Thermoplastic polyether sulfones for composite materials reinforced with fabrics

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Abstract. The results of conducted controlled synthesis of thermoplastic high-performance polyether sulfones with different molecular weight are presented. It is shown that control of reaction time with other synthesis parameters being fixed makes it possible to synthesize polyether sulfones with desired molecular weight and hence viscosity of their melts. The latter is important for making high quality thermoplastic prepregs reinforced with carbon fiber.

Keywords. Polyether sulfone, molecular weight, reduced viscosity, glass transition temperature, reinforced thermoplastic prepregs, carbon fiber.

1. Introduction

Polyether sulfones (PES) are high performance materials possessing high glass transition temperature (220-270 °C depending on chemical structure), tensile strength (500-800 MPa) and Young modulus (2,3-3,0 GPa) which makes them very promising materials for high performance thermoplastic composites reinforced with carbon fiber [1-19]. However, polyether sulfones, as well as other high-performance thermoplastics, have 2 significant drawbacks that hinder their widespread application in industrial setting: high costs and high melt viscosity. The cost of materials can be reduced by optimizing the technology of production of raw materials and the polymers themselves, and viscosity of the melts – through use of polymers with minimum molecular weight at which the polymer obtains adequate characteristics [1, 20, 21].

The goal of our work was to find the optimal conditions for the synthesis of polyethersulfone, to control molecular weight of the obtained polymer, to determine the dependance between glass transition temperature and molecular weight, and also to develop a method for manufacturing thermoplastic prepregs reinforced with carbon fibers using the synthesized polymer with desired molecular weight.

2. Experimental section

The synthesis of polyethersulfone (named PES-1) having glass transition temperature of 230°C was conducted using 4-(4-hydroxyphenyl)sulfonylphenol and 1-chloro-4-(4-chlorophenyl)sulfonylbenzene according to the following equation:

\[ n\text{HO} + n\text{Cl} \xrightarrow{T, \text{toluol}} + n\text{K}_2\text{CO}_3 \xrightarrow{T, \text{toluol}} n\text{O} \]

The reaction was conducted in N-methylpyrrolidone medium at temperature of 180°C for 22-24 hours while taking samples. At the end of the reaction the polymer was precipitated in distilled water.
acidified with oxalic acid taken in 5-6 fold excess by volume respective to the organic solvent while stirring. The precipitated polymer powder was filtered and repeatedly washed with demineralized water to remove the solvent and KCl formed during the reaction. Removal of the salt was controlled by a qualitative test for chlorine ions using AgNO₃. The washed polymer was then dried in air at 120°C for 6 hours. The polymer yield was 97-98%.

The molecular weight of the synthesized polyether sulfones was determined using gel permeation chromatography (GPC) with eluent dimethylformamide.

The reduced viscosity of 0.5% polymer solutions was determined in N-methylpyrrolidone using a Ubbelohde viscosimeter at 25°C according to GOST 18249-72 «Plastics. Method for determining the viscosity of dilute polymer solutions».

The glass transition temperature was determined according to GOST R 55135-2012 (ISO 11357-2:1999) «Plastics. Differential Scanning Calorimetry (DSC)» using «NETZH DSC 204 F1 Phoenix».

Ultrasonic treatment of carbon fabric during its impregnation with PES-1 solution was carried out in UZV-28 ultrasonic bath at maximum power.

3. Results and discussion

Weight-average molecular weight (Mw) of the synthesized polymers was 74 000-97 000 g/mol, number-average molecular weight (Mn) was 24 000-31 000 g/mol, molecular weight distribution (Mw/Mn) was 3.0-3.1. The general view of the GPC curve is shown in Fig. 1. Peaks to the right of the main peak correspond to cyclic oligomers, the content of which is usually 2-2.5 wt%, and to the residual solvent.

![Figure 1. GPC curve for polyether sulfone PES 1](image)

For ease and efficiency in assessing the value of molecular weight of the synthesized polymers, the value of reduced viscosity of their 0.5% solutions in N-methylpyrrolidone was determined. For the samples taken during the synthesis of PES-1, the viscosity ranged from 0.34 dl/g to 0.93 dl/g. For
In comparison, the viscosities of polyether sulfones Ultrason E3010 and Ultrason E6020 (BASF) in the same conditions were 0.6 dl/g and 0.73 dl/g respectively.

In Fig. 2 presented dependences of reduced viscosities and glass transition temperatures of the taken samples from reaction time. As can be seen from the figure, the maximum glass transition temperature is almost achieved when reduced viscosity value is equal to 0.45-0.5 dl/g. This suggests that upon reaching such a value the reaction can be terminated and precipitation of the polymer can begin. It is known that with increase in the molecular weight (MW) of a polymer most of its physical properties (such as glass transition temperature, strength, elongation at break) reach their maximum at a certain optimal molecular weight of the polymer [2-4]. An increase in the molecular weight beyond that optimal value leads to a significant increase of viscosity of the polymer’s melt without a noticeable increase in its physical properties, which significantly complicates its processing by methods of injection molding and extrusion or makes it impossible at all. Therefore, in practice, polymers are produced considering their molecular weight in the form of various grades intended for processing by casting method (grades with lower MW) or extrusion method (grades with higher MW).

The synthesized PES-1 with optimal reduced viscosity of 0.58 dl/g was used for manufacturing thermoplastic prepregs reinforced with carbon fiber.

Prepregs reinforced with unidirectional carbon fiber «UC230»(T700, 12K, with density of 243 g/m² manufactured by CIT, Italy) based on PES-1 were manufactured in two steps: first, the fabric was impregnated with a 7% polymer solution in dimethylformamide, and then surface of the fabric was sprinkled on one side with a predetermined amount of PES-1 flakes. Impregnation was conducted via ultrasonic treatment in a water bath for 5 minutes ensuring complete removal of air from the material and full wettability of all carbon fiber filaments. To preserve the fabric structure and to form smooth edges, sheets of carbon fabric with size of 400x400 mm were placed in aluminum frames with internal size of 315x315 mm specifically made for this task, and fabric was fixed with clumps (Fig. 3).
Figure 3. Aluminum frames and carbon fabric for impregnation with polyether sulfone solution

The impregnated carbon fabric was removed from polyether sulfone solution, the excess solution was allowed to stream down and then the fabric sheet was sprinkled with polyether sulfone flakes in the amount of 30-40% weight of the composite. Then carbon fabric was dried in the aluminum frames in an oven at 100 °C for 4 hours and then in a vacuum oven at 120 °C for 20 hours.

Figure 4. Prepregs after drying

The obtained prepregs were made for processing by hot pressing under pressure of 10 MPa at temperature of 320 °C in the form of sheets with size of 300x300x3mm. Physical, mechanical and thermal properties of the manufactured plates will be studied further.

4. Conclusions

1. A method for synthesis of high performance thermoplastics polyether sulfones was developed allowing to obtain polymers with desired molecular weight and ensuring good characteristics of composites reinforced with carbon fiber impregnated by the synthesized thermoplastics.

2. A method for manufacturing thermoplastic carbon reinforced prepregs was developed, including impregnation of the carbon fabric with polyether sulfone solution, sprinkling its surface with a certain amount of polyether sulfone flakes and removal of the solvent traces at elevated temperature.

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