Polymer composites based on halogen-containing oligoethers

R Ch Bazheva 1, A S Borodulin2, A N Kalinnikov2 and A M Charaev1

1Kabardino-Balkaria State University named after Kh. M. Berbekov, Nalchik, Chernyshevsky street, 173, Russian
2Intersectoral Engeneering Center “Composites of Russia”, Bauman Moscow State Technical University, Moscow

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. Conducted a physical modification of industrial polycarbonate bisphenol A oligosulfones obtained in a wide concentration range. 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 20 °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 loss on the dielectric loss tangent dependences on the temperature.

Keywords: oligosulfone, polycarbonate, viscometry, differential scanning calorimetry, compatibility.

Introduction
Recently, a noticeable expansion of scopes of rigid chain glassy polymers characterized by low resistance to cracking is largely due to the development of compositions 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 basic media, high melt viscosity, and hence the processing difficulty associated with this. In addition, the use of PC in construction also determines the increased requirements for flammability [1-12].

Despite numerous scientific studies on the modification of polycarbonate, the range of hand-made is small. 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 [13–37].

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.

Experimental
This work is licensed under the Creative Commons Attribution 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by/3.0/ or send a letter to Creative Commons, PO Box 1866, Mountain View, CA 94042, USA.
In a three-necked flask equipped with a stirrer, a reflux condenser with a Dean-Stark trap, a gas supply bubbler and a thermometer, 5.62281 g (0.02 mol) 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene are introduced, 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 n is added. sodium hydroxide solution. The temperature is raised to 140-145 °C and the azeotropic toluol-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.

The yield of light yellow product 97.5%; softening temperature 120-1220C; the content of the basic substance is not less than 99.9%; sodium chloride in the amount of not more than 0.05-0.1% is allowed as an impurity; they say m. = 776.52084; elemental composition, %: C = 61.87 / 61.75; H = 3.37 / 3.40; O = 12.36 / 12.31 (calculated in the numerator, found in the denominator). The content of hydroxyl groups - 4,38 / 4,431 (in the numerator, found in the denominator). In the IR spectra, the absorption bands in the region, cm – 1: 940 – 920 (ether bond), 1100, 1150, and 1290 (sulfonyl group), 980 (> C = CCl2 group), 3600 – 3300 (hydroxyl Group).

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. Solutions with relative viscosity = 1.1 were diluted for subsequent measurements of viscosity in such a way that the intervals of the obtained concentrations were approximately the same, and the η of the most diluted solution should not be less than 1.1. These limits of measurement specific viscosity η = 1.1-1.5 correspond to concentrations of polymer solutions for which the dependence of [ŋ] on the velocity gradient of fluid outflow from the capillary is not observed and with dilution there is no deviation from the linear dependence of ηsp / C or ln ηrel. / C from S.

Next, 0.75 is successively added to the viscometer; 1.00; 1.25; 2.00 ml and 4.00 ml of the solvent, and after each dilution the solution expiration time was measured. For the solvent and each polymer solution, the average value of the expiration time from three measurements was determined.

The concentration of the solutions was determined by the formula:

\[ C = \frac{a \cdot V}{V \cdot V_1 + V_2} \] (1)

where: a is the polymer sample, g; V, V1, V2 - 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.

On the basis of the data obtained, η / η0 = ti / t0, ηud = (ti-t0) / t0 (where ti is the expiration time of the polymer solution, s; t0 is the expiration time of the solvent, s), ηud were calculated. / C and t0 (η / η0 / C). Then built a graphical dependence ηud. / C or t0 (η / η0 / C) from C. Extrapolation of straight lines to the zero concentration of the polymer cuts an [ŋ] segment on the ordinate axis.

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 capillary viscometry on an IITT-M cargo capillary viscometer with a constant piston load of 21.19 N and a temperature of 220-280 °C. Every 5 min. the extruded melt was cut from 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 mass, between which did not exceed 5%. The melt flow rate (melt index) was calculated by the formula:

\[ i = \frac{10Q}{t} \]  

(2)

where: Q is the mass 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 as azeotropically. The resulting halogen-containing oligosulfone had the formula:

\[ \text{O} \]

\[ \text{O} \]

\[ \text{H} \]

\[ \text{Cl}_2 \]

\[ \text{C} \]

\[ \text{O} \]

\[ \text{S} \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{Cl}_2 \]

\[ \text{OH} \]

where \( n = 1-20 \).

The main properties of these oligosulfones are described in detail in [29-36].

Unambiguous methods for studying compatibility in polymer-plasticizer systems, polymer-polymer is not easy to find. 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 research methods. These criteria are, in principle, unambiguous criteria for compatibility, but in practice there may be some difficulties in using them. In particular, 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 temperatures 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.

Studies have shown that the nature of the surface composition depends on the composition. 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 depends on the composition of the composition and is for the sample containing from 0.31-3.13 microns.

Later, oligosulfone with a degree of polycondensation \( n = 5 \) (OC-5C-2) was used to modify PC.

All this is well illustrated in Fig. 1.
Fig. 1. SPM photographs of a PC composition with OC-5C-2, containing 5 (a) and 10 (b)% of the mass.

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 a given temperature, polymer-solvent systems (methylene chloride) were studied for composites containing various mass% oligosulfone, i.e. PC samples were injected from 1 to 10% of the mass. oligomer. It turned out that for these systems the maximum compatibility is observed at a ratio of 95% by weight. PC and 5% of the mass. OS-5C-2. The data are presented in Fig. 2.

Fig. 2. The dependence of the reduced viscosity of the solutions of composites from the content of OC-5C-2

The glass transition temperatures of composites found by differential scanning calorimetry are shown in Fig. 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.
Fig. 3. The dependence of the glass transition temperature of composites on the content of OS-5C-2

For the compositions obtained, the temperature dependences of the dielectric constant ($\varepsilon'$) 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 2000 °C. 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 loss on the dielectric loss tangent dependences on the temperature. The values of $\varepsilon'$ 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 (Fig. 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 mass. OS increases the PTR PC 1.5-2 times. Moreover, the introduction of small amounts is more effective - up to 5% by weight. OS.

Fig. 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 obtained composites easily dissolve in such easily volatile and relatively non-expensive solvents, such as 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 and 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 oligosulfones 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.

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

References
[1] Amerik V V, Radzinsky S A, Zolkina I Yu, Andreeva T I, Simonov-Emelyanov I D, Fedotova T I, Levchuk A V 2013 Polycarbonate - market analysis and development prospects, Plastic materials 11 10-13.
[2] Ponomareva V T, Likhacheva N N 2000 State and prospects of structural thermoplastics market. Plast. Masses 6
[3] Bolotina L M, Chebotarev V P 2003 Development of research in the field of chemistry and technology of aromatic polysulfones, Plast. Masses 11 3-7
[4] Alperstein D, Knani D, Borchmann N, Spekowius M, Hopmann C 2014 Prediction of environmental stress cracking in polycarbonate by molecular modeling Polymers for Advanced Technologies 25
[5] Ye Liu, Hui Zhou, Jia-Zhi Guo, Wei-Min Ren, Xiao-Bing Lu 2017 Completely Recyclable Monomers and Polycarbonate: Approach to Sustainable Polymers, Angewandte Chemie 129
[6] Wang J, McKenna G B 2015 Viscoelastic properties of ultrathin polycarbonate films by liquid dewetting, Journal of Polymer Science Part B: Polymer Physics 53
[7] Bagotia N, Choudhary V, Sharma D K 2018 A review on the mechanical, electrical and EMI shielding properties of carbon nanotubes and graphene reinforced polycarbonate nanocomposites, Polymers for Advanced Technologies 29
[8] Lee B Y, Park J Y, Kim Y C 2015 Effect of polycarbonate structure and reduction time on graphene oxide dispersion, Polymers for Advanced Technologies 26
[9] Militskova E A, Artemov S V, Andreeva T I, Kolerov A S 1991 Properties, processing and application of a number of complex aromatic polyesters, Production and processing of plastics and synthetic resins, m Niitekhim 65
[10] 2010 Polycarbonate, Application in modern construction (SPb: NOT) 200
[11] Wu X, Yang B, Zhuang S 2018 A novel polycarbonate composite for waveguides, Journal of Applied Polymer Science 135
[12] Sacher E 1995 Secondary structural motions in polycarbonate. II. Identification of the motions and their relation to impact strength, J. Macromol. Sci. 11 403-410.
[13] Bazheva R Ch, Kharayev A M, Mikitayev A K 2006 Temperature transitions in polycarbonate-polytetramethylenoxoide block copolymer resins, Polymers, Polymer Blends, Polymer Composites and Filled Polymers. Syntesis, Properties, Application, Nova Science Publishers pp. 115-120.
[14] Kharaev A M, Bazheva R Ch, Chaika A A, Barokova E B 2006 Chemical modification of polycarbonate (review), Plastics 9 25-30
[15] Bazhev R C, Kharaev A M, Storozhuk I P 2007 Synthesis and some properties of polycarbonate-polyalkylene oxide block copolymers, News of universities. North Caucasus region. Natural Sciences 3 pp.42-44.
[16] Bazheva R Ch, Bashorov M T, Kharaev A M, Mikitaev A K 2007 Study of temperature transitions in polycarbonate and polycarbonate-polytetramethylene oxide block copolymers, Chemical industry today 8 p. 35-40.
[17] Bazheva R Ch, Kharaev A M, Bazhev A Z, Inarkieva Z I, Beslaneeva Z L 2016 Fire-resistant copolycarbonates, Plastics 5-6 p. 26-30.
[18] Kharaev A M, Bazheva R Ch, Lukozhev R V 2014 Synthesis of polyesters based on oligosulfones containing a dichloethylene group, News of the Kabardino-Balkarian State University 6 62-68
[19] Bazheva R Ch, Kharaev A M, Inarkieva Z I, Beslaneeva Z L 2017 Copolycarbonates containing dichloroethylene groups in the main chain, Plastics 3-4 Pp. 32-35.
[20] Kharyayev A M, Bazheva R C, Chayka A A 2006 Polymers, Polymer Blends, Polymer Composites and Filled Polymers: Synthesis, Properties and Applications 115-120.
[21] Kharaev A M, Mikitaev A K, Bazheva R Ch and others 2006 Modified flame retardant aromatic polyesters, Chemical industry today 8 24-28.
[22] Kharaev A M, Bazheva R Ch, Chaika A A 2006 Composite materials based on polycarbonate Plastics 8 26-31.
[23] Kyarov A A, Bazhev R Ch, Kharaev A M 2010 Compatibility study of polycarbonate-based composite materials. In the collection: New polymer composite materials (Nalchik) p. 34-38.
[24] Zapornikov V A, Osipchik V S, Redkina A A 2014 Influence of modifying additives on manufacturability and physicomechanical properties of polycarbonate // News of higher educational institutions. Series: Chemistry and Chemical Technology 57 65-67.
[25] Petrova G N, Rumyantseva T V, Beyder E Ya 2013 The effect of modifying additives on the flame-retardant properties and manufacturability of polycarbonate, Trudy VIAM 6 6
[26] Simonov-Emelyanov I D, Yurkin A A, Surikov P V, Shembel N N, Andreeva T I, Radzinsky S A, Zolkina I Yu, Amerik V V 2015 Evaluation of the effectiveness of the action of rheological additives in the processing of polycarbonate, Plastics 7-8 pp. 37-40.
[27] Žubkova O A, Lapova T V, Gorlenko N P, Sarkisov Yu S, Konoplyansky D A, Reznikov I V, Smirnov A P 2015 Improving the sustainability of polycarbonate products to the action of ultraviolet radiation, Tomsk State University of Architecture and Civil Engineering Bulletin 6 (53) Pp. 135-140.
[28] Kharaev A M, Bazheva R Ch, Chaika A A 2007 Composite materials based on polycarbonate (review), International Polymer Science and Technology. 34 10 27-33
[29] Kharaev A M, Bazheva R C, Barokova E B 2008 Fireproof aromatic block copolymer resin on the basis of 1,1-dichlor-2,2 di(n-oxyphenyl) ethylene, Modern Tendencies in Organic and Bioorganic Chemistry: Today and Tomorrow (New York) 219-222.
[30] Barokova E B, Haraev A M, Bazheva R C, Haraeva R A 2010 Oligosulfons on the basis of 1,1-dichlor-2,2-di(4-oxyphenyl)ethylene and 4,4'-dichlorodiphenylsulfone obtained by high temperature polycrystallization, Handbook of Condensed Phase Chemistry 233-236.
[31] Nelyub V A 2016 A study of the microstructure of dressed glass fibers, Polymer Science - Series D 9 pp. 96-100
[32] Nelyub V A 2015 Determination of adhesion interaction between carbon fiber and epoxy binder, Polymer Science - Series D 8 (1) pp. 6-8.
[33] Nelyub V A, Borodulin A S, Kobets L P, Malysheva G V 2016 Capillary hydrodynamic of oligomer binder, Polymer Science – Series D 9(3) pp.322-325
[34] Nelyub V A, Borodulin A S, Kobets L P, Malysheva G V 2016 A study of structure formation in a binder depending on the surface microrelief of carbon fiber, *Polymer Science – Series D* 9(3) pp.286-289.

[35] Borodulin A S, Kalinnikov A N, Bazheva R C 2018 Receipt and investigation of performance characteristics of super constructions polyesters, *International Journal of Mechanical Engineering and Technology* 9 (13) pp. 1117-1127.

[36] Borodulin A S, Kalinnikov A N, Bazheva R C 2018 Synthesis and properties of aromatic polyethersulfones, *IJMET* 9 pp. 1109–1116.

[37] Borodulin A S, Kalinnikov A N, Kharaev A M 2018 New Polymeric Binders for the Production of Composit, *Materials today:proceedings* 11 pp. 1107–1111