

Antioxidative Activity of Carbon Nanotube and Nanofiber

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Abstract: Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have electron affinities similar to those of fullerenes C₆₀ and C₇₀ and they are therefore capable of acting as radical scavengers in free radical chain reactions, including polymerisation and the thermo-oxidative degradation of polymers. It is assumed that the CNTs and CNFs used as integral part of polymer composites are able to exhibit an antioxidant effect in these materials because of their radical accepting capacity.

To examine this presumption the antioxidative activity of original and purified commercial multiwall carbon nanotube MWCNT and carbon nanofibre of platelet structure CNF-PL has been studied by means of a model oxidation reaction of cumene initiated (2,2'-azobisisobutyronitrile, AIBN) in liquid phase. This model reaction was designed to simulate the thermo-oxidative processes in carbon-chain polymers and allows comparison and transfer of obtained results to a polymer system.

Kinetic measurements of oxidation rates showed that the effect of inhibition for the model oxidative reaction in the presence of the original and purified MWCNT and CNF-PL strongly depends on the presence of metals (Co, Fe) in the nanoparticles. Rates of oxidation $W_{O_2(CNT;CNF)}$ observed for the unrefined samples are result of the two competing rates - rate of inhibition $W_{inh(CNT;CNF)}$ caused by structures of the CNT or CNF and the rates of initiation $W_{i(M)}$ due to the following interaction: $ROOH + M (Co;Fe)$ i.e. $W_{O_2} \sim W_{inh(CNT;CNF)} + W_{i(M)}$.

The effective rate constants for the addition of cumyl radicals (R[·]) to MWCNT and CNF-PL have been determined. These constants reduced to the same concentration (0.5wt.%) and temperature (60°C) units have magnitudes: $k_{I(MWCNT)} [MWCNT] = (2.8 \pm 0.3) \times 10^4 \text{ s}^{-1}$ and $k_{I(CNF)} [CNF] = (6.0 \pm 1.0) \times 10^3 \text{ s}^{-1}$. Thus, the effective rate constant, reflecting the antioxidative activity for the CNT, is five times higher than that for the CNF, is about equal to the rate constant for HAS Chimassorb 2020: $k_{I(Chim.2020)} [Chim. 2020] = (2.2 \pm 0.3) \times 10^4 \text{ s}^{-1}$, is ten times less than that for the HAS Chimassorb 119FL: $k_{I(Chim.119FL)} [Chim. 119FL] = (2.8 \pm 0.3) \times 10^5 \text{ s}^{-1}$ and is about forty times less than that for the case of fullerene C₆₀: $k_{I(C60)} [C_{60}(353K)] = (1.2 \pm 0.2) \times 10^6 \text{ s}^{-1}$.

The kinetic data obtained specify the level of original antioxidative activity of MWCNTs and CNFs and scope of their rational use in polymer composites. It is believed that the results will be helpful for designing optimal profile of polymer composites filled by the CNT/CNFs.

Keywords: Model oxidation, Carbon nanotubes, Carbon nanofibres, Kinetics, Oxidation rate, Inhibiting activity, rate constant.

1. INTRODUCTION

Polymer composites with carbon nanotube (CNT) and carbon nanofibres (CNF), for example, used in or as electrical devices, are usually able to carry high current densities which undoubtedly afford Joule heating of the polymer. In particular, authors of Ref. [1] observed the high heating effects (above 200°C) of the polymer on the passage of direct current through such composites. The emitted heat leads to decreasing of the useful operating life-time of composites and therefore they need to be protected against the destructive thermal attack. On the other hand one can suppose quite significant antioxidative activity directly of CNT and/or CNFs as macromolecular analog of fullerenes. Actually

CNT/CNFs have electron affinities similar to those of fullerenes, and might therefore also be considered to behave as radical traps in chain reactions such as polymerisation and thermal degradation.

There are a number of publications on the thermal and thermo-oxidative degradation of polymers in the presence of fullerenes. These researches specified the apparent stabilizing role of fullerenes C₆₀ and C₇₀ in degradation processes of many polymers.

For instance, the stabilizing activity of fullerene C₆₀ which appeared to be purely comparable with the activity of the known stabilizer Irganox 1076 has been shown both, by means of model reaction of cumene initiated oxidation and in accelerated tests of polystyrene (PS) and polydimethylsiloxane (PDMS) rubber with the fullerene moieties [2].

It has also been shown in the Ref. [3] that fullerenes C₆₀ and C₇₀ are new high temperature antioxidants of polymers

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which are more effective than well-known inhibitors in the case of some polymers. C₆₀ also appears to be very effective in synergic mixtures with Neozone-D in the thermo-oxidative degradation of polystyrene.

The stabilizing effect of fullerenes for thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) and its blends with 1-4% fullerene C₆₀ or C₇₀ was confirmed by mass-spectrometric thermal analysis and DSC. The inhibiting effect of fullerene C₇₀ is stronger compared to C₆₀ [4].

Fullerene C₆₀ has been studied as thermal stabilizer and as antioxidant of both natural rubber (cis-1,4-polyisoprene) and synthetic cis-1,4-polyisoprene [5]. The study has been conducted respectively under nitrogen and air flow by simultaneous thermogravimetric analysis and differential thermal analysis (TGA-DTA) on rubber samples containing known quantities of fullerene in comparison to a "blank" of pure rubber. The results showed that C₆₀ fullerene (in absence of oxygen) is a thermal stabilizer of cis-1,4-polyisoprene because it reacts with the polyisoprene macroradicals formed by the thermally-induced chain scission reaction slowing down the degradation reaction. Conversely, under thermo-oxidative degradation conditions (in air flow) fullerene C₆₀ acts as an antioxidant for cis-1,4-polyisoprene, provided that the heating rate of the samples is low (5°C/min). At higher heating rates (20°C/min) C₆₀ does not show any antioxidant effect. This established result is extremely noteworthy. It proves that the fullerene loses its antioxidative capacity in the case of the polymer intensive oxidation affording the sharp increase of macropoxy radicals concentration, due to apparent insusceptibility towards oxygen-centred radicals.

Thermal stabilisation of isotactic polypropylene(i-PP) in the presence of fullerene C₆₀, its adduct with levopimaric acid, nanocarbon and carbon black is investigated by chemiluminescence at temperatures 170, 180 and 190°C [6]. The thermal oxidation of i-PP samples was carried out in air. Several kinetic parameters: oxidation induction time, half time of degradation, oxidation rate, maximum CL intensity and maximum oxidation times were calculated from CL measurements. The efficiency of additives places the studied compounds on the following order: fullerene C₆₀ < nanocarbon < carbon black < fullerene C₆₀ adduct.

Many works describe the influence of C₆₀ fullerene on the thermal and thermo-oxidative degradation of poly(methyl methacrylate)(PMMA).

Researches made on the effects of C₆₀ on the degradation of PMMA and PS in the stream of helium having 0.06% of oxygen and in dynamic oxygen showed that C₆₀ retards the degradation of the polymers [7]. Using thermogravimetry and DSC it was demonstrated that the presence of fullerene rises substantially induction periods on the curves of the polymers weight loss and considerably increases the temperatures of the onset of polymers degradation.

The C₆₀ additives inhibit the thermo-oxidative degradation of copolymers of MMA with styrene, butyl acrylate, glycidyl methacrylate and hydroxyethyl methacrylate for a long time. It is given the feasible schemes describing the reactions of C₆₀ fullerene with macroradicals produced by the thermo-oxidative degradation of copolymers and explaining the inhibiting effect of C₆₀ fullerene [8, 9].

This behaviour of fullerene C₆₀ is extended to atactic, anionic syndiotactic and isotactic forms of the PMMA. It is suggested that fullerene-containing polymers produced upon the thermal and thermo-oxidative degradation of PMMA together with the non-chain inhibition of PMMA's oxidation accounts for the stabilizing effect of fullerene [10].

For the thermal and thermo-oxidative degradation in fullerene (C₆₀, C₇₀) - polymer (PMMA, polystyrene) systems, concentration limits were observed for the stabilizing effect of fullerenes that depend on the solubility of the fullerene in a polymer: for polystyrene and PMMA, these values are 4×10^{-3} and 8×10^{-3} mol/kg of fullerene, respectively. For polystyrene-based systems containing C₆₀ or C₇₀, the temperature limit of thermal degradation was 380°C; for PMMA-based systems, this parameter amounted to 339 and 336°C for C₆₀ and C₇₀, respectively. For the thermo-oxidative degradation of these polymers and a polycarbonate, the temperature range of 335-340°C was the highest temperature limit for fullerene C₆₀ acting as an antioxidant, which was much lower than 370°C, the temperature corresponding to the onset of the intense oxidation of fullerene [11].

The strong antioxidative activity of fullerene C₆₀/C₇₀ has been found in model reaction of the initiated oxidation of styrene and then in accelerated tests the fullerenes mixtures with polystyrene. For the first time the rate constant for the addition of styryl radicals to C₆₀/C₇₀ has been determined to be $k_{(333\text{ K})} = (9.0 \pm 1.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. By means of thermal analysis of polystyrene using DSC and TGA methods it was demonstrated that fullerenes show a stabilizing effect purely comparable with that of for sterically-hindered phenol Irganox 1010 and amine Agerite White. The suggestion was made that the retarding effect of fullerenes is connected with its interaction with macroradicals R· leading to formation of less active compounds [12].

The presence of fullerene C₆₀ additives shifts the decomposition process of poly-*n*-alkyl acrylates and polymethacrylates under dynamical and isothermal conditions from a radical pathway to a non-radical mechanism [13]. For poly-*n*-alkyl acrylates the addition of fullerenes lead to the increase in the yields of olefin and alcohol, degradation products coming from non-radical pathways. On the other hand, the yields of the pyrolysis products deriving from the random main-chain scission, i.e. monomer, dimer, saturated diester, trimer, corresponding acetate and methacrylate, decrease. The stabilizing effect of fullerene is more noticeable in the thermal behaviour of poly-*n*-alkyl methacrylates, where enhancements of the temperature of maximum weight loss are 19–25°C. The mixtures containing fullerene give rise to a marked decrease of the monomer yield and, at the same time, an increase of olefin and methacrylic acid amounts. The fullerene acts as radical acceptor suppressing the unzipping process and favouring the non-radical side-chain reactions [13].

Thus, it is seen from short literature analysis the stabilizing role of fullerenes in the processes of oxidation of polymers. Because of their radical accepting capacity, CNTs and CNFs can also be expected to interrupt chain propagation, leading to antioxidant action in polymers.

To consider the detailed mechanisms of the activity of CNTs and CNFs and to obtain quantitative data it is obviously advisable to use also a certain chemical pure system simulating the thermo-oxidative degradation of polymers. The model system comprising a cumene initiated oxidation has proved to provide a useful basis as an efficient tool to describe the performance of antioxidants in an oxidizing medium [14-21], and this model is suitable for the designing the framework of thermo-oxidative processes in polymers [22-27].

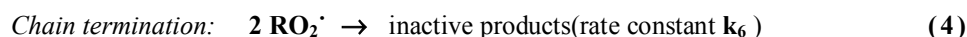
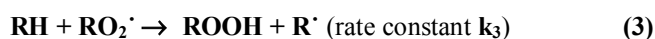
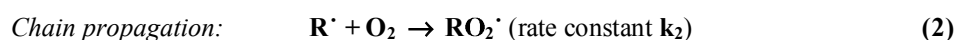
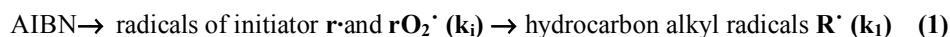
In this work an antioxidative effect of multiwall carbon nanotube MWCNT(Ib) and carbon nanofibre CNF-PL is tested using the oxidation of cumene as a model reaction. The proposed model oxidation is considered to simulate the thermo-oxidative degradation of carbon-chain polymers and it allows comparison of the results with those for a polymer system [21].

2. THEORETICAL CONSIDERATIONS

The model reactions of cumene initiated (initiator is 2,2'-azo-bisobutyronitrile, AIBN) oxidation are obligatory designed to proceed under steady state conditions with fairly long kinetic chains ($\nu > 10$) at moderate temperatures (40-80°C) [14, 15, 18 - 21]. The hydroperoxide does not contribute additionally to the initiation of oxidation. The air oxygen pressure is sufficient to not limit the process [$P_{O_2} = 20$ kPa (10^{-3} mol O_2 l $^{-1}$)].

For this case the model oxidation scheme may be represented in the following form:

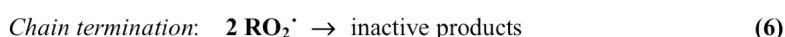
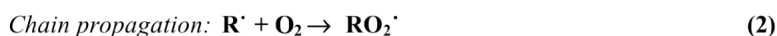
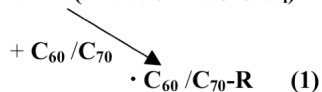
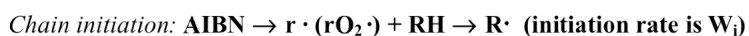
Chain initiation: generation of R^\cdot radicals (W_{iAIBN} is the initiation rate),



Scheme 1. Using the currently accepted rate constant numbering for elementary oxidation reactions [28, 29].

with **RH**: hydrocarbon, R^\cdot : alkyl radical, RO_2^\cdot : peroxy radical, **ROOH**: hydroperoxide.

The initiated oxidation scheme is changed in the presence of fullerenes C_{60} and/or C_{70} and can be represented as follows [2,12]:



Scheme 2.

where C_{60}/C_{70} - R: spin-adduct of fullerenes.

The fullerene plays an inhibiting role to reduce the initial initiation rate by interaction with R^\cdot cumylalkyl radicals. There is no interaction with cumylperoxy radicals.

For this scheme the rate of oxidation is described as

$$W_{O_2(C_{60}/C_{70})} = W_{i1}^{1/2} k_3 k_6^{-1/2} [RH] \quad /2/$$

where $W_{O_2(C_{60}/C_{70})}$ and W_{i1} are the oxidation and initiation rates in the presence of fullerenes, respectively: $W_{i1} = W_i - W_{full}$ and $W_{full} = k_1[R^\cdot] [C_{60}/C_{70}]$.

3. EXPERIMENTAL

The model reaction for cumene oxidation was conducted at the following initiation rates:

$W_i = 3.5 \cdot 10^{-8}$, $6.8 \cdot 10^{-8}$ and $1 \cdot 10^{-7}$ mol/l·s, temperatures were 40, 60 and 80 (± 0.02) °C and oxygen pressures were in each case $P_{O_2} = 20$ kPa (air).

2,2'-azobisisobutyronitrile (AIBN) was employed as the initiator. The volume of the reaction mixture was 10 cm³ (25°C). To achieve the stated initiation rates 100 mg (40°C), 10 mg (60°C) and 1 mg (80°C) of AIBN had to be added [30].

The CNT and CNF were the multiwall carbon nanotube MWCNT (Ib) and carbon nanofibre CNF-PL (platelet structure) manufactured by German Future Carbon GmbH with the following features:

MWCNT (Ib) - average diameter of particles: 10-20 nm; BET-surface ~ 200 m², content of the metal (Co) ≤ 1.5 wt. %

(Quality 1) (cf. Fig. 1a) and

CNF-PL (platelet structure) - average diameter of particles: 100-250 nm; BET-surface ~ 120 m², content of the metal (Fe) ≤ 5 wt. % (cf. Fig. 1b).

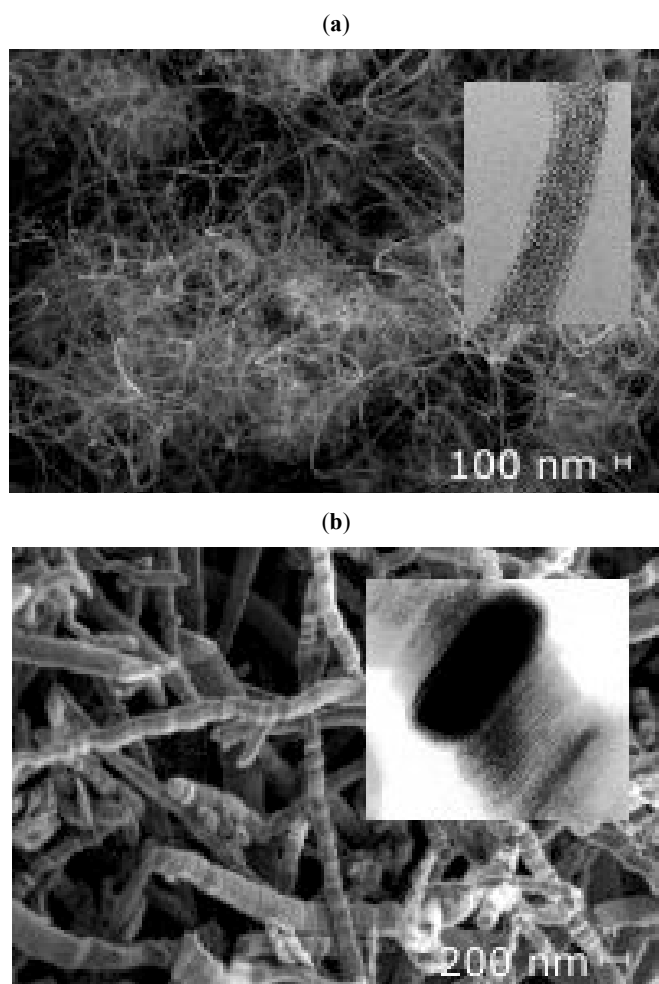
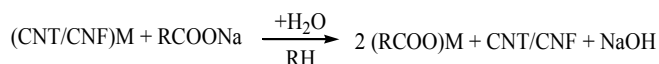


Fig. (1). SEM images of MWCNT (a) and CNF-PL (b)

Samples of the MWCNT and CNF-PL contain traces of metals and therefore must be underwent the purification to be applicable for study as potential antioxidants. In this investigation a new technique of purification is proposed. The matter of the purification consists of extraction of a metal from the CNT/CNF by means of processing of samples by sodium salts of distilled natural oil acids. In this case the following exchange interaction is taken place:



The indigenous oil acids are a complex mixture of mono-carboxylic aliphatic, alkyl-substituted alicyclic and aromatic acids. They were isolated from the Azerbaijanian offshore oils by the standard conventional method [31, 32].

The employed compounds were:

Distilled natural oil acid with acidity index – 285 mg KOH/g, molecular weight MW = 197 g/mole; Sodium hydroxide - 10% aqueous solution; Solvents – white spirit, butanol, benzene, petroleum-ether.

First, an amount of distilled oil acid providing full extraction of the metals is calculated. This amount is further saponified by 10% of the sodium hydroxide aqueous solution at temperatures 60-80°C and at continuous stirring. The saponification is considered to be completed when the value of the acid number of the reaction mix reaches 3-5 mg

KOH/mg. Then the mixture is diluted with the solvents (white spirit + butanol), and samples of the CNT/CNF are introduced inward. The reaction is conducted at 70-80°C for 1.5-2 hours with uninterrupted stirring. The exchange reaction proceeds according to the above stated pathway. The salt of oil acid, now containing the metal of CNT/CNF, is left in hydrocarbonic phase whereas the nanocarbon particles are directed to an aqueous phase. In order to enlarge the moiety of the aqueous phase hot water (70-80°C) is further added. The stirring is stopped and the mix is left for sedimentation for 24 hours.

The aqueous phase is separated from the hydrocarbonic, the nanoparticles are filtered out from the aqueous phase and then two times are washed out by hot water. Isolated nanoparticles, free of metal, are dried up to a fixed weight.

The rate constants of chain propagation and termination for the cumene oxidation at 40, 60 and 80°C respectively are: $k_3 = 0.58; 1.75; 3.45 \text{ l mol}^{-1} \text{ s}^{-1}$; $k_6 = 1.03 \times 10^5; 1.84 \times 10^5; 3.45 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$, concentration of cumene [RH] = 6.9 mol l⁻¹ [20, 28, 33].

Rates of oxidation were evaluated from the amount of oxygen consumed, which was measured volumetrically with the simple equipment as described in [14, 21, 27]. Oxidation rates were assessed both from slopes of kinetic curves of oxygen consumption in the case of steady rate values and also by means of differentiating the curve in the case of observed autocatalysis during a measuring period. Experiments were carried out at least in triplicate and the correctness of the oxidation rate values determined was within the range 1 - 4%.

4. RESULTS AND DISCUSSION

The Fig. (1) illustrates the kinetic curves profiles in the cumene-initiated oxidation in absence or presence of original and purified MWCNT (Ib) at 60°C.

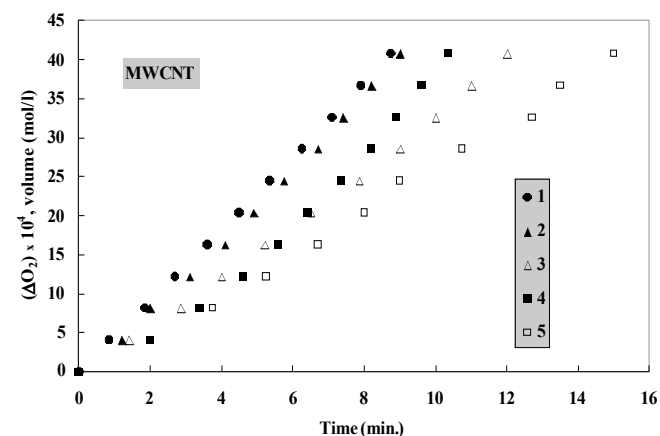


Fig. (2). Kinetic dependencies of oxygen-uptake for the model cumene initiated oxidation in the absence (1) and presence of original (2, 4) and purified (3, 5) form of multiwalled carbon nanotube MWCNT (Ib). The initiator was 2,2'-azobisisobutyronitrile (AIBN), and the initiation rate was $W_i = 6.8 \cdot 10^{-8} \text{ mol/l s}$, the reaction mixture volume was 10 ml, the oxygen pressure was $P_{O_2} = 20 \text{ kPa}$ (air), the temperature was kept at 60°C.

The concentration [MWCNT (Ib)], wt. % was (1) = 0; (2, 3) = 0.1; (4, 5) = 0.2.

The kinetic dependencies clearly showed reduced oxidation rates in the presence of the MWCNT (1b) which had steady values for purified samples during the measuring period. While the oxidation kinetic curves of the original unrefined MWCNT (1b) exhibit higher oxidation rates and slight autocatalytic shape because of the catalytic action of the cobalt metal (Co) contained in the MWCNT.

The measurements with CNF-PL samples displayed the same regularities for the kinetic curves running as those of for the MWCNT. Figs. (3-5) demonstrate the oxygen absorption for the cumene-initiated oxidation in the absence and presence of CNF-PL at 40, 60 and 80°C.

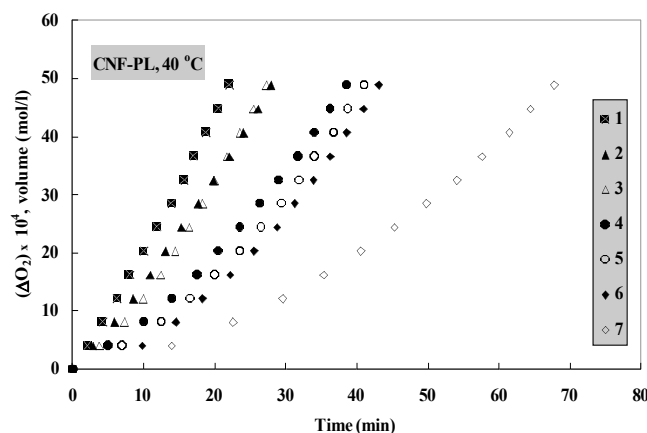


Fig. (3). Kinetic dependencies of oxygen-uptake for the model cumene initiated oxidation in the absence (1) and presence of original (2, 4, 6) and purified (3, 5, 7) form of the carbon nanofiber CNF-PL. The initiator was 2,2'- azobisisobutyronitrile (AIBN), and the initiation rate was $W_i = 3.5 \cdot 10^{-8}$ mol/l s, the reaction mixture volume was 10 ml, the oxygen pressure was $P_{O_2} = 20$ kPa (air), the temperature was 40°C.

The concentration [CNF-PL], wt. % was (1) = 0; (2, 3) = 0.3; (4, 5) = 1.0; (6, 7) = 2.0

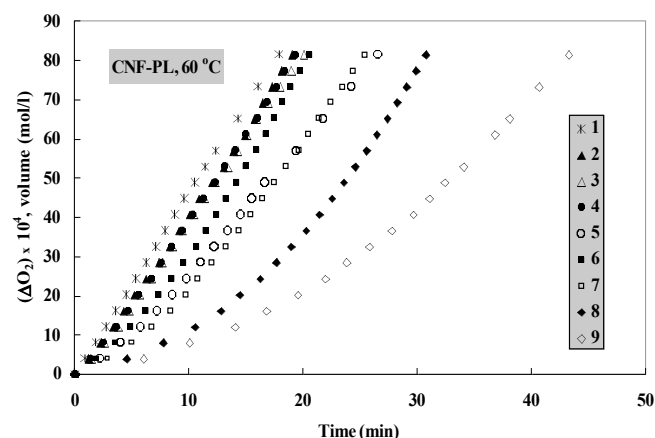


Fig. (4). Kinetic dependencies of oxygen-uptake for the model cumene initiated oxidation in the absence (1) and presence of original (2, 4, 6, 8) and purified (3, 5, 7, 9) form of the carbon nanofiber CNF-PL. The initiator was 2,2'- azobisisobutyronitrile (AIBN), and the initiation rate was $W_i = 6.8 \cdot 10^{-8}$ mol/l s, the reaction mixture volume was 10 ml, the oxygen pressure was $P_{O_2} = 20$ kPa (air), the temperature was 60°C.

The concentration [CNF-PL], wt. % was (1) = 0; (2, 3) = 0.3; (4, 5) = 0.5; (6, 7) = 1; (8, 9) = 2.

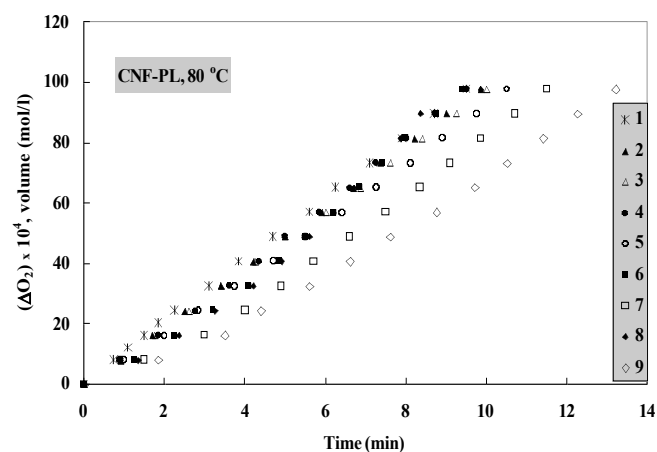


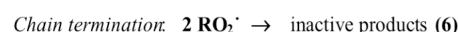
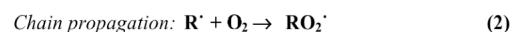
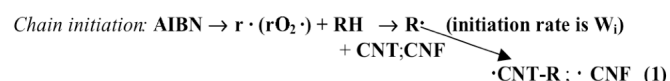
Fig. (5). Kinetic dependencies of oxygen-uptake for the model cumene initiated oxidation in the absence (1) and presence of original (2, 4, 6, 8) and purified (3, 5, 7, 9) form of the carbon nanofiber CNF-PL. The initiator was 2,2'- azobisisobutyronitrile (AIBN), and the initiation rate was $W_i = 1.0 \cdot 10^{-7}$ mol/l s, the reaction mixture volume was 10 ml, the oxygen pressure was $P_{O_2} = 20$ kPa (air), the temperature was 80°C.

The concentration [CNF-PL], wt. % was (1) = 0; (2, 3) = 0.3; (4, 5) = 0.5; (6, 7) = 1; (8, 9) = 2.

It is seen from the Figs. (3-5) that the effects of inhibition are displayed at more high concentrations of introduced CNF-PL than that for the MWCNT. In all cases the purification leads to more retardation in model oxidation which is pronounced for the high concentrations of the CN. The model oxidation proceeds with steady rate in the case of the purified samples, although at high concentrations the autocatalytic shape is retained (see curves 5, 7 of Fig. (3), and curves 7, 9 of both Figs. (4) and (5)).

The rates of oxidation $W_{O_2(MWCNT)}$ and $W_{O_2(CNF)}$ observed for the original nanosamples depends on two competing rates - the rates of inhibition W_{MWCNT} and W_{CNF} caused by the structures of the CNT and CNF, respectively and the rates of initiation $W_{(Co; Fe)}$ caused by the interaction $ROOH + M(Co; Fe)$ i.e. $W_{O_2(MWCNT; CNF)} \sim W_{(MWCNT; CNF)} + W_{(Co; Fe)}$

Thus according to the obtained results this scheme for the cumene model oxidation in the presence of the original MWCNT and CNF-PL can be represented in the following form:



Scheme 3.

where CNT: the MWCNT (1b), $\cdot CNT-R$ - spin-adduct of MWCNT (1b), CNF: the CNF-PL, $\cdot CNF-R$ - spin-adduct of CNF-PL, M^{n+} - the metals Co and Fe contained in the nanotube and the nanofibre, respectively.

Under steady-state conditions with the Scheme 3 the rates of forming and destruction of free radicals become equal:

$$dR\cdot/dT = W_i - k_2[R\cdot][O_2] - k_1[R\cdot][MWCNT;CNF] + k_3[RO_2\cdot][RH] = 0$$

$$dRO_2\cdot/dT = k_2[R\cdot][O_2] - k_3[RO_2\cdot][RH] + k_4[ROOH][M^{n+}] - k_6[RO_2\cdot]^2 = 0$$

Adding together these two equations we obtain the following expressions:

$$W_i - k_{1(MWCNT;CNF)}[R\cdot][MWCNT;CNF] + k_4[ROOH][M^{n+}] - k_6[RO_2\cdot]^2 =$$

$$W_i - W_{MWCNT}(W_{CNF}) + W_M - k_6[RO_2\cdot]^2 = 0 \text{ and}$$

$$[RO_2\cdot] = [(W_i - W_{MWCNT}(W_{CNF}) + W_M) / k_6]^{1/2}$$

$$\text{with } W_{MWCNT} = k_{1(MWCNT)}[R\cdot][MWCNT] / 3,$$

$$W_{CNF} = k_{1(CNF)}[R\cdot][CNF] / 4/$$

$$\text{and } W_M = k_4[ROOH][M(Co;Fe)^{n+}] / 5/$$

Thus the rates of oxidation are as follows:

$$W_{O_2(MWCNT)} = k_3[RO_2\cdot][RH] = (W_i - W_{MWCNT} + W_{Co})^{1/2} k_3 k_6^{-1/2}[RH] / 6/$$

$$W_{O_2(CNF)} = k_3[RO_2\cdot][RH] = (W_i - W_{CNF} + W_{Fe})^{1/2} k_3 k_6^{-1/2}[RH] / 7/$$

For the purified samples of CNT and CNF the rates $W_{MWCNT} \gg W_{Co}$ and $W_{CNF} \gg W_{Fe}$ and Eqs. /6/ and /7/ become simplified to

$$W_{O_2(MWCNT)} = (W_i - W_{MWCNT})^{1/2} k_3 k_6^{-1/2}[RH] = W_{iMWCNT}^{1/2} k_3 k_6^{-1/2}[RH] / 8/ \text{ and}$$

$$W_{O_2(CNF)} = (W_i - W_{CNF})^{1/2} k_3 k_6^{-1/2}[RH] = W_{iCNF}^{1/2} k_3 k_6^{-1/2}[RH] / 9/$$

wherein W_{iMWCNT} and W_{iCNF} are the rates of initiation in the presence of MWCNT (Ib) and CNF-PL, respectively. Hence

$$W_{MWCNT} = W_i - W_{iMWCNT} = W_i - W_{O_2(MWCNT)}^2 k_6 k_3^{-2}[RH]^2 / 10/$$

$$W_{CNF} = W_i - W_{iCNF} = W_i - W_{O_2(CNF)}^2 k_6 k_3^{-2}[RH]^2 / 11/$$

Under steady-state conditions of oxidation in the presence of MWCNT or CNF-PL the following equations are valid for fairly long chains [21, 28]:

$$k_2[R\cdot][O_2] = k_3[RO_2\cdot][RH] = W_{O_2(MWCNT;CNF)} / 12/$$

Using equations /3/, /4/, /8/ – /12/ the following expressions can be obtained for the calculation of effective rate constants $k_{1(MWCNT)}[MWCNT]$ and $k_{1(CNF)}[CNF]$:

$$[R\cdot] = W_{O_2(MWCNT;CNF)} / k_2[O_2] = W_{O_2(MWCNT;CNF)} / 10^6,$$

$$k_{1(MWCNT)}[MWCNT] = 10^6 W_{MWCNT} / W_{O_2(MWCNT)} = 10^6 \{W_i - W_{O_2(MWCNT)}^2 k_6 k_3^{-2}[RH]^{-2}\} / W_{O_2(MWCNT)} / 13/$$

$$k_{1(CNF)}[CNF] = 10^6 W_{CNF} / W_{O_2(CNF)} = 10^6 \{W_i - W_{O_2(CNF)}^2 k_6 k_3^{-2}[RH]^{-2}\} / W_{O_2(CNF)} / 14/$$

From the experimentally observed rates for the oxidation $W_{O_2(MWCNT)}$ and $W_{O_2(CNF)}$, assigned value of the initiation rate W_i and known constants for the cumene liquid phase oxidation, including $k_2 = 10^9$, l/mol s; $[O_2] = 10^{-3}$ mol/l [28, 33, 34] the effective rate constants may be calculated according to Equations /13/ and /14/. These values appeared to be

for the [MWCNT] within 0.1 – 0.2 wt. % $k_{1(MWCNT)}[MWCNT]_{(333-353K)} = (8.0 \pm 2.0) \times 10^3$ s⁻¹, and for [CNF-PL] within 0.5 – 2 wt. % $k_{1(CNF)}[CNF]_{(333-353K)} = (2.0 \pm 1.6) \times 10^4$ s⁻¹. If reducing the obtained constants to the same 0.5 wt.% concentration and temperature 60°C units the following magnitudes were kept: $k_{1(MWCNT)}[MWCNT]_{(333K)} = (2.8 \pm 0.3) \times 10^4$ s⁻¹, $k_{1(CNF)}[CNF]_{(333K)} = (6.0 \pm 1.0) \times 10^3$ s⁻¹. This appears that the effective rate constant which reflects the antioxidative activity for the CNT is five time higher than that for the CNF and is about fifty time less than that for the case of fullerene C₆₀ $k_{full}[C_{60}(0.5\%)]_{(333K)} = (1.2 \pm 0.2) \times 10^6$ s⁻¹ calculated from the data of Ref. [2]. The increased antioxidative activity of the CNT as compared with the CNF is presumably explained by the presence of fullerene moieties in the CNT structure.

It has been shown earlier in the works [21, 35] that the hindered piperidine HAS stabilizers retards the model thermal oxidation acting as acceptors of cumylalkyl R· radicals.

It is similar to the mechanism of inhibition for fullerenes and CNT/CNFs and therefore the comparison of the rate constants would be relevant.

The effective rate constants for the Chimassorb 2020 and 119 FL calculated from the data of Refs [21, 35] are $k_{1(Chim.2020)}[Chim. 2020]_{(333K)} = (2.2 \pm 0.3) \times 10^4$ s⁻¹ and $k_{1(Chim.119FL)}[Chim. 119FL]_{(333K)} = (2.8 \pm 0.3) \times 10^5$ s⁻¹. Hence the datum for the Chimassorb 2020 appears to be close to the region of rate constants obtained for the CNT/CNFs while the rate constant for Chimassorb 119FL is many times higher than those for the nanocarbon samples.

Thus, the results obtained in this paper specify the limits of rational use of carbon nanotubes and carbon nanofibers as antioxidants in polymer composites.

CONCLUSIONS

Presumptive anti-oxidative effect of the multiwalled carbon nanotube (MWCNT) and carbon nanofiber of platelet structure (CNF-PL) has been examined by means of the model reaction of cumene initiated oxidation. Experimental kinetic measurements of the oxygen uptake clearly showed reduced values of oxidation rates in the presence of the MWCNT and CNF-PL. The purified samples afford more profound inhibition of the model oxidation in comparison with original ones. Certain limitations for the retardation were attributed to the catalytic action of the metals (Co and Fe) originally contained in the commercial samples.

The concept of antioxidative behaviour of carbon nanotubes and nanofibres has basically been proved though further detailed quantitative studies of the modified representatives are required.

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