




Submitted: September 26, 2023

Revised: November 30, 2023

Accepted: December 15, 2023

Thermal transformation and mechanical properties of high-temperature-resistant matrix based polyetherketones

A.S. Shabaev¹, K.T. Shakhmurzova¹,  A.A. Zhansitov¹,  A.L. Slonov¹, I.N. Fomicheva², I.V. Dolbin¹ ,  S.Yu. Khashirova¹, ¹ Kh.M. Berbekov Kabardino-Balkarian State University, Nalchik, Russia² Tula State University, Tula, Russia

✉ i_dolbin@mail.ru

ABSTRACT

Of the entire variety of polyaryletherketones, the most promising representatives of this class of polymers with high thermal and mechanical properties (polyether ether ketone, polyether ketone ketone) were studied in this work. The dependence of the rate of thermal decomposition on the structure was revealed, and the temperature-time ranges for the onset of gas evolution were shown. The order of destruction of the main polymer chain depending on temperature has been established. Due to the complexity of processing this class of polymers into products, the possibilities of changing the temperatures of phase transitions were shown in order to improve the technological conditions of processing without loss of performance characteristics. Comparative studies of the kinetics of the release of the main gaseous degradation products for polyether ether ketones from various manufacturers were carried out. The influence of hydrogen formed during the destruction process on the rate of decomposition of polymers is shown, and the dependences of the formation of carbon oxide and carbon dioxide on the structure and manufacturer of polymer materials are revealed. It has been established that polyether ether ketone has slightly higher mechanical properties compared to polyether ketone ketone, which is associated with the lower crystallinity of the latter due to the content of a comonomer with an irregular structure - isophthaloyl chloride.

KEYWORDS

polyether ether ketone • synthesis • processing • heat resistance • mechanical properties

Acknowledgements. The study was carried out with the financial support of the Tula Region Committee for Science and Innovation under Agreement No. 10 dated 07.09.2022 "Development of a highly efficient import-substituting technology for the production of high-tech polyesterketoneketone with a long service life".

Citation: Shabaev AS, Shakhmurzova KT, Zhansitov AA, Slonov AL, Fomicheva IN, Dolbin IV, Khashirova SY. Thermal transformation and mechanical properties of high-temperature-resistant matrix based polyetherketones. *Materials Physics and Mechanics*. 2024;52(2): 123–132.

http://dx.doi.org/10.18149/MPM.5222024_13

Introduction

Polyaryletherketones (PEK) represent a group of aromatic polyethers possessing a ketone moiety, exhibiting exceptional resistance to high temperatures [1–9]. The enduring fascination with this particular polymer category arises from their ability to meet the most up-to-date demands for the performance characteristics of contemporary polymer materials, while also potentially serving as a binding agent in the fabrication of revolutionary polymer composite materials (PCM) [10–20].

The choice of matrix directly affects the physical, mechanical, and technical characteristics of the final product, as well as the manufacturing process itself. Among

these characteristics, thermal properties play a crucial role as they not only influence the properties of the resulting product, but also determine its reliability and operational range. In this context, the thermal changes of polyetherketones of various structures utilized in industry as part of PCM should be considered.

To date, several types of polyaryletherketones are known: polyether ether ketone (PEEK), polyether ether ether ketone (PEEEK), polyether ether ketone ether ketone (PEEKEK), polyether ketone (PEK), polyether ether ketone ketone (PEEKK), polyether ketone ether ketone ketone (PEKEKK), polyether ketone ketone (PEKK) (Table 1).

Table 1. The main representatives of a number of polyaryletherketones

| Name of the polymer | Polymer structure |
|---|-------------------|
| Polyetherketone (PEK) | |
| Polyether ether ketone (PEEK) | |
| Polyether ketone ketone (PEKK) | |
| Polyether ether ketone ketone (PEEKK) | |
| Polyether ketone ether ketone ketone (PEKEKK) | |
| Polyether ether ether ketone (PEEEK) | |

The composition of ether and carbonyl groups dictates the properties of the polymers listed in the table. Hence, as the concentration of carbonyl groups escalates, there is a corresponding elevation in the melting and glass transition temperatures (Table 2).

The level of crystallinity greatly influences impact strength, elasticity, and chemical resistance. The processing of PEK poses challenges due to its high melting point and melt viscosity. To achieve the desired operating characteristics, it is necessary to plan the processing operations that result in the appropriate level of crystallinity for PEK.

Polyetheretherketones (PEEK) have gained popularity due to their enhanced recyclability from melting, thanks to the inclusion of carbonyl and two ether linkages. In previous studies [21–23], researchers investigated the patterns of thermal degradation in polyetheretherketones with different structures and developed strategies for thermal

decomposition. The thermal degradation of polyether ketones was found to initiate with the breakage of the ketone group, and in the case of a diene fragment, with the separation of the methyl group and a simple ether bond (Fig. 1).

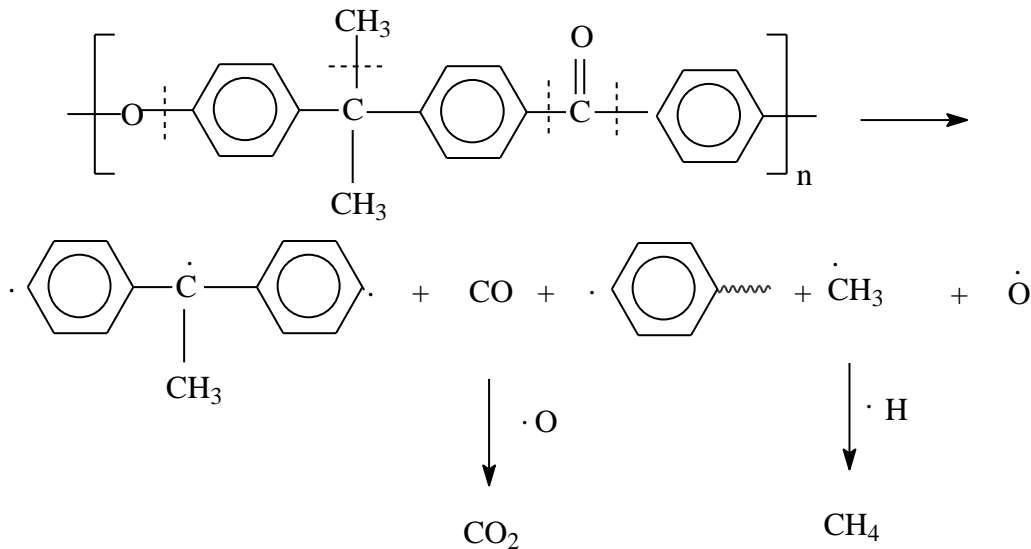


Fig. 1. Scheme of thermal decomposition of polyether ketones

Table 2. Values of melting and glass transition temperatures for various PEK [15]

| Polyethylene | Concentration of ketone groups, % | T_m , °C | T_g , °C |
|--------------------------------|-----------------------------------|------------|------------|
| Substituted polyphenyleneoxide | 0 | 285 | 110 |
| PEEEK | 25 | 324 | 129 |
| PEEK | 33 | 335 | 141 |
| PEK | 37,5 | 337 | 144 |
| PEEKEK | 40 | 345 | 148 |
| PEK | 50 | 365 | 152 |
| PEEKK | 50 | 365 | 150 |
| PEK | 57 | 374 (416) | 157 (160) |
| PEKEKK | 60 | 384 | 160 |
| PEKK | 67 | 391 | 165 |

The discovery of water during the pyrolysis processes, which had a significant impact on the degradation of polymer materials, was a prominent characteristic observed in nearly all studies conducted on polyaryletherketones.

Polyarylates, polyether sulfones, and polyimides are the most susceptible to thermohydrolysis of all known heat-resistant polymers [24,25]. When these polymers are pyrolyzed in a humid atmosphere, the start of breakdown changes to lower temperatures by 50-100 °C. According to studies on the influence of water, drying modes of polyether ketones on their thermal and physico-mechanical properties [26,27], polymer thermohydrolysis processes significantly worsen both the physico-mechanical and thermal properties of the products obtained. Simple ether groups are the most vulnerable to the impact of water.

Polyether ketones are typically processed into products in air at temperatures ranging from 360 to 420 °C. It is not always possible to keep the required qualities of items under such extreme circumstances. When researching the thermos-oxidative degradation of polyether ketones [28], it was discovered that PEEK thermos-oxidation begins around 325 °C and is followed by the loss of ketone groups. A rise in temperature causes parts of the benzene ring to oxidize. The authors were able to realize the potential of directional management of the depth of thermo-oxidative transformations for its processing without risk of deterioration of the major technical and operational properties with the aid of various stabilizers.

To ease processing, it is feasible to adjust both the melting point and the glass transition temperature in the synthesis of PEKK using isophthaloyl chloride. Furthermore, this substance has a high affinity for the tissues of live creatures and may be employed as an implant.

The goal of this work is to synthesize and investigate the thermal characteristics of PEKK and PEEK across a wide temperature range.

Methods

The study's subjects were the polyether ketone (PEKK) and polyether ether ketone (PEEK) of the following structure created at Kh.M. Berbekov Kabardino-Balkarian State University, Center for Advanced Materials and Additive Technologies (Fig. 2).

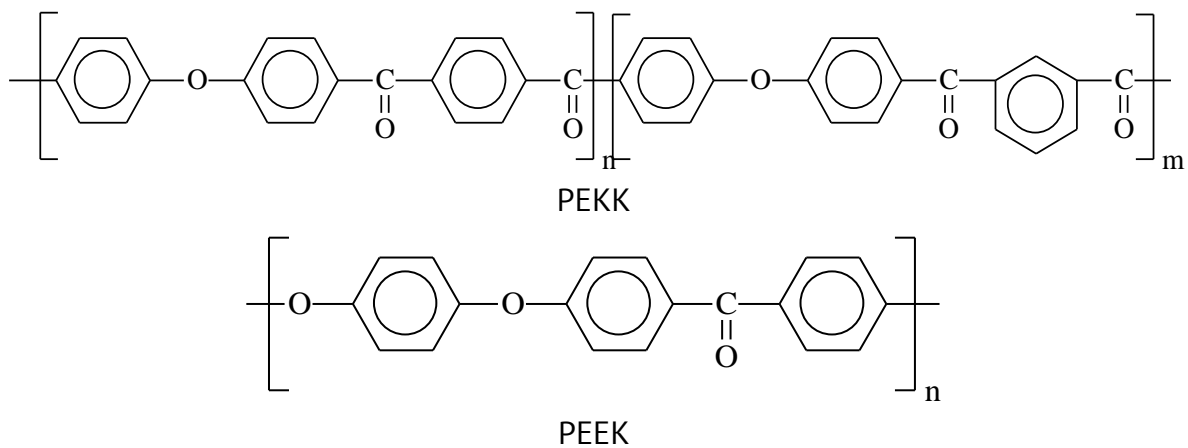


Fig. 2. Participation of atomic hydrogen in the destruction of the ketone group

Polyether ether ketone (PEKK) was synthesized via a low-temperature polycondensation process of electrophilic substitution via the Friedel-Crafts reaction. A glass reactor with a mechanical stirrer and a hydrogen chloride output was filled with diphenyl ether (DFE), terephthaloyl chloride (TPH), isophthaloyl chloride (IFX), a dispersant, and 1,2-dichloroethane. Lithium chloride, benzoic acid (BC), and guanidine methacrylate (MAG) were studied as dispersing chemicals. The reaction mixture was chilled to -20 °C before gradually adding aluminum chloride. After 1 hour, the temperature was gradually increased (0 °C – 30 min, 10 °C – 30 min) to 23-40 ± 2 °C, and the synthesis was completed in 7-20 hours. Depending on the synthesis conditions

used, the polymer precipitated from the solution over time in the form of a polymer gel or individual particles. Following synthesis, 1,2-dichloroethane with a portion of aluminum chloride was filtered from the polymer mass and subjected to regeneration, and PEKK was decomposed from the catalyst with a 3 % hydrochloric acid solution, and the resulting polymer powder was repeatedly washed with hot distilled water until a negative reaction to chlorine ions was observed. For 12 hours, the purified PEK was dried in a vacuum drying chamber at 120 °C.

The nucleophilic substitution procedure was used to synthesize polyether ether ketone (PEEK) via high-temperature polycondensation. 1,4-dihydroxybenzene 33.03 g (0.3 mol), 65.46 g (0.3 mol) 4,4'-difluorobenzophenone, 24.88 g (0.18 mol) potassium carbonate, 19.08 g (0.18 mol) sodium carbonate, and 300 g diphenyl sulfone. The reaction mass is heated to 320 °C for 2 hours and then continuously agitated in an inert gas current for 5 hours. The polymer is cooled to 250 °C and released into a metal pallet at the end of the synthesis. The cooled monolithic mass is crushed and washed with hot distilled water and acetone. For 12 hours, the powder is dried in a vacuum drying cabinet at 120 °C.

Thermogravimetric measurements were made on a Perkin-Elmer TGA-4000 derivatograph in an environment of air and nitrogen at a heating rate of 5 degrees/min. The principal gaseous pyrolysis products were analyzed using a gas chromatograph "Tsvet-800" equipped with a thermal conductivity detector, as described in [29]. The glass transition, melting, and crystallization temperatures were obtained using differential scanning calorimetry on a Perkin Elmer DSC 4000 equipment in an inert medium ranging from 30 to 370 °C, with a scanning speed of 10 °C/min. The study was based on the values of the glass transition and melting temperatures obtained during the second heating of the sample.

Results and Discussion

Figure 3 shows thermogravimetric weight loss curves for PEKK (1) and PEEK (2) in air. The study of the provided curves revealed that the temperatures for 2.5 and 10 wt. % loss for PEKK are 458, 513, and 537 °C, respectively, which is somewhat lower than for PEEK, which is 538, 553, and 561 °C. Nonetheless, the weight loss rate with PEEK is substantially greater and comprises three distinct phases (Fig. 4).

The maximal rate of weight loss for PEKK is significantly higher than for PEEK (619 and 567 °C, respectively). Given these findings, it can be hypothesized that PEKK decomposition happens by the normal homolytic break of the main polymer chain (a minor rate of weight loss), whereas PEEK breakdown occurs via a radical chain, which sometimes increases the rate of decomposition. Studies using differential scanning calorimetry are presented in Table 3.

Table 3. Values of glass transition, melting and crystallization temperatures

| Sample | T_g , °C | T_m , °C | T_{cr} , °C |
|--------|------------|------------|---------------|
| PEKK | 170 | 338 | 254 |
| PEEK | 147 | 348 | 306 |

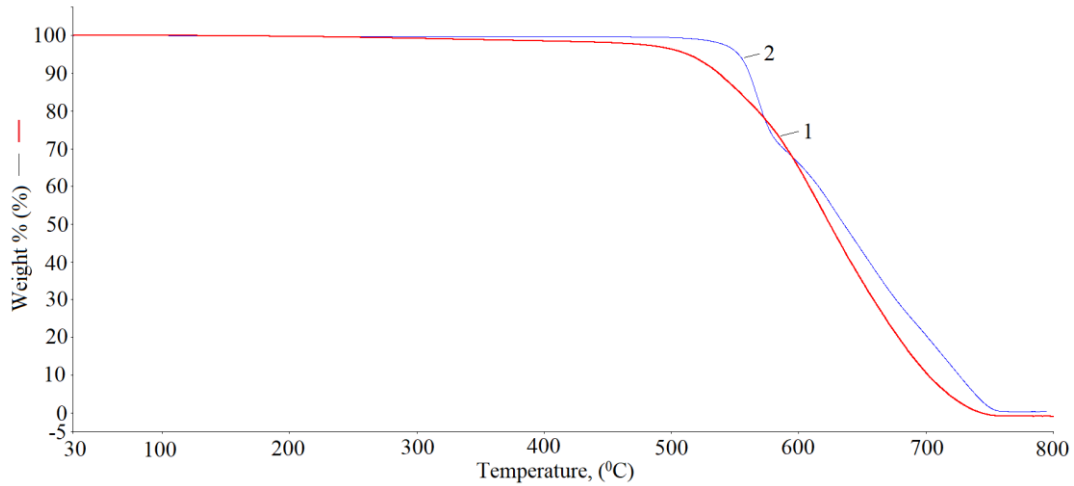


Fig. 3. Curves of weight loss in the air: 1 – PEKK, 2 – PEEK

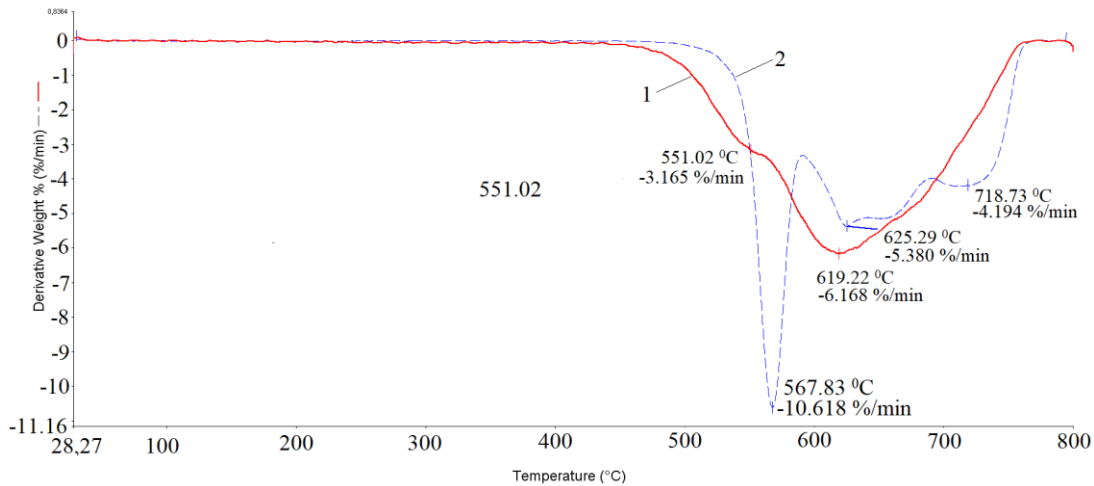


Fig. 4. The dependence of the rate of weight loss on temperature: 1 – PEKK, 2 – PEEK

Based on the results presented in Table 3, we can conclude that PEKK has more comfortable conditions for processing into products, which compensate for the lower temperatures at which weight loss begins.

Comparative investigations of the kinetics of the production of the main gaseous degradation products for PEKK produced in KBSU (PEKK-1) (1), PEKK brand CC-5801 (PEKK-2) (2) (China), and PEEK 450 P produced by Victrex (3) (Great Britain) were carried out using gas chromatography in a wide temperature range. The pyrolysis time was 30 minutes at all temperatures. For each temperature, a new sample of 20 mg was obtained.

No substantial quantities of hydrogen were discovered in any samples at temperatures ranging from 250 to 400 °C, which is most likely due to branching and crosslinking processes (Fig. 5). The hydrogen output for samples PEKK-2 and PEEK increases by an order of magnitude when the temperature is raised compared to PEKK-1.

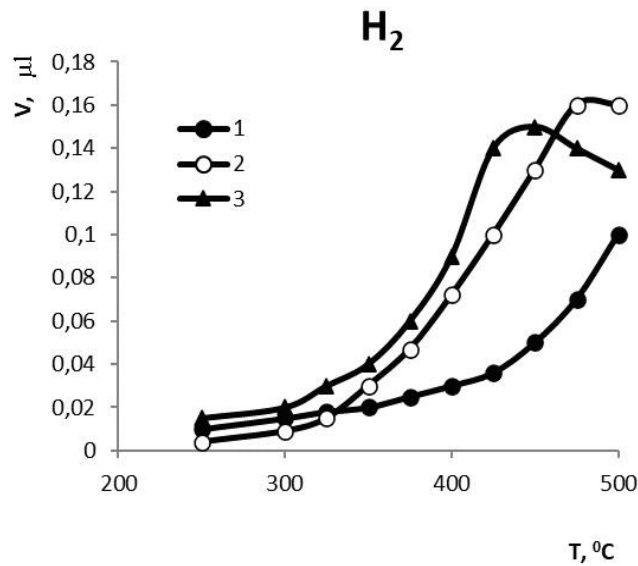


Fig. 5. Kinetic curves of hydrogen formation: 1 – PEKK-1, 2 – PEKK-2, 3 – PEEK

It decreases at temperatures over 450 °C, which is connected with its participation in subsequent polymer degradation processes, transforming homolytic decay into radical chain decay, which has a particular impact on the rate of mass loss for PEEK (Fig. 4).

Figure 6 depicts how active atomic hydrogen contributes to the breakdown of the ketone group by producing phenolic radicals, which also contribute to an increase in the rate of polymer decomposition.

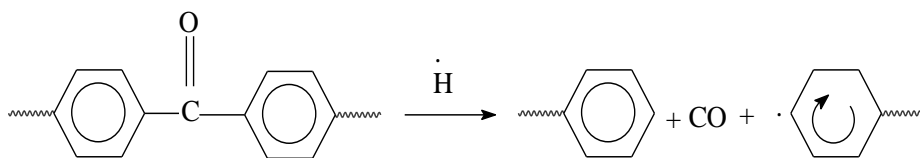


Fig. 6. Scheme of the influence of atomic hydrogen on the destruction of ketones

The presence of carbon monoxide in the breakdown products shows that the ketone group has been destroyed. However, carbon dioxide is found in the breakdown products in addition to CO (Fig. 7).

In [30], it was shown that the emergence of carbon dioxide with CO suggests that, at higher temperatures, the breaking of the simple ether link in the polymer happens concurrently with the release of oxygen, oxidizing CO to CO₂.

The figures show that the quantities of CO₂ for PEKK (1) are almost the same as the amounts of CO. The amount of carbon dioxide increases dramatically in sample (3), which has two simple ether groups in the structure, which is consistent with the results of the work [19]. The unusually high quantity of CO₂ observed in sample 2 is unknown. This is either the consequence of certain impurities remaining after synthesis or the breakdown of numerous stabilizers, plasticizers, and other additives added to the structure.

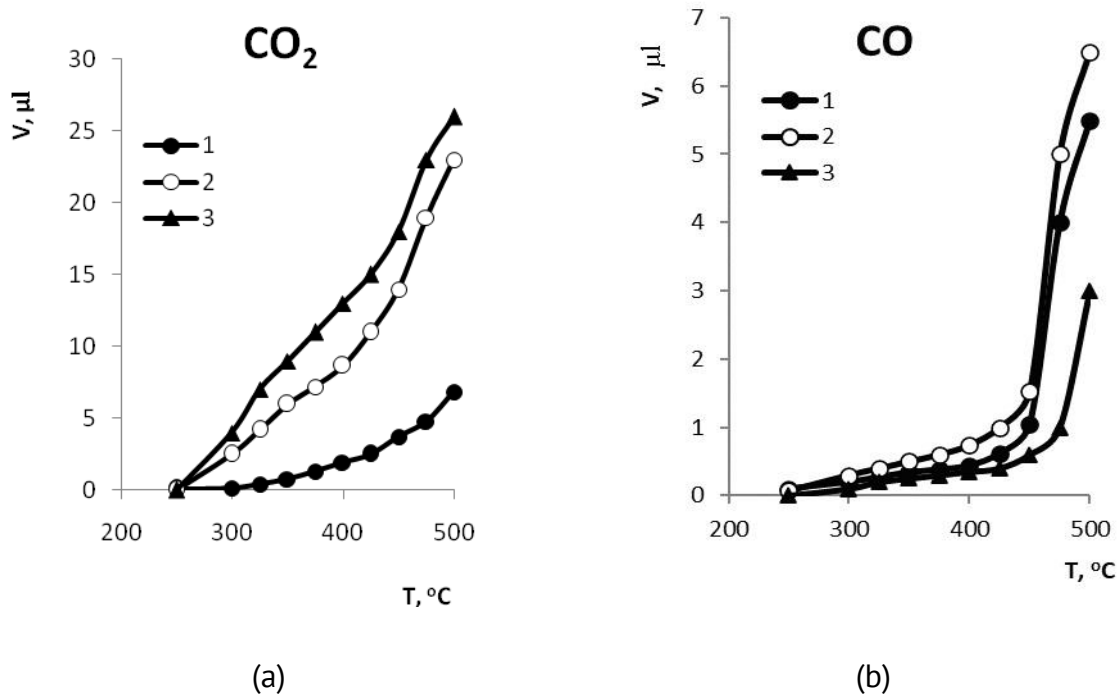


Fig. 7. Kinetic curves of CO₂ (a) and CO (b) formation: 1 – PEKK-1, 2 – PEKK-2, 3 – PEEK

In general, the revealed patterns indicate the possibility of directional regulation of the depth of thermal degradation processes of matrix with a decrease in phase transformation temperatures (T_{st} , T_m , T_{cr}) without risk of deterioration of the main technological and operational characteristics. The mechanical properties of polyaryletherketones were also investigated. The main properties are shown in Table 4.

Table 4. Mechanical properties of polyaryletherketones

| Sample | E_{fl} , GPa | E_{ten} , GPa | σ_{yield} , MPa | σ_{ten} , MPa | ϵ , % |
|--------------|----------------|-----------------|------------------------|----------------------|----------------|
| PEEK 450 P | 3.74 | 2.98 | 117.0 | 98.2 | 120.0 |
| PEKK CC-5801 | 3.17 | 2.66 | 77.4 | 61.5 | 22.6 |
| PEKK KBSU | 3.0 | 2.74 | - | 75.5 | 4.4 |

E_{fl} is the flexural modulus, E_{ten} is the tensile modulus, σ_{ten} is the tensile strength, σ_{yield} is the yield point, ϵ is the elongation at break.

A comparison of the mechanical properties of the studied polyaryletherketones showed that they all have a high range of mechanical characteristics. At the same time, it can be noted that PEEK has higher strength and elastic modulus than PEKK. Apparently, PEEK has superior properties due to its higher crystallinity, since the studied PEKK brands contain isophthaloyl chloride as a comonomer and resulting structure has a lower crystallization rate and degree of crystallinity, which causes lower mechanical properties. A significant difference in the properties of synthesized and industrial PEKK is the higher plasticity of the latter. The synthesized PEKK has a significantly lower elongation and does not exhibit a yield point, i.e., has a brittle character of destruction.

Conclusions

Thus, the conducted studies show that PEKK, due to its high thermal stability, good mechanical properties and lower melting point than PEEK, is a promising material for use as a for composite materials. A matrix based on PEKK is most suitable for creating various products, including implants for living organisms.

References

1. Bühler KU. *Spezialplaste*. Berlin: Akademik Verlag; 1978.
2. Mikhailin YA. *Heat-resistant polymers and polymer materials*. St. Petersburg: Profession; 2006. (In-Russian)
3. Korshak VV. *Chemical structure and temperature characteristics of polymers*. Moscow: Nauka; 1970. (In-Russian)
4. Baur E, Osswald TA, Rudolph N, Saechtling H. (eds.) *Saechtling Kunststoff Taschenbuch*. Carl Hanser Verlag GmbH & Co. KG; 2013.
5. Barvinsky IA, Barvinskaya IE. *Handbook of injection molding thermoplastic materials*. Moscow: 2018. (In-Russian)
6. Sheremetyev SV, Sergeeva EA, Bakirova IN, Zenitova LA, Abdullin ISh. The use of polyetheretherketones in medicine and other industries. Review. *Bulletin of Kazan Technological University*. 2012;15(20): 164–167. (In-Russian)
7. Harris JE, Robenson LM. Blends of poly(aryl ether ketones). In: *Multiphase Macromol. Syst.: Proc. Int. Symp. 14th Bienn. Meet. Div. Polym. Sci. Amer. Chem. Soc., San Diego, Calif., Nov. 19-23, 1988*. New York; 1989. p.519–546.
8. Werdinger W. High temperature performing plastics. *Automot.* 1991;44(11): 757–762.
9. Kuperman AM, Lebedeva OV, Puchkov LV, Zelensky ES, Gorbatkina YuA, Berlin AA. Reinforced plastics based on thermoplastic matrix. *Plasticheskie massy*. 1992;5: 9–10. (In-Russian).
10. Clavijo S, Membrives F, Boccaccini AR, Santillan MJ. Characterization of Polyetheretherketone Particle Suspensions for Electrophoretic Deposition. *J. Appl. Polym. Sci.* 2014;131(20): 40953.
11. Zhang G, Liao H L, Coddet C. Chapter 19 - Friction and wear behavior of PEEK and its composite coatings. *Tribology and Interface Engineering Series*. 2008;55: 458–482.
12. Small G. Outstanding physical properties make PEEK ideal for sealing applications. *Sealing Technology*. 2014;2014(4): 9–12.
13. Salamov AKh, Mikitaev AK, Beev AA, Beeva DA, Kumysheva YuA. Polyether etherketones (PEEK) as representatives of aromatic polyarylene etherketones. *Fundamental research*. 2016;1-1: 63–66. (In-Russian)
14. Yang D, Cao Y, Zhang Z, Yin Y, Li D. Effects of crystallinity control on mechanical properties of 3D-printed short-carbon-fiber-reinforced polyether ether ketone composites. *Polymer Testing*. 2021;97: 107149.
15. Murray BR, Doyle A, Feerick PJ, Semprimoschnig COA, Leen SB, Ó Brádaigh CM. Rotational moulding of PEEK polymer liners with carbon fiber/PEEK over tape-placement for space cryogenic fuel tanks. *Mater. Des.* 2017;132: 567–581.
16. Zhang Y, Tao W, Zhang Y, Tang L. Continuous carbon fiber/crosslinkable poly(ether ether ketone) laminated composites with outstanding mechanical properties, robust solvent resistance and excellent thermal stability. *Compos. Sci. Technol.* 2018;165: 148–153.
17. Monich PR, Henriques B, Novaes de Oliveira AP. Mechanical and biological behavior of biomedical PEEK matrix composites: a focused review. *Mater. Lett.* 2016;185: 593–597.
18. Shakhmurzova KT, Zhansitov AA, Kurdanova ZhI, Baykaziev AE, Salamov AKh, Khashirova SYu. Synthesis and characterization of copolyesteretherketone based on 1,4-dihydroxybenzene and 4,4-dihydroxydiphenyl. *Proceedings of the Kabardino-Balkarian State University*. 2016;6(3): 67–69. (In-Russian)
19. Rival G, Paulmier T, Dantras E. Influence of electronic irradiations on the chemical and structural properties of PEEK for space applications. *Polym. Degrad. Stabil.* 2019;168: 108943.
20. Sun W, Chen T, Liu X, Jiao Y, Zhu Y, Ye J. Microstructure-armed surface and its tribological effects on ultralow-wear PEEK/PTFE composites. *Polymer*. 2024;291: 126599.
21. Kirin BS, Kuznetsova KR, Petrova GN, Sorokin AE. Comparative analysis of the properties of polyetheretherketones of domestic and foreign production. *Proceedings of VIAM*. 2018;5(65): 34–43. (In-Russian)
22. Shabaev AS, Zhansitov AA, Kurdanova ZI, Kuchmenova LKh, Khashirova SYu. Investigation of thermal and thermo-oxidative degradation of poly(ether ether ketone) by gas chromatography. *Chin. J. Chromatogr.* 2018;36(4): 395–399.
23. Khakyasheva EV, Shabaev AS, Khashirova SYu. The effect of PEEK drying modes on its thermal stability. *Proceedings of the Kabardino-Balkarian State University*. 2018;8(3): 68–72. (In-Russian)
24. Saechtling H, Oberbach K. (eds.) *Kunststoff – Taschenbuch. 27 Ausgabe*. Munchen: Hanser Fachbuch; 1999.

25. Korshak VV. *Kinetics and mechanism of formation and transformation of macromolecules*. Moscow: Nauka; 1968. (In-Russian)
26. Krasnov YeP, Savinov VM, Sokolov LB, Logunova VI, Belyakov VK, Polyakova TA. Thermal stability of polyamides in various media. *Polymer Science U.S.S.R.* 1966;8(3): 413–421.
27. Kalra S, Munjal BS, Singh VR, Bhattacharya B. Investigations on the suitability of PEEK material under space environment conditions and its application in a parabolic space antenna. *Advances in Space Research.* 2019;63(12): 4039–4045.
28. Shabaev AS, Khakyasheva EV, Khashirova SYu. Effect of Water on the Thermal Properties of Polyetheretherketone. *Polymer Science, Series A.* 2022;64(5): 410–414.
29. Shabaev AS, Kalazhokov ZKh, Khashirova SYu, Kalazhokov KhKh, Dolbin IV. Stability of bridging groups of polyether ether ketone during thermal destruction and exposure to ion beams. *Russian Chemical Bulletin.* 2023;72(6): 1422–1429.
30. Shabaev AS, Zhansitov AA, Khakyasheva EV, Khashirova SYu. Study of thermo-oxidative transformations of unstabilized and stabilized poly(ether ether ketone). *Polymer Science, Series B.* 2019;61(5): 582–588.

About Authors

Al'bert S. Shabaev 

PhD in Chemistry

Senior Researcher (Kh.M. Berbekov Kabardino-Balkarian State University, Nalchik, Russia)

Kamila T. Shakhmurzova  

PhD in Chemistry

Senior Researcher (Tula State University, Tula, Russia)

Azamat A. Zhansitov  

PhD in Chemistry

Senior Researcher (Tula State University, Tula, Russia)

Azamat L. Slonov  

PhD in Technical Sciences

Senior Researcher (Tula State University, Tula, Russia)

Irina N. Fomicheva 

Junior Researcher (Tula State University, Tula, Russia)

Igor V. Dolbin  

PhD in Chemistry

Senior Researcher (Kh.M. Berbekov Kabardino-Balkarian State University, Nalchik, Russia)

Svetlana Yu. Khashirova  

Doctor of Chemical Sciences, Professor

Vice-Rector for Research (Kh.M. Berbekov Kabardino-Balkarian State University, Nalchik, Russia)