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ON THE PLASTICIZATION OF HIGHLY-FILLED POLYPHENYLENE SULFONE

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Abstract. The paper presents the results of a study of the plasticizing effect of oligomers based on 4.4′-dihydroxydiphenyl and 4.4′-dichlorodiphenylsulfone, as well as 4.4′-dihydroxydiphenylpropane (Diane) and 4.4′-dichlorodiphenylsulfone on polyphenylene sulfone and highly filled composites on its basis. It was established that these oligomers are quite effective plasticizers during processing, increasing the melt flow rate and retaining elastic-strength properties at concentrations up to 20%. At the same time, they have high heat resistance and the necessary compatibility with the matrix polymer.

Keywords: polyphenylene sulfone, composite material, glass fiber, carbon fiber, plasticization, oligomer

1. Introduction

The expansion of the field of application of high performance polymers in the technique requires its modification with the use of various fillers. Most often, the most affordable and effective reinforcing fillers, such as glass and carbon fibers (GF and CF), are used for these purposes [1].

The introduction of fillers with a high aspect ratio, i.e. a high ratio of longitudinal length to diameter, as a rule, along with an increase in mechanical characteristics, leads to a significant increase in melt viscosity and a decrease in manufacturability [2,3]. This is especially noticeable when processed by casting methods and 3D printing, where higher demands are placed on rheological properties material. In the case of 3D printing, the bond strength of the threads in the sample and, as a result, its mechanical properties depend on the fluidity of the material melt [4]. Proceeding from this, when creating highly filled materials, the problem of plasticization is acute, i.e. reduce melt viscosity during processing.

Industrial plasticizers and lubricants, such as diester, phosphorus-containing plasticizers, and polyesters (polyester plasticizers) [5] have low thermal properties (boiling points, flash points, etc.) [6] and are mainly used for standard or engineering plastics [7].

For the plasticization of high performance polymers, in particular, polyphenylene sulfone (PPSU), in addition to compatibility, chemical inertness and other requirements, plasticizers should have high boiling points and decomposition [8], since the processing temperatures of PPSU lie above 340°C, which makes industrially produced plasticizers unsuitable for these purposes.

Thus, there is the task of developing a plasticizing agent that has the necessary heat resistance and compatibility with PPSU, which could be used to reduce the viscosity of melts of highly filled composite materials.

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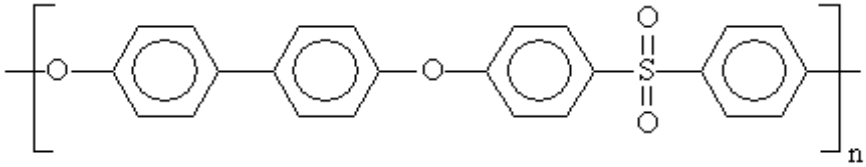
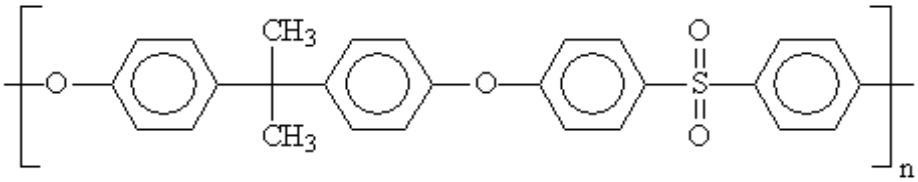
2. Experimental

On this basis, in the present work, the plasticizing effect of the synthesized heat-resistant oligomers [9,10] based on 4.4′-dihydroxydiphenyl and 4.4′-dichlorobiphenylsulfone with a molecular mass of about 15000 g/mole (plasticizer-1), as well as 4.4′ -dihydroxydiphenyl-propane (Diane) and 4.4′-dichlorodiphenylsulfone with a molecular mass of about 14.000 g/mole (plasticizer-2), the structural formulas of which are given in Fig. 1. These oligomers are solid powder and have high thermal stability.



plasticizer-1



plasticizer-2

Fig. 1. Plasticizer Schemes

Ground glass and carbon fibers with a particle length of 0.2 mm from R & G (Germany) were used as fillers. Composites were obtained by melt blending on a twin-screw Twin Tech micro-extruder (UK) with L / D = 30, with preliminary dry mixing of the starting components. Test specimens were obtained by injection molding on an SZS-20 machine from Haitai Machinery (China) at a material cylinder temperature of 400°C and a mold temperature of 180°C.

The melt flow index of composites (MFI) was determined on an IIRT-5 instrument at a temperature of 350°C and a load of 5 kg. The glass transition temperature (T_g) was determined by the method of differential scanning calorimetry (DSC) on a DSC 4000 instrument from Perkin Elmer (USA). Heat resistance was determined by thermogravimetric analysis on a TGA 4000 instrument from Perkin Elmer (USA).

Mechanical uniaxial tensile tests were performed on samples in the form of a double-sided blade with dimensions according to GOST 112 62-80 type 5. The tests were carried out on a Gotech Testing Machine CT-TCS 2000 universal testing machine (Taiwan) at a temperature of 23°C. Impact tests with a notch and without an incision were made by the Izod method according to GOST 19109-84 on a Gotech Testing Machine, model GT-7045-MD (Taiwan) with a pendulum energy of 11 J.

Initially, studies were carried out on pure unfilled PPSU with MM = 45000-50000 g/mole and melt flow index equal to 11 g/(10 min.) into which plasticizer-1 was injected in an amount of 5, 10, 20, 30, 40 wt %

3. Results and Discussion

DSC studies have shown that with an increase in the plasticizer-1 content up to 20%, a uniform decrease in the glass transition temperature (T_g) occurs, and upon reaching 30% concentration, a more dramatic and significant drop in T_g is observed (Figs. 2, 3). A similar nature of the change in properties is also observed on the graph of the MFI dependence on the plasticizer content, where up to 20% there is a uniform increase in melt flow, then a more

sharp increase upon reaching 30% concentration (Fig. 3). For a sample with 40% plasticizer, there is a decrease in T_g below the value for the original PPSU by 13.7%, and the MFI is higher by 645%.

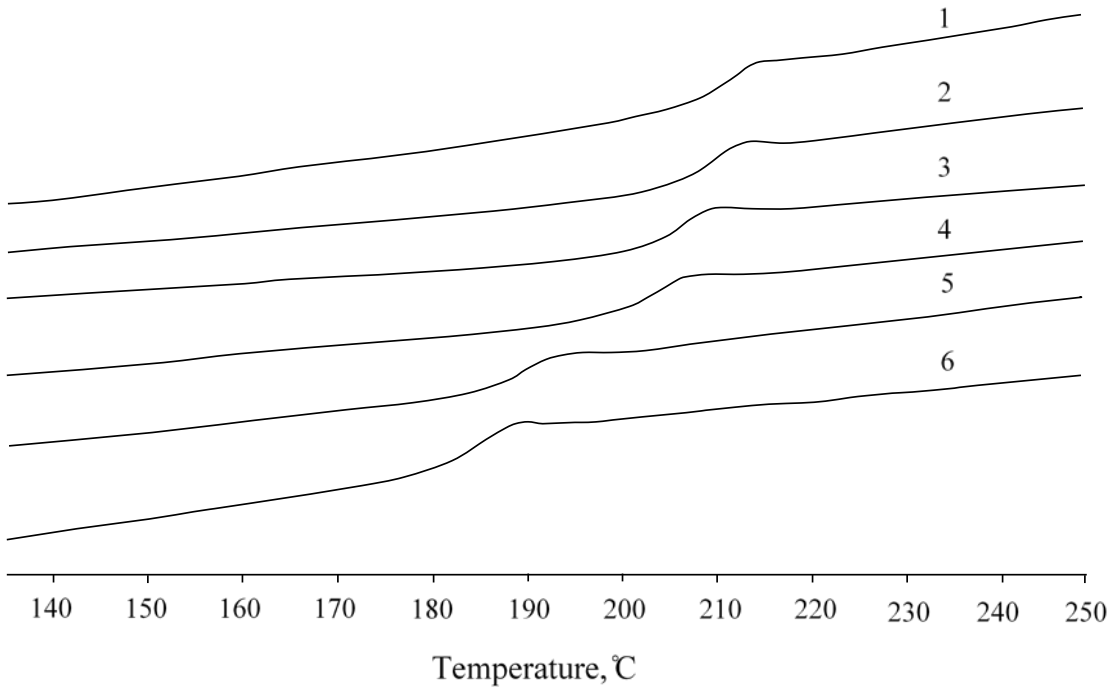


Fig. 2. DSC curves of PPSU with different content of plasticizer-1: 1 – 0%; 2 – 5%; 3 – 10%; 4 – 20%; 5 – 30%; 6 – 40%

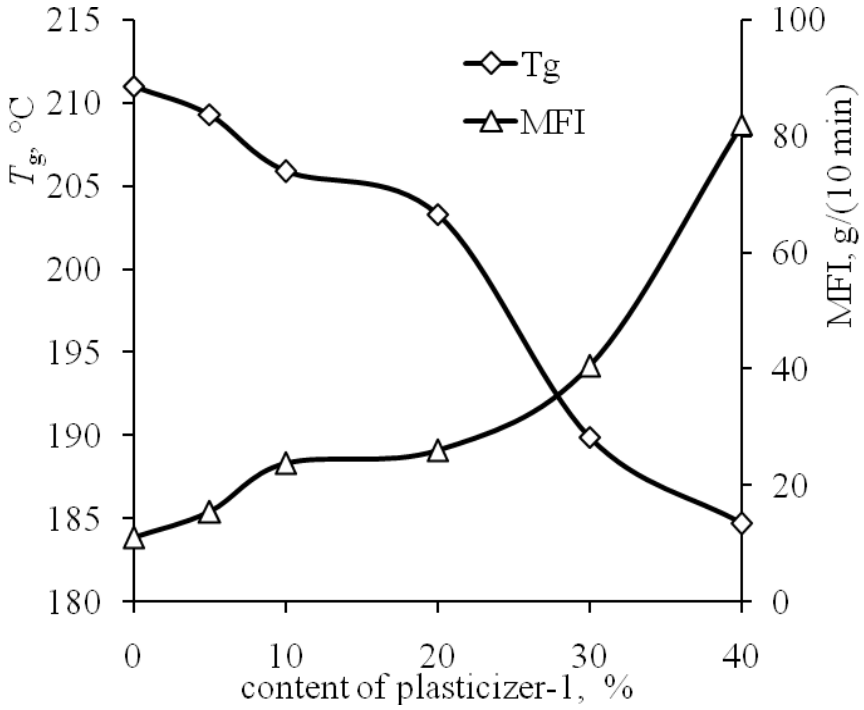


Fig. 3. Dependence of T_g and MFI of polyphenylene sulfone on the plasticizer-1 content

The study of physico-mechanical properties showed (Table 1) that with an increase in the content of the plasticizer, a uniform decrease in toughness and relative elongation at break occurs. When reaching 30-%-th concentration again there is a sharp drop in these properties.

In this case, the modulus of elasticity in bending and stretching reveals a tendency to increase. The tensile strength and yield strength under tension remain at the level of the original polymer with a plasticizer content of up to 20%, and upon reaching 30%, the strength is also significantly reduced. In this case, the yield strength in the uniaxial tension diagram is no longer detected, which indicates that the material loses its ability to plastic deformation.

Table 1. Physico-mechanical properties of PPSU with different content of plasticizer-1

The content of the plasticizer-1	Impact strength, kJ/m²		Flexural modulus, GPa	Tensile modulus, GPa	Tensile strength, MPa	Yield strength, MPa	Elong. at break,%
	unnotched	notched					
0	n/b*	20.1	2.5	2.04	68	82.5	16.6
5%	n/b	15	2.54	2.06	68	84.8	15.3
10%	176	16.5	2.56	2.1	68	84.9	12.6
20%	152	12.7	2.54	2.1	67	85.1	12
30%	21.2	6.3	2.7	2.12	52.2	-	3.5
40%	6.6	1.2	2.72	2.14	21.1	-	2.3

*n/b – not broken

Thus, with the introduction of plasticizer, on the one hand, we observe a decrease in the glass transition temperature, which indicates a decrease in intermolecular interaction and an increase in the flexibility of the chain, on the other, an increase in the elastic modulus and a decrease in plasticity, which differs from the action of classical plasticizers, the introduction of which leads to an increase in deformability and toughness [11]. On this basis, it can be assumed that this oligomer acts as an "anti-plasticizer", which is typical for rigid-chain polymers and plasticizers with a high glass transition temperature containing polar atoms [12].

It can be argued that the polymer and the plasticizer used for it are fully compatible, since they have similar chemical structures and only molecular mass are different. This is also confirmed by the fact that there are only single glass transition peaks on the DSC curves, regardless of the plasticizer concentration, and the fact that the samples of the mixtures remain optically transparent throughout the entire concentration range (Fig. 4).

Fig. 4. Images of cast samples: a - PPSU; b, c, d, e, f - PPSU + 5, 10, 20, 30, 40% plasticizer-1, respectively

At temperatures above the glass transition temperature, shorter and mobile molecules of the plasticizer can penetrate into the intermolecular space of PPSU, which results in easier movement of the polymer macromolecules relative to each other and an increase in the MFI.

However, at room temperatures, the plasticizer is also in the glassy state due to the high T_g, which causes high values of the modulus of elasticity and strength of the composites. Thus, it acts as a temporary plasticizer [11], increasing the mobility of molecules precisely at temperatures above T_g, i.e. in the highly elastic state, as evidenced by a decrease in polymer T_g, and viscous flow, which is manifested in an increase in melt flow. Therefore, in this case, it is not entirely correct to speak about inter- or intrastructural (molecular) plasticization, since plasticizer works only in the melt, where there are generally no structural elements. Due to the absolute affinity of plasticizer molecules with polymer macromolecules, when cooled, they can jointly form short-range structures, like molecular plasticizers, however, due to the high glass transition temperature of the plasticizer (150°C), the effect of plasticization at ordinary temperatures is absent.

A sharp decrease in T_g and mechanical properties, as well as an increase in the MFI when the concentration of the plasticizer reaches 30%, is apparently due to the fact that at a given mass concentration the molar content of the plasticizer exceeds the molar content of the polymer, which leads to a phase inversion in two-phase systems, i.e., the plasticizer becomes a continuous phase and the main component carrying the load.

Thus, this oligomer provides a fairly effective plasticizing effect in the processing of PPSU, significantly increasing the MFI. Also, the advantages of this plasticizer include the preservation of the elastic-strength properties of the polymer at concentrations up to 20%, which is a very positive factor in obtaining high-modulus reinforced composites. However, it meets a number of other requirements for plasticizers, namely: it has high heat resistance and compatibility with the polymer, low volatility, etc.

For further investigation of the possibility of plasticizing composite materials based on PPSU, compositions with a content of 30% carbon and glass fibers with a length of 0.2 mm were used. The choice of these concentrations of fillers is due, firstly, to the fact that this significantly increases the viscosity of the melts, and secondly, the composites have sufficiently high physico-mechanical properties [2,3]. Based on previous studies, plasticizers were introduced in the amount of 10, 15, 20 wt % relative to the polymer, while using oligomers of both structures (Fig. 1).

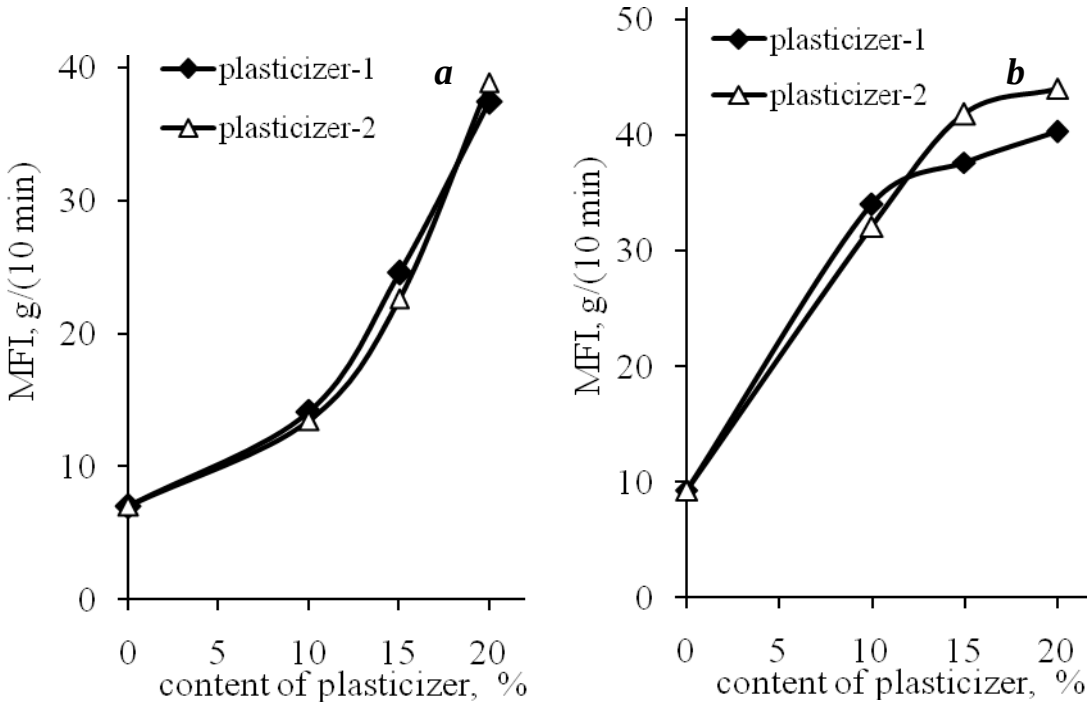


Fig. 4. Dependence of MFI of glass-filled (a) and carbon-filled (b) composites on the content of plasticizers

The study of the rheological properties of composites showed that with the introduction of oligomers, there is a significant increase in the MFI of the glass-filled composite (Fig. 5). It can be seen from the graph that the MFI values of the composites with the content of plasticizers of both structures are quite close. With the introduction of 10% of plasticizers, there is a sharp increase in the MFI (by about 254%), then a more gradual growth is observed. At 20-%-th concentration of plasticizers, the MFI of the composites is higher than that of the original glass-filled composite by an average of 350%.

The introduction of these oligomers into composite materials with a content of 30% CF also leads to an increase in the MFI (Fig. 5b). In this case, there is an almost linear dependence of the MFI on the content of plasticizers, regardless of their structure. The introduction of 10% of plasticizers leads to an increase in the MFI by 100%, and at its 20%-th concentration, the MFI exceeds the value of the initial composite by 440%.

Thus, these oligomers are quite effective temporary plasticizers for glass- and carbon-filled composites based on PPSU. The difference in the change in the viscosity of the melt of glass and carbon-filled composite is only in a more noticeable increase in MFI for the glass-filled composite, even at low concentrations, in contrast to the composite with carbon fibers, where the increase in MFI occurs monotonically with an increase in the content of plasticizers. Apparently, the greater brittleness of the GF and the lower adhesion to the polymer leads to a more significant plasticizing effect.

Table 2 presents the mechanical properties of composites with a content of 30% GF, depending on the type and concentration of the plasticizing oligomer.

As can be seen from the Table 2, the introduction of synthesized oligomers as plasticizers leads to a decrease in toughness and relative elongation at break, however, the elastic modulus of composites during bending and stretching is preserved and even increases somewhat, as in the case of unfilled PPSU. The introduction of plasticizers is also accompanied by a decrease in tensile strength and flexural strength (Table 2). At 10% concentration of plasticizers, the loss of strength is insignificant, but a further increase in their content leads to a significant decrease in these properties. Composites with a plasticizer-1 content demonstrate slightly higher rates for all tested properties.

Table 2. Physico-mechanical properties of glass-filled composites with a content of plasticizers of various structures

Composition	Impact strength, kJ/m²		Flexural modulus, GPa	Tensile modulus, GPa	Tensile strength, MPa	Flexural strength, MPa	Elong. at break,%
	unnotched	notched					
PPSUGF (PPSU + 30% GF)	21.8	6.2	5.5	4.34	71.7	117	3.2
Plasticizer-1							
PPSUGF + 10%	17.3	4.8	6.0	4.53	65.7	111	2.7
PPSUGF + 15%	15.5	4.26	5.9	4.55	61.4	89	2.2
PPSUGF + 20%	10.2	3.3	5.8	4.51	41.2	66	1.2
Plasticizer-2							
PPSUGF	17	4.2	5.94	4.47	64	105.5	2.5

+10%							
PPSUGF +15%	14	4.2	5.8	4.37	54	73.3	1.7
PPSUGF +20%	7.8	3	5.83	4.4	37	51	2

Similar studies were conducted with composites containing 30% CF. Table 3 shows the results of their physical and mechanical tests.

Table 3. Physico-mechanical properties of carbon fiber-filled composites with a content of plasticizers of various structures

Composition	Impact strength, kJ/m²		Flexural modulus, GPa	Tensile modulus, GPa	Tensile strength, MPa	Flexural strength, MPa	Elong. at break,%
	unnotched	notched					
PPSU CF (PPSU + 30% CF)	42	9.1	11.84	7.43	120	207	3.8
Plasticizer-1							
PPSU CF +10%	34.9	8.3	13.64	8.37	121	195	3.4
PPSU CF +15%	30	7.2	14.71	8.84	123.7	170	2.8
PPSU CF +20%	16	6.6	14.12	8.36	96.8	129	1.9
Plasticizer-2							
PPSU CF +10%	36.5	8.1	12.53	7.84	115.7	195.6	3.1
PPSU CF +15%	30.6	6.6	13.42	7.6	101.2	144.6	2.3
PPSU CF +20%	17.6	5.3	13.22	7.8	87.7	138	1.6

From Table 3 it can be seen that the introduction of plasticizers in carbon fiber-filled composites also leads to a decrease in toughness and a decrease in the relative elongation at break. At the same time there is a slight increase in the modulus of elasticity in bending and stretching. When tested without notching, the difference in impact of the structure of the plasticizer on impact resistance is insignificant, but composites with a content of plasticizer-1 are characterized by higher values of impact toughness with a notch.

Similarly, as in the case of glass-filled composites, the introduction of plasticizers into carbon-filled composites based on PPSU is accompanied by a decrease in strength, both during stretching and bending (Table 3). Composites with plasticizer-1 also demonstrate a slight superiority of properties.

The TGA method was used to study the heat resistance of composites with a content of plasticizers of various structures (Table 4).

Table 4. Heat resistance of fiber-filled composites with a content of plasticizers of various structures

Composition	$T_{2\%}$, °C	$T_{5\%}$, °C	$T_{10\%}$, °C
PPSU	504	529	550
Plasticizer-1	472	500	523
Plasticizer-2	454	486	499
Plasticizer-1			
GF			
PPSUGF (PPSU+30 % GF)	511	542	562
PPSUGF +10 %	506	540	560
PPSUGF +15 %	493	533	558
PPSUGF +20 %	482	530	556
CF			
PPSUCF (PPSU+30 % CF)	536	562	582
PPSUCF +10 %	536	562	580
PPSUCF +15 %	523	550	574
PPSUCF +20 %	518	547	572
Plasticizer-2			
GF			
PPSUGF +10 %	498	522	541
PPSUGF +15 %	486	512	532
PPSUGF +20 %	492	510	527
CF			
PPSUCF +10 %	502	530	551
PPSUCF +15 %	498	522	541
PPSUCF +20 %	497	518	535

From Table 4 it can be seen that plasticizers have high heat resistance, close to that of PPSU, and plasticizer-1 slightly exceeds thermal resistance of plasticizer-2. Similarly, we observe higher heat resistance and fiber-filled composites with plasticizer-1. The introduction of plasticizers slightly reduces the heat resistance of composites, however, despite this, in general, all composites have high decomposition temperatures.

4. Conclusions

Thus, we can conclude that the selected plasticizers rather effectively perform their main function - increasing the melt flow rate while maintaining the physico-mechanical properties and heat resistance at 10 -% content in the composite. Composites with plasticizer-1 have slightly higher properties, which, apparently, is due to its similar structure to the polymer, which ensures better compatibility.

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