



STUDY OF THE MECHANICAL PROPERTIES OF POLYPHENYLENE SULFIDE FILMS

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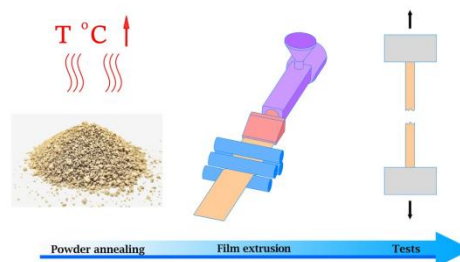
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Abstract

The mechanical properties of the films of various compositions based on polyphenylene sulfide (PPS) were studied. To obtain the films by extrusion, the PPS powder was subjected to heat treatment for 0/20/60 min. The compositions containing 3% of a plasticizer were also prepared. Each of the film types was tested in two forms: amorphous and crystallized. The crystallized films were obtained by holding the amorphous samples at the temperatures above the cold crystallization temperature. The mechanical properties were studied by conducting tensile tests of the standard film samples.

Key words: polyphenylene sulfide, films, crystallization, mechanical characteristics.



Introduction

Products based on PPS are common in various industries. They are used in electrical engineering, automotive industry, petrochemistry, *etc.* [1–3]. There is also a demand for chemically resistant polymer membranes in different areas of production.

Polyphenylene sulfide is a semi-crystalline thermoplastic with an asymmetrical rigid backbone chain consisting of *para*-substituted phenylene rings and sulfur atoms. As a hydrophobic material, PPS has high thermal stability and good mechanical properties. Moreover, it has excellent chemical resistance, including resistance to acids, alkali, chlorine, polar solvents, and caustic organic solutions [4].

Li *et al.* [5] performed the high-resolution thermogravimetric measurements in four atmospheres and revealed that there is no noticeable weight loss up to 490 °C, which indicates the thermal stability of PPS and rather low moisture content in it, since PPS was studied without preliminary drying.

Polymer membranes find extensive use in chemical and automotive industries, construction, as well as wastewater treatment plants. They are often used under relatively simple conditions, for water purification, separation of fractions of a dissolved polymer, removal of microorganisms, *etc.* [6, 7]. However, there are a number of applications of membranes in aggressive environments at high temperatures, when enhanced chemical resistance, heat resistance, and high mechanical characteristics for better flow resistance are required. High performance polymers, which include polyphenylene sulfide, are well suited for these purposes [8].

However, it is impossible to manufacture a membrane from PPS using traditional methods, such as non-solvent-induced

phase separation, since PPS is insoluble in any solvent at temperatures below 200 °C. Taking this into account, Fan *et al.* described the method of manufacturing membranes from PPS by thermally-induced phase separation. When mixing a polymer with a diluent at a sufficiently high temperature, this method affords a homogeneous solution of the polymer and diluent [9].

The properties of films or membranes based on PPS were studied in a number of works. Thus, Lu and Cebe [10] explored the thermal and relaxation properties of PPS films, some of which were additionally subjected to heat treatment. Based on the results obtained, the authors concluded that the annealing at 30–140 °C reduces the number of mobile chains in the amorphous phase of the polymer.

Rang and White [11] described the method for obtaining a biaxially oriented PPS film by producing a double bubble tubular film and studied the mechanical properties of these films. The authors found that the pre-annealed film samples have higher tensile strength and elastic modulus, but show lower maximum strain.

Bian *et al.* [8] reported the properties of membranes based on PPS, including the composite membranes reinforced with aramid and glass fabric. The results of this study showed that the mechanical characteristics of the membranes reinforced with the aramid fabric were many times higher than the analogous characteristics of the conventional membranes based on PPS. The properties of the glass fabric-reinforced membranes were also significantly higher than those of the conventional samples; however, they were more than twice as inferior to the membranes reinforced with the aramid fabric.

The mechanical properties of films or membranes based on PPS were studied in few reports. In order to expand the applicability of PPS-based membranes and their industrial production, the use of extrusion molding is necessary. Due to

the high fluidity of PPS, the extrusion of films is complicated. Therefore, the development of new compositions and subsequent investigation of the mechanical properties of polymeric film products obtained by various methods are required, which are the main goals of this work.

Materials and methods

A linear structure PPS powder with a melt flow rate (MFR) of 436 g/10 min (at 316 °C, 5 kg) was purchased from OOO "NTTs Ahmadulliny". Random ethylene-glycidyl methacrylate copolymer AX8840 produced by LOTADER was used as a plasticizer.

The granulation of the material was accomplished on a Scientific LTE 16–40 twin-screw extruder with water strand cooling. The heating temperature in the extruder zones were (loading-die) 290 – 295 – 300 – 305 – 310 – 310 – 315 – 315 – 320 – 325 °C. The films were obtained on an EX-25 (Welber) extrusion rolling line at die temperature of 330 °C and calendar temperature of 80 °C. The MFR measurement was carried out on a 2322 (SMARTTEST) plastometer at 316 °C and a load of 5 kg. The crystallinity degree of the printed samples was estimated using differential scanning calorimetry (DSC) on a DSC 214 Polyma (NETZSCH) device at a speed of 10 °C /min. The degree of crystallinity was calculated based on the enthalpy of melting of the samples. The tensile tests of the film samples were performed on a UTS-111 (Test systems) universal electromechanical testing machine with wedge-shaped grips and a deformation rate of 5 mm/min.

Results and discussion

For this study, different PPS-based films were obtained in terms of composition and processing method. The films based on the initial powder are designated as PPS-0, since the material has not been subjected to additional processing. As is known, the thermal treatment of PPS in an oxygen-containing environment leads to the curing of macromolecules, which causes a change in the crystallization process and mechanical properties of final products. For some film formulations, the starting powder was subjected to thermo-oxidative curing at 260 °C for 20 min (PPS-T20) and 60 min (PPS-T60). The MFR values of the cured PPS powders were 256 and 36 g/10 min, respectively. The effect of the plasticizer on the mechanical properties of the resulting films was also evaluated. The film samples containing 3 wt % of the plasticizer were designated as PPS-PEGMA. The thicknesses of the resulting films were 70–

150 µm.

Due to a high cooling rate, the films appeared to be transparent and had a predominantly amorphous structure, which was confirmed by the results of the DSC analysis, which showed the presence of a pronounced peak of cold crystallization. In this respect, some of the film samples were subjected to additional heat treatment at 150 °C for 40 min, which allowed them to crystallize. In this case, the DSC measurements showed the absence of a peak of cold crystallization. The amorphous samples were labeled "am", while the crystallized samples were labeled "cr".

The tensile tests of the film samples were carried out according to GOST (State Standard) 14236-81 for six samples. The test results are presented in Table 1. As can be seen, PPS-0 samples have the lowest mechanical characteristics. The curing of the initial powder for 20 min led to an increase in the tensile strength and elastic modulus of PPS-T20 samples. An increase in the curing time to 60 min significantly enhanced the strength to 89 MPa and the stiffness of the films, as well as increased their maximum relative strain from 2% to 10%. This effect is confirmed by the literature data and can be explained by the formation of longer macromolecular chains and transverse intermolecular bonds as a result of thermal curing, due to which the macromolecules have more elastic-active chains and intertwine with each other, improving the strength properties of the material [12]. The addition of the plasticizer to PPS-PEGMA samples also afforded a noticeable increase in the tensile strength and elastic modulus relative to PPS-0 owing to an increase in the material plasticity, which reduced the effect of stress concentrators on the mechanical properties.

The elongation at break also increased with an increase in the duration of heat treatment of the initial powder, but only for amorphous samples (Fig. 1). The maximum average elongation at break was 11.66% for the samples containing the plasticizer.

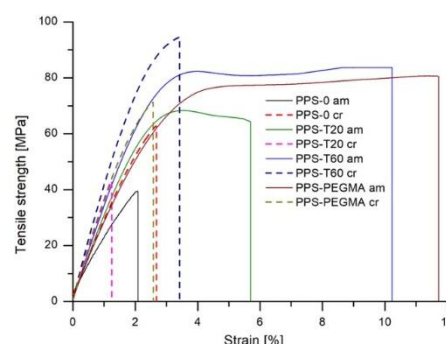


Figure 1. Results of the tensile tests of the film samples.

Table 1. Results of the tensile tests

Sample	Tensile strength, MPa	Standard deviation	Elastic modulus, MPa	Standard deviation	Elongation at break, %
PPS-0 am	41.4	7.8	2130	481	2.1
PPS-0 cr	63.6	4.9	2570	369	2.6
PPS-T20 am	67.6	1.9	3190	22	5.7
PPS-T20 cr	41.9	4.1	3860	89	1.2
PPS-T60 am	83.0	4.9	3500	191	10.2
PPS-T60 cr	88.8	13.9	4370	413	3.4
PPS-PEGMA am	73.8	10.3	2860	231	11.7
PPS-PEGMA cr	66.7	4.5	3510	558	2.4

In general, the amorphous films showed reduced mechanical characteristics compared to the crystallized ones. Although the elastic modulus increased with an increase in the crystallinity degree in all samples, which is associated with the appearance of a more rigid polymer phase, the tensile strength in some cases turned out to be less than that of the amorphous films. Furthermore, the average elongation at break was reduced in the crystallized samples, which did not change stably. This phenomenon may be associated with an increased degree of crystallinity of the samples, which led to their embrittlement.

Conclusions

Thus, the mechanical properties of the PPS films obtained from heat-treated powders as well as those containing the plasticizer were studied. An increase in the curing time of PPS led to an increase in their tensile strength, elastic modulus, and elongation at break, especially in the case of the amorphous samples, which offers opportunities for the production of membranes with improved mechanical properties. Moreover, these characteristics increased in the samples with the addition of the plasticizer. Although the elastic modulus of all crystalline films turned out to be higher, the other characteristics were unstable due to the high sensitivity of the crystalline samples to stress concentrators.

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