

The effects of UV irradiation to polyetheretherketone fibers – characterization by different techniques

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Keywords: PEEK, fiber, ultraviolet, rheology

Abstract

The effects of UV irradiation on polyetheretherketone (PEEK) fibers were investigated in this study. PEEK fibers were manufactured with a melt spinning system and then artificially aged with simulated solar UV light. Fibers were then characterized with mechanical tests, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), rheology, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). PEEK, best known for its excellent thermal stability, suffered greatly due to the effects of UV irradiation. The low UV stability could be observed as embrittlement of the fibers in the mechanical tests, increased crosslinking rate in the rheological tests, formation of carbonyl and hydroxyl groups and changes in the carbon-hydrogen bond nature in the FTIR, worsened thermal properties in the TGA and transverse cracks in the SEM photos. DSC was found to be an inaccurate technique in estimating the degradation level of PEEK fibers whereas the carbonyl index measured by FTIR was found to be the most convenient technique.

1. Introduction

UV irradiation of polymeric materials is an important area of research since many polymers have to withstand outdoor exposure. Long exposure to UV light causes polymers to degrade which can be observed as discolouring, embrittlement, loss of mechanical properties and thus as a greatly shortened lifetime of products [1-5]. The study of specialty and high performance polymers have gained more and more interest since their degradation behaviour, often occurring only in extreme conditions, is not as well studied as the commodity plastics [6-9].

Polyetheretherketone (PEEK) is a linear, aromatic, semicrystalline and rather expensive thermoplastic (Fig.1). It has excellent thermal properties and chemical resistance, low flammability, low water absorption and good radiation resistance. Because of these properties, PEEK is commonly used in high-tech applications such as

space products, medical devices, and as metal replacement [10, 11]. Commercial PEEK fibers can be found in process belting, filtration mesh, wiring harnesses, strings, threads and composites [12]. PEEK has a high processing temperature of 360–400 °C which limits the processing possibilities, because a typical extrusion or injection moulding equipment is not capable of temperatures this high.

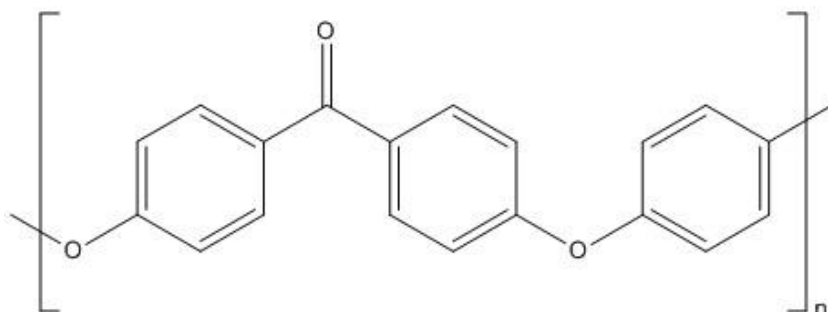


Fig. 1. The chemical structure of PEEK.

Most degradation studies of PEEK have concentrated on the high-temperature thermal behaviour [13-16] since PEEK has one of the highest continuous use temperatures (260 °C) among plastics. UV degradation of PEEK has been mostly studied from the chemical point of view [8, 17-19] and studies of mechanical properties are not as common [7]. Studies of the UV resistance of PEEK fibers were not found in the literature. Polymer fibers have often special characteristics in properties such as mechanical strength, sample thickness and polymer chain orientation which makes testing of fiber form samples desirable [20-23].

PEEK, like most linear polyaromatics, suffers from the effects of UV irradiation [7, 9, 24]. As an aromatic chain polymer PEEK absorbs practically all UV radiation of wavelengths under 380 nm [8]. As the incident solar spectrum begins from 290 nm, natural UV radiation is greatly absorbed by PEEK leading to photochemical oxidation reactions. Photooxidation also leads to products in the polymer sample that extend the absorption of light well into the visible region, leading to an observable yellowing caused by the absorption of blue light and further accelerating the rate of photodegradation. UV light induced ageing is thus a major factor affecting the lifetime and temperature resistance of PEEK products, and is of great economic value.

This article will concentrate on artificial UV testing of fiber form PEEK samples. UV testing of fibers has many advantages compared to sheets or tensile testing specimens that are more commonly tested. Fibers have a high surface area to volume ratio which makes ageing faster because the chemical reactions occur mostly in the surface layer. Samples were irradiated 0-1056 h after which the mechanical properties, DSC, TGA, FTIR, SEM and rheology were measured. Rheology is rarely used for studying the ageing of materials but it provides useful information of the degradation behaviour such as the relative amounts of competitive chain scission and

crosslinking reactions [25-27]. The goal of this article is to use a wide range of characterization techniques to measure the changes in the fibers and also estimate the suitability of the techniques in the study of photodegraded PEEK fibers.

2. Experimental

2.1 Samples and irradiation

Samples were made of Victrex (Lancashire, UK) PEEK grade 151G. This is a semicrystalline, easy flow grade with no inherent UV stabilizers. PEEK fibers were manufactured by a melt spinning process using a Göttfert Rheograph 6000 to melt and pump the material. The processing temperature was 380 °C, capillary dimensions 30/1 mm and piston speed 0.5 mm/s. Fibers were drawn by gravity because a spinning motor would have led to unnecessarily small fiber diameters. The final diameter of the fiber was very homogenous at 410 ± 10 μm .

The UV irradiation chamber (1260x710x450 mm) has four Q-Lab UVA-340 fluorescence lamps with peak intensity at 340 nm. Irradiance of the UVA-340 lamps corresponds well with sunlight at the critical short wavelength region [28]. The oldest lamp was changed every 400 h so the total working life of the lamps was 1600 h. For the UV irradiation tests, PEEK fibers were cut and taped in a 600x400 mm frame. PEEK samples were kept in the chamber for 0, 144, 384, 720, 1056 h so that both sides of the samples were irradiated for the same time. Temperature of the UV chamber was 33 °C.

2.2 Measurements

The tensile testing of the fibers was made with an Instron 5967 according to the standard ISO 5079:1995. The initial length was 20 mm and the drawing rate 20 mm/min. Instead of the recommended 50 measurements, only 10 samples per irradiation time was measured due to slowness of the testing procedure. The modulus was calculated by the software using linear regression technique according to the standards EN10002 and ASTM E8. Tests were made with a 2kN power shell.

FTIR measurements were made with a Bruker optics tensor 27 using ATR (attenuated total reflectance) mode. Samples were tested between 400-4000 cm^{-1} , using 16 measurements and resolution of 4 cm^{-1} . Measurements were made using four parallel fibers and the average of five measurements was used to minimize errors. The data was baseline corrected using the average absorbance of 3800–4000 cm^{-1} as a reference. The carbonyl index was calculated as the ratio of the aged and unaged peak intensities at 1716 cm^{-1} . To calculate the

peak areas for the crystallization measurements, the baseline corrected FTIR data was integrated using OPUS software.

DSC tests were carried out in a Netzsch DSC 204 F1 heat-flux DSC. All the tests were carried out in a nitrogen atmosphere. During the DSC tests, materials were heated from room temperature to 400 °C, then cooled down to room temperature and then heated once more. The heating/cooling rate was 20 °C/min. To minimize errors each fiber was measured 5 times.

Oscillatory shear measurements within the linear viscoelastic range were carried out for the samples using an Anton Paar Physica MCR 301 rheometer. All the experiments were performed in a nitrogen atmosphere using a 25 mm plate-plate geometry. The measuring points in the angular frequency range of 0.1–562 rad/s were recorded with decreasing frequency at 380 °C temperature.

TGA tests were made with a PerkinElmer TGA 6. Samples were heated from room temperature to 995 °C using synthetic air (20 % O₂/ 80 % N₂) and nitrogen (100 % N₂) with a heating rate of 10 °C/min.

A Philips XL30 scanning electron microscope (SEM) was used to investigate the morphology of the PEEK fibers. Liquid nitrogen was used to break the fibers for the transverse investigations.

3. Results and discussion

3.1 Tensile properties

Breaking strength, yield strength and Young's modulus decrease only a little as the irradiation time increases (Table 1). Fibers irradiated for 1056 h have lost approximately 5–15 % of their original strength and elastic modulus. These changes are small when compared with the changes in the elongations, because 1056 h irradiated fibers have lost 96 % of their original elongation at rupture becoming brittle. Pristine PEEK fibers were very ductile with over 300 % elongation at rupture. The changes in the elongations at rupture are fairly linear on a logarithmic scale as can be seen in Fig. 2. An exponential trendline gives R²-value of 0.87.

The relative variance in the elongations is the highest in the middle aged 144 h, 384 h and 720 h samples. UV irradiation causes chain scission reactions in the polymer chains which has a special significance in the fibers since they have a high degree of orientation. In pristine PEEK the polymer chains are untouched, thus the elongation at rupture is high and the variance is relatively low. UV irradiation starts randomly cutting the polymer chains leading to a rapid decrease in the rupture elongation. Existing flaws will induce new flaws at an increasing rate. High variance in the three middle aged samples can be explained by statistical reasons. If a sufficient amount

of material flaws are concentrated into a single area in any part of the fiber it leads to a rupture. In the 1056 h irradiated samples the amount of deterioration is so large that it inevitably ruptures the fiber very early, simultaneously decreasing the variance. Some of the variance can be explained by the spinning equipment [29]. There is no mixing in the capillary rheometer which can cause problems in the material homogeneity. Typical tensile testing curves for different samples can be seen in Fig. 3.

Previous mechanical tests for PEEK sheets have shown that photodegradation does not have a significant effect on the yield strength of PEEK which can even rise at first because of the crosslinking and hardening of the material [7, 24]. Also the embrittlement of the material was previously noticed with similar magnitude to our tests [7].

Table 1. Tensile properties of UV irradiated PEEK fibers.

Time [h]	Yield strength [MPa]	Tensile strength at rupture [MPa]	Elongation at rupture [%]	Modulus [MPa]
0	83.2 ± 2.0	87.6 ± 1.9	311 ± 9	2340 ± 55
144	80.5 ± 1.0	78.6 ± 0.8	173 ± 25	2290 ± 95
384	78.7 ± 1.5	78.0 ± 1.3	137 ± 23	2400 ± 71
720	79.6 ± 1.0	74.4 ± 1.0	49 ± 8	2200 ± 50
1056	77.8 ± 2.0	72.3 ± 1.6	13 ± 1	1980 ± 80

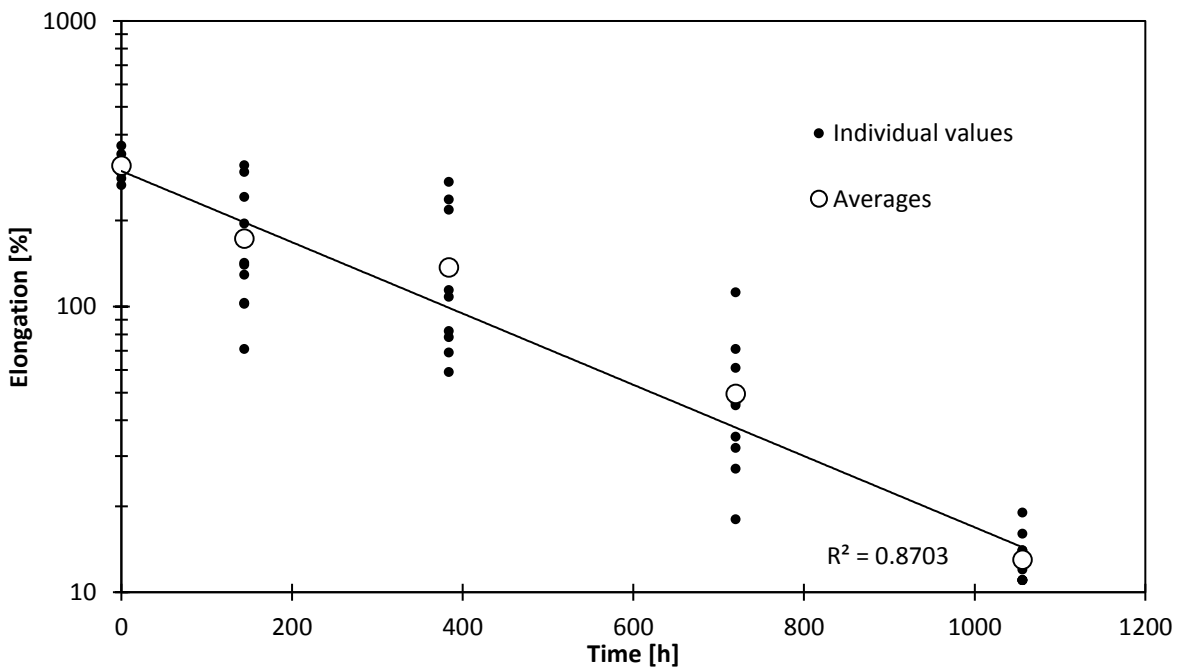


Fig. 2. Elongations at break on a logarithmic scale for UV irradiated PEEK fibers.

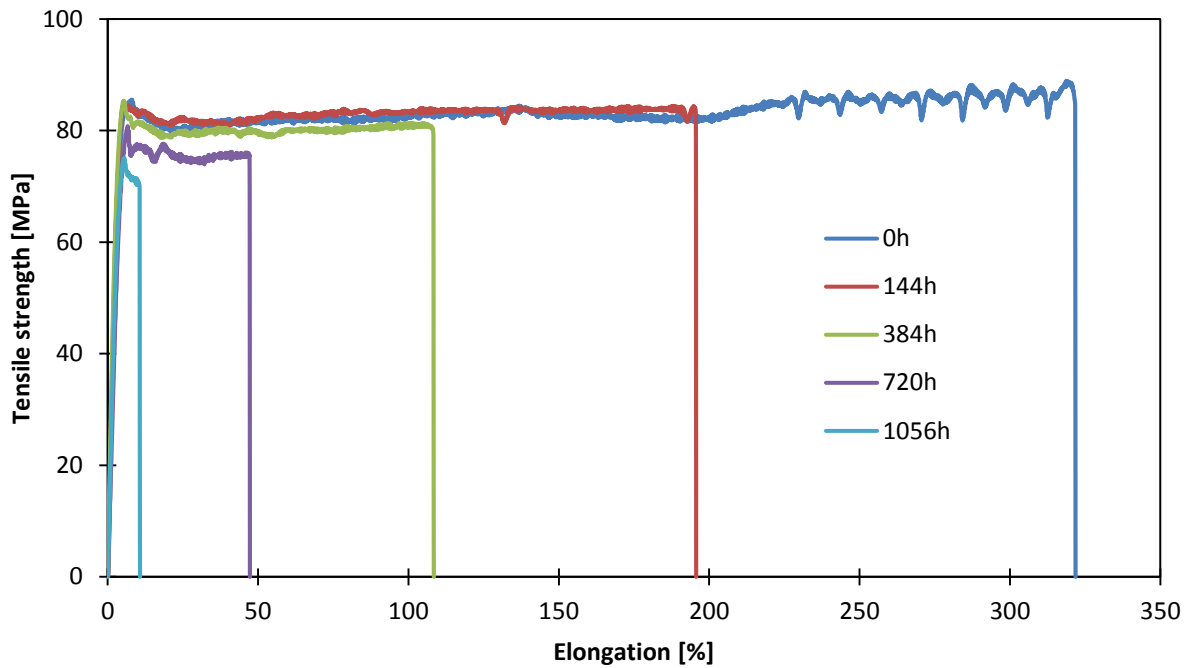


Fig. 3. Typical tensile testing curves for UV irradiated PEEK fibers.

3.2 FTIR

The most profound change in the IR spectra of UV irradiated PEEK is the formation of the carbonyl group absorption peak (Fig. 4), with a maximum at 1716 cm^{-1} and numerous shoulders indicating that several different carbonyl species (aldehydes, carboxylic acids and esters) are formed. Another typical change is the formation of the broad hydroxyl group absorption peak (Fig. 5), spanning from $2800\text{--}3700\text{ cm}^{-1}$ with a maximum at $\sim 3230\text{ cm}^{-1}$. In addition the two bands at $\sim 3050\text{ cm}^{-1}$ that correspond with the stretching C-H vibrations of phenyl groups decrease, indicating the opening of aromatic groups due to photodegradation.

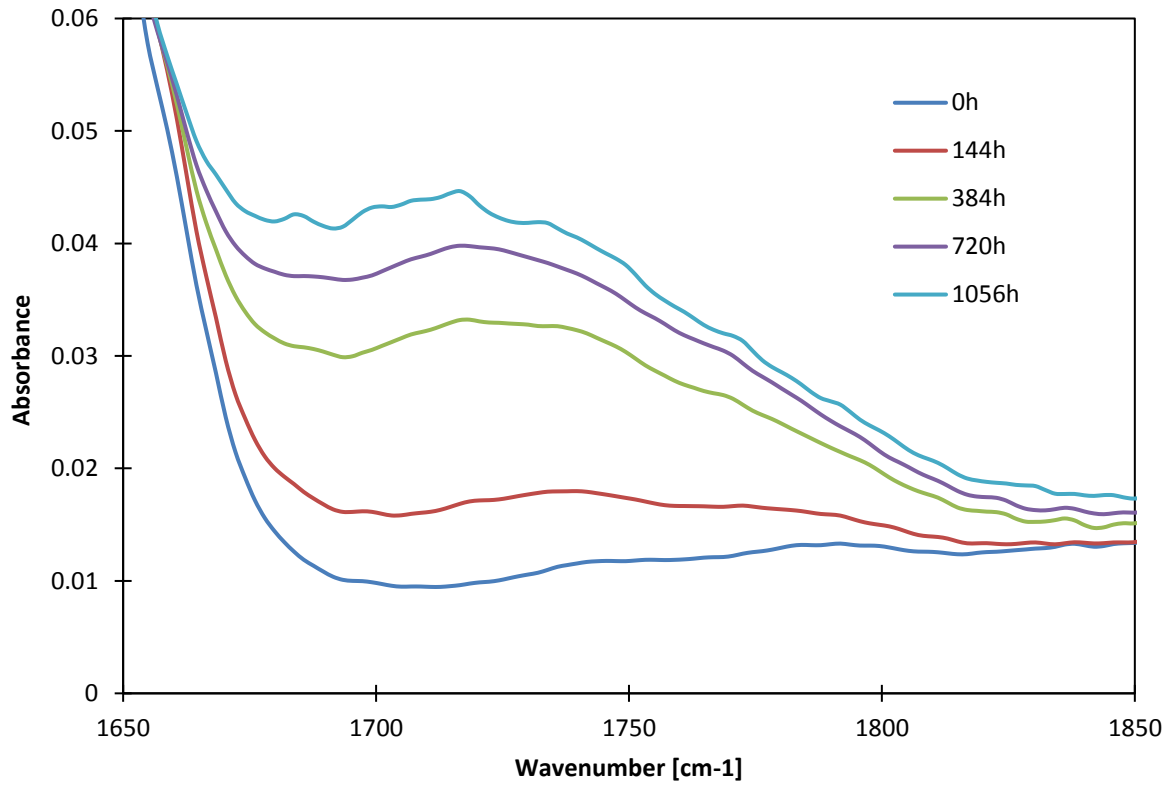


Fig. 4. FTIR spectrum of UV irradiated PEEK fibers in the carbonyl region.

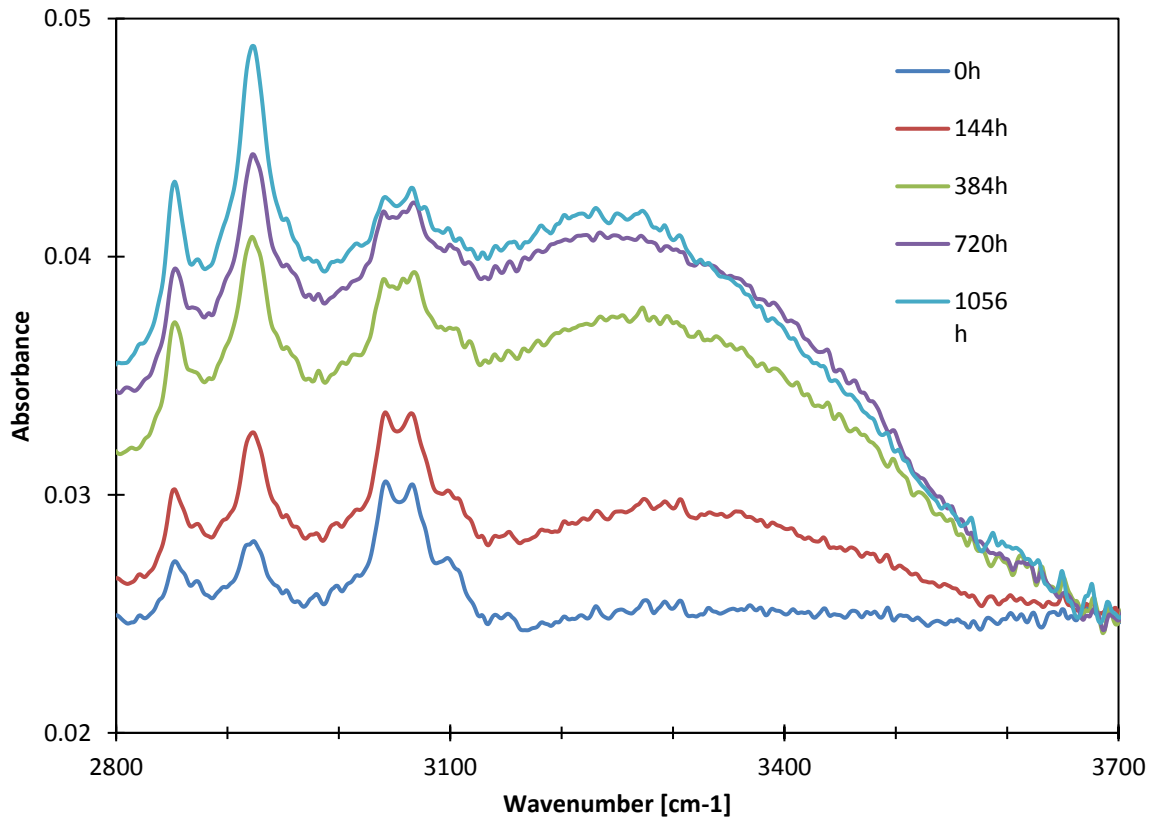


Fig. 5. FTIR spectrum of UV irradiated PEEK fibers in the hydroxyl region

The carbonyl index is one of the most used metrics in the study of polymer degradation. This is mainly due to the fact that the chemical degradation products often contain carbonyl groups and that the extinction coefficient of these groups is quite high, making the carbonyl group peaks very distinct in the FTIR-spectra. Since degradation reactions occur initially only in a thin surface layer of the sample, the increase in the concentration of carbonyl groups can often be observed well before mechanical properties change. The carbonyl index of PEEK fibers, shown in Fig. 6, rises with increasing irradiation time. The carbonyl index rises almost exponentially between 144-384 h, after which the rise continues at a much slower pace. This indicates a large number of carbonyl groups forming in the photodegradation of PEEK.

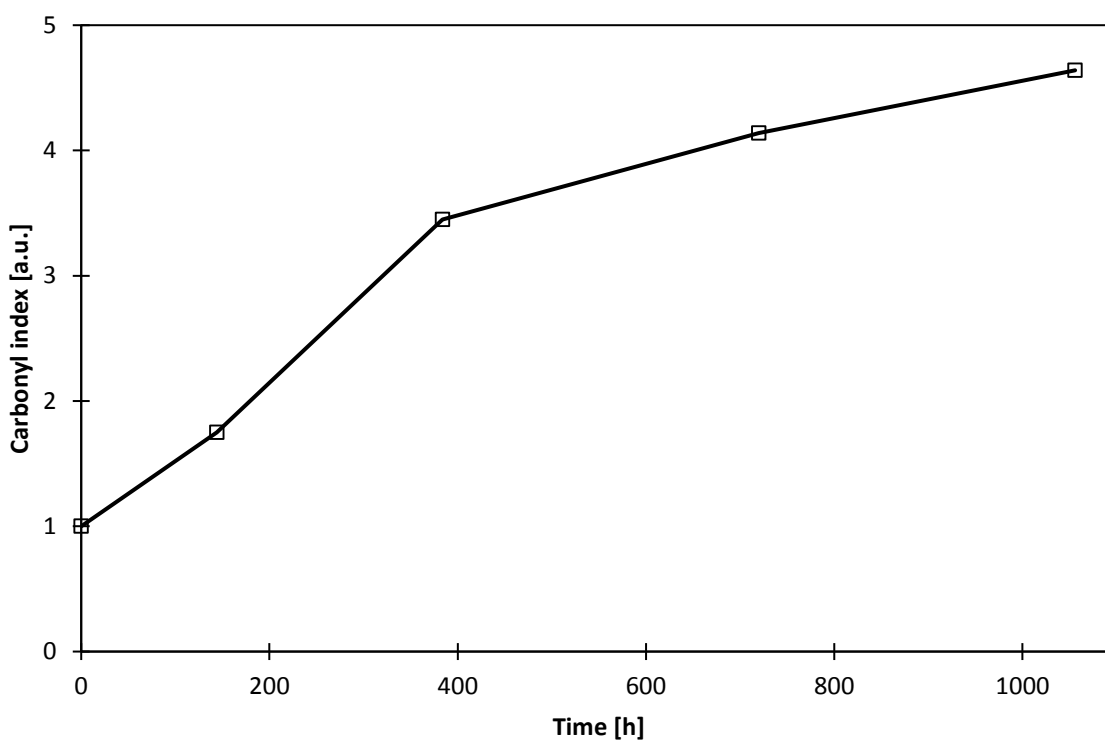


Fig. 6. Carbonyl index of UV irradiated PEEK fibers.

The rise of the aliphatic methylene group vibrations (symmetric CH_3 -stretching at 2853 cm^{-1} and anti-symmetric CH_3 -stretching at 2922 cm^{-1}) and the lowering of the CH -stretching vibration of the aromatic rings (at 3065 cm^{-1}) are clearly visible in Fig. 5. This result indicates that the photodegradation of PEEK fibers leads to a loss in aromaticity due to a ring breaking reaction. The relative changes of the absorptions are presented in Fig. 7.

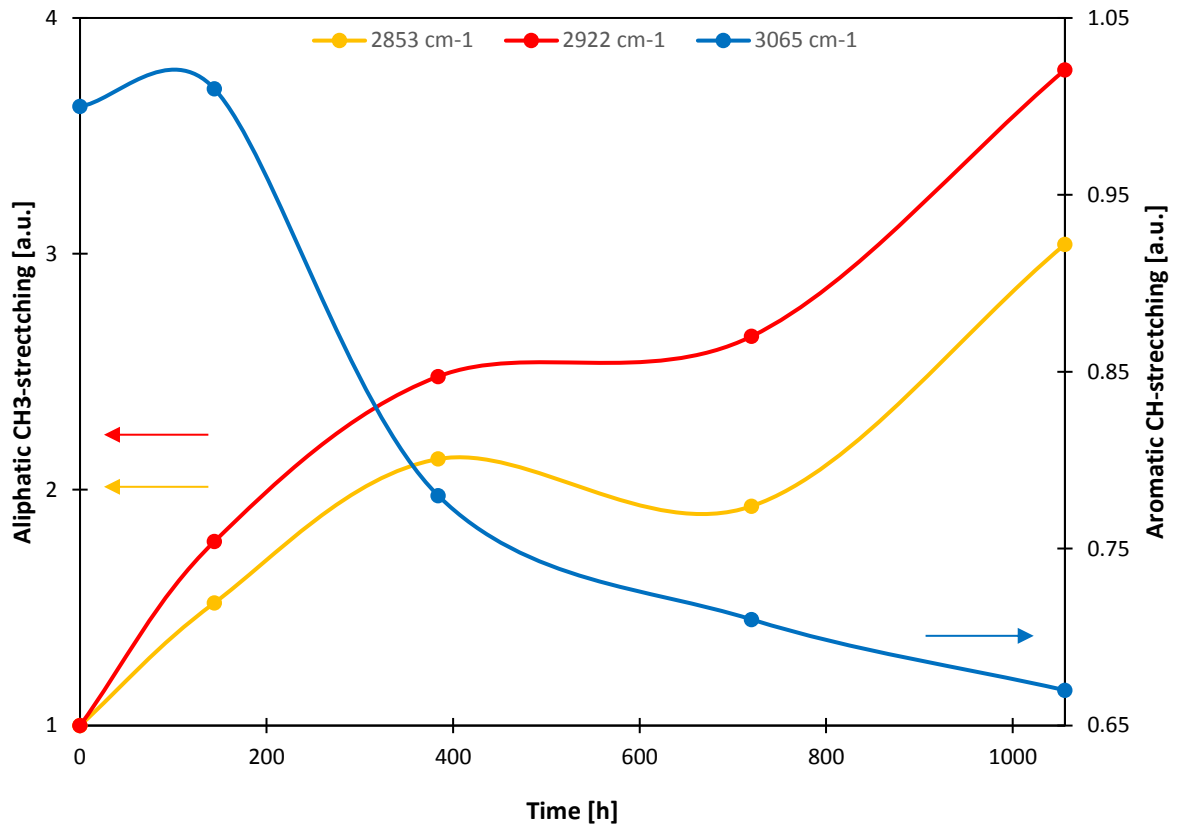


Fig. 7. Methylene CH₃- and aromatic CH-stretching vibration changes as a function of irradiation time.

Previous studies have shown that the degree of crystallinity and the ratio of certain IR absorption peaks have a linear relationship [30, 31]. Chalmers et. al. [30] reported that the ratios of the peak intensities at wavenumbers 1305cm⁻¹ / 1280cm⁻¹ and 970cm⁻¹ / 952cm⁻¹ increase as the degree of crystallinity increases. Jonas et. al. [32] later discovered that the peak 965 cm⁻¹ is not suitable for determination of crystallization degrees above 15 %. The ASTM F2778 standard uses the peak intensities at 1305 cm⁻¹ and 1280 cm⁻¹ to determine the degree of sample crystallinity [33].

Several authors have studied the determination of the degree of crystallinity of PEEK by different techniques. Specular reflectance FTIR (R-FTIR) is commonly considered to be the best technique for the task [31, 34, 35]. Also wide-angle x-ray scattering (WAXS) can be used for unfilled grades but it is slower and may need some complex curve fitting techniques to obtain the degree of crystallinity [34]. It has the advantage that it measures the crystallinity from the whole sample thickness whereas R-FTIR measures it only from the surface. The accuracy of DSC has been shown to be weak in the degree of crystallinity measurements of PEEK even though it is a commonly used technique. [32, 34]

ATR-FTIR is a very simple and common technique. It has received criticism due to its poorer absorption intensity and repeatability compared with R-FTIR [35] but despite that it is a commonly used to measure the degree of crystallinity of PEEK [31]. In this study the PEEK crystallinity was measured using ATR-FTIR (Table 2) and the results were compared with the DSC crystallinity measurements (Table 3). Both techniques indicate that there are no major changes in the degree of crystallinity caused by the photodegradation. DSC measurements give 35-36 % degree of crystallinity for all samples, but this value has to be considered with caution because of the limitations previously mentioned.

Table 2. Absorbance ratio $1305\text{cm}^{-1} / 1280\text{cm}^{-1}$ measured by FTIR to estimate the degree of crystallinity of PEEK.

Time [h]	0	144	384	720	1056
I^{1305}/I^{1280}	0.93	0.99	1.05	1.05	0.99

3.3 DSC

The glass transition temperature of PEEK rises quite linearly with increased irradiation time for both heating runs (Table 3 and Fig. 8). During the photo degradation T_{g2} is usually larger than T_{g1} . This is expected, since the glass transition temperature of a polymer is caused by a change of mobility of the amorphous regions. The photo degradation process induces crosslinks in the amorphous regions, limiting the mobility and free volume of the polymer chains. In the first heating run these tensions in the amorphous region lower the required energy to cause the glass transition process, because the polymer chains relax to lower tensions exothermically. During the cooling cycle the polymer crystallizes to a relaxed morphology, causing an increase in the temperature required to cause the glass transition.

According to the DSC tests, UV irradiation does not have an effect on the polymer crystallinity and melting point of the PEEK fibers tested.

Table 3. The results of DSC scans for UV irradiated PEEK fibers.

Time [h]	Crystallinity [%]	T_{g1} [°C]	T_{g2} [°C]	T_{m1} [°C]	T_{m2} [°C]
0	36.0 ± 0.5	143.6 ± 0.9	144.7 ± 1.1	342.9 ± 0.4	340.9 ± 0.1
144	36.4 ± 0.3	145.8 ± 0.5	148.4 ± 0.9	342.6 ± 0.2	341.2 ± 0.1
384	35.3 ± 0.4	145.9 ± 2.0	146.0 ± 1.3	342.2 ± 0.1	340.5 ± 0.1
720	35.9 ± 0.3	147.1 ± 1.4	146.0 ± 0.8	342.8 ± 0.1	340.7 ± 0.1
1056	35.4 ± 0.5	149.3 ± 1.3	151.3 ± 2.2	343.0 ± 0.2	340.6 ± 0.2

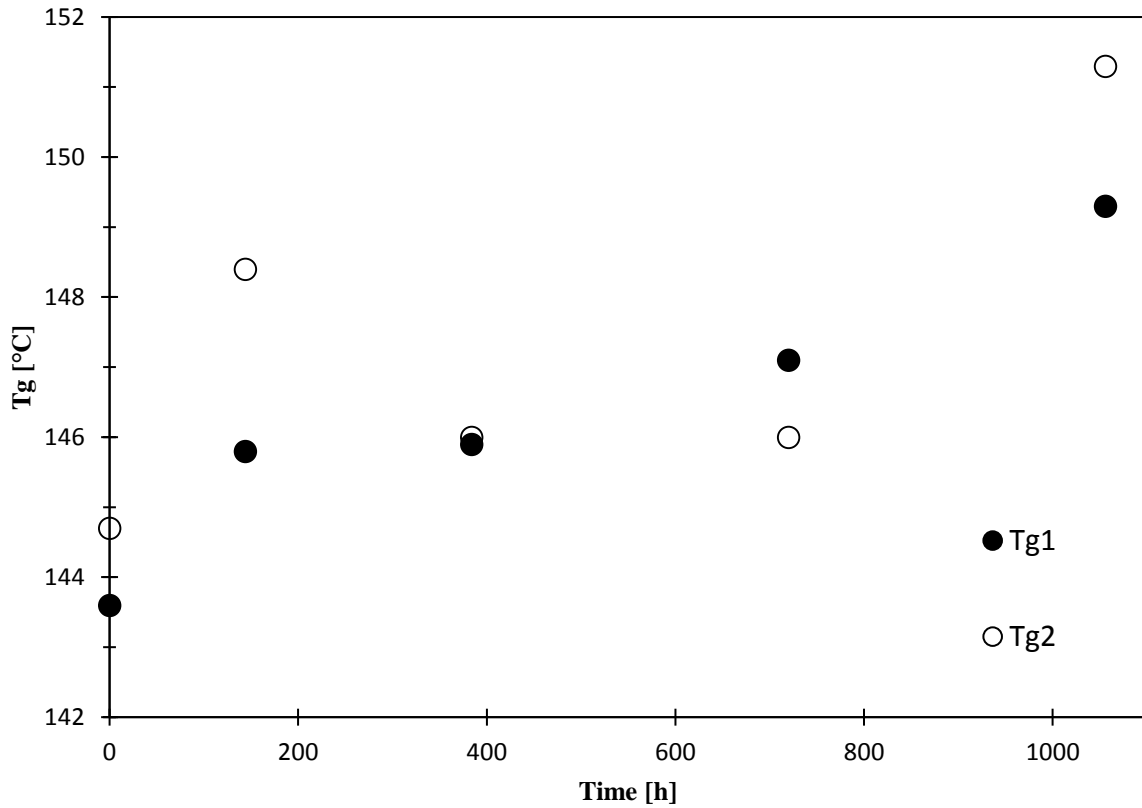


Fig. 8. Glass transition temperatures of UV irradiated PEEK fibers.

3.4 Rheology

The results of rheological tests in Fig. 9 show a steady increase in the zero shear viscosity with increased irradiation time. Also the amount of shear thinning increases during the irradiation so that the pristine PEEK samples have the lowest viscosity at low angular frequencies and the highest viscosity at high angular frequencies.

The zero shear viscosity of PEEK increases due crosslinking that was evident in the tensile tests and in DSC scans as well. As previously mentioned, UV- or ion irradiation has shown to increase the glass transition temperature because of crosslinking. [36-38]

The Cole-Cole plot is an old but often used experimental rheological model that can be used to study the changes in the polymer morphology [25, 26, 39]

$$\eta^*(\omega) = \frac{\eta_0}{1 + (i\omega\lambda_0)^{1-h}}$$

where η^* is the complex viscosity, ω angular frequency, η_0 zero shear viscosity, λ_0 average relaxation time and h parameter of the relaxation-time distribution. This model predicts that η'' versus η' curve (where η'' is the imaginary component of the complex viscosity and η' the real component) is an arc of a circle in the complex plane and that the extrapolated crossing point of the arc and the real axis is the zero shear viscosity η_0 . The zero shear viscosity η_0 and the molecular weight M_w have a well-known power law connection [40]

$$\eta_0 \propto M_w^a$$

Which means that changes in the arc radius correspond with changes in the molecular weight. According to the Cole-Cole-plot of PEEK, shown in Fig. 10, the crosslinking behaviour is very dominant after 144 h of irradiation. The samples that have been irradiated 0-384 h seem to have a double distribution behaviour because a straight line follows the arc. For 720 h and 1056 h irradiated samples the crosslinking rate is higher, with the curve being almost a straight line from the beginning. This is a typical sign of fully crosslinked material [25].

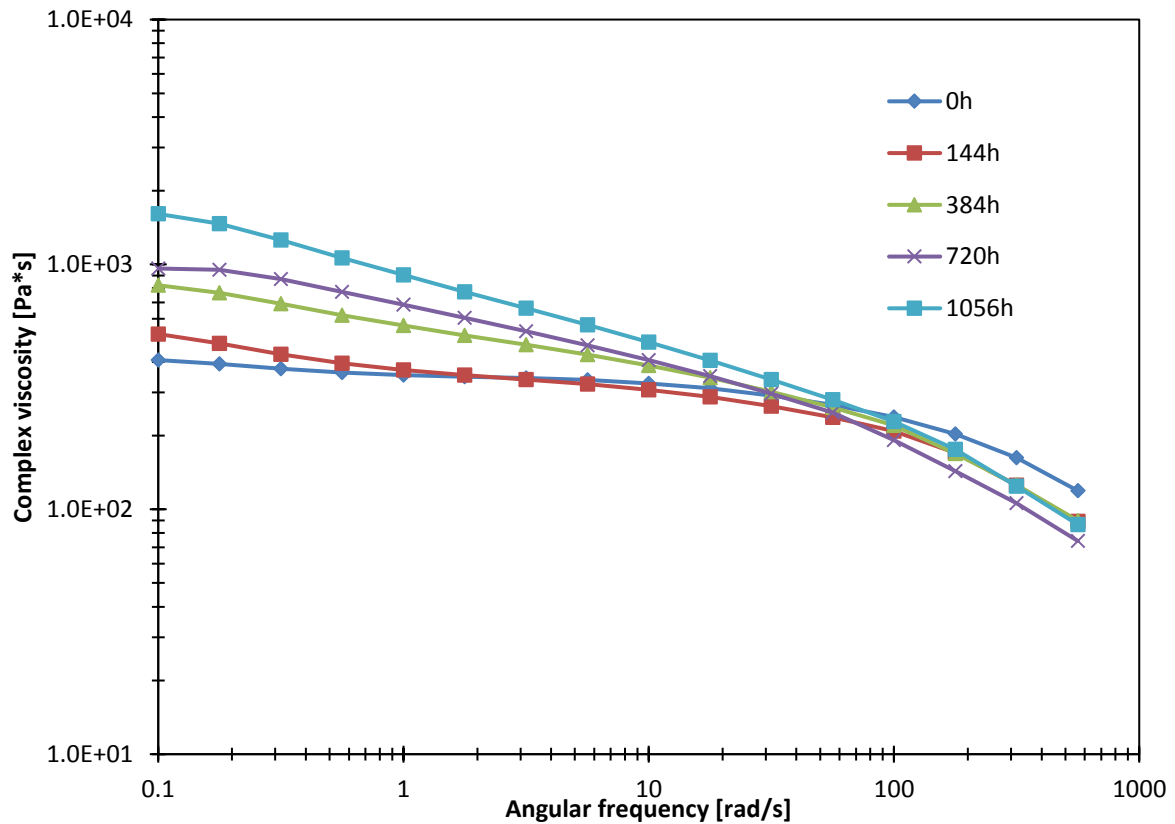


Fig. 9. Complex viscosity of UV irradiated PEEK fibers.

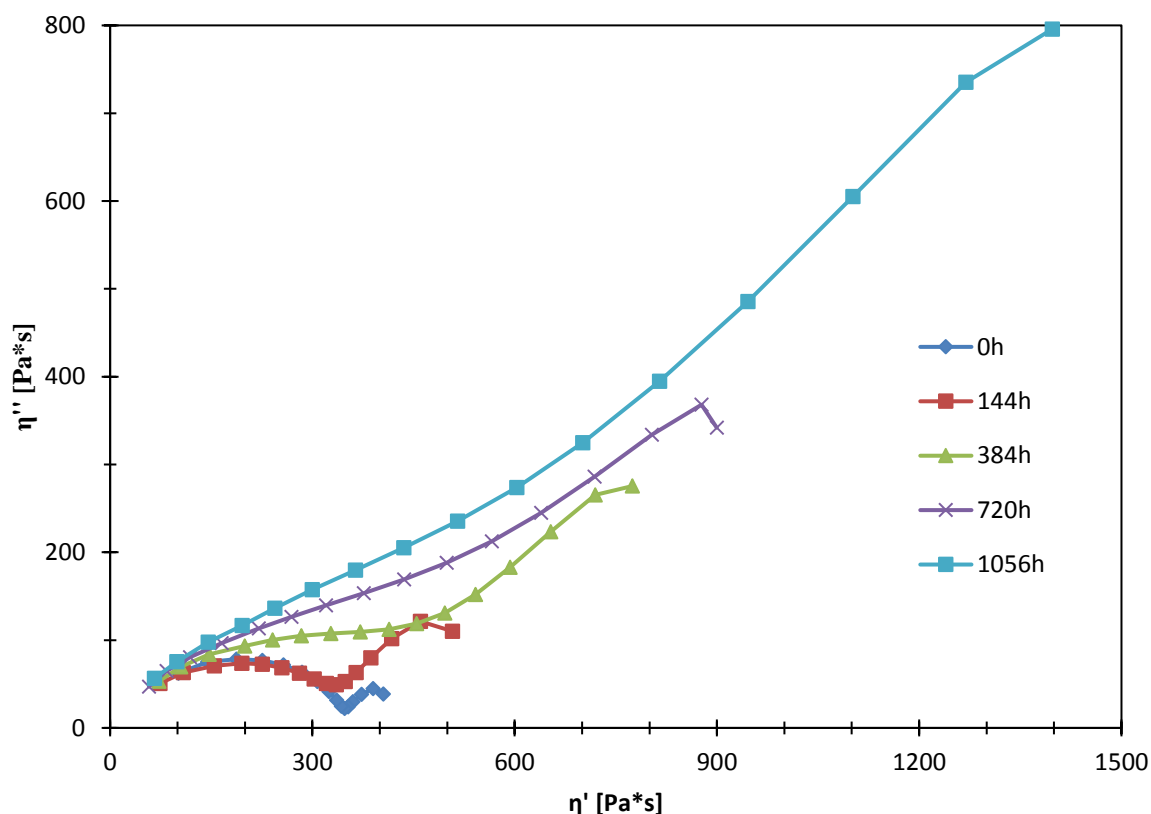


Fig. 10. Cole-Cole plot for UV irradiated PEEK fibers.

3.5 TGA

TGA tests were used to estimate the thermal resistance of the UV irradiated PEEK samples. The results measured in air (Fig. 11) and in nitrogen (Fig. 12) show that even a rather short exposure to UV light weakens thermal resistance significantly. The decrease in mass starts much earlier in aged samples than in pristine PEEK and depending on the definition of the starting point the difference can be up to 100 °C. The difference in the onset temperature is much smaller, only 10-20 °C as it can be seen in Table 4.

The differences between samples are larger when using synthetic air instead of nitrogen, since thermal degradation occurs faster in the presence of oxygen. Nitrogen purging inhibits the initiation of thermal degradation, even for photodegraded samples. The thermal properties of PEEK fibers are weakened significantly, which indicates a lower energetic barrier for the initiation of thermal degradation. The by-products formed in the photodegradation process are typically very labile radical and peroxide compounds, which lowers significantly the temperature barrier needed to start the thermal degradation process. One explanation of the weakened thermal properties is also found from the rheological tests that show significant changes in the molecular mass of the PEEK fibers.

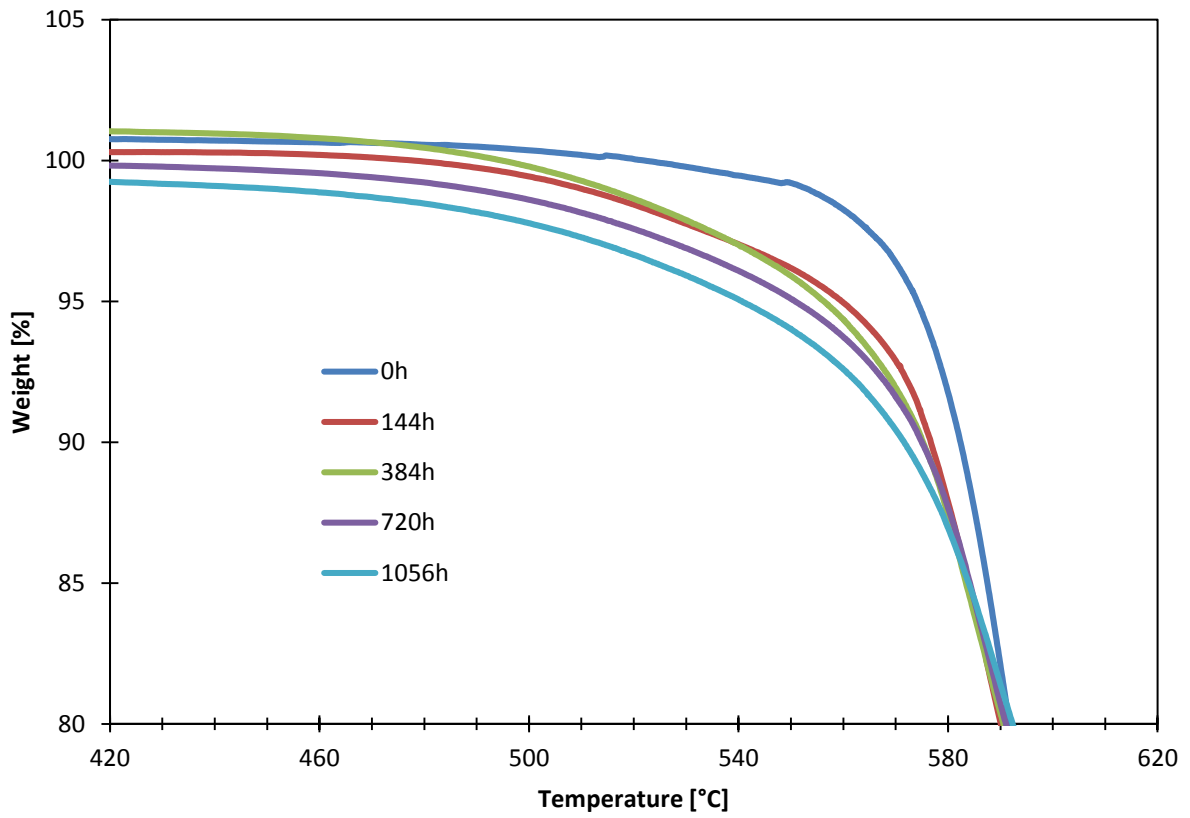


Fig. 11. TGA curve of UV irradiated PEEK fibers measured in air.

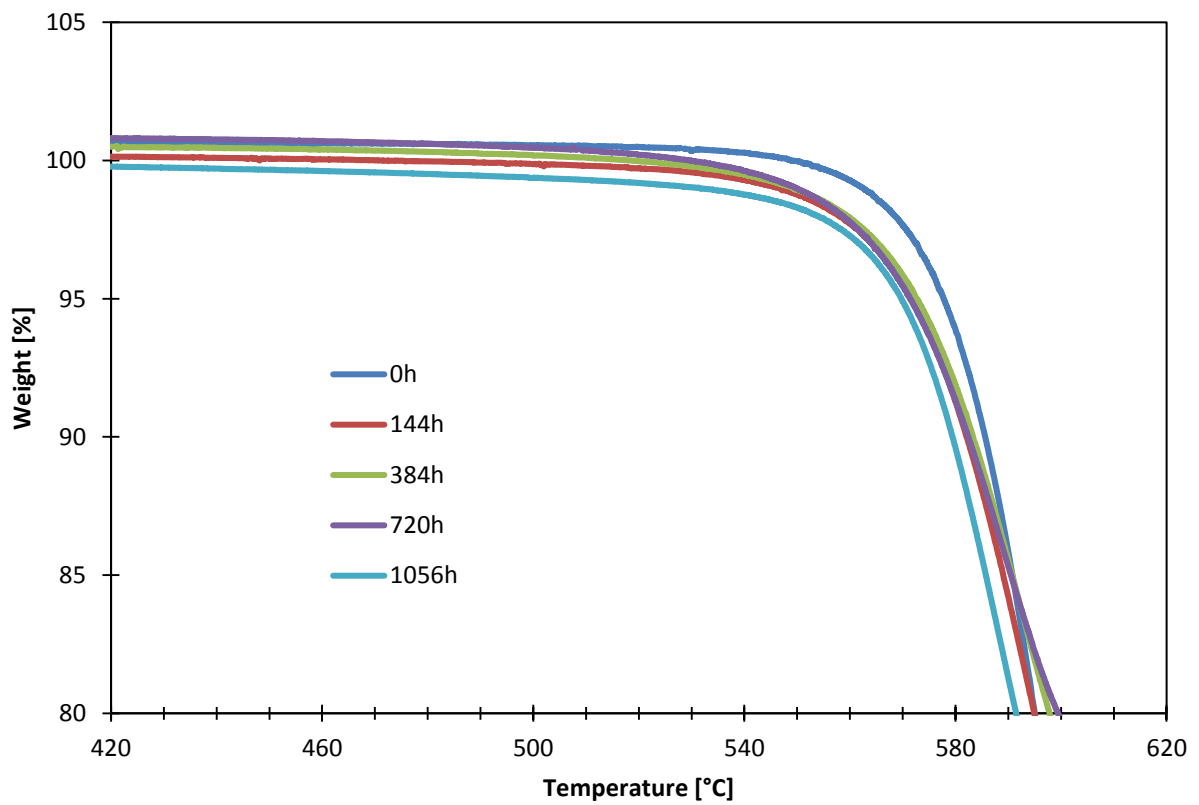


Fig. 12. TGA curve of UV irradiated PEEK fibers measured in nitrogen.

Table 4. Onset temperatures in TGA curves for UV irradiated PEEK fibers.

Irradiation time [h]	Onset temperature in air [°C]	Onset temperature in nitrogen [°C]
0	577	581
144	567	575
384	564	570
720	564	565
1056	564	569

3.6 SEM

In the longitudinal SEM photos there are no visible cracks even in the most irradiated 1056 h sample (Fig. 13 and Fig. 14) although there is a clear reduction in the mechanical properties. There are some particles and roughness on the surface of the fibers but these are most likely just impurities or scratches and not related to the UV irradiation. However, the changes are clearly visible in the transverse SEM photo of 1056 h irradiated sample compared to the pristine sample (Fig. 15 and Fig. 16). The cracks go to a depth of 20 μm which is significant in the case of fibers. Surprisingly the cracking is not visible in the longitudinal investigations.

Previous studies have shown that in the case of polypropylene (PP) it is possible to estimate the degradation level by using an optical or scanning electron microscope. Reconstruction of the amorphous content in the surface and increased crystallization shrinks the outer layer of the sample which leads to cracking [22, 23, 41]. The amount of cracking in PP is so significant that it is easily visible in the longitudinal investigations. The behaviour of the PEEK fibers is different because only transverse cracks were observed in the 1056 h irradiated sample. It is possible that longitudinal cracks would have emerged if the ageing would have been continued.

DSC tests indicate a stable crystallization degree of 36 % in all the samples which is very close to the theoretical maximum of 40 %. At least in the case of PP the high degree of crystallinity protects the fibres to some level from degradation and cracking [41]. PP studies have shown that changes in the mechanical properties can be observed before the changes in SEM photos because of micro cracks in the material [23]. Previous studies [7] and DSC and rheological tests have shown PEEK to harden by crosslinking, which can be confirmed from the transverse photos. Longitudinal investigations cannot be described as a very effective technique to estimate the degradation level of PEEK.

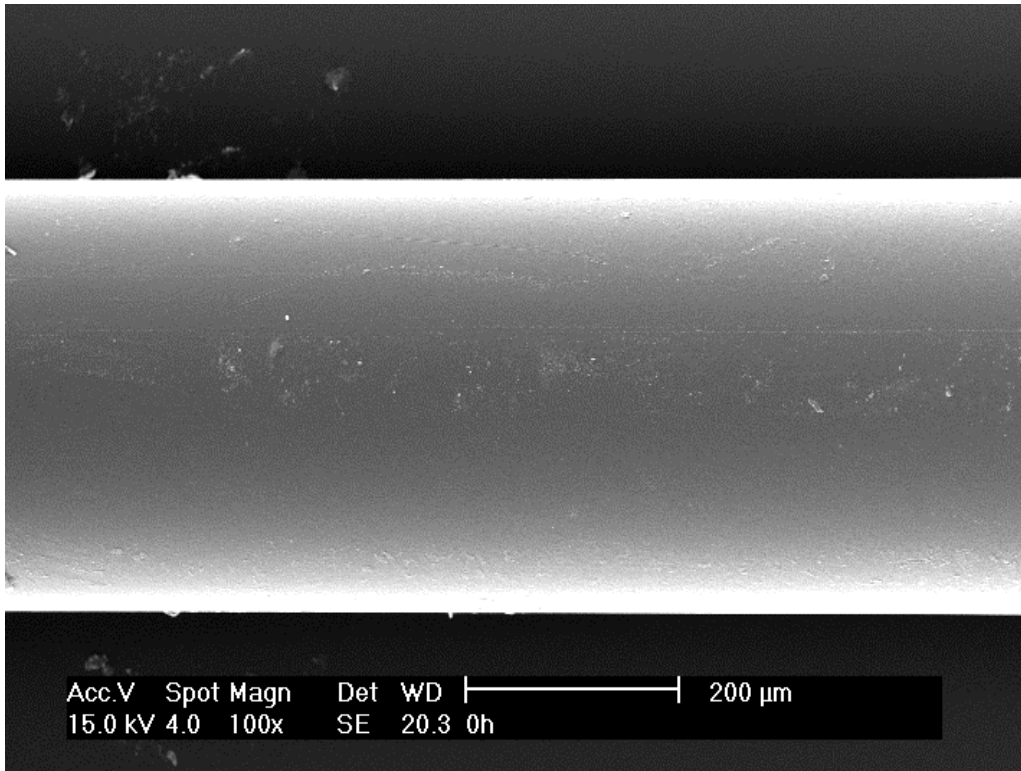


Fig. 13. Longitudinal SEM photo of pristine PEEK fiber.

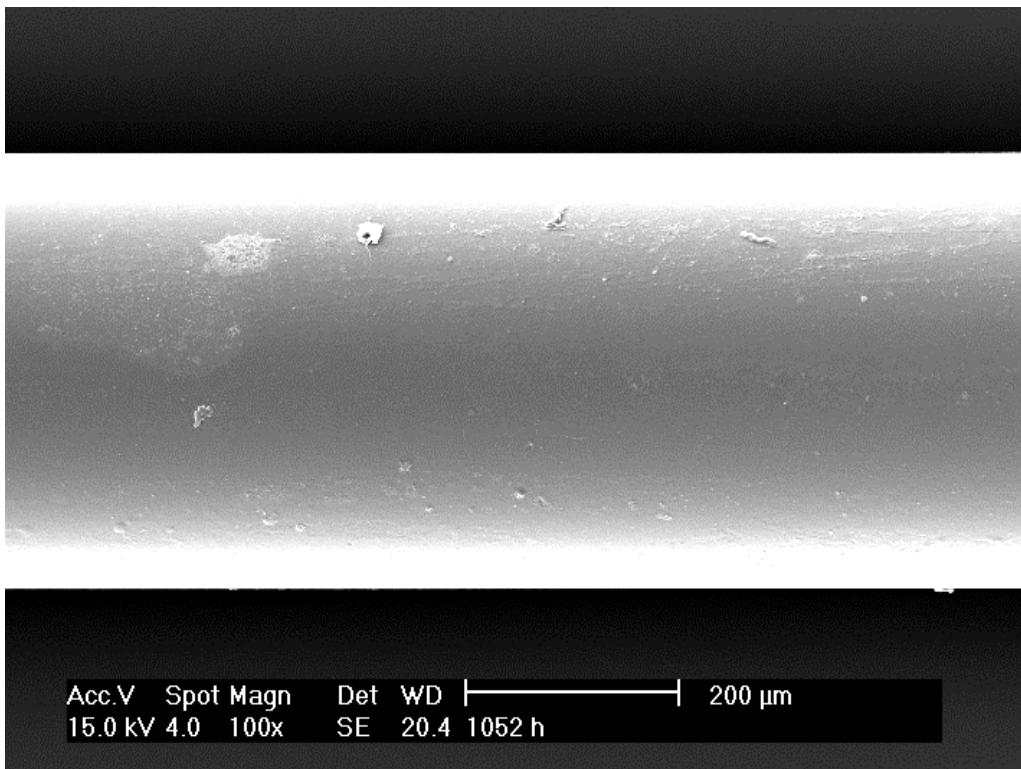


Fig. 14. Longitudinal SEM photo of 1056 h irradiated PEEK fiber.

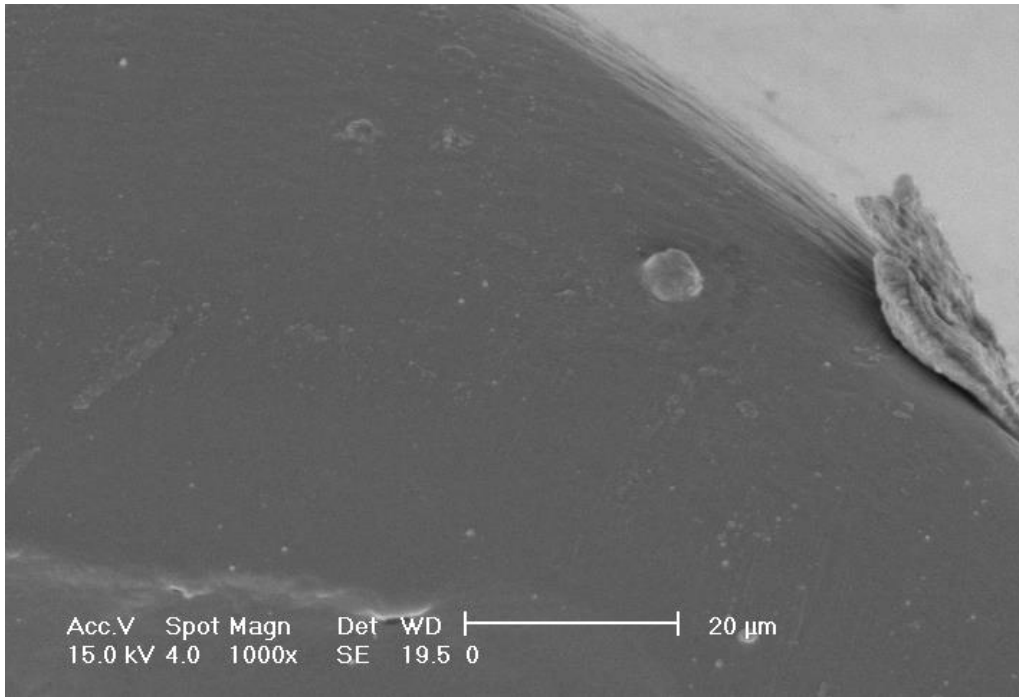


Fig. 15. Transverse SEM photo of pristine PEEK fiber.

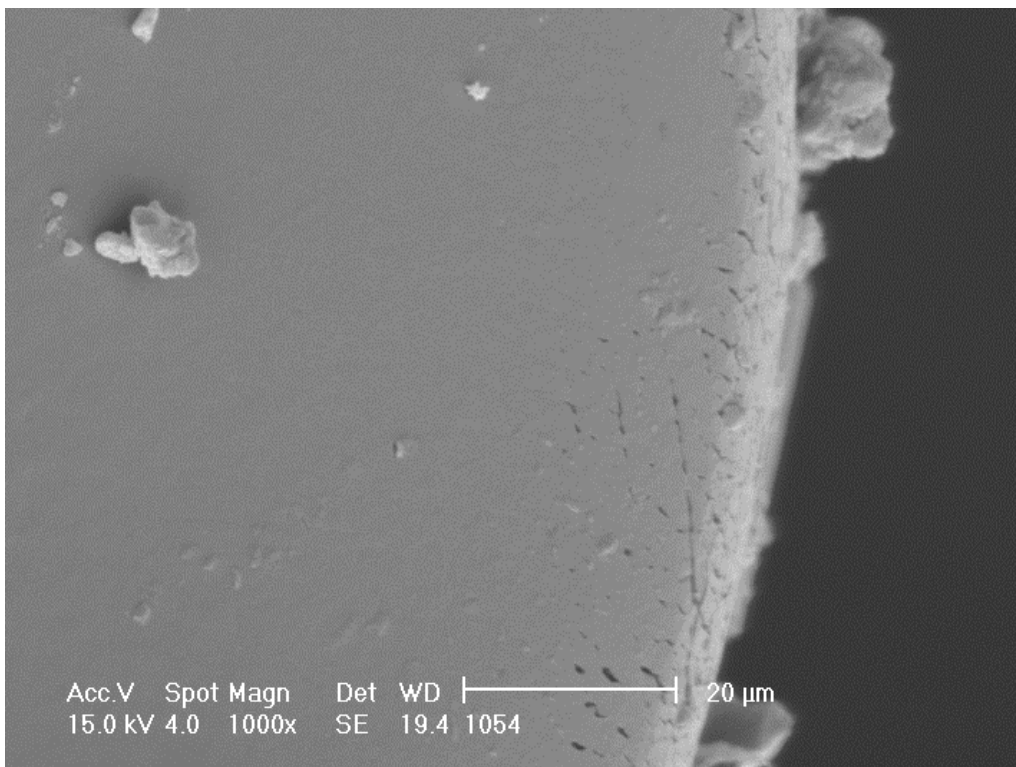


Fig. 16. Transverse SEM photo of 1056 h irradiated PEEK fiber.

4. Conclusion

According to these tests PEEK fibers should not be stored in direct sunlight and the limitations in outdoor use have to be considered carefully to avoid safety problems. A few weeks in direct sun light increases the crosslinking rate significantly making the fibers brittle. At the same time other mechanical as well as thermal properties are worsened which can be observed from the tensile tests, FTIR, TGA, SEM and rheological tests with some limitations. DSC cannot be considered a good technique to estimate the ageing of PEEK fibers. The carbonyl index measured by FTIR is the standard technique to show the first signs of photodegradation and it is suitable with PEEK fibers as well. To observe changes in deeper portions of the fibers TGA, rheological or tensile tests can be used.

Acknowledgements

The authors would like to acknowledge the financial support received from the Academy of Finland for the UVIADDEM project.

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