Polymer composites based on oligosulfones

R Ch Bazheva¹, Z I Inarkieva², Z Kh Sultygova² and A M Kharaev¹

¹Kabardino-Balkarian State University named after Kh.M. Berbekov, Nalchik, Chernyshevsky street, 173, Russia
²Ingush state University, Nazran, I.B. Zyazikov, 7, Russia

E-mail: r.bazheva@mail.ru

Abstract. Halogen-containing oligosulfones based on 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 4,4'-dichlorodiphenylsulfone on various degrees of condensation were synthesized in the solution by high-temperature polycondensation. Using the obtained oligosulfones, we conducted a physical modification of industrial bisphenol A polycarbonate in a wide range of concentrations. Physical and mechanical properties of composites are investigated. The compatibility of the obtained oligosulfones with polycarbonate was studied using viscometry, differential scanning calorimetry, and probe microscopy. It was shown that the introduction of oligosulfones into the polycarbonate matrix promotes an increase in the glass transition temperature, found by differential scanning calorimetry, at 3 to 200 °C, depending on the composition, the composites have good dielectric and technological properties. The temperature dependences of the dielectric properties of PCs and PC-based composites with different oligosulfone content are characterized by the presence of a single.

1. Introduction

Recently, a noticeable expansion of the applications of rigid chains of glassy polymers characterized by low resistance to cracking is largely due to the development of composites based on them. Bisphenol A (PC) polycarbonate, along with a complex of valuable properties, has a number of disadvantages, which significantly limit its fields of application. In particular, high internal (residual) stresses, which lead to cracking of products during operation, slow-going relaxation processes, low adhesion, low resistance to alkaline environment, high melt viscosity, and hence the processing difficulty associated with this [1-5].

Despite numerous scientific studies on modification of polycarbonate, its assortment is insignificant. Numerous attempts to modify polycarbonate with low-molecular compounds did not give positive results. Over 50 compounds of various classes have been tested. However, to date, modification of polycarbonate in order to improve a number of performance characteristics is relevant. In this direction, the most promising way is the physical modification, i.e. development of compositions based on polycarbonate and various modifiers. In addition, it is known that the introduction of halogen atoms into a polymer contributes to an increase in fire resistance [6-11].

In order to create polymer composites based on polycarbonate, oligosulfones based on 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 4,4'-dichlorobiphenyl sulfone were synthesized and some properties of the composites were studied.

2. Experimental
In a three-necked flask equipped with a mixer, a reflux condenser with a Dean-Stark trap, a gas supply bubbler and a thermometer, are entered 5.62281 g (0.02 mol) 1,1-dichloro-2,2-di-(4-hydroxyphenyl)ethylene, 40 ml of dimethyl sulfoxide (DMSO) and 30 ml of toluene. When stirring, nitrogen is passed in and the temperature is raised to 70 °C. After complete dissolution of 1,1-dichloro-2,2-di-(4-hydroxyphenyl)ethylene, 3.98406 ml of 10.04 normal solution of sodium hydroxide is added. The temperature is raised to 140-145 °C and the azeotropic toluene-water mixture is distilled off until the water is completely removed. The reaction mass is cooled to 40-50 °C and 2.87294 g (0.01 mol) of 4,4’-dichlorodiphenylsulfone is added. The reaction is carried out at 140-145 °C for 2 hours. The resulting mass is diluted with 10 ml of DMSO and precipitated into acidified distilled water. The precipitate formed is filtered off and washed with distilled water until the filtrate is negatively reacted with chlorine ion. The resulting oligoether sulfone is dried at 100 °C under vacuum for 24 hours.

Similarly, by changing the ratio of 1,1-dichloro-2,2-di-(4-hydroxyphenyl)ethylene and 4,4’-dichlorodiphenylsulfone, oligosulfones of various degrees of condensation were synthesized. In all cases, the amount of 1,1-dichloro-2,2-di-(4-hydroxyphenyl)ethylene is 1 mol more than the amount of 4,4’-dichlorodiphenylsulfone.

Ubbelohde viscometer was used to determine the intrinsic viscosity.

The concentration of the solutions was determined by the formula:

$$C = \frac{a V_1 \cdot 100}{V (V_1 + V_2)}$$

where $a$ is the polymer sample weight, g;
$V_1$, $V_2$ - respectively, the volumes of the solvent consumed to prepare the solution, the initial solution placed in the viscometer, and the solvent added to the viscometer upon dilution, ml.

Study of the surface of the samples on a scanning probe microscope. The sample is mounted on a polycore substrate 20x25x10 mm in size and then attached to the scanner in the horizontal position. A measuring head with removable probes is installed above the sample. Rapid supply of the probe is carried out by a stepper motor in about 1-3 minutes. The measurement time depends on the speed and field of the scan and is approximately 0.5-5 minutes.

Melt indices of polymers were measured by a capillary viscometer with a constant piston at a temperature of 220-280 °C. Every 5 minutes, the extruded melt was cut out of the capillary with a knife and weighed.

The test result was taken as the arithmetic average of two determinations on three pieces of material, the difference in weight, between which did not exceed 5%. The melt flow rate (melt index) was calculated by the formula:

$$i = \frac{10 \cdot Q}{t}$$

where $Q$ is the weight of the polymer, g;
$t$ - time extrusion, min.

Results and discussions
Oligosulfones based on 1,1-dichloro-2,2-di-(4-hydroxyphenyl)ethylene and 4,4’-dichlorodiphenylsulfone were synthesized by nucleophilic substitution in an aprotic dipolar solvent dimethyl sulfoxide at a temperature of 140-145 °C for 2 hours. Toluene was used to form an azeotrophic mixture. The resulting halogen-containing oligosulfone had the formula:
where n = 1-20.

The main properties of these oligosulfones are described in detail in [12].

Unambiguous methods of studying the compatibility in polymer-plasticizer systems, polymer-polymer find difficult. In the block state, compatible polymers form transparent films and fibers, which in a phase contrast microscope with high magnifications or in an electron microscope do not show a heterogeneous structure under any methods of contrasting. In addition, blends of compatible polymers should have the same glass transition temperature, regardless of the research methods. These criteria are, in principle, unambiguous criteria for compatibility, but in practice there may be some difficulties in using them. Particularly, incompatible polymers form transparent films if the refractive indices of both polymers are the same or if the refractive indices, although different, but the polymers can form a two-layer film that appears transparent when it is obtained by evaporating the solvent from the polymer solution. Such cases are not particularly difficult for analysis, since transparent films from blends of incompatible polymers are characterized by two glass transition temperatures corresponding to the glass transition temperature of the components, if the latter differ sufficiently and can be determined using the method of investigation used.

The above makes it critical to refer to any measurements on polymer blends, since it is very difficult to determine if the mixture is in an equilibrium state. Usually, without evidence, it is assumed that a film from a mixture of polymers obtained from a solution is in a more equilibrium state than samples obtained by mixing polymers in a block state. Everything said predetermined the need to determine the compatibility of polycarbonate with the obtained oligosulfones.

To determine the compatibility, as well as to determine the nature of the distribution of the synthesized oligosulfones in the PC matrix, we used the method of scanning probe microscopy.

Researches have shown, that properties of a surface depends on its structure, as illustrated in figure 1. However, in samples with a modifier content of up to 10% by weight, there is good compatibility between the components. Oligosulfones are evenly distributed in the polycarbonate matrix. The particle size of the modifier is from 0.31 to 3.13 microns and depends on the composition. Later, oligosulfone with a degree of polycondensation n = 5 (OC-5C-2) was used to modify PC.

![Figure 1](image)

Figure 1. SPM photographs of a PC composition with OC-5C-2, containing 5 (a) and 10 (b)% of the weight.

X-ray phase analysis showed that all compositions of composites are amorphous.
To determine the compatibility of the oligosulfones obtained, we also used the viscometric method. The studies were carried out in the Ubbelohde viscometer at a temperature of 25 °C. At this temperature, polymer-solvent systems containing from 1 to 10 weight % of oligosulfone were investigated. Methylene chloride was used as a solvent.

It turned out that for these systems the maximum compatibility is observed at a ratio of 95% by weight. PC and 5% of the weight. OS-5C-2. The data are presented in figure 2.

The glass transition temperatures of composites found by differential scanning calorimetry are shown in figure 3. As can be seen from the figure, with an increase in the content of oligosulfone in the composition, Tg increases. An increase in the glass transition temperature probably indicates the interaction of the filler with the matrix.

For the compositions obtained, the temperature dependences of the dielectric constant (ε ′) and the tangent of the dielectric loss angle were studied at a frequency of 104 Hz. The values of the dielectric constant of all the investigated samples of composites are ~ 3–3.6 and are stable in the temperature range from 20 to 200°C. Curves of dielectric properties as a function of temperature, for PCs and PC-based composites with different oligosulfone content, have the same dielectric loss tangent. The values of ε ′ for PC and all composites do not depend on the composition and, within the limits of error, coincide and correspond to values of 2.4-2.5.

Comparison of melt indices of the original PC and composites based on them (figure 4) showed that the introduction of small amounts of OC-5C-2 in PC significantly affects the melt flow rate (MFR) of these composites. Thus, the introduction of only 1-3% of the weight OS increases the PTR PC 1.5-2 times. Moreover, the introduction of small amounts is more effective - up to 5% by weight OS.

![Reduced viscosity, DL/g](image1)

**Figure 2.** The dependence of the reduced viscosity of the solutions of composites from the content of OC-5C-2.
The content of oligosulfone OS-5C-2, % of the mass

Figure 3. The dependence of the glass transition temperature of composites on the content of OS-5C-2.

Figure 4. The dependence of the melt flow index on the content of OC-5C-2 at a processing temperature of 260°C (▲) and 280°C (●).

All the composites obtained are dissolved in inexpensive and easily volatile solvents, for example, in chloroform, methylene chloride, dioxane, dimethylformamide, etc. This will allow their processing into film products from solutions, for example, in available and volatile methylene chloride.

Conclusion
Composite polymeric materials based on aromatic polycarbonate bisphenol A synthesized on the basis of 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 4,4'-dichloro diphenyl sulfone oligosulfones of various molecular weights were developed. The study of some properties of PC compositions with oligosulfone showed that these OS can be used to improve some of the performance properties of polycarbonate.

The compatibility of obtained OS with industrial polycarbonate has been studied by various methods. It was shown that the introduction of oligosulfones into the polycarbonate matrix promotes an increase in the glass transition temperature by 3 to 200 °C, depending on the composition. The resulting composites have good dielectric properties.
Comparison of the flow rates of PC melts and composites under various processing conditions allows us to conclude that these composites can be processed by extrusion and injection molding under milder conditions than bisphenol A polycarbonate.

References
[1] Amerik V V, Radzinsky S A, Zolkina I Yu, Andreeva T I, Simonov-Emelyanov I D, Fedotova T I and Levchuk A V 2013 Polycarbonate - market analysis and development prospects (Plastics vol 11) pp 10–13
[2] Ponomareva V T and Likhacheva N N 2000 State and prospects of structural thermoplastics market (Plastics vol 6)
[3] Bolotina I M and Chebotarev V P 2003 Development of research in the field of chemistry and technology of aromatic polysulfones (Plastics vol 11) pp 3–7
[4] Alperstein D, Knani D, Borchmann N, Spekowius M and Hopmann C 2014 Prediction of environmental stress cracking in polycarbonate by molecular modeling (Polymers for Advanced Technologies vol 25) I 12
[5] Jinhua Wang and Gregory B. McKenna 2015 Viscoelastic properties of ultrathin polycarbonate films by liquid dewetting (Journal of Polymer Science Part B: Polymer Physics vol 53) I 22
[6] Bazheva R Ch, Kharaev A M and Mikitaev A K 2006 Temperature transitions in polycarbonate-polytetramethylenoxide block copolymer resins Polymers, Polymer Blends, Polymer Composites and Filled Polymers. Syntesis, Properties, Application (Nova Science Publishers, Inc. New York) pp. 115–120
[7] Kharaev A M, Bazheva R Ch., Chaika A A and Barokova E B 2006 Chemical modification of polycarbonate (review) (Plastics vol 9) pp 25–30
[8] Bazheva R Ch, Bashorov M T, Kharaev A M and Mikitaev A K 2007 Study of temperature transitions in polycarbonate and polycarbonate-polytetramethylene oxide block copolymers (Chemical industry today vol 8) pp 35–40
[9] Bazheva R Ch, Kharaev A M, Bazhev A Z, Inarkieva Z I and Beslaneeva Z L 2016 Fire-resistant copolycarbonates (Plastics vol 5) pp 26–30
[10] Bazheva R Ch, Kharaev A M Inarkieva Z I and Beslaneeva Z L 2017 Copolycarbonates containing dichloroethylene groups in the main chain (Plastics vol 3) pp. 32–35
[11] Kharaev A M Bazheva R Ch and Chaika A A 2006 Composite materials based on polycarbonate (Plastics vol 8) pp 26–31
[12] Barokova E B, Haraev A M, Bazheva RC and Haraeva RA 2010 Oligosulfones on the basis of 1,1-dichlor-2,2-di(4-oxyphenyl)ethylene and 4,4′-dichlorodiphenylsulfone obtained by high temperature polycondensation Handbook of Condensed Phase Chemistry pp 233–236

Acknowledgments
The reported study was funded by RFBR according to the research project № 18-29-18063.