THERMO-OXIDATIVE DEGRADATION OF PEEK AT HIGH TEMPERATURES

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Abstract

In this study, the thermo-oxidative degradation of poly(ether ether ketone) (PEEK) during very short cycles, in the range of 30 up to 300 s, at temperatures higher than 400°C was investigated by differential scanning calorimetry (DSC). Apart from the surface degradation, thicker samples were also investigated via Fourier transform infrared (FTIR) spectroscopy and light transmission microscopy. In this case, longer cycles were applied in order to track the through-thickness degradation. It was observed that the boundary layer does not have a smooth transition but is clearly separated from the crystalline part of the polymer. In addition, it has been shown that the formation of the boundary layer is a diffusion-controlled process. As the processing temperature decreases, the maximum thickness of the edge layer increases. This is because the oxygen can further diffuse into the material before the crosslinked polymer at the edge of the material becomes impermeable to oxygen. In contrast, a high processing temperature results in a thinner, more concentrated edge layer that protects the underlying material.

1. Introduction

Semi-crystalline thermoplastic composites exhibit high toughness and temperature resistance that make them suitable for demanding applications [1, 2]. Among them, poly(ether ether ketone) (PEEK) is a reference material for the aeronautic industry and is mainly used in the form of semi-finished products. The quality of the composite parts is highly influenced by manufacturing conditions at every step in the production line – from PEEK compounding, semi-finished product manufacturing, composite processing, service and repair. Sufficient consolidation at fast production rates demand processing temperatures above melting point (343°C) at which PEEK can be damaged over time especially in the presence of oxygen. Therefore, an accurate process window needs to be determined.

Degradation mechanisms of long-time heated PEEK have been described in various studies [3-7]. A molecular deterioration results from overheating of the polymer. At elevated temperatures beyond melting point, components of the polymer chain backbone undergo random molecular scission and crosslinking [8]. These reactions cause changes at the molecular level and significant alteration of the optical, thermal, and mechanical properties. These changes appear to be accelerated in the presence of oxygen at elevated temperatures [9]. Various methods have been reported in the literature for the study of the degradation process above the melting point and for time cycles > 300 s. De Almeida et al. [10] used a plate-plate shear viscometer to rapidly heat neat PEEK samples to an isothermal temperature condition and measured the viscosity over time. The results show that in a first stage, PEEK viscosity

remains constant and a classical thermal dependence is observed. But degradation of PEEK progressively occurs resulting in a rapid increase of the PEEK viscosity. Phillips et al. [2] have investigated the thermal stability of carbon fibre-reinforced PEEK (PEEK/CF) in air via dynamic rheological analysis, DSC and thermogravimetral analysis (TGA). They showed that the processability of PEEK composites is strongly affected by the crosslinking of the PEEK resin.

For short-time heated PEEK (< 300 s), almost no studies can be found in the literature while a single detection method can hardly be applied in order evaluate the quality of the polymer. With the increased use of PEEK in fast manufacturing of advanced composites such methodologies and information are of high interest. Bayerl et al. [1] have investigated the thermal degradation behavior of short heated PEEK/CF in the range of 10 ms to 3 min. The material was heated by various methods including induction, IR and laser heating. DSC, TGA, FTIR spectroscopy and an optical analysis by scanning electron microscopy (SEM) were used to detect the changes. It was found that the degree of crystallinity and the melting point of laser-radiated CF/PEEK samples decreases significantly with increasing radiation time and higher power.

The scope of the present work focuses on the evaluation of the surface degradation state of short-time heated PEEK (in the range of 30 up to 300 s) in air by means of conventional analytical methods. Furthermore, in order to investigate the through-thickness degradation, thicker samples were heated for longer cycles and observed via Fourier transform infrared (FTIR) spectroscopy and light transmission microscopy.

2. Experimental

For the thermo-oxidative degradation during very short cycles, PEEK in powder form was tested as received. Samples of 5+/-0.05 mg were first heated in a small oven at temperatures of 400, 430, 460 and 490°C for 30, 60, 180 and 300 s. The degradated samples were then run in a DSC device (DSC Q1000 from TA Instruments) according to the following program: $0 - 360$°C with 10°C/min, $360 - 0$°C with 10°C/min and $0 - 400$°C with 10°C/min.

In order to track the through-thickness degradation, sliced samples from a semi-finished PEEK product (20 cm diameter rod from Cellpack) were tested. The samples were degradated in an oven using the configuration illustrated in Figure 1 and the program shown in Table 1. Their cross-section was first polished and then characterized via FTIR microscope (Centaurus from Thermo Nicolet). The received spectra were evaluated with the software OMNIC Version 9.2.32 from Thermo Fisher Scientific Inc. The positions of the measurements for the FTIR are schematically shown in Figure 2, where Position 1 represents the upper layer (surface) of the sample. Moreover, thin slices of the polished cross-section of the samples were cut using a microtome and then observed via light transmission optical microscope.
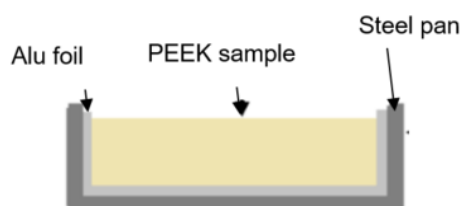

Figure 1. Schematic presentation of semi-finished PEEK sample for the degradation testing.

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Table 1. Degradation program.

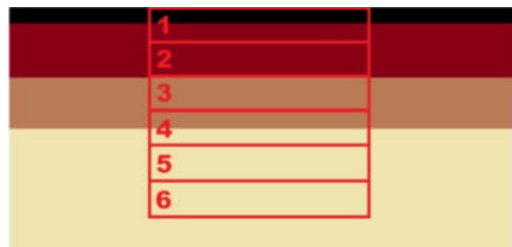| Temperature [°C]	Time [min]
370	80, 160, 320, 640
400	80, 160, 320
430	1, 5, 10, 20, 40, 80, 160
460	360

Figure 2. Schematic presentation of the observed positions for FTIR spectroscopy.

3. Results

Figures 3-5 show the effect of degradation temperature and time on glass transition temperature (T_g), melting point (T_m) and crystallinity of PEEK as observed via the DSC analysis. T_g shows the tendency to increase with degradation temperature and time indicating increase in the crosslinking density. At 490°C a rapid increase is observed with the first 60 s and then T_g tends to reach a plateau value. On the other hand, at 400°C no significant effect on T_m is noticed even for 300 s degradation time. Also the effect of degradation temperature for short cycles is minimal. Increase of both degradation time and temperature has a significant effect of T_m, shifting it towards lower temperatures. In general, the reduction in melting temperature can be assigned to chain scissoring effects and polymeric transformation mainly via crosslinking [4]. Similar tendencies are observed for crystallinity. At temperatures higher than 400 °C, crystallinity decreases dramatically, indicating that the amount of crystallizable material is decreasing as a result of increased exposure time and temperature. Similar tendencies have been reported in the literature for longer exposure times [1, 4].
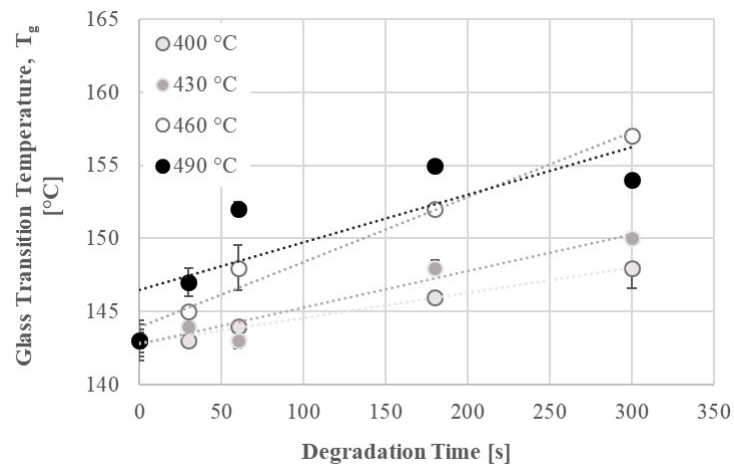
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Figure 3. Effect of degradation temperature and time on glass transition temperature, T_g.
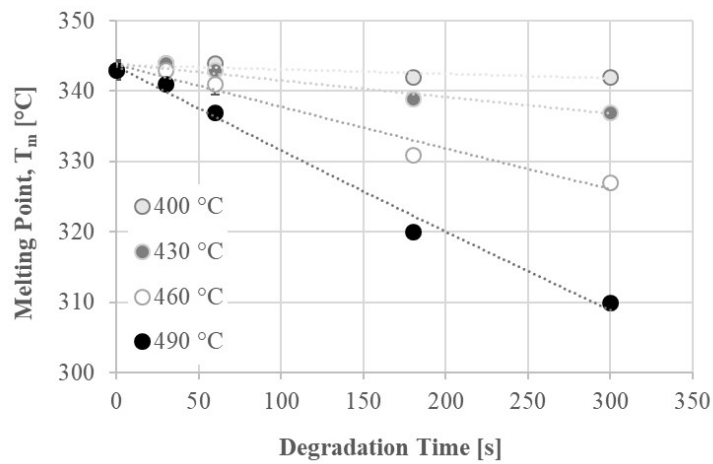

Figure 4. Effect of degradation temperature and time on melting point, T_m.
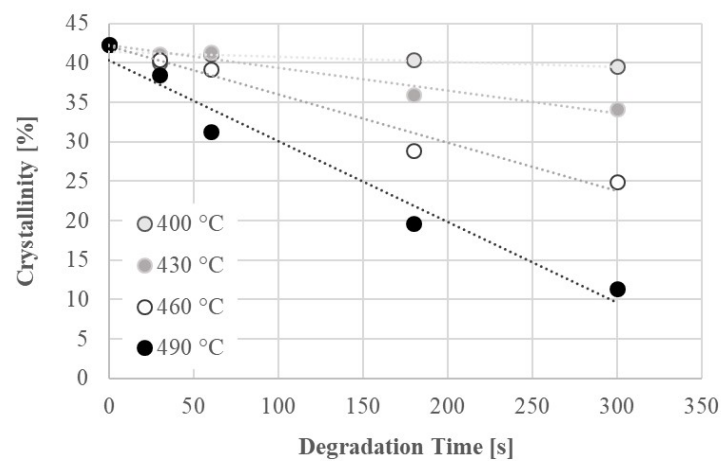

Figure 5. Effect of degradation temperature and time on the crystallinity.

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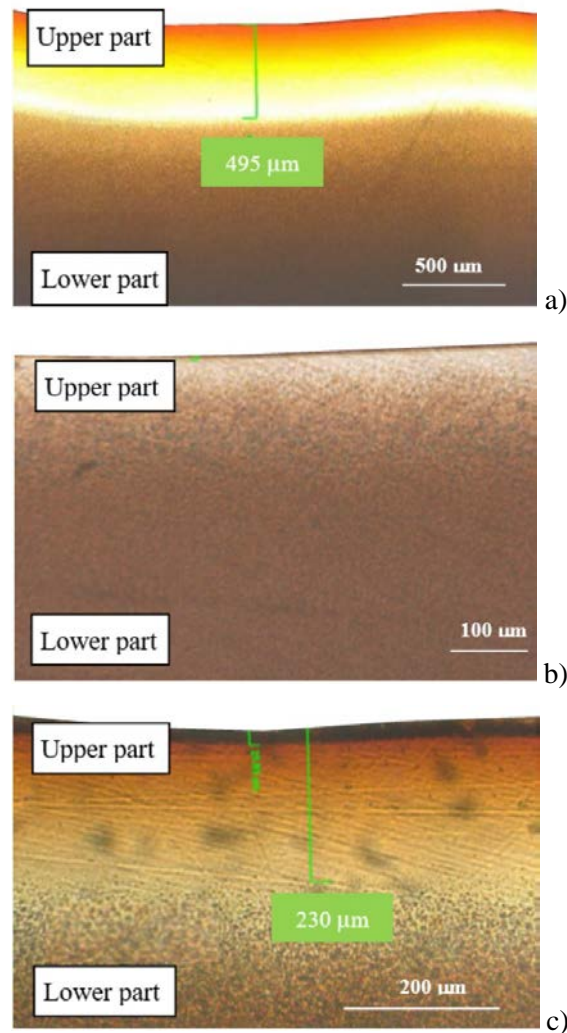
Figure 6. Thin cross-section samples of PEEK after degradated at a) 370 °C for 640 min, b) 430 °C for 10 min and c) 430 °C at 80 min as observed by the light transmission microscopy.

The investigation of the degradation process of the semi-finished PEEK samples revealed the creation of a layer (here called boundary layer) at the surface of the samples. The thickness and gradience of this layer depend on the degradation temperature and time. The images of thin slices of the samples degradated at 370 °C and 430 °C as observed by the transmission light microscopy are shown in Figure 6. The variation of the morphology of PEEK can be traced, with the degradated amorphous part (boundary layer) at the upper part of the material and a crystalline one at the lower one. At 370 °C the gradient transition can be seen and after 640 min a boundary layer of 500 μm is formed. Short degradation times result to a very thin boundary layer (8 μm for 10 min) even at 430 °C, while for longer exposure at this temperature a darker layer can been seen at the surface of the polymer (indicating a complete decomposition of the polymer), followed by the amorphous part. Based on the microscope images, the development of the boundary layer at 370, 400 and 430°C with time was estimated (Figure 7). For lower processing temperature, the maximum thickness of the boundary layer increases significantly. The formation of the boundary layer is a diffusion-controlled process. At lower temperatures, the oxygen can diffuse further into the material before the degradated polymer at the edge of the material becomes impermeable to oxygen. In contrast, a high processing temperature results in a thinner, more concentrated boundary layer that protects the underlying material.

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These results are in agreement with the observations of Day et al. [9] via TGA analysis. At lower temperatures (380 – 430 °C), the degradation reactions seem to be sufficiently slow that oxygen is able to diffuse to the reaction sites and initiate the oxidation process. For these temperatures, an activation energy E_α of about 120 J/mol has be reported in the literature for the degradation of PEEK in air [2, 6, 9]. This is much lower than that reported for the thermal degradation of PEEK in nitrogen, indicating a reduced thermal stability and faster weight loss of PEEK when heated in the presence of air. At higher temperatures (> 440 °C), the degradation process occurs much faster than the rate of oxygen diffusion. Therefore, they measured higher E_α values, similar to those for nitrogen atmosphere (210 J/mol)[5].

The FTIR analysis along the thickness of the samples showed differences between their upper and lower layer, which can be related to the observations from light transmission microscopy. Two main tendencies were observed with increasing temperature: a) decrease of the peak at about 840 cm^{-1} and broadening of the peaks at around 865 and 845 cm^{-1} and b) appearance of a shoulder between 1200 and 1280 cm^{-1}. According to the literature, these changes are related to C-H deformations in the region of the phenyl rings and straining of the ether groups, respectively. Additionally, changes in form and intensity in the region of about 1650 cm^{-1} support degradation reactions involving C=C and C=O groups. These results will be reported in detail in a forthcoming publication.
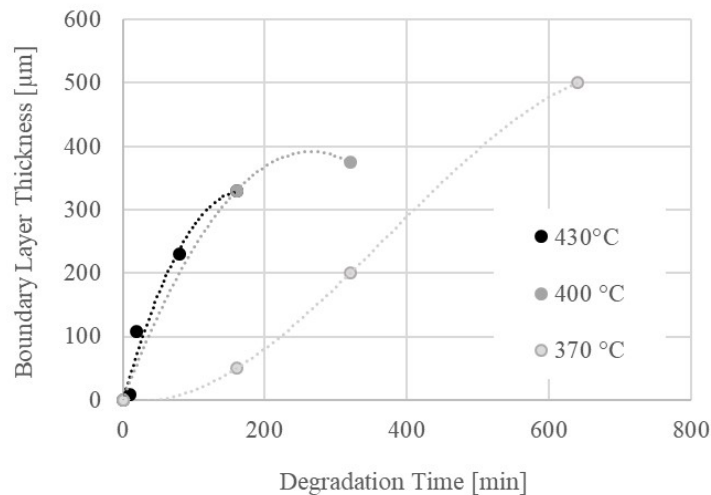

Figure 7. Development of the boundary layer with time at 370°C, 400°C and 430°C.

4. Conclusions

The investigation of the thermo-oxidative degradation of PEEK at temperatures above 400 °C and times below 300 s showed similar tendencies as those described in the literature for longer exposure times. In general, the melting point and crystallinity tend to decrease while T_g is increasing with increasing degradation temperature and time. From the DSC curves, these changes in melting behavior and crystallinity were used to estimate a safe processing window for PEEK between 30 to 300 s. The results are presented in Figure 8, together with estimations based on viscosity changes, by other authors, for longer degradation times (> 300 s) [2, 10]. In general, it has to be kept in mind that the thermal history in air affects significantly the processing properties of PEEK, especially on the surface. The investigation of the through thickness degradation of PEEK via transmission optical microscopy and FTIR spectroscopy in the presence of air indicated that at lower temperatures (< 400 °C) the degradation reactions are adequately slow as oxygen can diffuse through the surface of the material and initiate the oxidation process. At higher temperatures though, a faster degradation process

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takes place. This process induces a boundary layer on the surface of the material hindering in this way the oxygen diffusion. Although such a mechanism protects the inner part of the polymer from degradation, it damages thoroughly its surface, minimizing in this way its consolidation ability during further processing.
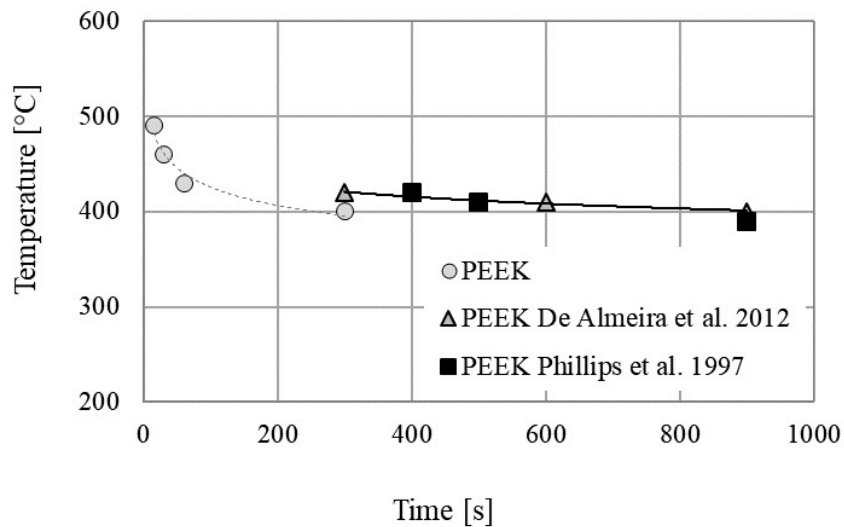

Figure 8: PEEK processing window.

References

[1]   T. Bayerl, Brzeski, M., Martı, M., Martinez-Tafalla, M., Schledjewski, R., Mitschang, P., "Thermal degradation analysis of short-time heated polymers," *Journal of Themoplastic Comsposite Materials,* vol. 28, pp. 390-414, 2015.

[2]   R. Phillips, Glauser, T., Manson, J.-A. E., "Thermal stability of PEEK/carbon fiber in air and its influence on consolidation " *Polymer Composites,* vol. 18, pp. 500-508, 1997.

[3]   K. C. Cole and I. Casella, "Fourier transform infrared spectroscopic study of thermal degradation in films of poly(etheretherketone)," *Thermochimica Acta,* vol. 211, pp. 209-228, 1992.

[4]   M. Day, Suprunchuk, T., Cooney, J. D., Wiles, D. M. , "Thermal degradation of poly(aryl-ether–ether-ketone) (PEEK): A differential scanning calorimetry study," *Journal of Applied Polymer Science,* vol. 36, pp. 1097-1106, 1988.

[5]   M. Day, J. D. Cooney, and D. M. Wiles, "A kinetic study of the thermal decomposition of poly(aryl-ether-ether-ketone) (PEEK) in nitrogen," *Polymer Engineering & Science,* vol. 29, pp. 19-22, 1989.

[6]   M. Day, J. D. Cooney, and D. M. Wiles, "The thermal stability of poly(aryl-ether–ether-ketone) as assessed by thermogravimetry," *Journal of Applied Polymer Science,* vol. 38, pp. 323-337, 1989.

[7]   P. Patel, Hull, T.R., McCabe, R.W., Flath, D., Grasmeder, J., Percy, M., "Mechanism of thermal decomposition of poy(ether ether ketone) (PEEK) from a review of

decomposition studies," *Polymer Degradation and Stability,* vol. 95, pp. 709-718, 2010.

[8]   M. Day, D. Sally, and D. M. J. Wiles, "Thermal degradation of poly(aryl-ether-ether-ketone): Experimental evaluation of crosslinking reactions," *Journal of Applied Polymer Science,* vol. 40, pp. 1615-1625, 1990.

[9]   J. D. C. M. Day, D.M. Wiles, "The kinetics of the oxidative degradation of poly(aryl-ether-ether-ketone) (PEEK)," *Thermochimica Acta,* vol. 147, pp. 189-197, 1989.

[10]   O. De Almeida, Bessard, E., Bernhart, G., "Influence of processing parameters and semi-finished product on consolidation of carbon/PEEK laminates," in *ECCM15 - 15th European Conference on Composite Materials*, Venice, Italy, 2012.