Fullerene Derivatives, Preparation, Identification and Use

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Received: March 01, 2013 / Accepted: April 06, 2013 / Published: June 25, 2013.

Abstract: This article is focused on oxidation and halogenation of fullerene, identification of the prepared products and their potential application. The Fourier transform infrared (FTIR) spectrometry was used for analysis of oxidized fullerene derivative and material balance and elemental analysis were used to identify the summary composition of the prepared fullerene halogen derivatives. We have confirmed yet the radioprotective ability of oxidized fullerene in our recently published work radioprotective properties and toxicity test of C₆₀ fullerene derivative *in vivo* & *in vitro*. Since radioprotective properties are associated with the ability to recapture free radicals in the system (formed due to radiolysis of water in the physiological environment), this property is closely connected also with fire-retarder properties, when the fire is also a radical mechanism. We tested thermal properties of polyvinyl alcohol (hereinafter PVA) nanofibers prepared with C₆₀ and its derivatives as nanocomposites. The TG-DTA and TG-DSC analysis were used for this purpose. We have demonstrated experimentally that a retarder on C₆₀oxi basis and C₆₀ halogenderivative has good results in increasing of thermal resistance of PVA-based nanofibers.

Key words: C₆₀ derivative, oxidation, halogenation, radioprotectivity, fire-retarder, nanofibres.

1. Introduction

Fullerenes are condensed polycyclic carbon substances with cage structure, with even numbers of carbon atoms arranged preferably into pentagons or hexagons. The most perfect spherical shape has the fullerene C₆₀. Its surface is made up of 20 hexagons and 12 pentagons (similar to a classical sewn soccer ball). The pentagons are made of single covalent bonds and the hexagons are made up of a system of alternating single and double bonds.

The principal difference from graphite and diamond is the solubility of C₆₀ in non-polar organic substances and its reactivity. Its typical reactions are associated with a transformation of arrangement from sp² to sp³ and thus with a reduction of tension in the molecule. The C₆₀ molecule is electropositive which means that

it prefers nucleophilic or radical addition on a multiple bond. Fullerene C₆₀ can be used for hydrogenation, alkylation, halogenation, oxidation, polymerization etc.

Substances identified as fire retarders are designed to slow down or stop the burning process, both by physical and chemical mechanisms.

The physical mechanism of fire retardation is based on endothermic decomposition of the retarder, flame cooling and dilution of combustible gases (e.g., Al(OH)₃·xH₂O).

The chemical mechanism is based on a substitution of radicals H· and OH· with less reactive radicals or inert molecules produced by reactions with fire retarders. The exothermic reaction is slowed down and the temperature and production of combustion products decrease.

For polymer material, the treatment with a fire retarder may be applied on the polymer surface or “in

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bulk during the polymer processing; the retarders may be thus divided into those that do not react with the polymer (composites) and those that are integrated in the polymer chain.

Composites with at least one dimension in the nanometric area are identified as nanocomposites.

Apart from the fire-retarder properties, nanocomposites mostly also provide polymers prepared in this manner with additional desirable mechanical and physical properties. The most widespread nanoparticles used in industrial mass production are stratified nanoclays (stratified silicates, such as montmorillonite, kesterite, saponite). Synthesis of stratified nanoclays with polymer matrix, depending on the conditions and methods of preparation, enables to produce three main types of nanocomposites:

- phase separated;
- intercalated nanocomposites;
- exfoliated nanocomposites.

In intercalated nanocomposites polymer molecules permeate between the layers of silicate aggregates, they slightly expand but remain together, while in exfoliated nanocomposites, the individual layers are essentially dispersed in the individual matrix. This leads to optimization of mechanical properties, such as strength, elasticity, and to improvement of thermal stability (retardation). For phase-separated nanocomposites, the polymer matrix is unable to intercalate between clay layers so it only wraps them up. Clay particles in this case only perform the function of a microfilter.

Other investigated nanoparticles-based fire retarders were quartz flakes [1], metal oxides TiO_2 , Fe_2O_3 [2] and carbon-based nanoparticles. The latter included oxidized graphite, carbon singlewall nanotubes (SWNT), multiwall nanotubes (MWNT) and carbon fibers. In most cases, an improved thermal stability of the polymers was found and a significant reduction of the rate of released heat [3, 4]. The degree of dispersion of nanoparticles in the polymer is

of essence [3].

In our earlier works [5, 6], we published a change of thermal stability of polyvinyl alcohol (hereinafter PVA) nanofibers after addition of C_{60}oxi which increased the thermal stability of nanofibers. In this work, we have focused on testing of thermal resistance of the nanofibers depending on the concentration of the added C_{60}oxi . The quantity of C_{60}oxi in relation to PVA before spinning was in the range 1-3 wt.%.

2. Materials and Methods

2.1 Preparation of Fullerene Derivatives

The pristine fullerene C_{60} with 99.5% purity was obtained from SES Research, Houston, USA.

2.1.1 Fullerene Oxidation with Peracetic Acid

500 mg of C_{60} fullerene was mixed with 600 mL of 35% peracetic acid (Penta, Pharmaceutical division Prague). The mixture was constantly stirred at the laboratory temperature and a dark brown dispersion solution was obtained within half an hour which was heated and evaporated to ca. 100 mL. The heating accelerated the process while the same result may be achieved after a longer period of time at the laboratory temperature when the peracetic acid evaporates spontaneously. After the acid was evaporated to 100 mL, the clayey modified fullerene was settled with a centrifuge (3,500 rev/min, for 5 min). By decanting the liquid portion, the peracetic acid, or its chemical residue, was removed. The solid part was repeatedly washed with small quantities of water, centrifuged again and the liquid portion was decanted. During washing with water always a certain part of the hydroxylated fullerene passed into the liquid portion, which was demonstrated by a light brown color of the acidic part. Decantation of that portion represents a certain weight loss of the product; however, the washing and repeated centrifugation was necessary and it was repeated at least three times. The achievement of neutral pH was a precondition for further use of the product in radioprotectivity biotests,

as we published in Refs. [7, 8]. We tested preparation of C₆₀oxi for several years to always achieve reproducible results with optimum solubility in water so that it can be used as a radioprotective substance.

2.1.2 Fullerene Bromination

Fullerene C₆₀ (4 g) was added into liquid bromine 27.5 mL (85.3 g) and the mixture was agitated at the laboratory temperature for 72 h. Subsequently, the excessive bromine was removed by drying at 75 °C for ca. 24 h until a constant weight was achieved. The product was 9.9 g of a green-brown substance. Based on the weight increase, the average composition was C₆₀Br₁₄ which has been confirmed by an elemental analysis of bromine.

2.1.3 Chlorination of Bromofullerene

The earlier prepared bromoderivative C₆₀Br₁₄ (5 g) was added into 300 mL of tetra chloromethane. Subsequently, the mixture was percolated with gaseous chlorine of 99.8% purity released from a pressure cylinder. The reaction mixture was in contact for three days, the percolation with gaseous chlorine was performed with an interruption under slight reflux for 16.5 h. Tetra chloromethane was replenished during the reaction time with additional 100 mL. After evaporation of tetra chloromethane in a rotation evaporator the resulting red-brown powder was dried at 75 °C until a constant weight was achieved, while the total product was 4.65 g. Based on a calculation and elemental analysis, the summary formula was determined as C₆₀Br₁₀Cl₄.

2.2 Identification of the Prepared Fullerene Derivatives

Fourier transform infrared (FTIR) spectroscopy was used to identify fullerene oxoderivative. attenuated total reflection (ATR) analysis with FTIR spectrometry was performed on Brucker Sloha/FT-IR spectrometer, ATR crystal (Id. platinum Diamond 1 Refl), software OPUS 6.5, source IR SiC Globar. Measuring parameters are: number of spectrum scans 24, resolution 4 cm⁻¹, spectrum range 375-4,000 cm⁻¹.

Material balance and elemental analysis were used to identify the summary composition of fullerene

halogen derivatives. Subsequently ATR analysis with FTIR spectrometry (the same as above) was used.

2.3 Preparation of Nanofibres with C₆₀ and Its Derivatives as Nanocomposites

The nanofibers were prepared by electrospinning (Department of Non-woven Textiles, Technical University Liberec).

The polyvinylalcohol (PVA, Mowiol 18-88, average mol wt. 130.000 from Kuraray) water solution 10 wt.% with crosslinking agents (4 wt.% of 40 wt.% glyoxal solution and 3 wt.% of 85 wt.% phosphoric acid solution from dry PVA content) were electrospun and subsequently crosslinked at 135 °C for 5 min. The material was used as a control sample. Then PVA nanofibers with addition of 1 wt.%, 2 wt.% and 3 wt.% of C₆₀oxi were produced. Used voltage for electrospinning was 20-25 kV. After electrospinning the same crosslinking process as for the control sample was used. Couptiss Ultra Sons HS30 with power 30 W and frequency 30 kHz (Calemar, France) was applied for 60 s for dispersion of fullerenes inside the water. The final structure of electrospun nanofibers can be seen in Fig. 1.

The diameters of nanofibers measured by image analysis are: control sample 210 ± 56 nm; 1 wt.% C₆₀oxi 214 ± 73 nm; 2 wt.% C₆₀oxi 219 ± 74 nm; 3 wt.% C₆₀oxi 224 ± 72 nm.

A change of thermal stability of the produced nanofibrous materials was assessed at Fire Rescue Service of Czech Republic, by means of TGA and TG-DSC method. Measurements of weight loss and relaxed-consumed thermal energy depending on used temperature and time are principles of these methods. The tests were performed according to accredited methods, apparatus STA 1500 THASS (mentioned in Table 1). The employed devices for TGA and DSC are provided in Table 1.

A similar method, including the subsequent analysis, was used to prepare nanofiber samples with added fullerene bromo- and bromochloroderivatives. Only an demonstrative electron microscope image of nanofibers

Fig. 1 Scanning electron images of control PVA nanofibers (a) PVA with 2 wt.%; (b) and with 3 wt.%; (c) $C_{60}oxi$ (magnification of all images is 10,000 $\times$).

Table 1 Measuring instruments and devices.

Name of the measuring instrument/device	Measuring range	Calibration period (years)
Barometer GPB 2300	(50-1,300) mbar	2
Digital thermometer /humidity meter BONECO	(-20 to 50) $^{\circ}C$, (20% to 100%)	5
Analytical scales SUMMIT, SI 234-A	(0-230) g	2
Ball flow meter	(10-50) mL/min	5
STA i 1500 (Instrument Specialists Incorporated-THASS), device for simultaneous TG-DTA and TG-DSC analysis		

with fullerene bromochloro-derivative (3 wt.%) is shown in Fig. 2.

3. Results

3.1 Fullerene Oxidated with Peracetic Acid

Obtained FTIR spectrum demonstrated presence of functional -OH and -COOH groups, Fig. 3.

The presence of the bands of valence vibrations of -OH groups of the fullerene oxoderivative is obvious at 3,379 and 3,198 cm^{-1} , with -COOH groups at 1,770, 1,746, 1,707 and 1,636 cm^{-1} and C-O groups at 1,034 cm^{-1} .

TGA curves of samples No. 1 through No. 4 (Fig. 4 and Table 2) may be divided into several curves with different slopes, i.e., rate of weight reduction. The division with corresponding temperature ranges and corresponding weight reductions is provided in Table 2. Table 3 indicates parameters of the detected thermal processes on the DSC curve. The thermal energy changes (ΔH) were determined as areas of the individual peaks that represent the respective thermal

Fig. 2 Scanning electron images of PVA nanofibers with 3 wt.% bromochlorofullerene composite (magnification of image is 10,000 $\times$).

Fig. 3 IR spectrum of the pristine fullerene C_{60} (upper curve) and its oxoderivative (lower curve).

Fig. 4 Thermal analysis of PVA nanofibers without composite and with C₆₀Oxi composite in the order: (a) PVA, blank; (b) PVA, 1 wt.% of C₆₀Oxi; (c) PVA, 2 wt.% of C₆₀Oxi; (d) PVA, 3 wt.% of C₆₀Oxi; degradation medium, air, air flow rate 20 mL/min, temperature regime 25-600 °C, heating rate 10 °C/min, weighted quantity 6.4 mg.

Table 2 Division of the TGA curve into temperature intervals.

Sample No.	Interval No.	Temperature range (°C)	Weight loss (%)
1 PVA-blank	1	25.0-176.5	4.9
	2	176.5-235.2	11.2
	3	235.2-294.8	34.2
	4	294.8-469.3	33.3
	5	469.3-532.4	23.4
2 PVA-1% C ₆₀ Oxi	1	25.0-81.4	5.2
	2	81.4-202.9	4.3
	3	202.9-241.8	7.5
	4	241.8-287.2	39.3
	5	287.2-453.3	21.2
	6	453.3-498.1	19.3
3 PVA-2% C ₆₀ Oxi	1	25.0-293.8	11.9
	2	293.8-385.0	52.8
	3	385.0-437.5	20.9
	4	437.5-545.7	27.3
4 PVA-3% C ₆₀ Oxi	1	25.0-288.9	12.9
	2	288.9-377.0	47.6
	3	377.0-450.1	27.7
	4	450.1-512.2	25.0

Table 3 Parameters of the ongoing thermal processes (DSC) for nanofibers PVA without and with C₆₀oxi addition.

Sample No.	Thermal process No.	Temperature range (°C)	ΔH (kJ/kg)	H_n (mW)	Overall thermal energy change ΔH (kJ/kg)
1 PVA-blank	1	25.0-95.5	-457.8	6.0	5,040.4
	2	154.1-195.7	-56.6	2.1	
	3	220.4-389.1	4,176.4	95.8	
	4	441.6-565.5	1,378.4	17.3	
2 PVA 1% C ₆₀ oxi	1	25.0-89.2	-508.2	5.2	4,458.6
	2	146.1-180.8	-38.2	4.2	
	3	234.7-293.6	3,042.1	248.7	
	4	295.2-377.7	368.0	14.5	
	5	438.9-520.5	1,594.9	65.9	
3 PVA 2% C ₆₀ oxi	1	25.0-83.1	-426.6	3.6	916.6
	2	178.0-215.4	-41.0	1.5	
	3	428.1-442.4	41.5	10.6	
	4	451.8-483.1	1,156.3	168.0	
	5	483.1-503.7	186.4	37.2	
4 PVA 3% C ₆₀ oxi	1	25.0-81.4	-418.8	3.0	2,000.3
	2	174.5-210.9	-43.9	2.2	
	3	426.3-453.1	243.5	32.1	
	4	453.1-501.9	1,454.2	109.1	
	5	501.9-538.2	765.3	75.7	

ΔH : Thermal energy change based on DSC curves ($\Delta H > 0$: exothermic process, $\Delta H < 0$: endothermic process);

H_n : Peak height of a thermal process on a DSC curve in the absolute value related to the point representing the beginning of the thermal process.

process, i.e., the area outlined with the DSC curve and a line between points that indicate the beginning and the end of the thermal process. The peak area is directly proportional to the heat released or consumed during the reaction and the peak height (H_n) is directly proportional to the reaction rate.

From 25 °C (i.e., from the beginning of the analysis) all samples demonstrated an endothermic process with the peak area on the DSC curve up to 510 kJ/kg. It probably represents evaporation of moisture. Then, at 145-180 °C, another endothermic process occurred with the peak area on the DSC curve up to 60 kJ/kg. All samples demonstrated a very distinct exothermic process with the peak area on the DSC curve above 1,000 kJ/kg. In samples No. 1 and 2 this exothermic process started as early as at 220.4 °C (sample No. 1) and 234.7 °C (sample No. 2) and the peak area on the DSC curve was 4,176.4 kJ/kg (sample No. 1) and 3,042.1 kJ/kg (sample No. 2). In samples No. 3 and No. 4 the distinct exothermic process started only at around 450 °C and the peak area on the DSC curve did

not exceed 1,500 kJ/kg. In samples No. 1 and No. 2 there were two very noticeable exothermic processes, while in samples No. 3 and No. 4 there was only one, as described above.

The thermal analysis of Fig. 4 and values of the total ΔH (Table 3) indicate that the thermal resistance of nanofibers containing 3% of C₆₀oxi deteriorated in comparison with nanofibers with 2%. A rapid decrease of thermal resistance occurred in samples containing 4% and 5% of C₆₀oxi. The total thermal energy change accompanying decomposition of the prepared nanofibers exceeded even the value of "clean" (non-composite) PVA nanofibers. Addition of 4% and 5% of C₆₀oxi causes thermal instability of the nanofibers.

3.2 Fullerene Halogenated with Bromine and Chlorine

The result of interpretation of the IR spectrum of the bromo- and bromochloroderivative might be that the substances are the same, see the measured

spectrums in Fig. 5 and Fig. 6. Maximum vibrations at 844 cm^{-1} and 773 cm^{-1} corresponds to the halogen presence. However, the TGA and DSC analyses have demonstrated different behavior of the substances during thermal stress, see the TGA and DSC curves in Fig. 7 and Fig. 8.

Fig. 5 IR spectrum of fullerene bromoderivative.

Fig. 6 IR spectrum of fullerene bromochloroderivative.

Fig. 7 Thermal analysis of fullerene bromoderivative (degradation medium is air, air flow rate 20 mL/min, temperature regime 25-550 °C, heating rate 10 °C/min, weighted quantity 12.3 mg).

Both the substances first demonstrated an end effect with the highest weight loss for $\text{C}_{60}\text{Br}_{14}$ (Table 4) which started at 126 °C; for $\text{C}_{60}\text{Br}_{10}\text{Cl}_4$ it was at a higher temperature, specifically at 152 °C. A significant exothermic process occurred for bromochloroderivative at 390 °C and for bromoderivative at 418 °C, with the peak area on the DSC curve, which corresponds to 2,084 kJ/kg for bromochloroderivative and to 4,233 kJ/kg for bromoderivative. At temperatures over above 450 °C bromochloroderivative demonstrated two more exothermic processes (Table 5 and Fig. 8).

The sum of the ΔH value of the overall thermal process of both the substances has shown that the exothermic process of bromoderivative (3,906 kJ/kg) is practically double of that of bromochloroderivative (2,270 kJ/kg).

For further specification of differences between the two substances, we heated both the samples, under identical condition as during their TGA and DSC measurements, to 250 °C, and the samples were subsequently subject to IR analysis. The resulting spectrums after the heating are provided in Figs. 9 and 10. Comparisons of IR spectrums of both the derivatives before and after the heating are shown in Figs. 11-13 compares IR spectrums of products generated after heating of the derivatives to 250 °C.

Fig. 8 Thermal analysis of fullerene bromochloroderivative (degradation medium is air, air flow rate 20 mL/min, temperature regime 25-550 °C, heating rate 10 °C/min, weighted quantity 10.4 mg).

Table 4 Division of the TGA curve into temperature intervals for fullerene bromo- and bromochloroderivative.

Sample	Interval No.	Temperature range °C)	Weight loss (%)
C ₆₀ Br ₁₄ bromoderivative	1	25.0-126.8	1.0
	2	126.8-188.3	56.1
	3	188.3-445.2	10.5
	4	445.2-495.6	32.0
C ₆₀ Br ₁₀ Cl ₄ bromochloroderivative	1	25.0-152.0	1.8
	2	152.0-191.9	51.2
	3	191.9-435.7	16.5
	4	435.7-466.6	21.9
	5	466.6-527.9	15.8

Table 5 Parameters of ongoing thermal processes (DSC) in fullerene bromo- and bromochloroderivatives.

Sample	Thermal process No.	Temperature range (°C)	ΔH (kJ/kg)	H _n (mW)	Total thermal change ΔH (kJ/kg)
C ₆₀ Br ₁₄ bromoderivative	1	122.2-195.1	-326.8	16.8	3,906.2
	2	418.1-504.2	4233.0	306.7	
C ₆₀ Br ₁₀ Cl ₄ bromochloroderivative	1	152.4-199.8	-297.1	24.2	2,270.6
	2	390.0-449.0	2084.0	335.5	
	3	449.0-490.5	437.2	24.9	
	4	506.3-528.3	46.5	9.4	

ΔH: Total thermal change during the process according to DSC curves (ΔH > 0, exothermic process, ΔH < 0, endothermic process);

H_n: Peak height of the thermal process on the DSC curve in the absolute value related to the point which represents the beginning of the thermal process.

Fig. 9 IR spectrum of fullerene bromoderivative after heating to 250 °C. **Fig. 11** Comparison of IR spectra of the initial fullerene bromoderivative (upper spectrum) and of the same substance after its heating to 250 °C (lower spectrum). **Fig. 10** IR spectrum of fullerene bromochloroderivative after heating to 250 °C. **Fig. 12** Comparison of IR spectra of the initial fullerene bromochloroderivative (upper spectrum) and of the same substance after its heating to 250 °C (lower spectrum).

Fig. 13 Comparison of IR spectrums of the derivatives after the heating to 250 °C (upper spectrum, bromochloroderivative; lower spectrum, bromoderivative).

The results indicate that in case of thermal stress of the bromoderivative beyond the temperature of its endoeffect, i.e., after a probable release of bromine, we obtained an IR spectrum practically identical with that of the initial fullerene (compare Figs. 6 and Fig. 11).

A different result was found for bromochloroderivative sample exposed to thermal stress, where in the interval 861-710 cm^{-1} , the wave numbers (peaks) are characteristic for C-Cl bonds.

Meanwhile, the spectrum makes it possible to identify vibration of groups typical for oxidation products of carbon, such as C=O ca. 1,683 cm^{-1} (1,683-1,636 cm^{-1}), -C-O ca. 3,700-3,750 cm^{-1} and skeleton -C-C=C 1,556 cm^{-1} . Peaks characterizing vibration of the C-Br bond were not identified in either case. Therefore we can conclude that all bromine was released before reaching 250 °C, probably by a radical mechanism. One can also assume that the pentadiene circle radical was probably stabilized with chlorine atoms, which enabled its reaction with atmospheric oxygen and formation of carbonyl or carboxyl groups on a chlorinated C_{60} molecule.

(a)

(b)

(c)

(d)

Fig. 14 Thermal analysis of PVA nanofibers without and with fullerene bromochloroderivative composite in the order: (a) PVA, blank; (b) PVA, 1 wt.% of bromochloroderivative, (c) PVA, 2 wt.% of bromochloroderivative, (d) PVA, 3 wt.% of bromochloroderivative; degradation medium, air, air flow rate 20 mL/min, temperature regime from 25 to 600 °C, heating rate 10 °C /1min, weighted quantity 6.4 mg.

Table 6 Division of the TGA curve into temperature intervals.

Sample No.	Interval No.	Temperature range (°C)	Weight loss (%)
1 PVA-1% bromochloroderivative	1	25.0-67.3	2.1
	2	67.3-158.7	2.6
	3	158.7-230.2	10.6
	4	230.2-282.5	36.0
	5	282.5-418.4	13.4
	6	418.4-518.5	32.6
2 PVA-2% bromochloroderivative	1	25-75.7	3.1
	2	75.7-168.9	2.1
	3	168.9-228.8	9.6
	4	228.8-277.0	38.6
	5	277.0-435.5	18.5
	6	435.5-512.3	31.7
3 PVA-3% bromochloroderivative	1	25.0-72.3	3.6
	2	72.3-153.5	1.9
	3	153.5-226.2	11.1
	4	226.2-276.6	37.9
	5	276.6-402.0	11.6
	6	402.0-532.3	39.5
4 PVA-1% bromoderivative	1	25.0-64.8	2.3
	2	64.8-163.5	2.9
	3	163.5-231.2	11.4
	4	231.2-287.8	33.0
	5	287.8-475.9	32.4
	6	475.9-557.3	23.7
5 PVA-2% bromoderivative	1	25.0-75.9	3.0
	2	75.9-157.2	1.9
	3	157.2-223.1	10.8
	4	223.1-282.6	31.3
	5	282.6-395.5	14.6
	6	395.5-547.5	42.6
6 PVA-3% bromoderivative	1	25.0-76.0	3.2
	2	76.0-152.2	1.9
	3	152.2-213.6	7.9
	4	213.6-277.6	32.0
	5	277.6-472.1	32.3
	6	472.1-537.3	24.8

Interpretation of results of thermal tests of the prepared PVA nanofibers, fullerene bromochloro- and bromoderivatives is that:

Visible differences in the course of thermal decomposition of PVA nanofibers with composites made of fullerene bromochloro- and bromoderivatives are shown in the measured TGA and DSC curves, (Figs. 14 and 15 and Tables 6 and 7).

PVA nanofibers with fullerene bromochloroderivative undergo thermal

decomposition in the air with three exothermic effects while bromoderivative demonstrates two exothermic effects, even through the first one is partly non-formed.

The total thermal change of the decomposition of nanofibers with bromochloroderivative is essentially the same (Table 7, range 1% of the value) regardless of the weight content of the composites, within 1%-3% it is lower than in case of bromoderivative. For bromoderivatives one can identify a certain

dependence of a decline (cca. by 10%) of the total thermal change on the content of bromoderivative in nanofibres, see the ΔH values in Table 7. The decline of ΔH corresponds always to ca. 10% when the composite concentration changes by 1%.

4. Discussion

There are a number of publications dealing with halogen derivatives of fullerenes [9-16] that describe preparation and identification of bromo- and chloroderivatives of fullerene C_{60} . The content of bromine in $C_{60}Br_n$ has been defined in the range $2 < n < 24$, depending on reaction conditions (direct contact with bromine, reaction in a solvent, reaction time and temperature etc.), a higher content of bromine than $n = 24$ is ascribed to an adduct with bromine and

bromination in solvents may also produce adducts with a solvent, e.g., CS_2 , $CHBr_3$, $C_6H_4Cl_2$, etc..

The most frequently used methods for identification of the prepared products included:

Elemental analysis, IR spectroscopy, X-ray analysis, TGA analysis. Identical IR spectrums were measured both for the bromoderivative and bromochloroderivative: 1,242 w, 911 w, 844 vs, 773 vs, 749 m, 718 m and 543 m(cm^{-1}).

Only the most prominent peaks (vs) are indicated below for the published spectrums:

$C_{60}Br_{24}$: 851 cm^{-1} [10]; $C_{60}Br_8$: 849 cm^{-1} [10]; $C_{60}Br_8$: 847 cm^{-1} [11]; $C_{60}Br_{24}$: 849 cm^{-1} [11]; $C_{60}Br_{14}$: 842 cm^{-1} [11]; $C_{60}Br_8 \cdot 2Br_2$: 720 cm^{-1} , 846 cm^{-1} [11]; $C_{60}Br_{14} \cdot Br_2$: 842 cm^{-1} [12]; $C_{60}Br_{24} \cdot 2Br_2$: 846 cm^{-1} [12].

Fig. 15 Thermal analysis of PVA without and with fullerene bromoderivative composite in the order: (a) PVA, blank, (b) PVA, 1 wt.% of bromochloroderivative, (c) PVA, 2 wt.% of bromochloroderivative, PVA, (d) 3 wt.% of bromochloroderivative; degradation medium, air, air flow rate 20 mL/min, temperature regime from 25-600 °C, heating rate 10 °C/min, weighted quantity 6.4 mg.

Table 7 Parameters of the ongoing thermal processes (DSC).

Sample No.	Temperature range (°C)	ΔH (kJ/kg)	H_{fi} (mW)	Total thermal energy change ΔH (kJ/kg)
1 PVA-1% bromochloroderivative	25.0-97.7	-404.9	5.7	4,273.2
	218.3-290.7	2,402.6	192.6	
	290.7-378.5	630.9	21.5	
	432.3-544.2	1,644.6	43.2	
2 PVA-2% bromochloroderivative	25.0-105.3	-520.1	7.7	4,279.0
	204.1-289.9	2,671.5	232.3	
	289.9-372.4	517.7	18.7	
	433.7-541.5	1,609.9	59.9	
3 PVA-3% bromochloroderivative	25.0-100.4	-361.7	7.1	4,338.9
	211.7-284.5	2,527.4	216.9	
	285.9-369.7	639.6	25.1	
	424.8-530.5	1,533.6	44.9	
4 PVA-1% bromoderivative	25.0-106.5	-492.2	11.7	5,679.9
	199.5-414.5	4353.8	94.8	
	414.5-581.9	1817.3	23.3	
5 PVA-2% bromoderivative	25.0-110.3	-471.3	6.9	5,138.3
	200.6-393.8	3,939.9	79.7	
	429.0-574.1	1,669.7	23.9	
6 PVA-3% bromoderivative	25.0-124.2	-532.5	9.3	4,521.2
	203.2-394.8	3,764.9	77.1	
	441.4-555.5	1,288.8	23.5	

ΔH : thermal energy change accompanying the process based on DSC curves ($\Delta H > 0$, exothermic process, $\Delta H < 0$, endothermic process);

H_{fi} : height of the peak of the thermal process on the DSC curve in the absolute value related to the point which represents the beginning of the thermal process.

The following data have been published about the thermal stability of the prepared products: $C_{60}Br_{24}$: two levels of decomposition at 45 °C and 170 °C [12]. $C_{60}Br_{24}$: beginning of decomposition at 100 °C, maximum at 162 °C [13, 14] $C_{60}Br_{24}$: at 90 °C [10] $C_{60}Br_8$: beginning of decomposition at 70 °C [10] Pressure of developing gases was measured during decomposition of $C_{60}Br_6$ [13] and based on the obtained values the authors anticipated gradual decomposition with partial maximums at 138 °C, 175 °C and 204 °C, while one atom of bromine releases from cyclopentane circle in the temperature interval 90-187 °C and cyclopentadienyl radical operates as a intermediary product of decomposition, followed by release of the remaining five bromine atoms. The authors anticipate a similar course of decomposition

also for $C_{60}Br_{24}$.

The shapes of DSC curves of our products in the endo effect area are different. It is the area where we anticipate release of bromine. For bromoderivative the range is 62 °C (126-188 °C), the shape of the DSC curve is softer (Fig. 7), potentially hiding partial maximums, which may reflect gradual release of bromine through intermediate products of decomposition, e.g., $C_{60}Br_8$. For bromochloroderivative the range is smaller, 40 °C (152-192 °C) with a positive maximum on the DSC curve (Fig. 8). In respect to the composition of our bromoderivative $C_{60}Br_{14}$, the publication [12] states that the substance with this ratio of fullerene and bromine is an intermediate product before obtaining the final product $C_{60}Br_{24}$.

Programs MOPAC/AM1 [12] were used to calculate ΔH values and two stable isomers were proposed for 14 Br, including their structure in form of a Schlegel diagram. A certain difference between our results and their derivative was that they prepared their derivative during 30 min of contact between fullerene and bromine and after 10 h they obtained their product $C_{60}Br_{24}$.

The contact to prepare our product lasted 72 h in total. One year later the essentially same authors [11] described an experiment in which they extended the contact time of fullerene and bromine to 1-2 d. The reaction product, adduct $C_{60}Br_{14}\cdot Br_2$, subsequently spontaneously decomposed to $C_{60}Br_{14}$ and bromine and its thermal decomposition occurred in one stage.

Fullerene chloroderivatives can not be prepared by a direct reaction of gaseous or liquid chlorine and fullerene C_{60} . It can be synthesized by means of chlorination reagents, e.g., $SbCl_5$, VCl_4 , $KICl_4$, $VOCl_3$, ICl at temperatures 200-300 °C using relatively long reaction times (days).

Derivatives $C_{60}Cl_n$ have been described, where $n = 6, 8, 10, 12, 26$ and 30 [14]. The least stable derivative $C_{60}Cl_6$ (prepared by reaction of fullerene with ICl in benzene) may be used for a direct reaction with bromine to prepare $C_{60}Br_{24}$ [16]. The same reaction in case of more stable fullerene chloroderivatives, such as $C_{60}Cl_n$, where $n = 8, 12, 14$, results with a very low degree of conversion even after a long reaction time.

Fullerene bromoderivative $C_{60}Br_{24}$ has been successfully chlorinated with $SbCl_5$ at 140 °C for 14 d with $KICl_4$ at 150 °C for 90 d. The prepared $C_{60}Cl_{24}$ has the same tetrahedral structure as the initial $C_{60}Br_{24}$.

Fullerene chloroderivatives are thermally more stable than bromoderivatives and they decompose to chlorine and fullerene. $C_{60}Cl_{24}$ decomposes thermally at 280-390 °C and $C_{60}Cl_{30}$ decomposes at 400-550 °C. The latter thermally stable substance has a "drum" structure, i.e., the spherical molecule of the original fullerene is flattened. The strongest peaks in the IR

spectrum are at 775, 822, 854, 895, 903, 918 cm^{-1} . The search for information has shown that it is possible to brominate a partly chlorinated (non-stable) fullerene $C_{60}Cl_6$ with elemental bromine when using long reaction times or, on the other hand, to chlorinate bromoderivatives with $SbCl_5$ or $KICl_4$ at a relatively high temperature [14, 16]. In our opinion, the temperature used for chlorination (140 °C) is above the decomposition temperature of the bromoderivative so the probable mechanism is chlorination of activated fullerene molecule after the bromine is released and the bromine is trapped by 5-valent antimony.

The comparison of the prepared halogen derivatives of fullerene with literary data has confirmed that the resulting halogen content depends on reaction conditions. Results depend on whether the reaction occurs directly in a solution, on reaction temperature, reaction time and also on the halogenating agent.

We have demonstrated experimentally that a retarder on $C_{60}oxi$ basis has good results in increasing of thermal resistance of PVA-based nanofibers. The optimum concentration in the nanofiber is cca. 2 wt.%. However, a further increase of its content above 3% has a negative effect on thermal stability of nanofibers. A similar result indicating that an additional increase of composite weight in polymer deteriorates its thermal resistance was published, e.g., for polypropylene with added MWNT [4].

Based on the functional groups bonded to fullerene molecules in $C_{60}oxi$ (the IR spectrum in Fig. 3), we can expect reactions with -OH groups on PVA by acetylation, esterification or formation of hydrogen bonds between -OH groups of polymers and $C_{60}oxi$.

Higher concentrations of $C_{60}oxi$ probably affect chemical properties of the polymer which may have an impact on deteriorating stability of nanofibers. Organic bromoderivatives in general are often successfully used as fire retarders and therefore we hoped to apply our fullerene bromoderivative to achieve a significant thermal resistance of nanofibers. The explanation can be found in preparation of the

initial polymer, during its cross-linking which is performed for 4 min at 135 °C. During this process we observed yellowing of the initial material. The temperature of cross-linking was close to the temperature at which the bromoderivative has been demonstrated to decompose and to release bromine, see the TGA and DSC curves and Fig. 7. This means that the composite was in this case probably a debrominated fullerene whose retarder effect slightly increased with its increasing content in the fiber. The bromochloroderivative changed the course of thermal decomposition of nanofibers and the total thermal energy change of the decomposition was approximately same as for nanofibers prepared from composite C₆₀oxi containing 1 wt.%.

5. Conclusions

Oxidation of fullerene with peracetic acid was used to produce C₆₀oxi, the so-called oxoderivative, which is partly soluble in water and numerous experiments have demonstrated its radioprotective properties [7, 8, 17]. Earlier in published work [7, 18] we demonstrated its sufficient solubility in water and low toxicity to the sensitive organism *Danio rerio* and its radioprotective effect which led to increasing in D₅₀ (in Gy) of about 100%. It has been demonstrated that the substance is able to eliminate superoxide radicals, OH radicals and other oxidizing agents that attack lipids, proteins, PVA and other macromolecules.

Oxoderivative fullerene preparation for the purpose of the ionizing radiation protection resulted in the preparation of material with ability to recapture free radicals has inspired to retardation experiments with combustion, which is also the radical process. Demonstration of decreased fire activity of aerosol with C₆₀oxi [19] confirmed that there was prepared highly active “free radical scavenger” and it opens many perspectives for research into its use in the protection and safety of persons related effects and chemical aggressiveness of reactive radical forms.

Testing the possibility of using halogen- and oxo-derivatives of C₆₀ in nanofibres as nanocomposites using thermogravimetric analysis demonstrated the inhibitory effect in the thermo-oxidative degradation of the prepared nanowires. It opens up possibilities for further study of thermal properties of these materials, which can be applied in the area of the security and fire protection.

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