

Characterization of thermally aged polyetheretherketone fibres - mechanical, thermal, rheological and chemical property changes

Ville Mylläri^a, Tero-Petri Ruoko^b, Jyrki Vuorinen^a, Helge Lemmetyinen^b

^aDepartment of Material Science, Tampere University of Technology, Tampere 33101, Finland

^bDepartment of Chemistry and Bioengineering, Tampere University of Technology, Tampere 33101, Finland

Corresponding author: Ville Mylläri, E-mail address: ville.myllari@tut.fi, phone number: +358401981683

Keywords: PEEK, fibre, thermal degradation

Abstract

This paper investigates the effects of thermal degradation on polyetheretherketone (PEEK) fibres. PEEK samples were aged at a constant temperature of 250 °C for 1–128 days and characterized with mechanical tests, FTIR (Fourier Transform Infrared Spectroscopy), DSC (Differential Scanning Calorimetry), rheology, TGA (Thermogravimetric Analysis), SEM (Scanning Electron Microscopy), and UV-Vis diffuse reflectance spectroscopy. The short-term thermal annealing had a positive effect on the mechanical properties, due to the formation and growth of secondary crystals. Crosslinking in the material was verified by rheological inspections. The crosslinking increased the mechanical strength and modulus but reduced the elongation at break of the fibres. FTIR tests showed that carbonyl and hydroxyl groups were slowly formed on the surface of the fibres while ring opening reactions took place. The thermal ageing reduced the thermal stability of PEEK. The decreased stability was observed in the decomposition onset temperature after 8 d and in the melting point and the glass transition temperature after 32 d. The first signs of degradation, crosslinking, embrittlement, and reduced thermal stability, were visible roughly after 8 d of ageing, whereas the deterioration in general usability occurred after 64 d.

1. Introduction

Polyetheretherketone (PEEK) is a linear, semicrystalline thermoplastic polymer and is probably best known for its outstanding thermal properties. A continued use temperature of 250–260 °C combined with excellent mechanical properties and chemical resistance make it an excellent candidate for replacing metals in demanding

applications. A melt spinning of PEEK has been conducted from the 1980's, and the spinnability of the fibres is typically excellent [1]. The applications of the fibres are similar to those of bulk PEEK, extreme environmental conditions where conventional thermoplastic are inadequate. The PEEK fibres are currently used in process conveyor belts, filters, protective braids, reinforced rubber gaskets, industrial bristles, protective clothing, sports strings, music strings, and thermoplastic composites [2]. The chemical structure of PEEK is presented in Fig.1, where a PEEK monomer is composed of three phenyl rings, linked to each other with either a carbonyl or ether group.

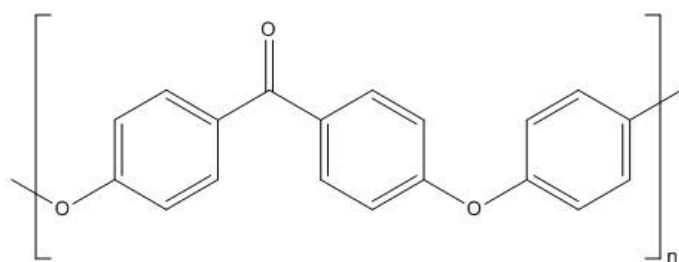


Fig. 1. The chemical structure of PEEK.

The high temperature behaviour of PEEK under both short- and long-term exposures, as well as the decomposition products formed have been well characterized with different approaches and methods, including FTIR (Fourier Transform Infrared Spectroscopy) [3, 4], TGA (Thermogravimetric Analysis) [5-7], mass spectroscopy [8, 9], UV-Vis [10], and NMR (Nuclear Magnetic Resonance) [10] spectroscopies, DSC (Differential Scanning Calorimetry) [11–13], WAXS (Wide Angle X-ray Scattering) [11], and mechanical tests [12–15]. However, most of the studies have concentrated only on one or two methods making the comparison between the results difficult. To the best of the authors' knowledge, any systematic studies regarding the thermal degradation of the PEEK fibres have not yet published. Fibres have typically high degree of orientation and crystallinity, and small diameter, which can cause differences in results compared to other sample forms.

Initially, the thermal ageing of PEEK has many advantages. Annealing PEEK between the glass transition (T_g) and melting temperature (T_m) for various time periods has been studied since the 1980's. According to the manufacturer recommendations, a typical annealing time is 40 h at 250 °C [13]. The annealing increases the crystallinity [13] and changes the crystal morphology [12, 16, 17]. According to the TEM (Transmission Electron Microscope) micrographs, PEEK has two populations of crystals [18]. The annealing grows these secondary crystals, which can be observed in the DSC scans as a minor secondary peak at a temperature a little bit higher than the annealing temperature [12].

The goal of this article is to study the effects of the maximum use temperature (250 °C) on PEEK fibres using numerous complementary characterization methods. By using a long timescale, the onset of different phenomena, whether positive or negative or occurring on a microscopic or macroscopic scale, should be observed during the tests. In addition, the results are compared with our previous research on the photodegradation of PEEK fibres [19]. This research offers valuable information for the applications of PEEK fibres in different environments.

2. Experimental

2.1 Samples and ageing

Samples were made of Victrex (Lancashire, UK) PEEK grade 151G, a semicrystalline, easy flow grade PEEK with no inherent UV stabilizers. PEEK fibres were manufactured by a melt spinning process using a Göttfert Rheograph 6000. The processing temperature was 380 °C, capillary dimensions 30/1 mm and piston speed 0.5 mm/s. Fibres were drawn by gravity since the use of a spinning motor would have led to unnecessarily small fibre diameters. The draw ratio ($v_{\text{capillary}}/v_{\text{final}}$) of the fibres was 5.9, resulting in a very homogenous final diameter of $410 \pm 10 \mu\text{m}$.

2.2 Ageing

The samples were aged using a modified Ahma GO600 oven. The original temperature controller was replaced with an Omron E5CN control unit and a PT100 platinum resistance thermocouple. The annealing conditions were kept stable at a temperature of $250 \pm 0.1 \text{ °C}$ during the artificial ageing process. The samples were attached to a horizontal grill attached on the same level as the thermocouple. The aged fibres were cut from the grill so that the fibres in close contact with metal were discarded because the high thermal conductivity of the grill results in accelerated ageing.

2.3 Measurements

DSC thermograms were recorded with a Netzsch DSC 204 F1 heat-flux DSC. All measurements were performed under a nitrogen atmosphere. During the DSC tests, materials were heated from room temperature to 400 °C, cooled to room temperature, and heated once more. The heating rate was 20 °C/min. Two samples from each fibre were measured.

FTIR spectra of the fibres were measured with a Bruker optics tensor 27 using ATR (attenuated total reflectance) mode in the wavenumber range 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and averaging 32 scans. Measurements were performed using three parallel fibres and results were an average of three measurements. A baseline correction was performed using the average absorbance between 3800–4000 cm^{-1} as a reference. The carbonyl index was calculated as the ratio of the aged and unaged peak intensities at 1740 cm^{-1} , corresponding to a carbonyl vibration in ester groups produced by the oxidation of carbonyl groups [3].

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

TGA thermograms were recorded with a PerkinElmer TGA 6. The samples were heated from room temperature to 995 °C in synthetic air (20 % O_2 / 80 % N_2) with a heating rate of 10 °C/min. The onset temperature was defined as the intersection point of the extrapolated baseline and the tangent of the inflection point.

The tensile properties of the fibres were tested with an Instron 5967 according to the ISO 5079:1995 standard. The initial length was 50 mm with a crosshead speed of 20 mm/min. Instead of the recommended 50 measurements, only 15 samples per annealing time were measured due to the long total duration of the mechanical tests. The modulus was calculated using linear regression techniques according to the EN10002 and ASTM E8 standards. A 2 kN force shell was used in the measurements.

The morphology of the PEEK fibres was investigated with a Philips XL30 scanning electron microscope (SEM). The fibres were broken in liquid nitrogen for transverse imaging.

UV-Vis diffuse reflectance spectra were measured with a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and ISR-3100 integrating sphere. All spectra were recorded in the wavelength range 350–750 nm.

3. Results and discussion

3.1 DCS tests

The annealing induces a secondary endotherm slightly above the maximum use temperature of PEEK, as observed also in previous studies [12, 13, 16]. After 1 d of ageing this peak is at 275 °C, shifting to higher temperature during the ageing so that it merges with the primary melting peak for the 128 d aged samples (Fig.

2). Melting of PEEK removes this secondary endotherm and it is not visible during the second DSC scan due to the thermal history of the sample being wiped in the first scan (Fig. 3). The disappearance of the secondary peak reduces the melting endotherm area of the 128 d aged sample to almost half compared to the first scan.

The melting point of PEEK remains at 345 °C for the first 32 d of ageing (Fig. 4). A sudden drop in T_m is noticeable with the additional ageing. By 128 d of ageing the T_m is 15 °C lower, a sign of significant degradation in the bulk of the fibres.

The glass transition temperature of the PEEK fibres increased with the ageing (Fig. 5). According to the previous literature, this change is caused by significant crosslinking induced decrease in the molecular mobility [20, 21]. The latter study claims that if both the T_g and Young's modulus are increased simultaneously, this can only be justified by the material crosslinking. T_{g2} (glass transition during the second heating run) starts to increase after 16 d of ageing. Even 1 d of ageing increases T_{g1} (glass transition during the first heating run) from 148 °C to 164 °C presumably due to the formation of secondary crystals, leading to chemical and mechanical changes in the amorphous portions of the fibres and crosslinking induced tensions inside the fibres.

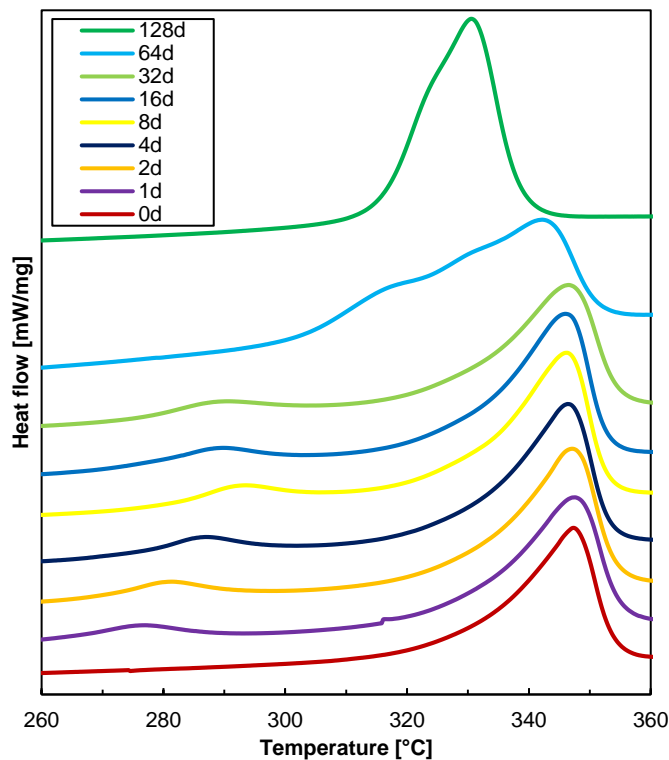


Fig. 2. DSC traces of thermally aged PEEK fibres, first heating.

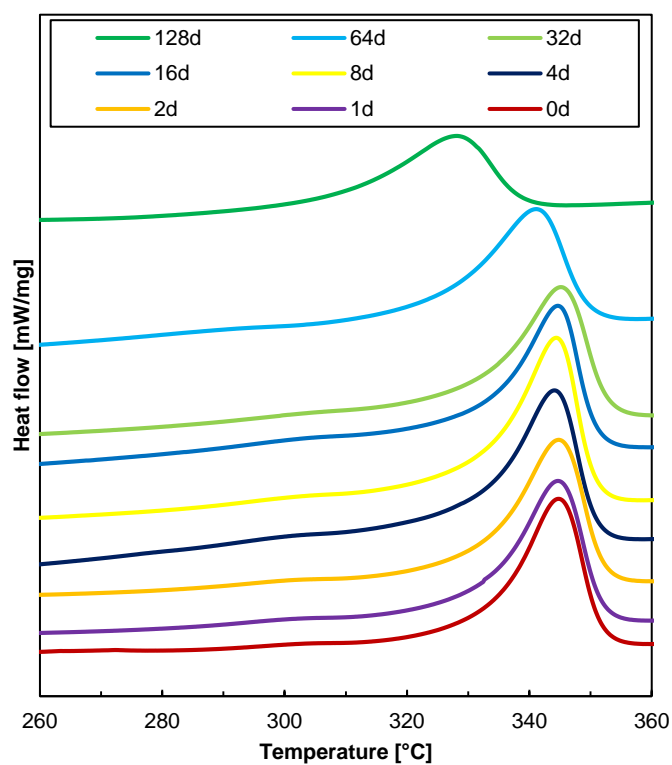


Fig. 3. DSC traces of thermally aged PEEK fibres, second heating.

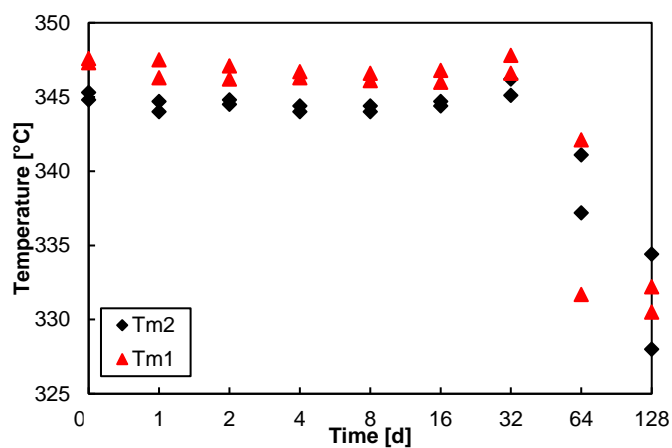


Fig. 4. Melting temperature of thermally aged PEEK fibres. T_{m1} during the first heating and T_{m2} during the second.

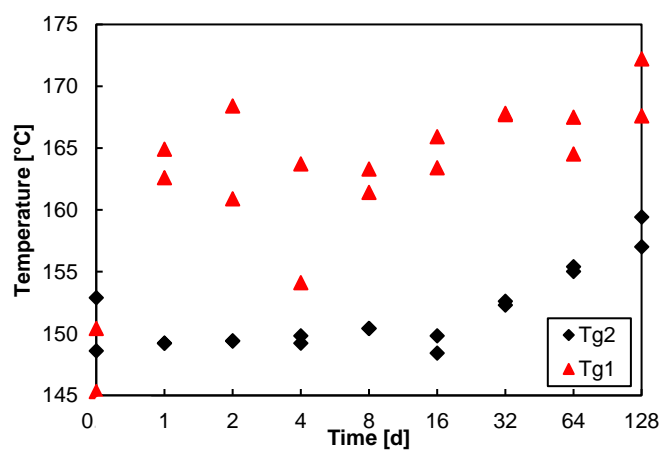


Fig. 5. Glass transition temperature of thermally aged PEEK fibres. T_{g1} during the first heating, T_{g2} during the second heating.

3.2 FTIR

The most common changes in the FTIR spectrum during the polymer degradation is the formation of an absorption band specific to the carbonyl absorption. The carbonyl group (C=O) absorbs the IR radiation in the wavenumber region of 1540–1870 cm^{-1} , with the exact wavenumber depending on the chemical structure of the polymer chain (Fig. 6). Another typical change during the ageing of PEEK is the formation of a broad hydroxyl group (–OH) absorption at 2800–3700 cm^{-1} with a maximum at $\sim 3260 \text{ cm}^{-1}$ (Fig. 7).

The rise in the carbonyl index is steady, but moderate compared to the photodegradation (Fig. 8). The carbonyl peak intensity maximum is located at 1740 cm^{-1} which is different from the photodegradation study where the intensity maximum was at 1716 cm^{-1} . This is an interesting result because it indicates that the ageing goes through a different degradation route between the thermal- and photodegradation and illustrates the fact that the photodegradation of aromatic polymers rarely occurs by the well-known hydroperoxide mechanism that is typical for aliphatic polymers and general thermal degradation. [22, 23]

The good thermal stability of PEEK, and many other polymers, is connected to aromatic groups in the molecular structure. The repeating unit of PEEK includes three phenyl rings. According to the FTIR tests (Fig. 9), the relative number of the phenyl rings decreases and the number of aliphatic groups increases during ageing, which indicate that ring opening reactions occur during ageing. This is one probable reason for the decreased thermal stability at longer degradation times, which is observed as a reduction in the melting point with DSC.

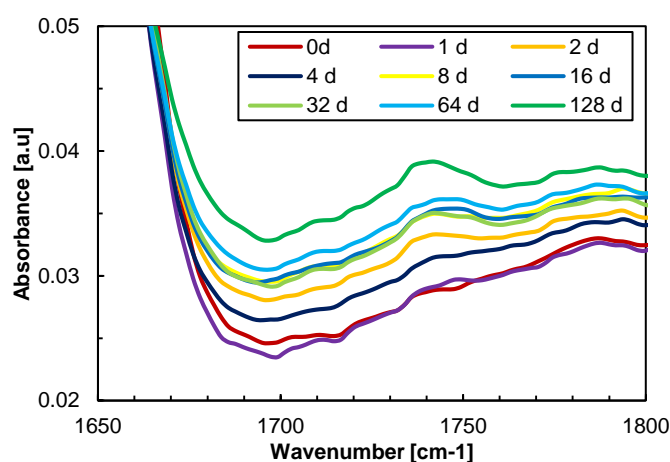


Fig.6. FTIR spectra of thermally aged PEEK fibres in the carbonyl region.

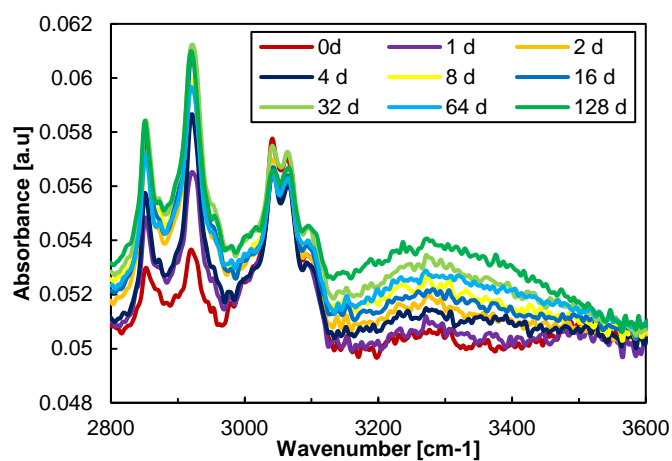


Fig. 7. FTIR spectra of thermally aged PEEK fibres in the hydroxyl region.

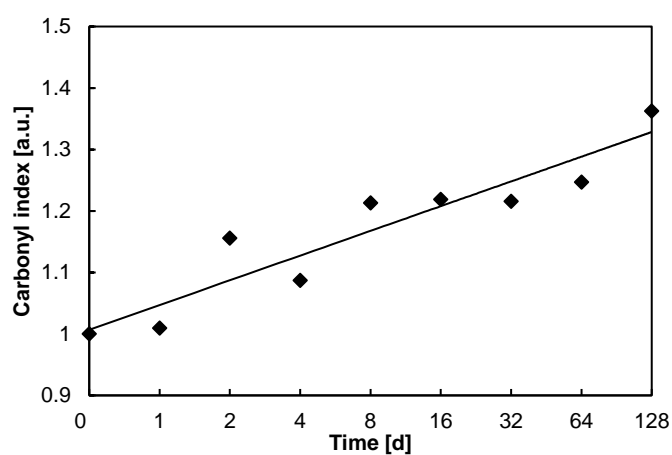


Fig. 8. Carbonyl index [$1740\text{ cm}^{-1}/1740\text{cm}^{-1}$ ($t = 0$)] of PEEK fibres aged at $250\text{ }^{\circ}\text{C}$

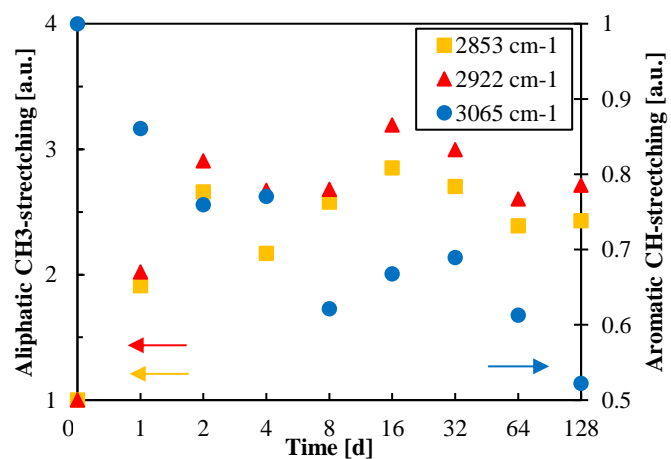


Fig. 9. Methylene CH_3 - and aromatic CH -stretching vibrations of thermally aged PEEK fibres as a function of ageing time.

3.3 Rheology

Rheology is not a commonly used tool for studying the ageing of polymer fibres. The challenge is obtaining a sufficient volume of fibres, up to several kilometres of length which are needed in the case of ultrafine fibres when using a typical rheometer. On the other hand, rheology is a powerful tool in estimating changes occurring in the whole fibre, not just at the surface. When studying materials degradation, rheology can be utilized to estimate which of the two competitive reactions is dominant, the chain scission or the crosslinking. Due to PEEK's aromatic structure, it has a tendency to crosslink when aged with the UV light [20], which can be observed as increased zero shear viscosity and shear thinning [19].

With regard to rheology, the thermal ageing (Fig. 10) causes somewhat similar effects as the photodegradation [19]. The zero shear (or 0.1 1/s in this case) viscosity increases slowly in the early phases of ageing and very rapidly after 16 d. Even 1 d of the thermal ageing causes a significant reduction in the viscosity at the high angular frequencies. This behaviour is different from the photodegradation, where more changes occurred at low angular frequencies. The 32 d aged sample was the last that could be measured. The 64 and 128 d aged samples had very interesting properties, since they did not melt during the tests (Fig. 11). Evidently, at that point the material is highly crosslinked, behaving more like a thermoset than a thermoplastic.

Relative molecular weights were estimated using the experimental Cole-Cole model [24, 25]. In theory, the curves should form a circular arc where the x-axis crossing point is the zero shear viscosity. The curves were extrapolated using 2nd degree polynomial fitting, and the relative molecular weights were calculated with equation 1 [26]

$$\eta_0 \propto M_w^{3.4} \quad (1)$$

where η_0 is the zero shear viscosity and M_w the average molecular weight. The results shown in Fig. 12 indicate that a slow increase in M_w happens until 16 d, after which the crosslinking rate increases, thus significantly increasing the average molecular weight. T_m and T_{g2} , measured with DSC, start to change roughly at the same time (32 d) as the increased crosslinking is observed with the rheology. This is an expected correlation, since a high amount of crosslinking leads to changes in the relative amounts of crystalline and amorphous material, directly observed as changes in the melting point and the glass transition temperature with DSC.

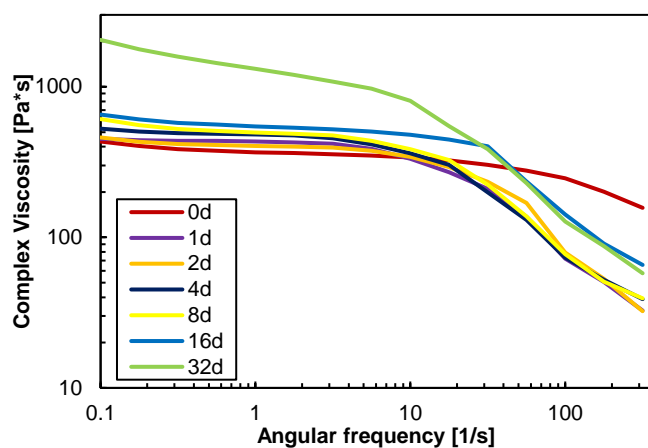


Fig. 10. Complex viscosity curves of PEEK fibres aged at 250 °C.



Fig. 11. 128 d aged PEEK fibres after rotational rheometer measurement. The fibres were heated 15 min at 450 °C using 50 N compression without changes in the fibre form. The photo was taken while heating was still on.

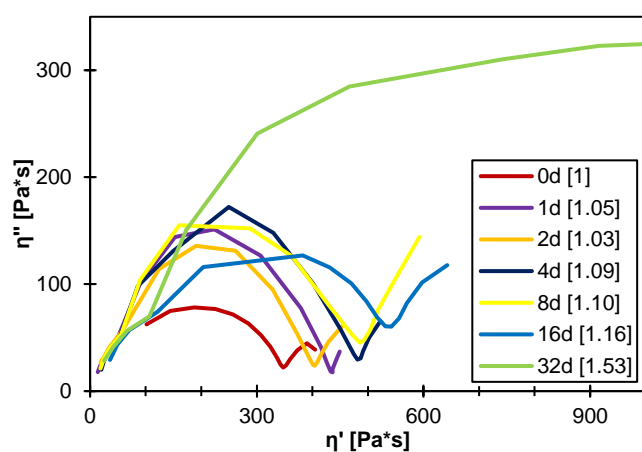


Fig. 12. Cole-Cole plot of PEEK fibres aged at 250 °C. Calculated relative molecular weights are within the brackets.

3.4 TGA

TGA tests (Fig. 13) show that thermal ageing reduces the thermal stability of PEEK, a result observed in the DSC tests as well. The first significant changes are observed after 8 d of ageing. Even though the difference in degradation onset temperature (Fig. 14) is only 13 °C between the virgin sample and the 128 d aged sample, the curvatures of the mass loss curves are drastically different. With the increased ageing the mass loss begins at noticeably lower temperatures. Thermal degradation causes similar effects in TGA as photodegradation [19].

Even though the 64 d and 128 d aged samples did not melt during the rheological investigations, they have the worst thermal stability according to TGA. The confirmed crosslinking of the material during the ageing evidently reduces the gap between the material melting point and the decomposition temperature. In the case of virgin PEEK the gap is over 200 °C but it decreases to almost zero, like in the case of the thermosets. The loss of aromaticity that is observed with FTIR also supports this decrease in thermal stability, since phenyl rings are much more stable than aliphatic chains in the polymers. Both TGA and rheology give information on the whole samples volume, not only surface, and their ability to detect degradation in the bulk of the PEEK fibres is fairly similar. On the other hand, FTIR method is surface sensitive, thus observing the changes in aromaticity long before the lowered bulk thermal stability becomes visible.

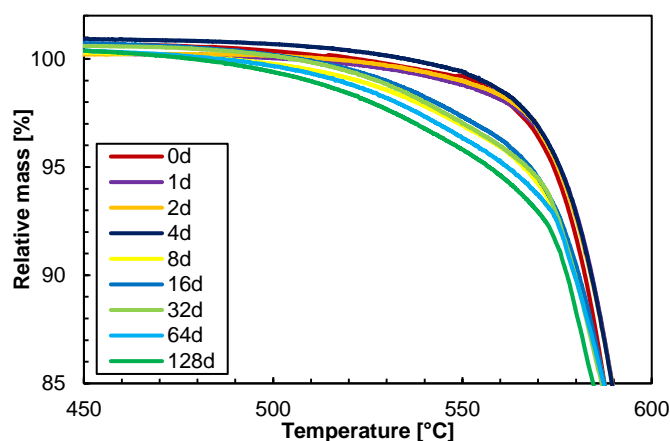


Fig. 13. TGA of PEEK fibres aged at 250 °C.

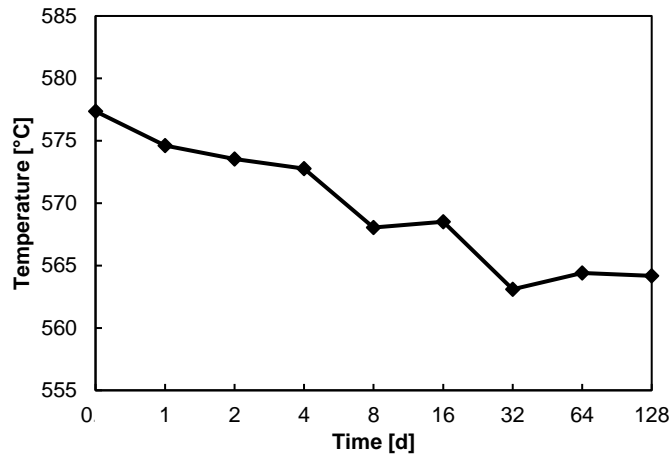


Fig. 14. Oxidation onset temperature of PEEK fibres measured in air.

3.5 Tensile properties

The tensile properties changed significantly during the first day of ageing; the tensile strength (Fig. 15) increased from 92 to 105 MPa and the modulus (Fig. 16) from 2.6 to 2.9 GPa. The properties were unchanged within standard errors until 64 d of ageing. The maximum values were reached after 128 d; a tensile strength of 123 MPa and a modulus of 3.0 GPa. PEEK typically turns brittle during the ageing. The elongation (Fig. 17) was reduced step by step from 315 % to 8 %. An untypical testing procedure, where the elongation was the maximum value of 15 measurements, was chosen because of equipment limitations. A stress concentration was generated near the jaws which often caused the fibre to break at the yield point. The modified method turned out to be suitable in this case. It provided a good way to estimate the elongation and reduced the amount of measurements needed compared to the conventional method. Typical tensile testing curves can be found in Fig. 18.

The effect of the annealing on the mechanical properties of PEEK has been intensively studied. According to literature, the annealing improves both short- and long-term mechanical properties of PEEK. [12,15,18] This was clearly visible in our short-term tensile tests as well. Crosslinking of the material, confirmed in section 3.3, is another explanation for the improved mechanical properties and reduced elongation [14,20]. On the other hand, the crosslinking is not desirable in the case of fibres because they become very brittle, thus reducing usability.

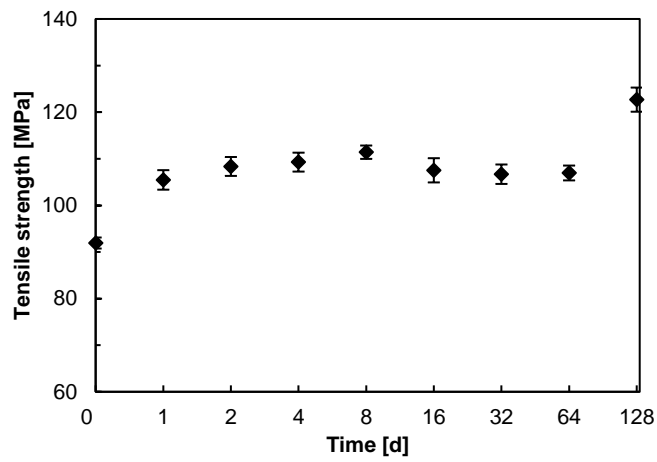


Fig. 15. Tensile strength of PEEK fibres aged at 250 °C.

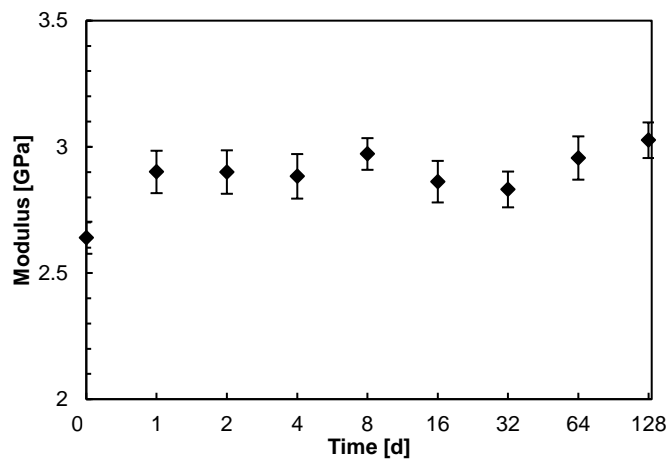


Fig. 16. Modulus of PEEK fibres aged at 250 °C.

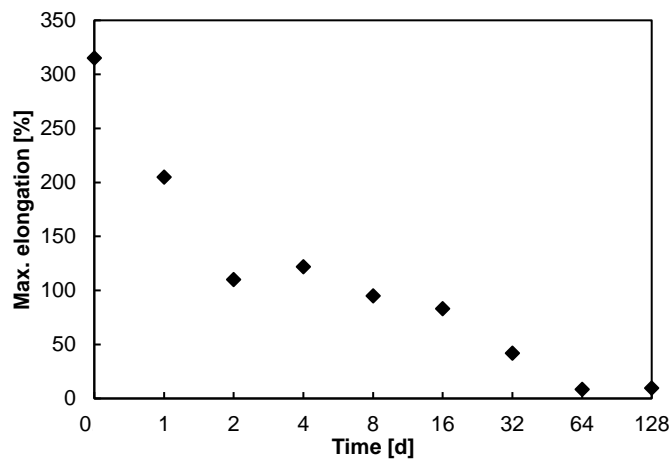


Fig. 17. Maximum elongation of PEEK fibres aged at 250 °C.

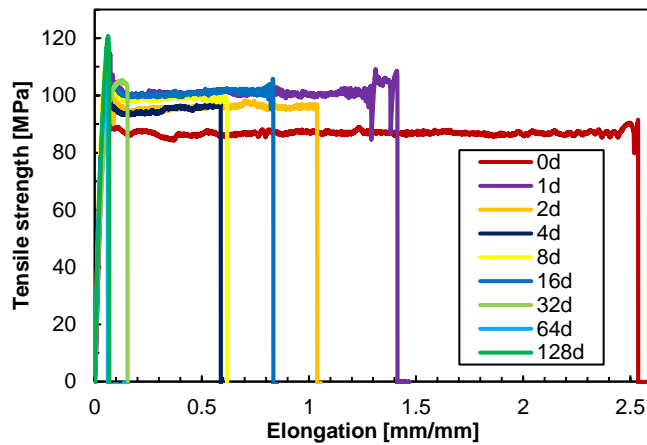
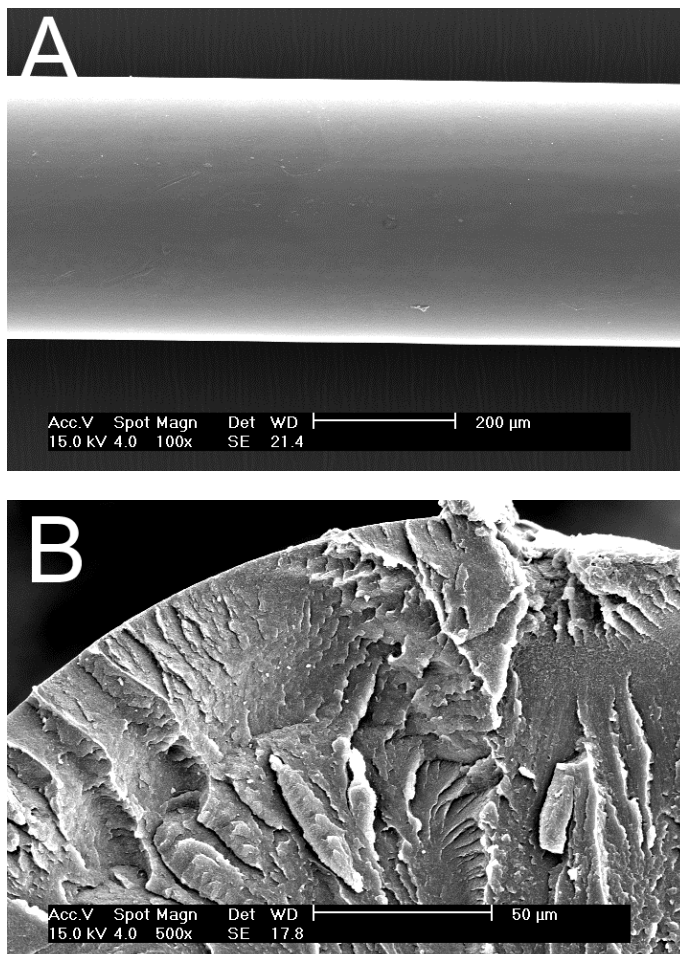


Fig. 18. Typical tensile testing curves.

3.6 SEM

There are no observable changes in the SEM micrographs during the ageing (Fig. 19). The photodegradation has been shown to cause solidification and shrinkage of the outer layer of the fibre causing observable cracking, but this was not evident with the thermal degradation. This is logical considering that the thermal degradation affects the whole sample, whereas the photodegradation mostly the sample surface.



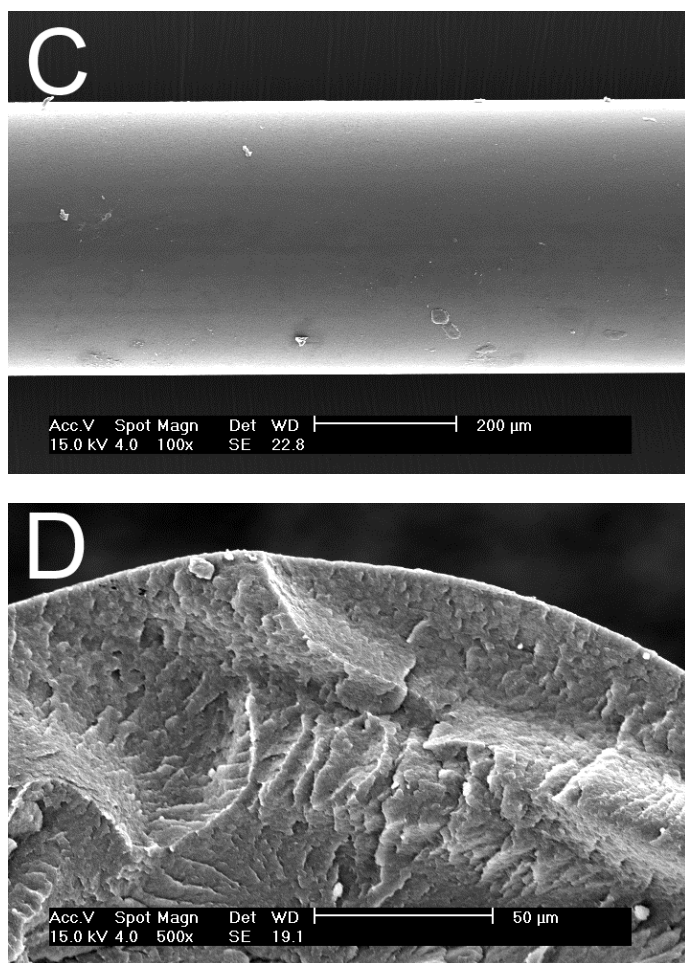


Fig 19. Longitudinal SEM photo of pristine PEEK fibre (A), transverse SEM photo of pristine PEEK fibre (B), longitudinal SEM photo of 128 d aged PEEK fibre (C), and transverse SEM photo of 128 d aged PEEK fibre (D).

3.7 UV-Vis

The originally yellowish PEEK fibres turned brownish red with the increased ageing. The diffuse reflectance spectra of the samples (Fig. 20) show how pristine PEEK fibres mainly absorb the UV radiation below 410 nm, which explains the yellow color. With the increased ageing, the onset of the absorption gradually moves to higher wavelengths with an absorption band forming in the visible region between 400–750 nm. The 128 d aged fibres have an absorption onset of 550 nm, corresponding to a brownish red color. The color changes are presumably due to surface oxidation of the material, similar to what is observed during the burning of polymers.

Since the PEEK fibres are completely opaque, the absorption of the samples can be presented as $A = 1 - R$, where A is absorbance and R is reflectance. The relative changes in absorption at 500 nm (Fig. 21) show a clear logarithmic increase in the absorption of the PEEK fibres with increased annealing time, as illustrated by the logarithmic trend line ($R^2 = 0.94$). The colour changes are mainly due to the formation of conjugation of the PEEK chains and the formation of small molecular degradation products.

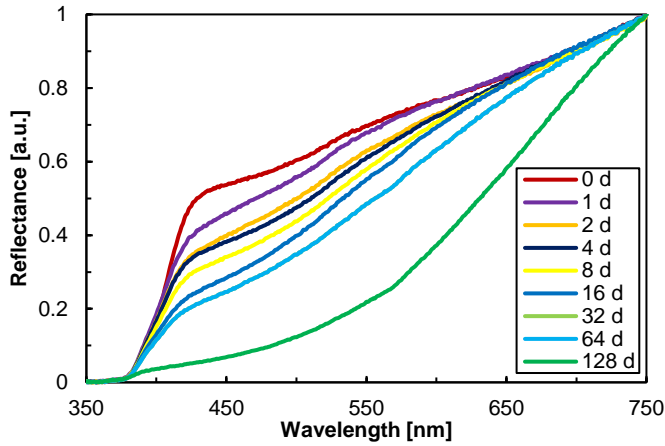


Fig. 20. UV-Vis diffuse reflectance spectra of PEEK fibres aged at 250 °C.

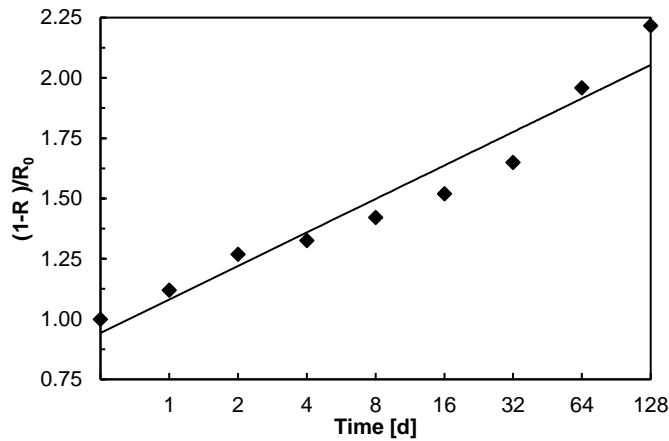


Fig. 21. Relative change in the absorbance of the PEEK fibres at 500 nm.

4. Conclusion

The PEEK fibres were aged 1–128 d at 250 °C. The ageing process can be divided into four steps. The first step is the formation of secondary crystals in the first phases of ageing. The effects of the initial annealing are mostly positive: the mechanical strength and modulus increase without changes in the thermal properties or rheology. The second step occurs roughly between 8–16 d when the first signs of degradation become visible mainly with the surface sensitive methods, but the usability of the fibres remains good. The crosslinking is observed with the rheology, elongation of the material decreases, TGA demonstrates changes in the thermal decomposition behaviour, FTIR indicates the opening of phenyl rings, and the colour of the material is turning darker. The third step, the reduced usability, depends strongly on the intended application, but is located roughly between 32–64 d of the ageing. The material has become highly crosslinked and brittle. The decrease in the melting point can be measured with DSC and the colour of the fibres has turned brown. The fourth step would

have been the degradation beyond the point of usability. However, this would have required a longer degradation time than 128 d.

The changes were only partly similar to those caused by the photodegradation [19]. Both ageing methods caused the material to crosslink, increasing the zero-shear-viscosity and shear thinning, and making the most aged samples brittle. The ageing increased the mechanical strength, more so during the thermal tests because of the positive effects of the annealing. The photodegradation increased both T_{g1} and T_{g2} but did not affect T_m . On the other hand, thermal ageing increased significantly T_{g1} due to the formation of secondary crystals, whereas there were no observable changes in T_{g2} and T_m before 32 d of the ageing. The carbonyl index rose rapidly due to the photodegradation compared to the thermal ageing, and the main peak was located at a slightly different wavenumber, indicating that a different carbonyl group containing degradation product was dominant. According to the FTIR tests, both ageing types caused ring breaking reactions in the polymer chain. TGA revealed reduced thermal stability, however, it was inaccurate for quantitative analysis. SEM was not considered a good method for studying the thermal degradation, since no changes were observable. Combining both the studies, the carbonyl index is the most accurate method to study the degree of degradation on the PEEK fibres. It can even separate the degradation source because the intensity maximum is located at a different wavenumber in the thermal- and photodegradations. If no equipment is available, colour changes or elongation at break can be used as easy alternatives.

Acknowledgements

The research was partly funded by the Academy of Finland UVIADDEM project (Grant no 253655). The authors would like to thank Sinikka Pohjonen and Maija Järventausta for performing the TGA, DSC, and SEM measurements.

References

- [1] Golzar M. Melt spinning of fine PEEK filaments. Dissertation. Technischen Universität Dresden; 2004.
- [2] Hearle J, editor. High performance fibres. Boca Raton: Woodhead Publishing; 2001. p. 344.
- [3] Cole K, Casella I. Fourier transform infra-red spectroscopic study of thermal degradation in poly(ether ether ketone)-carbon composites. Polym 1993;34:740–5.

- [4] Cole KC, Casella IG. Fourier transform infrared spectroscopic study of thermal degradation in films of poly(ether ether ketone). *Thermochim Acta* 1992;211:209–28.
- [5] Yao F, Zheng J, Qi M, Wang W, Qi Z. The thermal decomposition kinetics of poly(ether-ether-ketone) (PEEK) and its carbon fiber composite. *Thermochim Acta* 1991;183:91–97.
- [6] Nandan B, Kandpal LD, Mathur GN. Poly(ether ether ketone)/poly(aryl ether sulphone) blends: thermal degradation behaviour. *Europ Polym J* 2003;39:193–8.
- [7] Huo R-Z, Luo Y-F, Hang L-K, Jin X-G, Karasz FE. Kinetic studies on thermal degradation of poly(aryl ether ether ketone) and sulphonated poly(aryl ether ether ketone) by thermogravimetry. *J Funct Polym* 1990;4:426–33.
- [8] Perng LH, Tsai CJ, Ling YC. Mechanism and kinetic modelling of PEEK pyrolysis by TG/MS. *Polym* 1999;49:7321–9.
- [9] Tsai CJ, Perng LH, Ling YC. A study of thermal degradation of poly(aryl-ether-ether-ketone) using stepwise pyrolysis/gas chromatography/mass spectrometry. *Rapid Commun Mass Spectrom* 1997;11:1987–95.
- [10] Day M, Sally D, Wiles DM. Thermal degradation of poly(aryl-ether-ether-ketone): experimental evaluation of crosslinking reactions. *J Appl Polymer Sci* 1990;40:1615–20.
- [11] Buggy M, Carew A. The effect of thermal ageing on carbon fibre reinforced polyetheretherketone (PEEK). Part II Morphological changes. *J Mater Sci* 1994;29:2255–9.
- [12] Jar P-Y, Kausch HH, Cantwell WJ, Davies P, Richard H. The effect of annealing on the short and long term behavior of PEEK. *Polym Bull* 1990;24:657–64.
- [13] Berer M, Major Z, Pinter G, Constantinescu DM, Marsavina L. Investigation of the dynamic mechanical behaviour of polyetheretherketone (PEEK) in the high stress tensile regime. *Mech Time-Depend Mater* 2014;18:663–84.
- [14] Buggy M, Carew A. The effect of thermal ageing on carbon fibre reinforced polyetheretherketone (PEEK). Part I Static and dynamic flexural properties. *J Mater Sci* 1994;29:1925–9.
- [15] Jar P-Y, Kausch HH. Annealing effect on mechanical behavior of PEEK. *J Polym Sci B Polym Phys*. 1992;30:775-8.
- [16] Lee LH, Vanselow JJ, Schneider NS. Effects of mechanical drawing on the structure and properties of peek. *Polym Eng Sci* 1988;28:181–7.
- [17] Ostberg GMK, Seferis JC. Annealing effects on the crystallinity of polyetheretherketone (PEEK) and its carbon fiber composite. *J Appl Polym Sci* 1987;33:29–39.

- [18] Lattimer MP, Hobbs JK, Hill MJ, Barham PJ. On the origin of the multiple endotherms in PEEK. *Polym* 1992;33:3971–3.
- [19] Mylläri V, Ruoko T-P, Järvelä P. The effects of UV irradiation to polyetheretherketone fibres – characterization by different techniques. *Polym Degrad Stab* 2014;109:278–84.
- [20] Nakamura H, Nakamura T, Noguchi T, Imagawa K. Photodegradation of PEEK sheets under tensile stress. *Polym Degrad Stab* 2006;91:740–6.
- [21] Claude B, Gonon L, Duchet J, Verney V, Gardette JL. Surface cross-linking of polycarbonate under irradiation at long wavelengths. *Polym Degrad Stab* 2004;83:237–40.
- [22] Carlsson D, Wiles D. The photodegradation of polypropylene films. II. Photolysis of ketonic oxidation products. *Macromolecules* 1969;2:587–97.
- [23] Carlsson D, Wiles D. The photodegradation of polypropylene films. III. Photolysis of polypropylene hydroperoxides. *Macromolecules* 1969;2:597–606.
- [24] Dealy JM, Larson RG, editors. *Structure and Rheology of Molten Polymers*. Munich: Hanser Publishers; 2006. p. 530.
- [25] Commereuc S, Askanian H, Verney V, Celli A, Marchese P, Berti C. About the end life of novel aliphatic-aromatic (co)polyesters after UV-weathering: Structure/degradability relationships. *Polym Degrad Stab* 2013;98:1321–8.
- [26] Han CD. *Rheology and processing of polymeric materials: volume 1: polymer rheology*. New York: Oxford University Press; 2007. p. 736.