

Synthesis and study of block copolymer polyarylates

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Abstract. In order to reduce the viscosity of a polyarylate melt based on phenolphthalein and terephthalic acid dichloride with a glass transition temperature of 280°C, polyarylate-polysulfone block copolymers with a glass transition temperature of 240 to 260°C capable of processing through a melt at 340°C were synthesized and studied.

1 Introduction

Among superstructural thermoplastics, a prominent place is occupied by polyarylates, which are aromatic polyesters based on bisphenols and aromatic dicarboxylic acids or dichlorides based on them [1–4].

Polyarylates are characterized by high heat resistance, physical-mechanical and dielectric properties, which practically do not change over a wide temperature range. They are characterized by good resistance to aggressive media (diluted mineral acids and alkalis, gasoline, oils, fats and most organic solvents), as well as ionizing radiation [5–7].

Thermoplastic polyarylates obtained by emulsion or high-temperature polycondensation of equimolar mixtures of iso- and terephthalic acid dichlorides with bisphenol A (diphenylolpropane), for example, polyarylates of the DV grades (RF, Sverdlov Plant), U-polymers (Japan, Unitica Ltd), Ardel, Arilef. Liquid-crystalline thermotropic polyarylates (Vextra, Xidar, Ultrax, etc.) also find practical application, which are obtained by high-temperature polycondensation in bulk from dicarboxylic and hydroxycarboxylic acids with bisphenol diacetates, for example, terephthalic acid and 4-hydroxybenzoic acid acetate with diacetate 4,4'-dihydroxybiphenyl. A highly crystalline polyarylate based on p-hydroxybenzoic acid, known as Econol (USA), surpasses polyimides in heat resistance (380–400°C) and has a chemical resistance close to that of fluoroplastics [8–12].

2 Aim of the work.

The aim of our work was the synthesis and study of the properties of a modified polyarylate based on phenolphthalein and terephthalic acid dichloride, previously known as F-2 [1–3]. This amorphous carded polyarylate is obtained from a relatively affordable raw material, it has a high glass transition temperature (280 °C), good solubility in available organic

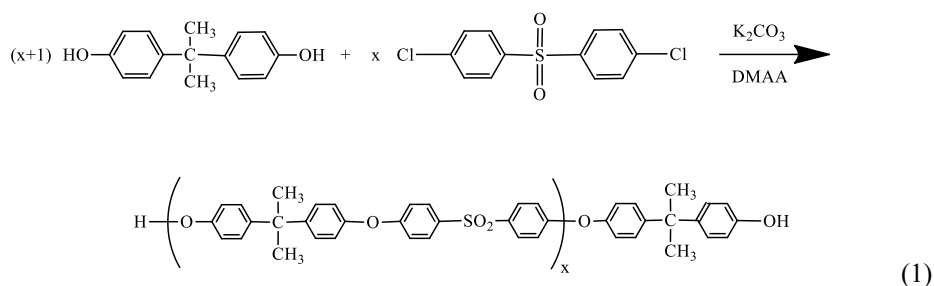
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solvents, and has high mechanical and dielectric properties. However, despite a number of attractive characteristics, this thermoplastic did not become industrial due to the high viscosity of the melt and the difficulties in processing it from the melt. In order to overcome this shortcoming, we modified the chemical structure of the considered polyarylate by introducing blocks of easily processed aromatic polysulfone into its macromolecules, which could act as a chemically bound plasticizer.

3 The discussion of the results.

As is known, one of the ways to improve the processability of rigid-chain thermoplastics is the synthesis of block copolymers (BCP), in which one of the blocks belongs to a thermoplastic with good melt flow and high thermal and oxidative stability [13–15]. As a chemically bound plasticizer, we chose blocks of aromatic polysulfone based on bisphenol A and 4,4'-dichlorodiphenylsulfone, which is well processed from a melt at 310–330°C and has a high thermal and oxidative stability [5–7, 16].

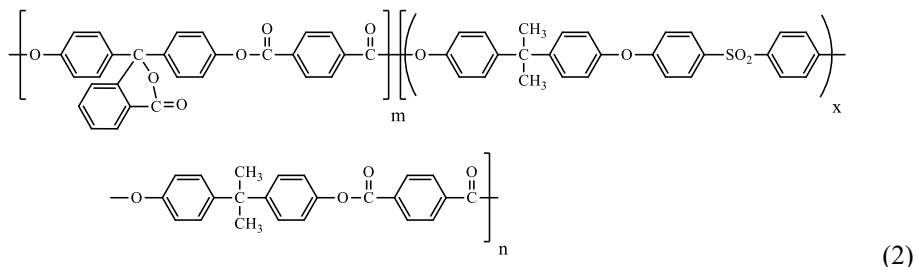
For the synthesis of polyarylate-polysulfone (PAR-PSU) block copolymers, oligosulfones with terminal phenolic groups and the degree of polycondensation $x=10$ and 30 were specially synthesized, which corresponds to a molecular weight of 4500 and 13400 Da. The synthesis of oligosulfones was carried out according to the following reaction equation (1):



where: $x=10$ and 30 .

The structure of the synthesized oligosulfones was confirmed by IR and NMR spectroscopy data, and the molecular weight by GPC data.

Synthesis of polyarylate-polysulfone block copolymers was carried out under the conditions of acceptor-catalytic polycondensation in dipolar aprotic solvents in the presence of triethylamine. The structural formula of the BCP is represented by equation (2), where: m and n are the polycondensation coefficients, which are statistical values from 1 to $25-50$, depending on the molecular weight of the polymer.



The content of PSU blocks in block copolymers was 10, 30, and 50 wt%. The composition and some properties of the synthesized block copolymers are shown in Table 1.

Table 1. Composition of PAR-PSU block copolymers and some of their properties.

| № | PAR code | The content of PSU blocks, wt %. | | η reduced, dl/g DMF, 25 °C | Tc, °C (DSC) | TGA data | | MFR, g/10 min 340°C |
|----|-------------|----------------------------------|------|---------------------------------|--------------|----------|-----|---------------------|
| | | x=10 | x=30 | | | 5% | 10% | |
| 1 | F-2 (F-200) | - | - | 0,16 | - | - | - | - |
| 2 | | | | 0,32 | - | - | - | 0,4 |
| 3 | | | | 0,42 | 280 | 456 | 471 | 0,2 |
| 4 | F-210/30 | - | 10 | 0,80 | 295 | - | - | - |
| 5 | | | | 0,26 | - | - | - | - |
| 6 | | | | 0,17 | - | 422 | 448 | - |
| 7 | F-230/10 | 30 | - | 0,48 | 239 | 466 | 457 | - |
| 8 | | | | 0,43 | 239 | - | - | 5,6 |
| 9 | | | | 0,43 | 238 | 424 | 438 | 5,6 |
| 10 | F-230/30 | - | 30 | 0,44 | 203/260 | 448 | 463 | 3,0 |
| 11 | | | | 0,4-0,6 | 200/260 | 451 | 460 | 0,8-9,8 |
| 12 | F-250/30 | - | 50 | 0,43 | 203/259 | 444 | 457 | 7,2 |

Where: 210/30) - the numerator reflects the content (% wt.) of PSU blocks, and the denominator - the degree of polycondensation of oligosulfone "x".

The glass transition temperatures of F-2 polyarylate (F-200) and block copolymers were determined using differential scanning calorimetry (DSC) on a NETZH DSC 204 F1 Phoenix instrument. The temperature rise rate was 10°C per minute; argon was used as an inert atmosphere. The weight of the samples was 12-13 mg. To obtain curves with the best kink configurations for calculation, the polymer powders were compressed using a hand press into tablets 5 mm in diameter and 0.2 mm high. Figure 1 shows the dependence of the

thermal effect on temperature for a sample of F-2 polyarylate. As can be seen, the glass transition temperature of F-2 polyarylate is 280°C.

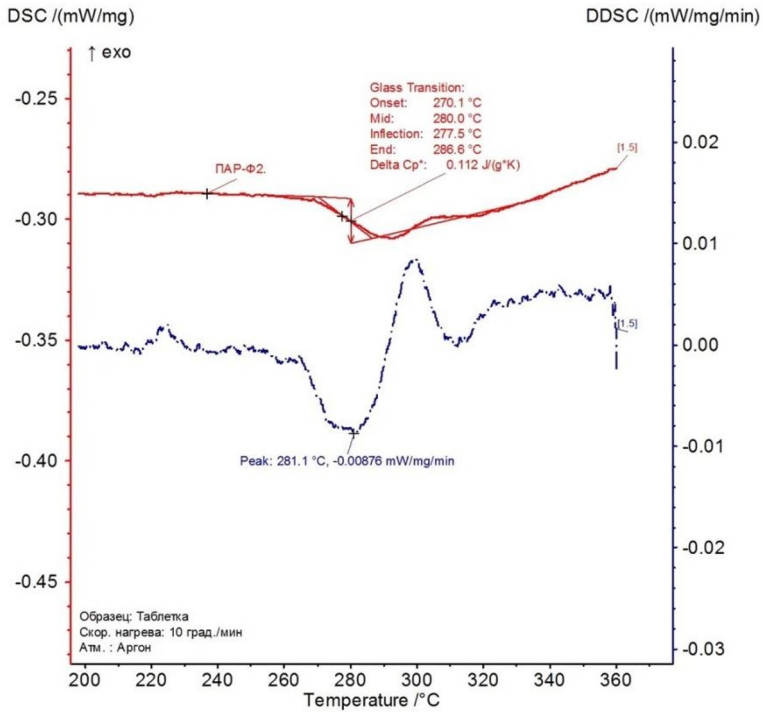


Fig. 1. Dependence of the thermal effect on temperature, obtained using the DSC method for F-2 polyarylate.

Figure 2 shows a typical thermal effect versus temperature curve for PAR-PSU block copolymer F-230/10. And here it is necessary to pay attention (Fig. 2 and Table 1) to the fact that F-230/10, containing 30% mass of PSU blocks with a degree of polycondensation $x=10$, has one glass transition temperature (239°C) for a mixed polyarylate-polysulfone phase. While for a block copolymer containing 30% wt. PSU blocks with a degree of polycondensation $x=30$, two glass transition temperatures are observed (Fig. 3): for the phase consisting of PSU blocks, $T_c=200-203$ °C and for the phase consisting of plasticized polyarylate blocks with a glass transition temperature of about 260 °C.

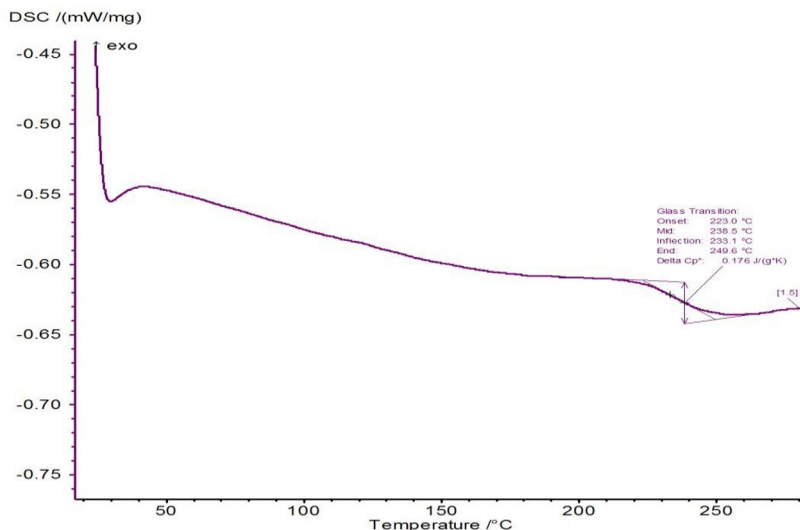


Fig. 2. Dependence of the thermal effect on temperature, obtained using the DSC method for the BCP F-230/10.

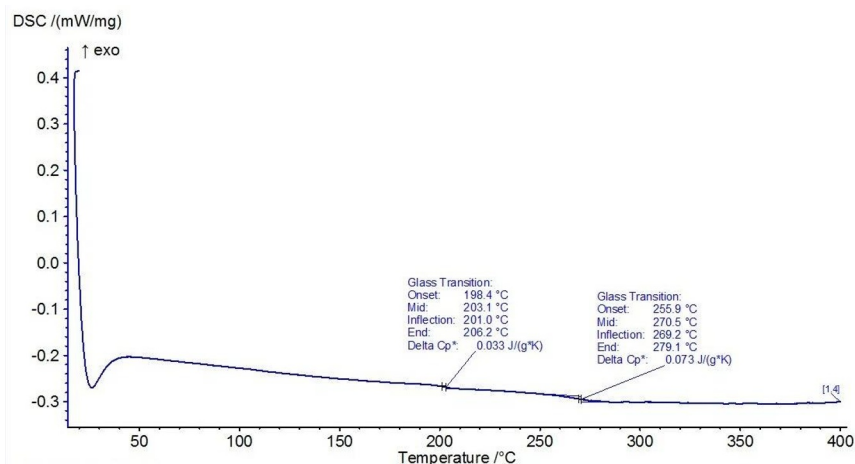


Fig. 3. Dependence of the thermal effect on temperature, obtained using the DSC method for F-230/30 polyarylate.

It is also noteworthy that the DSC readings for samples of the same composition but different syntheses slightly differ from each other by about 3–5 degrees, which may be due to a number of reasons: different molecular weight distribution of macromolecules or different the holding time of the polymer melt during the transition from the first heating to the second, which is usually taken as the basis for measuring T_c .

The thermal-oxidative stability of F-2 polyarylate melts (Fig. 4) and PAR-PSU block copolymer melts was evaluated using the thermogravimetric analysis (TGA) method in air. The measurements were carried out on a NETZH TG 209 F1 Libra instrument at a constant heating rate of 5 degrees per minute. The temperatures of 5% (T5%) and 10% (T10%) weight loss were recorded.

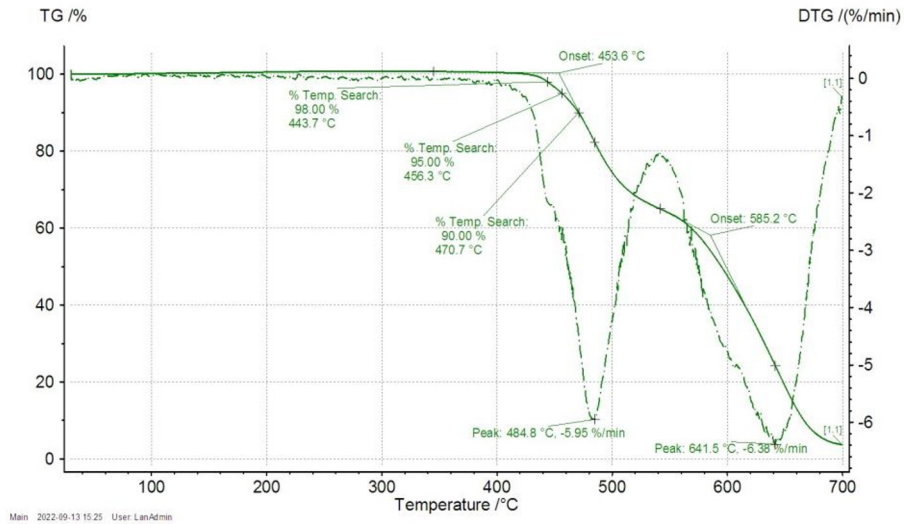


Fig. 4. Dependence of the F-2 sample weight reduction on temperature, obtained using the TGA method in air.

As can be seen from Figure 4, a noticeable thermal-oxidative degradation of the F-2 polyarylate melt in air begins at a temperature above 420°C, a 5% sample weight loss is recorded at 456.3°C. The decomposition of the sample proceeds in two stages and practically does not lead to the formation of coke.

The two-stage thermal-oxidative process is obviously explained by the fact that at the first stage of decomposition of the polyarylate melt, carbon dioxide is split off and an intermediate heat-resistant product is formed, which later, at the second stage of decomposition, decomposes into low molecular weight products.

The high thermal and oxidative stability of F-2, shown by the TGA method, when the polymer melt begins to degrade above 420°C, made it possible to hope for a good thermal stability of the polymer during its processing in real conditions on processing equipment (granulator, injection molding machine or extruder). However, in the course of testing by the method of assessing the melt flow index (MFR), it was found that the temperature of the viscous state of the polymer is close to the temperature of thermal-oxidative degradation. In particular, it was found that the MFR of the F-2 melt with a reduced viscosity of 0.57 dl/g at $T = 340^{\circ}\text{C}$ is only 0.2 g/10 min, and that the reduced viscosity of the polymer after processing the powder into strands noticeably decreases (from 0.57 to 0.40 dl/g). In this regard, additional attention was paid to the practically important issue of processing the synthesized polyarylates from the melt and their thermal and oxidative stability.

The determination of the melt flow index for the synthesized polymers was carried out in air using a PTR-LAB-11 device. Table 1 shows the MFR for various polymers at 340°C and a load of 5 kg. As can be seen, in contrast to the base polyarylate F-2 PAR-PSU, block copolymers have significantly higher MFR values.

Using the F-230/30 block copolymer as an example, the dependence of the MFR on the melt temperature was determined (Fig. 5). The resulting curve is exponential, on average, an increase in temperature by 20°C doubles the MFR. Usually, on the basis of these data, the conditions for processing the thermoplastic are selected.

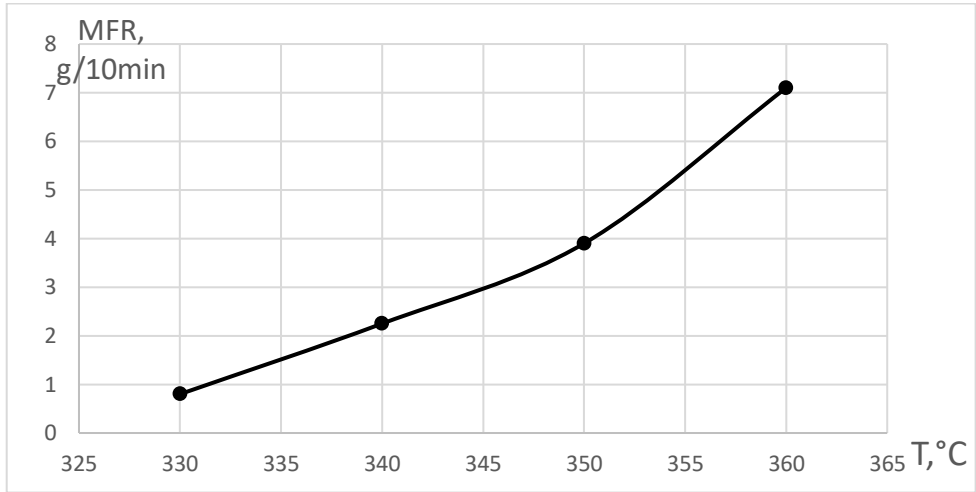


Fig. 5. Dependence of the melt flow index (MFR) on the melt temperature for F-230/30 with a reduced viscosity of 0.43 dl/g.

Figure 6 shows the dependence of the MFR value on the reduced viscosity of the F-230/30 block copolymer (BCP), from which it can be seen how strongly the molecular weight of the polymer affects the fluidity of its melt.

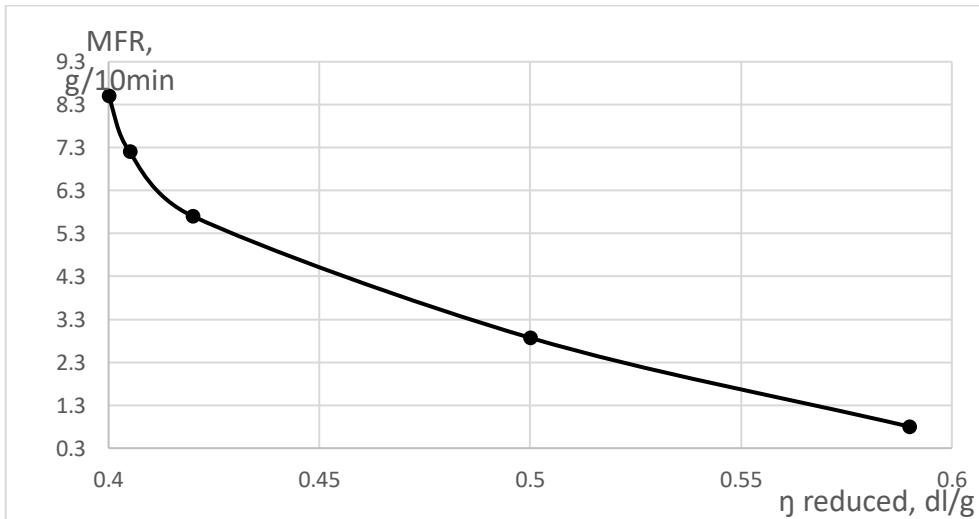
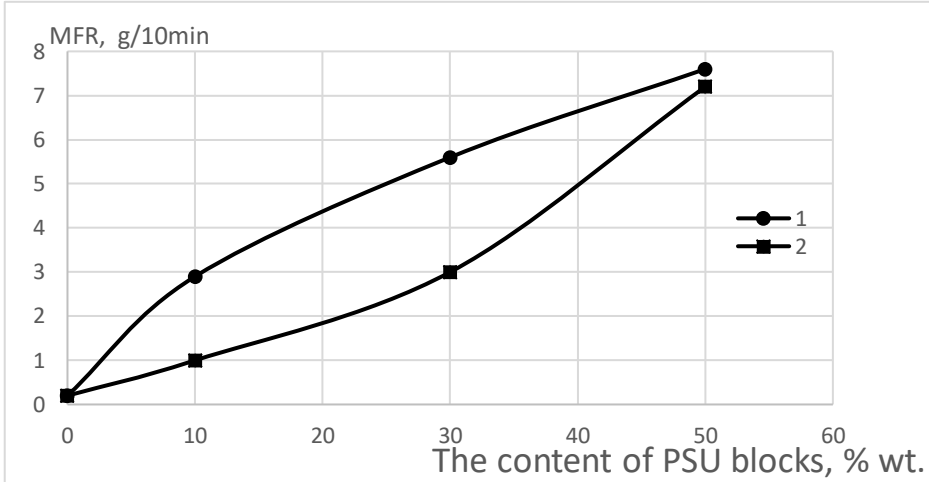


Fig. 6. Dependence of the melt flow index (MFR) F-230/30 on the reduced viscosity of the polymer.

Based on the data obtained, the influence of the degree of polycondensation of PSU blocks on the value of MFR was considered. Figure 7 shows such a dependence for two block copolymers F-230/10 and F-230/30, in which $x=10$ and 30 and the same content of PSU blocks (30 wt %). As can be seen, curve 1 for BCP with $x=10$ lies above curve 2 for BCP with $x=30$. This suggests that the plasticizing effect, that is, the ability to reduce the viscosity of the melt, is higher in the case of short PSU blocks with $MM=4500$. This is obviously due to the fact that, at the same weight content, high-molecular blocks of PSU with $x=30$ in BCP macromolecules are in a smaller amount compared to blocks with $x=10$, and, in addition, they tend to separate into an independent group for thermodynamic

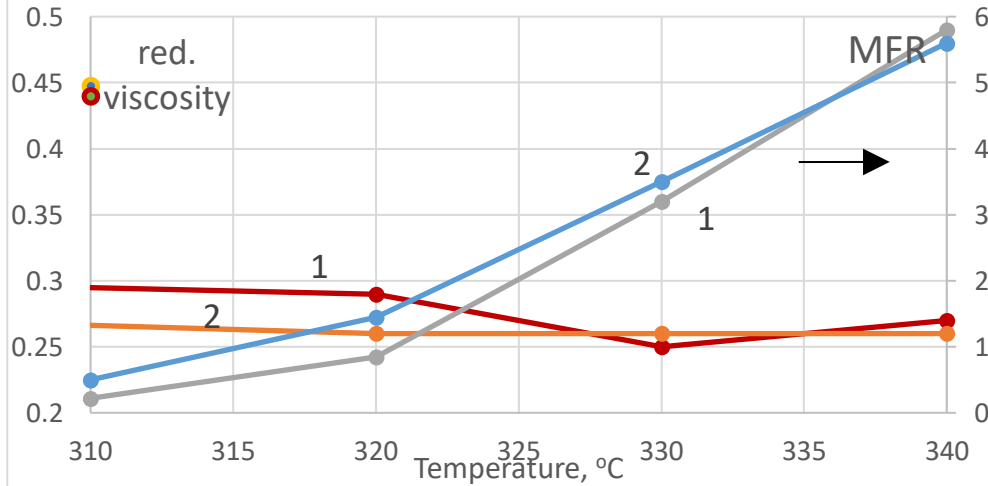
reasons. a phase that has a less plasticizing effect on the more rigid polyarylate matrix. Low molecular weight PSU blocks with $x=10$ form a mixed phase with PAR blocks, therefore, they more effectively reduce the viscosity of the PAR melt, since they have a lower T_c ($\approx 190^\circ\text{C}$) and are in a highly elastic state when the polyarylate phase is still in a glassy state ($T_c \approx 260^\circ\text{C}$).



1 - BCP with PSU blocks with $x=10$, 2 - BCP with PSU blocks with $x=30$.

Fig. 7. Dependence of MFR for PAR-PSU block copolymers on the content of PSU blocks

Figure 8 for two samples of PAR-PSU block copolymer F-230/10 with a similar molecular weight shows the dependences of the reduced viscosity of the polymers in strands (after determining the MFR) and the MFR values on the processing temperature. The decrease in the reduced viscosity of the BCP after holding the powder and melt in the chamber of the device and determining the MFR for 15-20 minutes is up to 36%. From this it follows that keeping the melt of PAR-PSU block copolymers at a temperature $70-100^\circ\text{C}$ higher than the T_c of polymers leads to a noticeable decrease in their MW, and hence their physical and mechanical properties.



1 - F-230/10 with an initial reduced viscosity of 0.45 dl / g
 2 - F-230/10 with an initial reduced viscosity of 0.44 dl / g

Fig. 8. Dependence of the reduced viscosity of the polymer in strands and MFR on the processing temperature of PAR-PSU block copolymer F-230/10.

4 Conclusion

Thus, the synthesized polyarylate-polysulfone block copolymers with a glass transition temperature of 240-260°C have improved processability from the melt, compared to F-2 carded polyarylate, but due to the ongoing destructive thermal-oxidative processes in the melt, their processing into products must be carried out by methods with a short thermal exposure cycle, for example, direct pressing, injection molding or injection molding with rapid cooling of the melt [17, 18].

5 Acknowledgement

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References

1. B. B. Korshak, C. B. Vinogradova, *Poliarilaty*. Moscow, Nauka, 72 (1964)
2. A. A. Askadskiy, *Fiziko-khimiya poliarilatov*. Moscow, Khimiya, 216 (1968)
3. S. V. Vinogradova, V. A. Vasnev, *Polikondensatsionnyye protsessy i polimery*, Moscow, Nauka, MAIK «Nauka/Interperiodika», 373 (2000)
4. L. B. Sokolov, *Osnovy sinteza polimerov metodom polikondensatsii*, Moscow, Khimiya, 264 (1979)
5. YU. A. Mikhaylin, *Termoustoychivyye polimery i polimernyye materialy*. Saint-Petersburg:, TSOP Professiya, 480 (2013)
6. K.-U. Byuller, *Teplo- i termostoykiye polimery*; Per. s nem. Vygodskogo, Moscow, Khimiya, 1056 (1984)
7. V. K. Kryzhanovskiy, *Tekhnicheskiye svoystva plastmass*. Saint-Petersburg, TSOP Professiya, 248 (2014)
8. A. Ye. Sorokin, M. V. Goroshkov, A. V. Naumkin, G. F. Zyuzina, V. A. Solov'yeva, A. P. Krasnov, *Vliyaniye sposoba i usloviy pererabotki na svoystva poliarilata, Aviatsionnyye materialy i tekhnologii*, 50(1), 32-38 (2018)
9. A. Ye. Sorokin, A. P. Krasnov, G. F. Zyuzina, V. B. Bazhenova, L. F. Klabukova, P. A. Shcheglov, *Vliyaniye gibkosti polimernoy tsepi na tribologicheskiye svoystva poliarilatov DV i FV, Voprosy materialovedeniya*, 4, 223-230 (2012)
10. T. Nobuhide. *Polyarylates «U-polymers»*, Japan Energy and Technology Intelligence, **6**, 69–72 (1986)
11. B. Y. Mapleston, *Polyesters: properties spectrum in broadening*, Modern Plastic International, **7**, 26–27 (1993)
12. A. I. Burya, O. P. Chigvintseva, *The influence of carbon fibre content on the tribological properties of polyarylate based somposites materials*, Science in China (Series A), **44**. 281–286 (2001)

13. A. Noshey, Dzh. Mak-Grat, Blok-sopolimery. Kriticheskiy obzor, Moscow, Mir, 478 (1980)
14. P. M. Valetskiy, I. P. Storozhuk, Blok-sopolimery polikondensatsionnogo tipa, *Uspekhi khimii*, 48(1), 75-114 (1979)
15. I. P. Storozhuk, P. M. Valetskiy, S. V. Vinogradova, V. V. Korshak, Polikondensatsionnyye puti sinteza blok-sopolimerov, V kn.: Sintez i svoystva blok-sopolimerov, Kiyev, 18-53 (1983)
16. I. P. Storozhuk, P. M. Valetskiy, Zakonomernosti obrazovaniya i svoystva poliarilensul'fonoksidov, V kn.: Itogi nauki i tekhniki. Khimiya i tekhnologiya vysokomolekulyarnykh soyedineniy, Tom 12, Moscow, VINITI, 127-176 (1978)
17. V. K. Kryzhanovskiy, M. L. Kerber, V. V. Burlov, A. D. Panimatchenko, Proizvodstvo izdeliy iz polimernykh materialov. SPb: Professiya, 464 (2004)
18. G. S. Golovkin, Proyektirovaniye tekhnologicheskikh protsessov izgotovleniya izdeliy iz polimernykh materialov, Moscow, Khimiya, KolosS, 399 (2007)
19. V. A. Nelyub, Adhesive-Strength Evaluation via the Pull-Out Method in a Binder—Elementary-Filament System at Various Treatments of Filaments. *Polym. Sci. Ser. D* **11**, 263–266 (2018) <https://doi.org/10.1134/S1995421218030127>
20. P. A. Belov, A. S. Borodulin, L. P. Kobets, et al., Kinetics of fiber impregnation by a binder. Gradient generalization of Navier–Stokes–Darcy equations. *Polym. Sci. Ser. D* **9**, 205–208 (2016) <https://doi.org/10.1134/S1995421216020039>