==== **SHORT COMMUNICATIONS** ====

Thermal and Thermo-Oxidation Stability of Plasticized Fiber-Filled Composite Materials Based on Polyphenylene Sulfone

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Abstract—The effect of plasticization on the thermal properties of carbon- and glass-filled composites based on polyphenylene sulfone was studied with the methods of thermogravimetric analysis and gas chromatography. A relationship is established between the composition of composites and the nature of fiber fillers, as well as the effect of the composition on the thermal and thermo-oxidative properties of materials.

INTRODUCTION

The development of modern technology contributes to the development of new polymeric materials with high values of their thermophysical properties. These include polyphenylene sulfone (PPSF). Issues related to the chemical transformations of polysulfone (PSF) at high temperatures (above 400°C) were studied in detail earlier in [1–6], in which various gaseous and liquid thermal decomposition products were discovered. In [7–9], studies were carried out in a wider temperature range, which made it possible to study the processes of "stitching" at lower temperatures (300–400°C) and to establish the basic mechanisms of decomposition at higher temperatures. However, the thermophysical properties of composite materials based on PPSF, which have increased heat resistance, high physical, mechanical, and dielectric properties, radiation resistance, and fire resistance, remain practically unstudied. In addition, their application in promising fields of science and technology is limited by the difficulty of processing, which is associated with high melt viscosity, especially in the case of fiber-filled composites. The plasticization of high performance polymers to increase their manufacturability often leads to a decrease in the values of their thermophysical properties. Moreover, there is practically no literature data that can become the basis for the selection of the maximum allowable plasticizer content in high performance polymers and in composites based on them to maintain stability in a given temperature range.

In the present work, we studied the effect of a plasticizer on the thermal stability of carbon- and glass-filled composites based on a high-temperature thermoplastic-PPSF.

RESEARCH METHODS

The studies were carried out on composites based on polyphenylene sulfone synthesized at the Center for Advanced Materials and Additive Technologies at KBSU, with a 30% content of carbon (CF) and glass (GF) fibers with a length of 0.2 mm from R&G (Germany). The choice of these compositions is due, first, to the fact that the melt viscosity increases significantly at given filler concentrations, and, second, the composites have enhanced physical and mechanical properties. An oligomer based on 4,4'-dihydroxydiphenyl and 4,4'-dichlorodiphenylsulfone with a molecular weight of about 15000 g/mol previously synthesized according to the method described in [10] was used as a plasticizer. The plasticizer and fillers were introduced into the polymer matrix via melt mixing on a TWINTECH SCREW 10 mm $L/D = 3$ extruder (UK) with five heating zones, a screw speed of 60 rpm, and a direct feed of ingredients through the hopper. The temperatures in the heating zones ranged from 200 to 355°C.

Thermogravimetric studies were carried out on a Perkin Elmer TGA 4000 device in air and in an inert medium (the flow rate in both cases was 20 mL/min) with a rate of temperature increase of 10°C/min.

The analysis of the main gaseous products of thermal and thermal oxidative degradation was performed on a Tsvet-800 gas chromatograph according to the procedure described in [11]. The thermal oxidative stability of composites was studied at a temperature of 350°C, and the thermal stability was determined at 450°C. The temperature control time in both cases was 30 min. The samples were heated at a rate of 50°C/min with a closed hydraulic lock. For all composites, the weight was 60 mg.

RESULTS AND DISCUSSION

Thermogravimetric analysis showed (Table 1) that the temperature of the onset of mass loss in the air of all composites lies in the range from 480 to 540°C.

Table 1. Heat resistance of fiber-filled composites with different plasticizer contents

Composition	$T_{2\%}$, °C	$T_{5\%}$, °C	$T_{10\%}$, °C
PPSF	504	529	550
PPSF+GF (PPSF + 30% GF)	511	542	562
PPSF+GF + 10% plasticizer	506	540	560
PPSF+GF + 15% plasticizer	493	533	558
PPSF+GF + 20% plasticizer	482	530	556
PPSF+CF (PPSF + 30% CF)	536	562	582
PPSF+CF + 10% plasticizer	536	562	580
PPSF+CF + 15% plasticizer	523	550	574
PPSF+CF + 20% plasticizer	518	547	572

Subscripts denote temperatures at which 2%, 5%, and 10% loss of the sample weight upon heating.

With an increase in the plasticizer content, the heat resistance of composites decreases (Table 1). Moreover, composites with CF are more heat resistant than composites with GF.

Since sample heating in thermogravimetric studies is carried out with a rate of temperature increase of 10 deg./min, this method does not make it possible to determine the actual temperature of the beginning of thermal decomposition of the samples and the beginning of gas evolution. Therefore, it is necessary to study in more detail via gas chromatography the composition of the released gaseous products of the thermal destruction of composites at temperatures higher than those the above.

Gas chromatography allows the minimum gas evolution or absorption of oxygen to be recorded, even if it totals 0.001% by sample weight.
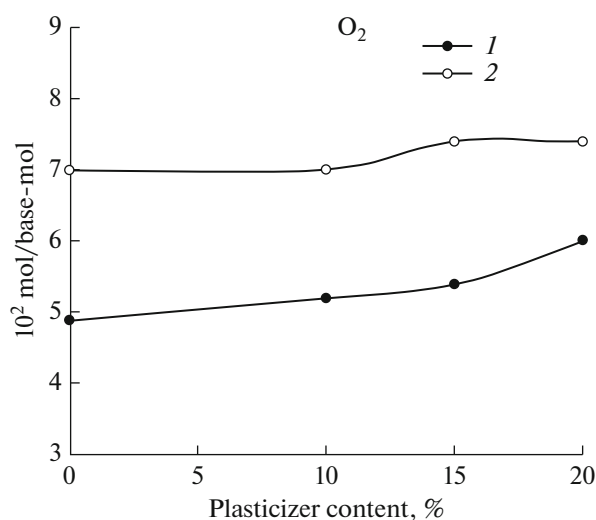

Fig. 1. Oxygen absorption curves of carbon fiber (*1*) and fiberglass (*2*) composites
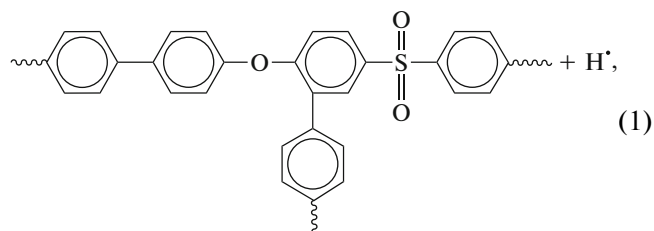
Since the processing into products, the obtainment of filaments for 3D printing, the printing itself, and the measurement of the melt flow rate of these composite materials are carried out in air at a temperature range of 320−400°C, a temperature of 350°C was chosen to study the thermo-oxidative stability.

It should be noted immediately that no noticeable amounts of sulfur-containing gases (SO_2, H_2S) were found with these pyrolysis modes.

Figure 1 shows the curves of oxygen absorption by composites, which differ in the percentage of plasticizer. Composites with GF absorb significantly more oxygen than carbon-filled composites. With an increase in the percentage of plasticizer, the amount of oxygen absorbed for both composites changes insignificantly.

The method used in this work [11] allows, in addition to research on O_2 absorption, simultaneous analysis of the gaseous products that form during the oxidation process, among which hydrogen and carbon dioxide were detected. Figure 2 shows the kinetic curves of hydrogen evolution from glass- and carbon-filled composites with respect to the content of plasticizer.

The hydrogen yield for composites filled with GF is noticeably higher (Fig. 2, curve *2*) already with the minimal amount of plasticizer. At the research temperature (350°C), we cannot speak of about the destruction of the main polymer chain of the matrix, therefore, the H_2 output is associated only with the structuring processes that occur during the interaction of terminal hydroxyl groups with a macromolecule of the main polymer chain:
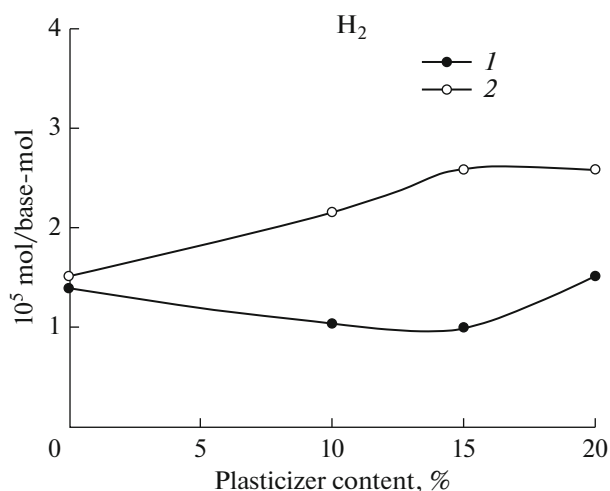

$$(1)$$

Fig. 2. Hydrogen emission curves of carbon fiber (*1*) and fiberglass (*2*) composites.
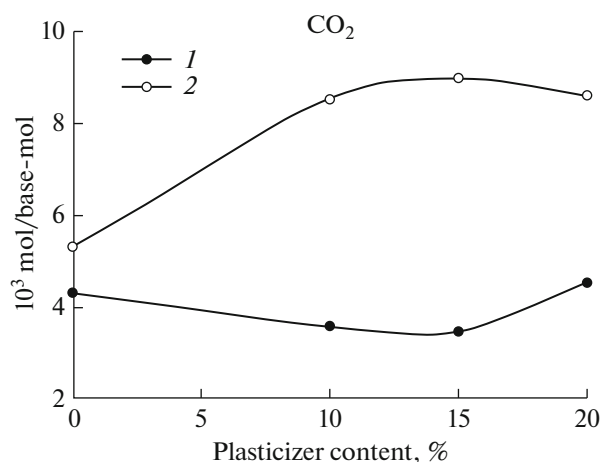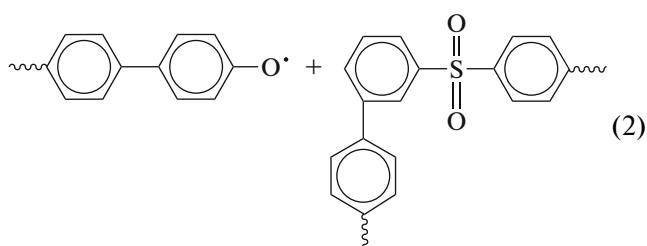

Fig. 3. CO emission curves carbon fiber (*1*) and fiberglass (*2*) composites.

$$(2)$$

Reaction (1) leads to crosslinking, which is accompanied by the release of atomic hydrogen; reaction (2) is responsible for the destruction of the main polymer chain. At relatively low temperatures, as in the considered case, the reactions proceed mainly according to scheme (1). Indirect confirmation of the occurrence of such reactions can be seen in the slight increase in the amount of hydrogen released with the introduction of a plasticizer. With an increase in its percentage, the hydrogen yield also increases. In a low molecular weight oligomer, more mobile terminal hydroxyl groups are able to increase the intensity of crosslinking processes.

Although the amount of hydrogen formed in all cases is insignificant, the contribution of structuring processes to the formation of the physicomechanical properties of the finished product should not be disregarded.

A somewhat different picture is observed in the case of CO_2 formation in the process of thermal oxidation (Fig. 3).

The source of carbon dioxide formation is not entirely clear. These are either defects in the structure of the matrix and the used plasticizers or are residual products of thermal degradation of the epoxy resins used to process the fillers. The best results were shown for CF composites in which a small amount of carbon dioxide begins to be released only when the plasticizer content is 20%. In samples with GF, the carbon dioxide yield more than doubled already at a plasticizer

content of 10% (Fig. 3, curve *2*) Therefore, during the processing of plasticized glass-filled high-temperature thermoplastics into products, the probability of the formation of defects in the form of cavities is high, which will certainly lead to deterioration of the physical and mechanical properties.

It is interesting to note that a decrease in the amounts of hydrogen and carbon dioxide that form for carbon-filled composites is observed with the addition of 10 and 15% plasticizer (Figs. 2 and 3). The discovered phenomenon indicates a slowdown in structural transformations in carbon-filled composites. For an increase in the volume of H_2 and CO_2, with the addition of plasticizer in an amount of 20% (curves *1*, Fig. 2, 3) the plasticizer itself is responsible, which becomes an additional source of gas formation.

The authors of [12] found earlier that anomalous heat capacities appear in composites filled with carbon nanotubes, which are explained by defects in the filler subsystem. Apparently, in the present case, the plasticizer better wets the hydrocarbon, and its introduction into carbon-filled composites contributes to the filling of numerous filler defects and the formation of a more ordered structure.

Thermogravimetric analysis showed that the onset of mass loss in an inert medium of all composites lies in a temperature range of 500–570°C. In this regard, a temperature of 450°C, which precedes the onset of intense mass loss (pyrolysis time of 30 min), was chosen for the analysis of the main products of thermal destruction of composites.

Table 2 shows the results of a study of composites, which include 30% filler (carbon fiber or fiberglass) and 20% plasticizer.

As in the case of studies on thermal oxidative stability, the best results were found for composite materials with hydrocarbons. The yield of all detected gaseous

Table 2. Compositions and Volumes *V* of the formed gaseous products

Composites	V, μL			
	H_2	CO	CH_4	CO_2
PPSF + GF + 20% plasticizer	0.15	1.25	−	10.29
PPSF + CF + 20% plasticizer	0.07	0.53	−	6.74

products of thermal degradation is several times lower for them than for composites with carbon fibers.

CONCLUSIONS

Experimental studies show that the thermal stability of plasticized, fiber-filled composites depends on the nature of the filler and the amount of introduced plasticizer. The yield of all detected gaseous degradation products, as well as the amount of oxygen absorbed for carbon fiber composites, is significantly lower as compared to glass-filled composites. Under the studied temperature-time regimes, no appreciable damage to the main polymer chain of the matrix is observed.

FUNDING

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