Super engineering polyesters: synthesis and performance characteristics

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Abstract. The method of polycondensation allows to produce aromatic polyesters of various composition and structure. In this study, the structure and performance characteristics of the synthesized polymers have been investigated. It has been explained that the resulted aromatic polyesters have appropriate performance characteristics for using them as the base for producing prepregs and engineering polymeric materials with desired parameters in order to replace essential parts made of metals and metal alloys with the similar plastic ones in various industrial equipment.

In general, the group of super-engineering, or high temperature thermoplastics includes the following aromatic polyesters: polyetherimides, polysulfones, polyethersulfones, polyether ether ketones (PEEK), polyphenylene sulfide (PPS), etc. [1] Due to their high heat, thermal, and fire resistance (where smoke emission is less than that of polytetrafluoroethylene (PTFE) or polycarbonates), UV resistance, and unique resistance to hot water and steam exposure, engineering plastic materials based on aromatic polyesters, as well as fusible powdered varnishes and enamels based on them, are used for insulation of wires and cables in aircraft manufacturing, military and nuclear industries, likewise in the manufacture of explosion-proof equipment for underground works, electronics, etc. [2—7].

In this case, to improve a technology for producing aromatic polyesters obtained by the nucleophilic substitution reaction shall mean to sophisticate each technological stage that is included in the full production cycle regarding these polymers and that, as a rule, significantly contributes to the final set of their performance characteristics.

One of the line to follow when enhancing the aromatic polyester synthesis technology is to reduce the number of stages within the production process, together with reducing the time of synthesis and mastering operational modes used to obtain the final product at lower temperatures.

Based on these considerations, three technological solutions regarding aromatic polyester synthesis were considered.

The first option is to obtain aromatic polyesters with the following structural formula shown in Figure 1. They are produced using the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligosulfones based on 4,4'-dihydroxy-2,2-diphenylpropane with degrees of condensation equal to 1-20.
Figure 1. Aromatic polyester obtained as a result of the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligosulfones based on 4,4'-dihydroxy-2,2-diphenylpropane with degrees of condensation equal to 1-20.

The polyester is synthesized in an organic solvent that dissolves the polyester itself. However, it does not dissolve the polycondensation product of low molecular weight. Thus, it is possible to separate the polymer solution from the solid synthesis product of low molecular weight.

Oligosulfone with n=1 and dichloroethane are transferred into the reactor equipped with a mechanical stirrer. While stirring, triethylamine is added there. Once the oligomer completely dissolved, the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene is transferred into the reaction flask. The reaction is carried out at room temperature for 1 hour. The reaction mass is then diluted with dichloroethane; the polymer solution is allowed to stay without stirring for 1 hour. Once separated, the lower clear solution (free from triethylamine hydrochloride), is drained and used as a finished varnish product; or it is swaged in the presence of isopropyl alcohol and filtered off without further purification, dried to constant weight, and used for its intended purpose. The structure of the synthesized compound was confirmed by IR spectroscopy. The spectra of the synthesized compounds were recorded using a Nicolet iS10 FTIR-spectrometer with a spectral range of 7 800 — 350 cm⁻¹ with a resolution of at least 0.4 cm⁻¹. The following absorption bands were detected in the IR spectra in the frequency range indicated as follows: 940–920 cm⁻¹ (ether bond), 1100 cm⁻¹, 1150 cm⁻¹, and 1290 cm⁻¹ (sulfonyl group), 980 cm⁻¹ (> C = CCl₂ — dichloroethylene group), the absorption bands of the C–O bond, consisting of two bands at 1266 cm⁻¹ and 1170 cm⁻¹. In the IR spectrum, the aromatic ring is detected as a moderate peak of C–H stretching vibrations around 3030 cm⁻¹, stretching vibrations of aromatic C—C bonds at 1600 cm⁻¹ and 1475 cm⁻¹, and intense absorption in the range of 800 – 690 cm⁻¹ due to deformation vibrations of C–H, which confirms the structure of the synthesized polyester shown in Figure 1.

The performance characteristics of the synthesized polyester are given in Table 1.

| Reduced viscosity, ηr, dL/g | Glass transition temperature, Tg °C | Thermal degradation temperature at different weight loss of the sample, °C | Oxygen index, % | Tensile strength, MPa |
|-----------------------------|-----------------------------------|-----------------------------------------------------------------|----------------|--------------------------|
| 0,84                        | 208                               | 398                                                            | 587            | 40,5                     | 79,6                      |

The second option is the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligoethersulfones based on 1,1-dichloro-2,2-di(n-
hydroxyphenyl) ethylene with degrees of condensation equal to 1-20 in accordance with the procedure given in [8] and resulted in producing of aromatic polyesters with the following structural formula shown in Figure 2.

\[ \text{Figure 2. Aromatic polyester obtained as a result of the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligo(ether-sulfones) based on 1,1-dichloro-2,2-di (n-hydroxyphenyl) ethylene with degrees of condensation equal to 1-20.} \]

The common process is as follows. Oligoether sulfone with \( n=1 \) and diphenyloxide (or ditolylmethane) are loaded into a reactor equipped with a mechanical stirrer and a nitrogen supply system. While stirring, triethylamine is added there. Once the oligomer completely dissolved, the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene is transferred into the reaction flask. While stirring, the temperature is raised up to 180°C within 0.5 hour and the reaction is carried out for 3 hours with intensive passage of nitrogen over the reaction mass. The polymer solution is diluted by pouring it into a mixer with heated tetrachloroethane being stirred. Then, the polymer is swaged in the presence of isopropanol. The polymer is washed twice with the same alcohol to eliminate traces of high-boiling solvent, and dried to constant weight at 150°C. The polymer does not contain any traces of low molecular weight polycondensation product.

The spectra of the synthesized compounds were recorded using a Nicolet iS10 FTIR spectrometer. The following absorption bands were detected in the IR spectra in the frequency range indicated as follows: 940–920 cm\(^{-1}\) (ether bond), 1100 cm\(^{-1}\), 1150 cm\(^{-1}\), and 1290 cm\(^{-1}\) (sulfonyl group), 980 cm\(^{-1}\) (> C = CC\(_2\) — dichloroethylene group), the absorption bands of the C–O bond, consisting of two bands at 1266 cm\(^{-1}\) and 1170 cm\(^{-1}\). In the IR spectrum, the aromatic ring is detected as a moderate peak of C–H stretching vibrations around 3030 cm\(^{-1}\), stretching vibrations of aromatic C–C bonds at 1600 cm\(^{-1}\) and 1475 cm\(^{-1}\), and intense absorption in the range of 800–690 cm\(^{-1}\) due to deformation vibrations of C–H, which confirms the structure of the synthesized polyester shown in Figure 2.

Sublimed triethylamine hydrochloride is deposited on the reactor lid surface and is ready for use as intended. The performance characteristics of the produced polyester are given in Table 2.

| Reduced viscosity, \( \eta_r \), dL/g | Glass transition temperature, \( T_g \) °C | Thermal degradation temperature at different weight loss of the sample, °C | Oxygen index, % | Tensile strength, MPa |
|----------------------------------|---------------------------------|---------------------------------|----------------|---------------------|
| 0,97                             | 223                             | 370                             | 456            | 43,0                | 86,8                |

The third option is the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligosulfones based on phenolphthalein with degrees of
condensation equal to 1-20. The process results in producing of aromatic polyesters with the following structural formula shown in Figure 3.

\[
\begin{align*}
\text{Figure 3. Aromatic polyester obtained as a result of the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligosulfones based on phenolphthalein with degrees of condensation equal to 1-20.}
\end{align*}
\]

The common process is as follows. Oligosulfone with \(n=1\) and ditolylmethane are transferred into the reactor equipped with a mechanical stirrer. While stirring, triethylamine is added there. Once the oligomer completely dissolved, the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene is transferred into the reaction flask. While stirring, the temperature is raised up to 60°C and the reaction is carried out for 1 hour. Then, the temperature is raised up to 200-220°C and the reaction is carried out for another 1 hour. The polymer solution is poured into a mixer with heated tetrachloroethane being stirred. Then, the polymer is swaged in the presence of isopropanol. The polymer is washed twice with the same alcohol to eliminate traces of high-boiling solvent, and dried to constant weight at 150°C. The synthesized polymer does not contain any traces of low molecular weight polycondensation product.

The spectra of the synthesized compounds were recorded using a Nicolet iS10 FTIR spectrometer. The following absorption bands were detected in the IR spectra in the frequency range indicated as follows: 940–920 cm\(^{-1}\) (ether bond), 1100 cm\(^{-1}\), 1150 cm\(^{-1}\), and 1290 cm\(^{-1}\) (sulfonyl group), 980 cm\(^{-1}\) (\(\text{> C = CCl}_2\) — dichloroethylene group), the absorption bands of the C–O bond, consisting of two bands at 1266 cm\(^{-1}\) and 1170 cm\(^{-1}\). In the IR spectrum, the aromatic ring is detected as a moderate peak of C–H stretching vibrations around 3030 cm\(^{-1}\), stretching vibrations of aromatic C–C bonds at 1600 cm\(^{-1}\) and 1475 cm\(^{-1}\), and intense absorption in the range of 800–690 cm\(^{-1}\) due to deformation vibrations of C–H, which confirms the structure of the synthesized polyester shown in Figure 3.

Sublimed triethylamine hydrochloride is deposited on the reactor lid surface and is ready for use as intended. Synthesis can be also performed in the presence of diphenyloxide. The performance characteristics of the produced polyester are given in Table 3.

**Table 3.** Some performance characteristics of an aromatic polyester obtained as a result of the equimolar mixture of terephthaloyl chloride and 1,1-dichloro-2,2-di (4-carboxyphenyl) ethylene interacting with oligosulfones based on phenolphthalein with degrees of condensation equal to 1-20.

| Reduced viscosity, \(\eta_r\), dL/g | Glass transition temperature, \(T_g\) °C | Thermal degradation temperature at different weight loss of the sample, °C | Oxygen index, % | Tensile strength, MPa |
|----------------------------------|---------------------------------|---------------------------------|---------------|---------------------|
| 0.63                             | 264                             | 377                             | 414           | 41.0                | 73.7               |

As a result of the analysis performed regarding characteristics of the synthesized aromatic polyesters presented above, it was revealed that all three aforementioned synthesis options can be used to obtain materials, characteristics of which determine their reference to super engineering plastic. The main
advantage of the obtained aromatic polyesters is their high manufacturability, a relatively low synthesis time compared to the polysulfone synthesis by the method of high-temperature polycondensation (at least 6 hours for the latter), and lower temperature modes at synthesis. Available domestic raw materials also determine the viability of the proposed methods in the context of addressing import substitution issues.

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