/tan δ DMA data (Fig. 3B)) and led to an increase in the modulus above and below T_g. The plasticization of PEEK chains in the network enabled the formation of small polymer crystallites despite the presence of the crosslinked network. These crystallites serve to reinforce the polymeric matrix, leading to stiffer, higher modulus materials. In the case of the oil-exposed PEEK 10%, it appears that the crystallinity of the sample treated to oil exposure may actually be higher than that of the original uncrosslinked, unplasticized Victrex. This is likely due to annealing effects; the oil exposure test conditions take place at temperatures close to the glass transition for extended time periods. As would be expected, based on the argument of increased crystallinity in the oil-exposed PEEK 10%, above the glass transition temperature, a step-wise drop in storage modulus is observed, which is common for semicrystalline polymers. With further temperature increases, the modulus eventually drops to values close to the original PEEK 10% as the crystallites that had formed melt away. It is also known that absorption of most solvents by PEEK is a reversible dynamic process [10,11]. One of the observations that was made during our DMA experiments is that when an oil-exposed PEEK 10% sample was subjected to DMA testing for a second time, it generated a response curve identical to the original PEEK 10%, implying that mechanical loading during the first DMA run leads to desorption of oil and yields a material with identical morphology to the original PEEK 10% before swelling. To shed more light on this particular aspect of the thermomechanical behavior of the crosslinked PEEK materials we conducted swelling tests and DSC experiments.

3.4. Differential scanning calorimetry (DSC)

DSC is one of the methods, along with densitometry, WAXS and IR spectroscopy that can estimate crystallinity of PEEK polymers [12]. The DSC method is based on the measurement of the enthalpy of crystallites (ΔH_m) melting in a first DSC heating scan of the PEEK material. Knowing the theoretical heat of fusion for the pure crystalline phase of PEEK (130 J/g) [12], one can estimate the mass fraction of the crystalline phase in the polymer investigated. The disadvantage of DSC is that it overlooks additional crystallization that can take place during the first heating scan due to induced chain mobility for temperatures $T_g < T < T_m$. In some cases, an exotherm is observed for additional in-situ crystallization, but it is argued that even when such an exotherm is not visible, some additional crystallization happens inevitably [13]. Therefore, DSC measurements tend to yield higher values of the percent crystallinity (especially for samples with low crystallinity), than, for example, WAXS measurements taken at room temperature [11,13]. In the case of crosslinked PEEKs, additional crystallization during the first heating scan in DSC was never observed. In accordance with the earlier report on crosslinked PEEK systems [3], no melting point transitions were observed for processed PEEK 10% either in the heating, or in the cooling scans (Fig. 2). From this, we can conclude that PEEK 10% is completely amorphous (0% crystallinity). However, both IRM 903 oil-exposed PEEK 10% and PEEK 5% exhibited melting transitions (Fig. 4). The DSC thermograms of PEEK 5% and oil-exposed PEEK revealed several melting transitions, which are attributed to different sizes of crystallites and/or polymorphs [14]. It is the presence of the range of melting temperatures exhibited by these various crystallites that lead to the observation of a step-wise decrease in the modulus (as measured in DMA) of PEEK 5% and oil-exposed PEEK 10% during temperature sweeps (Fig. 3). For an approximate calculation of crystallinity for these samples, the melting enthalpies of each sample were summed. Using the method described above [12] the crystallinity of PEEK 5% sample was determined to be 11%. Solvent induced crystallinity was apparent from the large crystallite melting endotherm in oil-exposed PEEK 10%. Applying the same method we calculated 20% crystallinity. It was also interesting that upon cooling this sample did not display any recrystallization exotherms, resembling pristine amorphous PEEK 10%. This once again supports the dynamic model of absorption/desorption of ASTM oil in/from the crosslinked PEEK.

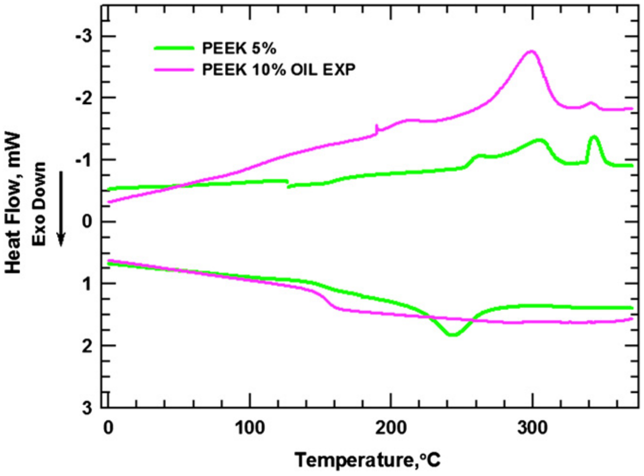


Fig. 4. Differential scanning calorimetry thermograms of PEEK samples. First heating (upper curves) and cooling scans (heating/cooling rate 10 °C/min).

3.5. Swelling tests

The affinity of PEEK polymers to methylene chloride is well established. The nature of relatively high absorption of methylene chloride by PEEK materials is not well understood; however, it has been determined that the amount of methylene chloride absorbed is directly related to the PEEK sample crystallinity [10,15]. The more crystalline the PEEK, the lower the solvent uptake. In this experiment we exposed two crosslinked PEEK

Table 3
Swelling tests of PEEK samples in methylene chloride at 22 °C for 22 days. Average of 2 measurements is reported.

Sample	Weight percent gain
Victrex 151G	6.2 ± 0.2%
ASTM oil-exposed PEEK 10%	21.3 ± 0.4%
PEEK 10%	32.1 ± 0.6%

Table 4

Tensile properties of PEEK samples with various degree of crosslinking and crystallinity (as determined by DSC, * – as claimed by manufacturer for an average sample).

Sample name	Victrex 151G	PEEK 5%	PEEK 10%
Crystallinity	29% (35)%* Crystallinity	11% Crystallinity	0% Crystallinity
Young's modulus @ 220 °C, MPa	443	180	6
Ultimate elongation @ 220 °C, %	215	41	28

samples and non-crosslinked Victrex 151G. The samples were soaked in methylene chloride for an extended period of time (22 days) to ensure equilibration and the resulting weight gains are reported in Table 3. The degree of swelling in our materials depended both on crystallinity and the concentration of crosslinks introduced. However, our experiments indicated that the amount of crosslinks introduced could not compensate for a complete loss of crystallinity in PEEK 10% and that was why the swelling ratio was higher in our crosslinked materials than in pristine PEEK. Data in Table 3 also supports the assertion that oil-exposed PEEK 10% was more crystalline than PEEK 10% itself, providing additional evidence that small amounts of ASTM oil in the swollen matrix acts as a crystallization-inducing plasticizer for the 10% crosslinked PEEK.

3.6. *Tensile properties at high strain*

The tensile properties of a series of PEEK compounds at 220 °C can be found in Table 4. It can be seen from the above results that introduction of rigid linkers not only effectively disrupts crystallinity but significantly reduces the tensile properties of PEEK, such as ultimate elongation and elastic modulus (Fig. 5).

To gain additional insight into the elastomeric properties of crosslinked PEEK materials, PEEK 5% and Victrex 151G were subjected to 20% strain level for three uniaxial deformation cycles at 220 °C as shown in Fig. 6. The original Victrex 151G material exhibited a large residual strain (~11.5%) (Fig. 6B) in the first deformation cycle, whereas the 5% crosslinked PEEK showed somewhat improved elastic behavior with a permanent set of only ~7% at the same conditions (Fig. 6A). A significant *permanent set* was observed in both cases due to the disruption of the original microstructural orientation of the material. Once the microstructure becomes disrupted during the first cycle, it does not have time to completely "reheal" before the next cycle is initiated, thus a much lower mechanical hysteresis and *permanent set* is observed in subsequent cycles, indicating a more elastomeric polymer matrix.

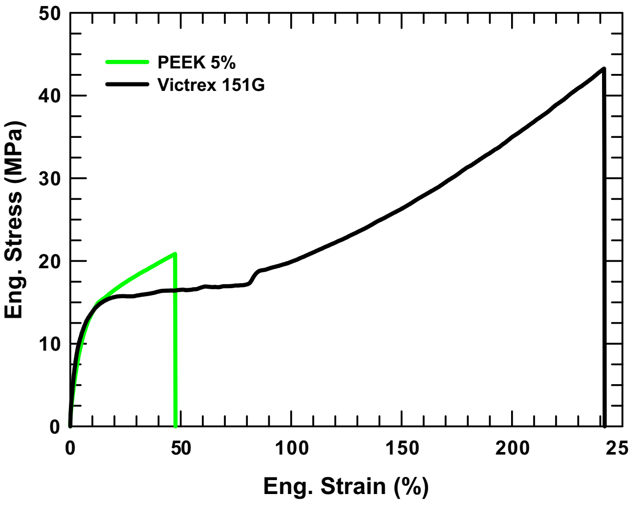


Fig. 5. Stress–strain curves at 220 °C for crosslinked PEEK (5%) and original Victrex 151G. Measured on Zwick Mechanical tester at 45 mm/min.

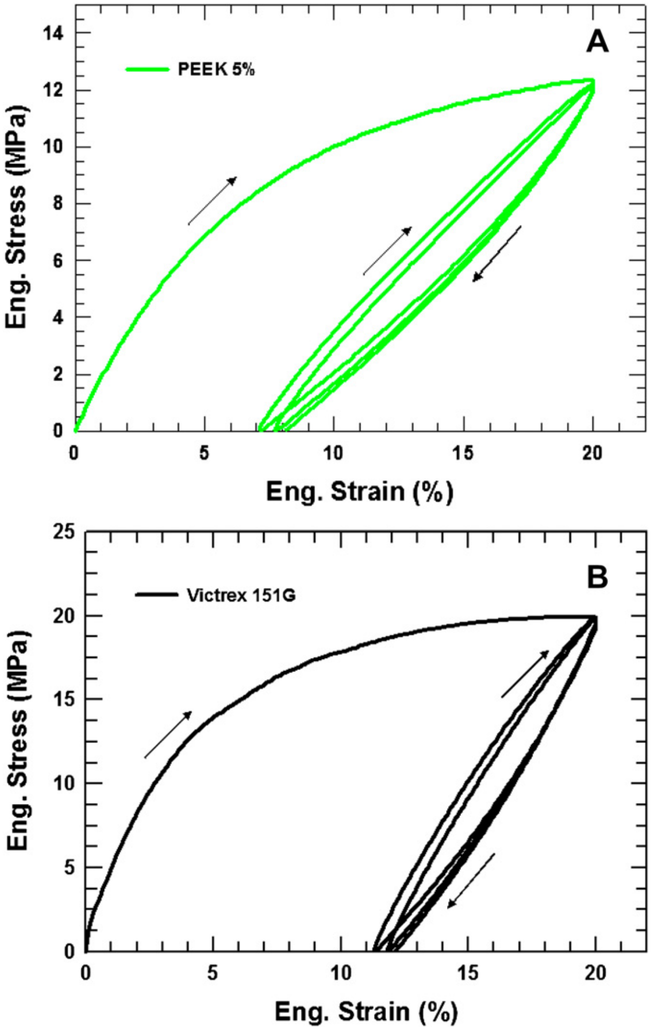


Fig. 6. Uniaxial cyclic tensile test of PEEK 5% (A) and Victrex 151G (B) at 220 °C.

3.7. *Creep data*

Samples of the 5% crosslinked PEEK and the virgin Victrex 151G sample were subjected to 3 MPa stress for 2 h at 280 °C. After 2 h of constant stress loading, the sample was allowed to relax for 20 min. The evolution in sample strain was recorded in this experiment. High temperatures for this test are needed because it is known that the creep modulus of PEEK strongly depends on temperature and not time [16]. In Fig. 7A the strain values have been normalized to the maximum strain achieved by each sample after 120 min loading. In Fig. 7B, creep compliance is plotted vs time, where creep compliance is the measured strain divided by imposed constant stress (3 MPa). This experiment demonstrates that crosslinked PEEK is more compliant (soft), but shows less irreversible plastic deformation, as also confirmed by a cyclic tensile test.

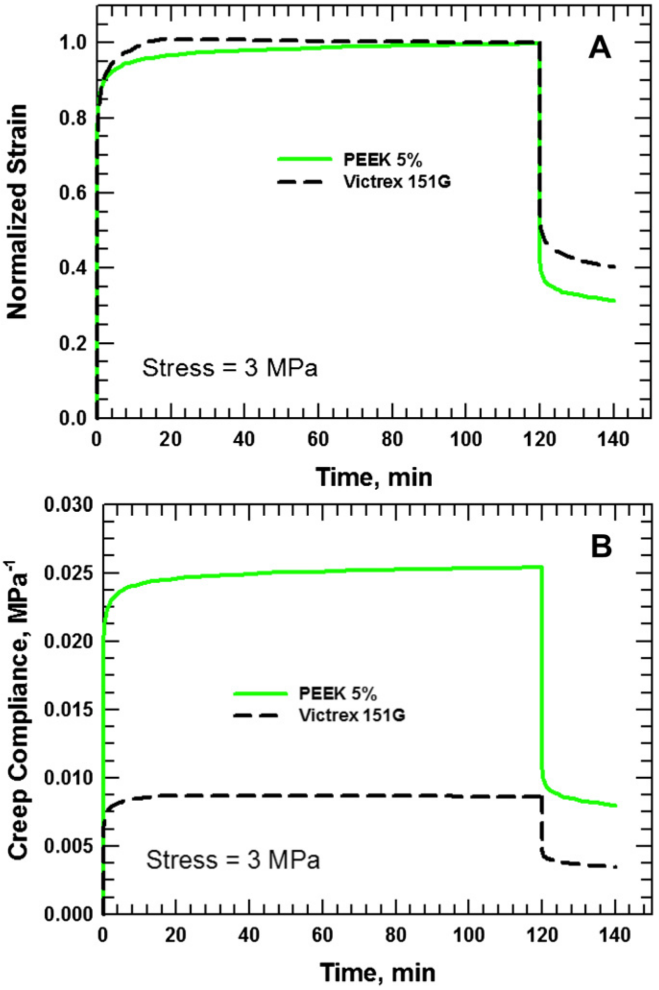


Fig. 7. Creep tests for 5% crosslinked PEEK and Victrex 151G at 3 MPa stress and 280 °C. A. Victrex 151G curve is normalized to 2.58% strain and PEEK 5% at 7.63% strain.

4. Conclusions

A reliable synthetic protocol has been demonstrated that allows for a reproducible and traceable introduction of rigid crosslinkers within a linear PEEK polymer matrix. The resulting thermoset elastomeric materials were found to be extremely thermally stable (up to 500 °C for small periods of time). The crosslinked PEEK (PEEK 10%) showed excellent resistance towards various aggressive media at high temperatures, which was comparable to pristine PEEK (Victrex 151G), and in particular was significantly less susceptible to swelling in oil than other traditional rubber materials. It was shown by means of DSC and methylene chloride uptake tests that introduction of even small amounts of rigid crosslinkers disrupts crystallinity of the original polymer matrix very efficiently. In the case of amorphous PEEK 10% it was demonstrated that additional crystallinity could not be induced by thermal treatment alone, but only when coupled with solvent exposure (ASTM oil IRM 903). Furthermore, the additional crystallinity is introduced reversibly and can be controlled by oil absorption and desorption. As revealed by high temperature tensile tests, tensile properties (elastic modulus, ultimate elongation) of PEEK materials strongly depend on the crystallinity of the samples tested. Crosslinking reduces the crystallinity of the PEEK materials and therefore also decreases the Young's modulus, at high temperatures. DMA tests show that we are able to create truly crosslinked polymer networks (PEEK 10% and PEEK 5%), which do not flow up to very high temperatures (<400 °C). PEEK 10% exhibited a very broad rubbery plateau in the storage modulus, as determined by DMA at small strains. The crosslinked PEEK (PEEK 5%) also showed improved creep resistance at high temperature, compared to original unmodified PEEK, in terms of a reduced irreversible creep component. This is accompanied by a reduction in the maximum extensibility that can be achieved under loading, as shown in Fig. 6; although extensibilities of 40% can still be achieved at very light levels of crosslinking.

In summary, by crosslinking commercial PEEK engineering materials we were able to produce softer more rubbery materials (see the results of cyclic testing) with useful elastomeric properties for high temperature applications. A possible application of such swell-resistant elastomeric materials can be in areas where low strain/low stress high temperature applications with improved creep resistance are required, especially in hostile thermal/chemical environments.

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Appendix. Supplementary information

Supplementary information associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.01.056.

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