DOI 10.1007/s10692-018-9911-5
Fibre Chemistry, Vol. 49, No. 6, March, 2018 (Russian Original No. 6, November-December, 2017)

SYNTHESIS AND PROPERTIES OF POLYETHERETHERKETONES FOR 3D PRINTING

A. A. Zhansitov, A. L. Slonov, R. A. Shetov,
A. E. Baikaziev,K. T. Shakhmurzova,
Zh. I. Kurdanova, and S. Yu. Khashirova

UDC 547.6

Polyetheretherketones (PEEKs) of different molecular masses were synthesized via high-temperature polycondensation using nucleophilic substitution by varying the excess of 4,42-difluorobenzophenone. The dependences of the thermal and physicomechanical properties of the PEEKs on the intrinsic viscosity were studied. The conditions for synthesizing PEEKs that produced a polymer powder with the property set needed for high-quality 3D printing using SLS technology were determined.

3D printing or so-called additive manufacturing is becoming popular for producing items made of polymers. In contrast with traditional polymer processing techniques (extrusion, injection molding, pressing), the new technology can produce items of any complexity and geometry from digital models. 3D printing has enormous potential for reducing both the cycle time and the production cost [1].

Platform polymers such as polyetheretherketone (PEEK), polyetherimide, polyphenylenesulfone, and others are promising for application to 3D printing. They have high thermal stability and mechanical strength, are resistant to chemicals and radiation, exhibit biocompatibility [2], and can be used in a broad spectrum of sectors including the aerospace, automobile, electronic, and medical industries [3].

An analysis of all worldwide experimental results obtained until now showed that polymeric 3D items have poorer properties than molded ones. Most 3D-printed products are used as before as conceptual prototypes and not functional parts [4]. Such deficiencies limit broad industrial application of 3D-printed polymers.

The manufacturing process or characteristics of the final items were the focus of most research on 3D printing of polymers [5-9]. Although the behavior of polymers is fully studied for traditional manufacturing processes such as spinning and cold pressing [5, 10, 11], very little attention has been paid to the effects of the properties (flow, morphology, etc.) of the 3D printing materials on the quality of the produced items.

The goal of the present research was to find synthetic features that could improve the production method and properties of PEEK used in 3D printing.

PEEK is a polycrystalline polymer with a unique combination of high mechanical properties, thermal stability, and chemical resistance [12, 13]. Selective laser sintering (SLS) is the main method used to fabricate 3D items from PEEK.

SLS technology is based on successive sintering of layers of powdered material using high-power lasers [14]. The sintering occurs in two or three layers because the laser should not only melt the powder but also sinter it to the preceding layer.

A drawback of SLS technology is the lack of pressure, which leads to the formation of porous structures. As a result, the mechanical properties are inferior to those of molded items. This problem is solved by using polymers with the optimum melt viscosity.

In addition, the phase-transition (melting and crystallization) temperatures must be well separated to ensure high-quality sintering of the layers. The region between the temperatures of the start of melting and the start of crystallization is thermodynamically stable and favorable for sintering because the material cannot manage to crystallize

---

Kh. M. Berbekov Kabardino-Balkarian State University, Nalchik; E-mail: azamat-z@mail.ru. Translated from *Khimicheskie Volokna*, No. 6, pp. 68-73, November—December, 2017.

in that temperature range [15]. Rapid crystallization from the melt can lead to poor adhesion of the sintered layers. Therefore, the temperature must be kept high in the powder layer to suppress crystallization.

The upper limit on particle size should be <150 μm and 90% of the particles should be <135 μm according to the requirements for powders for high-quality SLS printing [16]. The powder particles must be spherical to guarantee an even and smooth surface on the powder layer and item. The powder must also have enough friability and bulk density to deposit an even layer. The layer thickness in SLS is usually 100-150 μm. Therefore, a particle size that is one half of that is recommended [17]. The powder flow may be hindered if the particles are too fine. Other researchers also discussed the undesirability of particles <15 μm in size and the best flow of spherical particles (less friction) [5].

Therefore, systematic studies are needed to optimize the production method for polymer powders with sets of properties required to ensure high-quality SLS 3D-printing of items.

PEEK was synthesized using nucleophilic substitution of 4,42-difluorobenzophenone (DFBP) by hydroquinone in mole ratios from 1:1 to 1.04:1 in the presence of anhydrous K_2CO_3 in diphenylsulfone (Scheme 1, Appendix). The reaction was conducted under N_2 with constant stirring and the temperature gradually increasing to 320°C. The reaction mixture was unloaded after 5 h at 320°C and cooled. The resulting solid was ground. Diphenylsulfone and inorganic salts were rinsed away successively with Me_2CO (2×), H_2O (3×), and *i*-PrOH (2×). The resulting solid polymer was dried at 150°C in vacuo for 12 h.

The melt flow index (MFI) was determined on an IIRT-5 capillary viscometer at 350°C with a load of 5 kg.

Mechanical tests used a Gotech Testing Machine CT-TCS-2000 universal testing machine (Taichung Industry Park, Taichung City, Taiwan) at 23°C. Izod impact tests used samples with and without a notch on a Gotech Testing Machine GT-7045-MD pendulum impact tester (Taichung Industry Park) at pendulum energy 11 J.

Differential scanning calorimetry was performed according to GOST R 55134-2012 on a DSC 4000 (PerkinElmer) in air at 25-390°C. The scan rate was 5°C/min. The temperatures of the glass transition and melting that were obtained during the second heating of the sample were taken as the analytical results. Polymer samples were dried in a vacuum drying cabinet in several stages at temperatures from 90 to 150°C before the studies.

The degrees of crystallinity of PEEK and SPEEK were calculated using the formula $\chi_{cr} = (\Delta H/H_{100\%})\cdot 100\%$, where ΔH is the sample enthalpy of fusion; $H_{100\%}$, enthalpy of fusion of absolutely crystalline PEEK (130 J/g).

The structures of the obtained composites were studied using scanning electron microscopy (SEM) on a Vega 3 LMH scanning electron microscope (Tescan, Czech Rep.).

The MFI of the polymer is one of the most important parameters controlling the ability to use polymers in 3D printing. It depends directly on the molecular mass (MM). Strictly defined MFI values and; therefore, MMs, are required for high-quality printing of items. The reproducibility of the MMs from synthesis to synthesis is a factor that is just as important. Polymers with high MMs but low MFI values that do not allow processing by injection molding and 3D printing are produced if the polyetherketone is synthesized with an equimolar ratio of components. Attempts to regulate the MM by changing the synthesis time and dynamic viscosity of the reaction mixture or blocking active propagation centers in various synthetic steps did not produce polymers with high reproducibility.

The PEEK MM can be effectively regulated by using the functional group non-equivalence rule to produce polymers with strictly given intrinsic viscosities and a broad range of MFI values [18, 19]. The polymer chain in a non-equilibrium polycondensation stops growing in the presence of an excess of one of the starting components because the macromolecules formed in a certain reaction step will have identical functional groups of the component in excess on both ends, which precludes further propagation of the polymer chain [20] (Scheme 2, Appendix).

The PEEKs were synthesized with identical temperature—time regimes (320°C, 5 h) and varying excesses of DFBP. DFBP was chosen as the terminal group blocker because polymers with halide terminal groups are more heat-, fire-, and water-resistant than those with terminal hydroxyls [21-23].

It is noteworthy that the intrinsic viscosity continued to increase after 5 h with an equimolar ratio of monomers although it reached a certain value after which it practically did not increase further if an excess was used. The intrinsic and characteristic viscosities are exceedingly difficult to measure because PEEK dissolves only in protic solvents (e.g., conc. H_2SO_4) or at temperatures close to its melting point. Thus, DSC is a rather convenient and accurate method for detecting changes of PEEK MM using the glass-transition temperature.

The glass-transition temperature is known to increase at first very rapidly and then more slowly and finally to become constant as the polymer MM increases [24]. DSC results for the synthesized PEEKs showed that the glass-

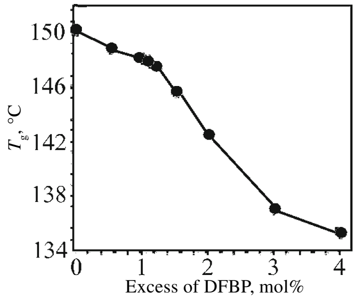


Fig. 1.

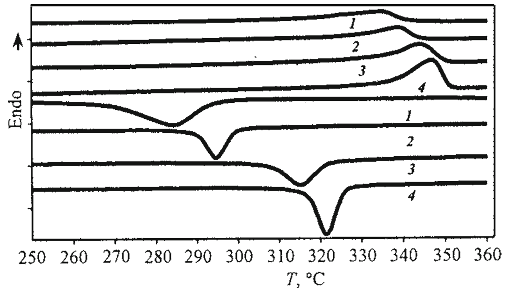


Fig. 2.

Fig. 1. Effect of excess of DFBP on PEEK glass-transition temperature.

Fig. 2. DSC curves: 1) PEEK-1; 2) PEEK-3; 3) PEEK-7; 4) PEEK-8.

Table 1. Thermal Properties of PEEKs

Sample	Excess of DFBP, %	T_g, °C	T_{cr}, °C	mp, °C	χ_{cr}, %
PEEK-1	0	150.35	285.87	334.23	19.79
PEEK-2	0.5	148.94	290.66	335.96	27.31
PEEK-3	1	148.42	294.60	338.55	30.65
PEEK-4	1.1	147.81	297.50	339.96	31.49
PEEK-5	1.2	147.74	301.47	341.33	32.43
PEEK-6	1.5	145.80	309.84	342.30	36.45
PEEK-7	2	142.74	315.18	344.46	42.75
PEEK-8	3	137.2	321.7	347.5	53.4
PEEK-9	4	135.4	326.0	348.4	57.0

Note: T_g, T_{cr}, and T_{mp} are the glass-transition and crystallization temperatures and melting point, respectively; χ_{cr}, the degree of crystallinity.

Table 2. Physicomechanical and Rheological Properties of PEEKs

Sample	T_g, °C	MFI, g/(10 min)	A_p, kJ/m^2		E_{ben}, GPa	E_{ten}, GPa	σ_t, MPa	σ_f, MPa	ε_f, %
			wo/n	w/n					
PEEK-1	150.35	0.15	n/d	16.8	3.60	2.85	118	1050.0	30.0
PEEK-2	148.94	0.7	n/d	11.2	3.78	3.02	110	95.0	82.0
PEEK-3	148.42	2.66	n/d	10.2	3.6	3.20	105	99.3	67.0
PEEK-4	147.81	8.6	n/d	9.4	3.74	2.97	104.6	96.2	86
PEEK-5	147.74	25.4	n/d	9.0	3.67	3.15	104	96.5	85.5
PEEK-6	145.80	52	32.4	–	3.90	3.05	90.5	–	5
PEEK-7	142.74	80	9.3	–	4.00	3.30	68	–	3
PEEK-8	137.2	111	10.7	–	4.50	3.50	63	–	2.5
PEEK-9	135.4	Leaked	5	–	4.8	–	–	–	–

Note: A_p is Izod impact viscosity; wo/n, without notch; w/n, with notch; n/d, not destroyed, i.e., the pendulum hammer did not have enough energy to break the sample without a notch.

transition temperature decreased smoothly as the excess of DFBP was increased and, as a result, the polymer MM decreased (Fig. 1).

DSC analyses also demonstrated that the melting point and PEEK crystallization temperature increased with increasing excess of DFBP (Table 1). This was related to the greater mobility of short macromolecular chains, which facilitated their reorientation during crystallization to form more perfect crystal structures that increased the melting point. The degree of crystallization of the synthesized polymers also noticeably increased.

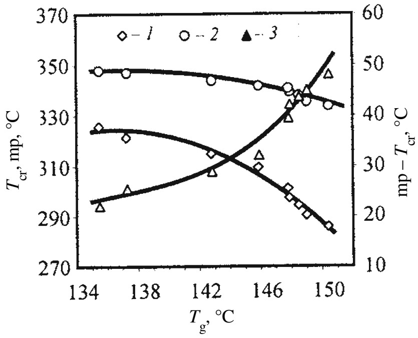


Fig. 3.

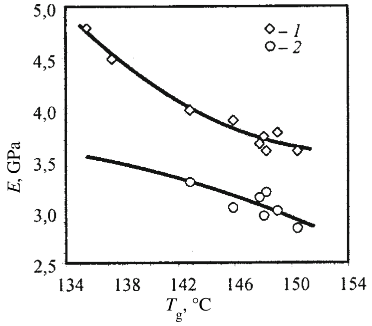


Fig. 4.

Fig. 3. Crystallization temperature T_{cr}, melting point mp, and difference between them mp – T_{cr} as functions of PEEK glass-transition temperature T_g.

Fig. 4. Moduli of bending elasticity E-$_{ben}$ (1) and tension E_{ten} (2) of PEEK samples as functions of glass-transition temperature T_g.

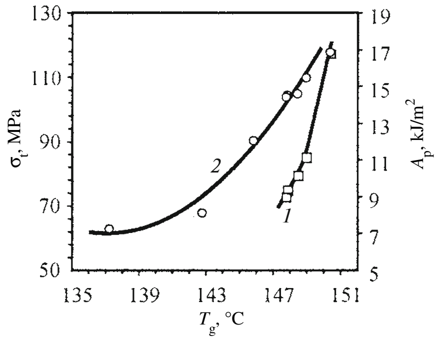


Fig. 5. Impact viscosity A_p and tensile strength σ_t of PEEK samples as functions of glass-transition temperature T_g.

It is noteworthy that the melting point and crystallization temperature did not increase in proportion to each other as the excess of DFBP was increased and the MM was correspondingly decreased (Fig. 2). Thus, whereas the melting point of PEEK-9 increased by 14°C as compared with PEEK-1, the difference of the crystallization temperatures was 40°C. Therefore, the temperature interval between melting and crystallization contracted (Fig. 3). As stated above, the phase-transition temperatures (melting and crystallization) must be well separated to ensure high-quality sintering of layers in SLS 3D-printing technology.

Table 2 presents results for the physicomechanical properties of the synthesized PEEKs fabricated by injection molding. It can be seen that PEEK with glass-transition temperature 147.8-148.5°C exhibited high mechanical properties and was technically suitable for 3D printing.

A clear tendency of the polymer rigidity to decrease was observed as the glass-transition temperature increased (Table 2, Fig. 4). In turn, this was directly dependent on the MM.

The higher elasticity moduli of samples with low MM (with low T_g) was obviously related to the lower flexibility of short macromolecular chains that limited the number of possible conformations and also to their greater ability to reorient during crystallization that led to the formation of more perfect crystal structures. This was confirmed by the elevated melting points and crystallization temperatures of samples with a low glass-transition temperature.

The strength of the PEEKs increased smoothly with increasing MM because the total energy of intermolecular bonds increased as the chain length increased, leading to increased strength (Fig. 5). This was especially characteristic of polymers containing polar groups and; therefore, with stronger intermolecular interactions.

The strength increased by almost 100% from the low MM samples to those with high MMs. The impact viscosity increased analogously as the MM increased. The amount of energy absorbed during the impact was greater for stronger and more plastic (ability to deform) materials. Increased MM is known to increase these properties.

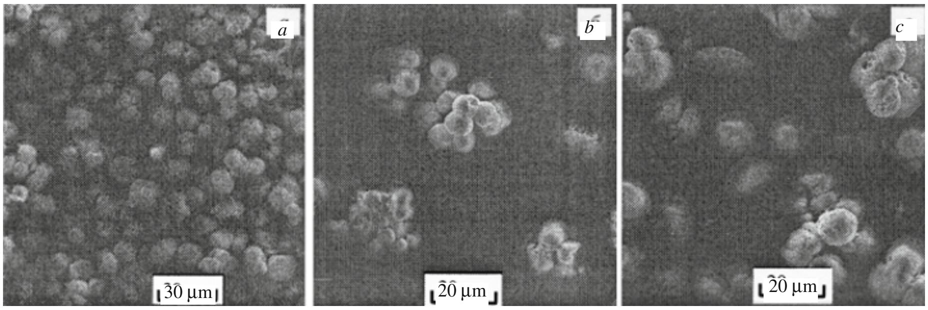


Fig. 6. SEM photographs: a) PEEK-7; b) PEEK-6; c) PEEK-3.

SEM was used to determine the PEEK particle size. It was concluded that samples with low MM had rather small particle sizes (10-15 μm) that increased with increasing MM (Fig. 6). Samples prepared with an excess of DFBP (1-1.1%) had the optimal thermal and physicomechanical properties and the optimal powder particle sizes (30-50 μm) necessary for high-quality 3D printing.

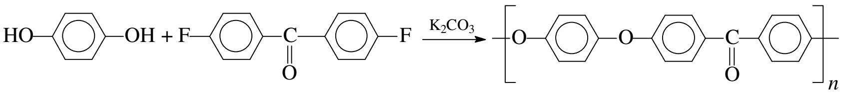
It should also be mentioned that the obtained particles were spherical, which was optimal for even sintering of the layers.

The work was performed in the framework of Contract No. 14.577.21.0240 with the Ministry of Education and Science of the Russian Federation dated Sept. 26, 2017; project identifier RFMEFI57717X0240.

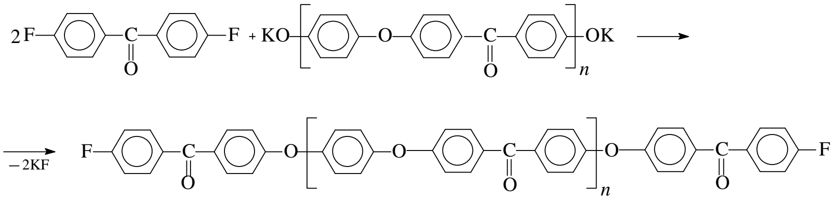
REFERENCES

1. S. Ahn, M. Montero, et al., *Rapid Prototyping J.*, No. 8, 248-257 (2003).
2. K.-W. Buehler, *Heat- and Thermally Stable Polymers* [Russian translation], Ya. S. Vygodskii (ed.), Khimiya, Moscow, 1984, 1056 pp.
3. A. A. Zhansitov, S. Y. Khashirova, et al., *High Perform. Polym.*, 29, No. 6, 724-729 (2017).
4. X. Wang, M. Jiang, et al., “A review and prospective,” *Composites, Part B*, 110, 442-458 (2016).
5. S. Berretta, O. Ghita, and K. E. Evans, *Eur. Polymer J.*, 59, 218-229 (2014).
6. H. Zarringhalam, N. Hopkinson, et al., *Mater. Sci. Eng., A*, 435-436, 172-180 (2006).
7. R. D. Goodridge, R. J. M. Hague, and C. J. Tuck, *Polym. Test.*, 29, No. 4, 483-493 (2010).
8. R. D. Goodridge, C. J. Tuck, and R. J. M. Hague, *Prog. Mater. Sci.*, 57, No. 2, 229-267 (2012).
9. S. R. Athreya, K. Kalaitzidou, and S. Das, *Compos. Sci. Technol.*, 71, No. 4, 506-510 (2011).
10. R. W. Truss et al., *Polym. Eng. Sci.*, 20, No. 11, 747-755 (1980).
11. J. Olinek, C. Anand, and C. T. Bellehumeur, *Polym. Eng. Sci.*, 45, No. 1, 62-73 (2005).
12. B. Nandan, L. D. Kandpal, and G. N. Mathur, *J. Appl. Polym. Sci.*, 90, 2906 (2003).
13. C. N. Velisaris and J. C. Seferis, *Polym. Eng. Sci.*, 26, 1574-1581 (1986).
14. http://3dtoday.ru/wiki/SLS_print/
15. M. Schmid, A. Amado, and K. Wegener, *AIP Conf. Proc.*, 1664, No. 160009, 1-5 (2015).
16. F. Muller, A. Pfister, and M. Leuterer, EP Pat. 2,115,043 B1, Nov. 11, 2009.
17. R. D. Goodridge, C. J. Tuck, and R. J. M. Hague, *Prog. Mater. Sci.*, 57, No. 2, 229-267 (2012).
18. V. V. Shaposhnikova, Candidate Dissertation in Chemical Sciences, INEOS RAS, Moscow, 1993, 141 pp.
19. V. V. Shaposhnikova, S. N. Salazkin, et al., *Izv. Akad. Nauk, Ser. Khim.*, No. 10, 2526-2530 (1996).
20. V. V. Korshak and S. V. Vinogradova, *Nonequilibrium Polycondensation* [in Russian], Nauka, Moscow, 1972, 445 pp.
21. L. I. Danilina, E. N. Teleshov, and A. N. Pravednikov, *Vysokomol. Soedin., Ser. A*, 16, No. 3, 581 (1974).
22. V. B. Gavalyan, V. I. Nedel2 kin, et al., *Vysokomol. Soedin.*, 20, No. 10, 768-771 (1978).
23. N. D. Badikova, E. A. Militskova, and N. V. Andrianova, in: *Production and Processing of Plastics and Synthetic Resins* [in Russian], NIITEKhim, Moscow, 1974, No. 10, pp. 54-57.
24. A. A. Tager, *Physical Chemistry of Polymers* [in Russian], Khimiya, Moscow, 1978, 544 pp.

Appendix



Scheme 1



Scheme 2