ИЗВЕСТИЯ ВЫСШИХ УЧЕБНЫХ ЗАВЕДЕНИЙ.
Т 63 (11) Серия «**ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ**» 2020

IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENII
V 63 (11) **KHIMIYA KHIMICHESKAYA TEKHNOLOGIYA** 2020
RUSSIAN JOURNAL OF CHEMISTRY AND CHEMICAL TECHNOLOGY

DOI: 10.6060/ivkkt.20206311.6213

ВЛИЯНИЕ ДОБАВОК НАНОУГЛЕРОДА НА СТАБИЛЬНОСТЬ ПОЛИМЕРНЫХ КОМПОЗИТОВ

Э.Б. Зейналов, М.М. Агагусейнова, Н.И. Салманова

Эльдар Багадур Зейналов

Лаборатория окисления пероксидом водорода в присутствии нанокатализаторов, Институт катализа и неорганической химии АН Азербайджана, просп. Г.Джавид, 113, Баку, AZ1143, Азербайджан
E-mail: elzey@mail.ru

Минира Магомед Али Кызы Агагусейнова*, Назиля Искандар Салманова

Кафедра химии и технологии неорганических веществ, Азербайджанский государственный университет нефти и промышленности, просп. Азадлыг, 20, Баку, AZ1010, Азербайджан
E-mail: minira_baku@yahoo.com*, nazilya.salmanova@gmail.com

В этом обзоре кратко описывается состояние исследований по влиянию фуллеренов и углеродных нанотрубок (УНТ) на долговечность различных полимерных композиционных материалов, эксплуатируемых в экстремальных условиях. Фуллерены C_{60}, C_{70}, фуллереновая сажа и УНТ, введённые в полимерную матрицу, эффективно предотвращают процессы как термической, так и термо- фотоокислительной деструкции. Механизм стабилизации углеродных наносоединений (УНС) практически идентичен и состоит в обрыве цепей окисления на наноуглеродном каркасе. При этом все данные однозначно указывают на преимущественное присоединение к УНС углерод-центрированных алкильных радикалов. Таким образом, указанные углеродные наноструктуры могут рассматриваться как редкий класс эффективных базовых антиоксидантов, действие которых заключается в снижении скорости зарождения цепей термоокислительной деструкции на самом первом этапе. Для этого такие антиоксиданты должны обладать очень высокой константой скорости присоединения алкильных радикалов, чтобы составить конкуренцию реакции $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$. В данной работе рассмотрены различные полимерные композиционные материалы на основе полиолефинов, полиакрилатов, полиамидов, поликарбонатов, эластомеров. Описанные подходы направлены, в основном, на решение задачи повышения стабильности полимерных композитов путем введения в их состав различных комбинаций наноуглеродных добавок. Оптимальная дозировка УНС и межфазная совместимость между полимером и наполнителями могут значительно повысить термостойкость композитов. Замена атомов углерода в молекуле фуллерена гетероатомами также может изменить ее электронные свойства и улучшить антирадикальную и антиокислительную активность. Области эффективного использования фуллерена C_{60} в водных средах могут быть значительно расширены путем их модификации гидрофильными полимерами. Таким образом, эффективность УНС как стабилизаторов-антиоксидантов для полимерных материалов сравнима с действием сильных синтетических стабилизаторов. УНС обладают хорошими перспективами для реального промышленного применения.

Ключевые слова: фуллерены, углеродные нанотрубки, полимерные композиты, термоокислительная деградация, акцепторы радикалов, стабилизаторы

Для цитирования:
Зейналов Э.Б., Агагусейнова М.М., Салманова Н.И. Влияние добавок наноуглерода на стабильность полимерных композитов. *Изв. вузов. Химия и хим. технология*. 2020. Т. 63. Вып. 11. С. 4–12
For citation:
Zeynalov E.B., Agaguseynova M.M., Salmanova N.I. Effect of nanocarbon additives on stability of polymer composites. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. [Russ. J. Chem. & Chem. Tech.]. 2020. V. 63. N 11. P. 4–12

EFFECT OF NANOCARBON ADDITIVES ON STABILITY OF POLYMER COMPOSITES

E.B. Zeynalov, M.M. Agaguseynova, N.I. Salmanova

Eldar B. Zeynalov

Laboratory of Oxidation by Hydrogen Peroxide in the Presence of Carbon Nanocatalysts, Institute of Catalysis & Inorganic Chemistry of ANAS, H. Javid ave., 113, Baku, AZ1143, Azerbaijan
E-mail: elzey@mail.ru

Minira M. Agaguseynova*, Nazila I. Salmanova

Department of Chemistry and Technology of Inorganic Substances, Azerbaijan State Oil and Industry University, Azadlig ave., 20, Baku, AZ1010, Azerbaijan
E-mail: minira_baku@yahoo.com*, nazilya.salmanova@gmail.com

This review briefly describes a state of research on the effect of fullerenes and carbon nanotubes (CNTs) on a durability of various polymer composite materials under extreme conditions. Fullerenes C_{60}, C_{70}, fullerene soot and CNTs integrated into the polymer matrix effectively prevent both thermal and thermo-oxidative degradation, as well as photo-oxidation processes. The stabilization mechanism of the carbon nanocompounds (CNC) is likewise and consists of the substantial end-capping termination of oxidation destructive chains on the nanocarbon skeleton. At that, the data array unequivocally indicates the predominant addition of carbon-centered alkyl radicals. Various polymer composite materials based on polyolefins, polyacrylates, polyamides, polycarbonates, elastomers are involved into the consideration. The approaches described are mostly aimed to increase the level of stabilizing activity of the polymer composites using different combinations of nanocarbon additives. The optimal dosage of CNC and interfacial compatibility between the polymer and fillers can significantly increase the heat resistance of the composites. The replacement of carbon atoms in the fullerene molecule with heteroatoms can also change its electronic properties and improve the antiradical and antioxidant activity. Areas for the effective use of fullerene C_{60} in aqueous media can be significantly expanded by modification with hydrophilic polymers. Thus, the performance of CNC integrated in the polymer composites is similar with those for strong synthetic stabilizers. CNC have good prospects for real industrial applications.

Key words: fullerenes, carbon nanotubes, polymer composites, thermooxidative degradation, radical scavengers, stabilizers

GENERAL INTRODUCTION

Nanoscience area is exemplified by numerous studies and important results having high scientific and applied significance.

Polymer nanocomposites are currently the main targets of contemporary polymer chemistry and hence, the issue of their stability and durability during storage and performance is one of the most important [1, 2]. This review presents some noteworthy results in this field recently published and indexed in the Web of Science.

REVIEW OF THE PUBLICATIONS

Issues on the effect of disparity of carbon nanomaterials (CNMs) along the matrix and their interaction with the polymer were considered. It is postulated that the uniform distribution of CNMs can be significantly improved by functionalization of a surface of carbon nanofillers, as well as by optimal processing the preparing nanocomposites. Potential carbon nanofillers, such as CNTs, graphene, fullerene and carbon nanofibers (CNF) significantly increase the thermal stability of polymer compositions by way of several mechanisms. The optimal dosage of CNMs and interfacial compatibility between polymer and fillers can increase the heat resistance of composites to greater extent. CNMs can also significantly change the glass transition temperature and crystallization, as well as degree of crystallinity of a composite polymer phase [3].

Nanocarbon compounds have a peculiar electronic structure making possible the intensive attachment of various nucleophilic particles, such as electrons, free radicals, anions, hydrogen atoms to their walls or surfaces [4]. For instance, fullerenes possess high electron affinity within the range 2.65 eV (C_{60})-3.5 eV (C_{84}) [4]. Hence, the high electron affinity allows fullerenes intensively attach electron-deficient organic radicals, such as benzyl and tert-butyl radicals [5-7]. The active addition of alkyl radicals to fullerenes is also confirmed by high values of the rate constants – ca = $10^{8\pm1}$ $M^{-1}s^{-1}$ [8-12]. Thus, fullerenes can act as effective terminators of radicals in radical chain processes, including thermal and thermooxidative degradation of polymers. The chain processes are ruled by alkyl and peroxide macroradicals and therefore can be retarded and even suspended by compounds which capable to trap such radicals.

Actually, there are a series of publications in the literature showing the stabilizing role of fullerenes while polymer materials are subjected to ageing or disruption.

One of the first works proving the inhibiting activity of fullerene C_{60} in oxidizing hydrocarbon medium was Ref. [11]. There was demonstrated both using model reaction of cumene initiated oxidation and by thermooxidative degradation of polystyrene and polydimethylsiloxane rubber [11].

Another study was undertaken to determine the antioxidant activity of a number of C_{60}-C_{70} fullerenes and their mixtures, in order to set them according to the efficiency [9]. The low-temperature model cumene oxidation reaction initiated by 2,2'-azo-bisisobutyronitrile was used. Kinetic measurements of the oxidation rate in the presence of various fullerenes showed that there is a satisfactory correlation between the rate constant values and electron affinity for fullerene molecules. At the same time it has been found the discrepancy in the inhibition mechanism for fullerenes C_{60}, C_{70} and fullerene soot: – all fullerenes – C_{60} (99%), C_{60}/C_{70} (93/7, mixture 1), C_{60}/C_{70} (80 ± 5/20 ± 5, mixture 2) and C_{70} operate in the mode of acceptance of alkyl radicals, while fullerene soot unexpectedly exerts mechanism of double mode – first, similar to that for C_{60}-C_{70} fullerenes, and the second, like action of many primary phenolic and amine antioxidants. It was found for C_{60} and C_{70} that the oxidation rates linearly depend on the inverse square root of the fullerene's concentration in a fairly wide range thereby confirming the mechanism of addition of $R^{\bullet}$ alkyl radicals to a fullerene core. This fact is in accordance with well-known published data about preferences of alkyl radicals in the described reactions. The rate constants of the cumyl $R^{\bullet}$ radicals attachment to fullerenes were determined to be $k_{(333K)} = (1.9 \pm 0.2)\cdot10^8$ (C_{60}); $(2.3 \pm 0.2)\cdot10^8$ (C_{60}/C_{70}, mixture 1); $(2.7 \pm 0.2)\cdot10^8$ (C_{60}/C_{70}, mixture 2); $(3.0 \pm 0.3)\cdot10^8$ (C_{70}), $M^{-1}s^{-1}$. An increase of C_{70} portion in the fullerene mixture leads to corresponding increase in the rate constant. Fullerene soot inhibits the oxidation in accordance with mechanism of peroxide radicals capture. In this case, the oxidation proceeds with induction period and exemplified by kinetic curves which are well straightened in semilogarithmic coordinates. Effective concentrations of inhibitory centers and inhibition rate constants for fullerene soot were first determined as:

fn [C_{60}-soot] = $(2.0 \pm 0.1)\cdot10^{-4}$ mol g^{-1} and $k_{in.} = (6.5 \pm 1.5)\cdot10^3$ M^{-1} s^{-1}, respectively [9].

It was shown that fullerenes C_{60} and C_{70} are new high-temperature antioxidants of polymers and operate more effective than known inhibitors of the polymer oxidation. It was found that C_{60} forms a synergistic mixture with Ph_3Sb and phenyl-beta-naphthylamine (Neozone-D) upon thermo-oxidative degradation of polystyrene. These synergistic fullerene-based mixtures are proposed as new high-temperature antioxidants for polystyrene (PS) [13].

Although fullerene C_{60} is considered as a strong acceptor of alkyl radicals, it is unexpectedly not susceptible to peroxide radicals. It seems the replacement of carbon atoms in the fullerene cage with heteroatoms can change the electronic background of the molecule and improve antiradical and antioxidant activity [14]. In the study being under this consideration, the antiradical and antioxidant activity of azafullerenes $C_{40}N_{20}$ and $C_{42}N_{18}$ were studied and compared with those for C_{60} using method of calculating the electronic structure (DFT). The process of adsorption of several alkyl and peroxide radicals on the most active sites of various separated isomers of these azafullerenes was studied. The results unambiguously showed that both isomers of azafullerenes exhibit stronger antiradical activity than C_{60} [14].

Areas for effective use of fullerene C_{60} in aqueous media can be significantly expanded by modification with hydrophilic polymers. Kinetics of radical addition for four water-soluble fullerene polymer systems (C_{60}-PAA-C_{60}, PAA-C_{60}, PEO-b-PAA-C_{60} and PDMA-C_{60} was studied by using calorimetric analysis. The measure of these compounds to accept stable 1,1-diphenyl-picryl-hydrazyl radical (DPPH) showed a two-stage kinetic tendency that correlates with the self-assembly behavior of fullerene-polymer systems in aqueous solutions. Since there was a mixture of unimers and micelles, the first kinetic process was explained by the inherent scavenging property of more accessible unimers, while the second stage was concerned to the scavenging behavior of micelles. The micellar scavenging reaction rate depends on the size of a micelle: for larger micelles the reaction is going faster, especially if larger number fullerenes are available for the scavenging reaction. The results demonstrate the effect of nanostructure on the antioxidant efficiency of fullerene polymers solutions. Such knowledge will contribute to the development of optimally effective fullerene-polymer systems for inhibition of radical processes [15].

The stabilizing effect of 1-4% C_{60} or C_{70} additives on the thermal decomposition of poly-2,6-dimethyl-1,4-phenylene oxide and its mixtures was studied using mass spectrometric thermal analysis and differential scanning calorimetry (DSC). It was shown that the addition of fullerenes shifts the onset of thermal decomposition of the polymer with formation of gaseous products in the area of higher temperatures range. The inhibitory effect of fullerene C_{70} is more pronounced than that for fullerene C_{60} [16].

Fullerene C_{60} was studied as promising thermal stabilizer and antioxidant for natural and synthetic rubber (cis-1,4-polyisoprene) [17]. The study was carried out in a stream of nitrogen and air. Thermogravimetric and differential thermal analysis (TGA-DTA) methods were used. The results showed that fullerene C_{60} (in the absence of oxygen) is good thermostabilizer for cis-1,4-polyisoprene due to active interaction with polyisoprene macroradicals formed by the thermally induced chain breaking reaction. Supportively, under conditions of thermal oxidative degradation (in the air stream), C_{60} fullerene acts as antioxidant for cis-1,4-polyisoprene provided that the heating rate of samples is low (5 °C/min). However, at higher heating rates (20 °C/min) C_{60} does not exhibit any additional antioxidant effect. This result is extremely noteworthy since is evidence that fullerene C_{60} reduces the intrinsic antioxidant efficiency in the intense oxidation condition and high amount of macro-peroxide radicals. This is due to obvious indifference to radicals centered on oxygen atom.

Thermostabilization of isotactic polypropylene (i-PP) in the presence of C_{60} fullerene and adducts with resin acid, nanocarbon, and soot was studied by chemiluminescence (CL) [18]. Thermal oxidation of i-PP samples was carried out in air at 170, 180, and 190 °C. Several kinetic parameters were determined: oxidation induction period, half-life of polymer matrix structure, oxidation rate, maximum CL intensity, and maximum oxidation time. According to their effectiveness, the additives were arranged in the following order: fullerene C_{60} < nanocarbon < soot < adduct of fullerene C_{60}.

Many studies describe the effect of fullerene C_{60} on the thermal and thermooxidative decomposition of polymethylmethacrylate (PMMA). In particular, DTA and TG studies were performed on the effect of C_{60} on decomposition of PMMA and PS in helium stream, containing 0.06% oxygen and pure oxygen at 282 and 238 °C [19]. It was shown by the TG method that C_{60} retards polymer degradation – the induction periods, curves of mass loss of polymers – all data indicate substantial shift of the temperature onset. Similar results were obtained by using DTA method. It was established that C_{60} significantly increases the decomposition temperature point of polymer oxidation. As of the degradation mechanism, it has been suggested that in the case of thermal degradation, the inhibition effect of C_{60} is associated with interaction with $R^\bullet$ macroradicals affording inactive particles. During thermo-oxidative degradation of PMMA at elevated temperatures, the inhibitory effect of C_{60} is ruled by interaction not only with $R^\bullet$ but also with oxygen-containing radicals. In the case of PS, the inhibitory effect of fullerene is mainly associated with its reaction with oxygen-containing radicals, although the interaction $C_{60} + R^\bullet$ is also not excluded [19].

The introduction of additional MMA units (5-15 mol.%) in PMMA reduces the rate of thermooxidative degradation due to the formation of anhydride rings interacted between adjacent co-monomer units. C_{60} additives inhibit the thermal oxidative degradation of MMA copolymers with styrene, butyl acrylate, glycidyl methacrylate and hydroxyethyl methacrylate for a long time. Possible schemes describing the reactions of fullerene C_{60} with macroradicals formed as a result of thermooxidative degradation of copolymers are presented. The scheme shows the inhibitory effect of fullerene C_{60} [20, 21].

Other authors also described similar research results on the effect of fullerene C_{60} on the processes of thermal and oxidative degradation of PMMA [22-24]. DSC, TG, (DTG and mass spectrometry (MS) were involved in these studies. It has been established that during PMMA oxidative aerobic degradation three processes occur almost simultaneously: thermal degradation or chains breaking, oxidation or incorporation of oxygen atoms in polymer chains and decomposition products and sublimation of decomposition products. The introduction of small amounts of C_{60} into the system leads to the replacement of one oxidizing agent (oxygen) with less active (with fullerene) and, as a result, to partial prevention of oxidation. As a result, in the first stage fewer oxidation products are formed than expected theoretically. C_{60} molecules are conventionally subdivided during oxidative degradation of

PMMA into two groups: linked (about 20%) and unrelated to PMMA macroradicals. Unbound C_{60} molecules, in turn, are subdivided into oxidized and sublime, that is, not oxidized and not decomposed. The inhibitory effect of C_{60} on thermal oxidative degradation is reduced mainly to two processes: chain transfer with formation of fullerene-containing macromolecules and inhibition of the non-chain oxidation pathway. This behavior of fullerene C_{60} extends to atactic, anionic syndiotactic, and isotactic forms of PMMA [25].

Fullerene C_{60} inhibits high-temperature oxidative degradation of PMMA copolymers and methyl methacrylate with methacrylic acid [26]. The copolymers of methyl methacrylate with methacrylamides undergo thermal oxidative degradation less actively than PMMA. C_{60} fullerene supplements inhibit degradation [27].

Study of the thermal and thermooxidative decomposition processes in polymer (PMMA, polystyrene)- fullerene (C_{60}, C_{70}) – systems detected limits for the stabilizing effect of fullerenes. The constraint depend on solubility of fullerene in the polymers: for PS and PMMA these values are $4 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol/kg, respectively. For PS-based systems containing C_{60} or C_{70}, the thermal decomposition temperature limit was 380 °C; for PMMA-based systems, this parameter was 339 and 336 °C for C_{60} and C_{70}, respectively. For the thermo-oxidative degradation of these polymers and polycarbonate, the temperature range of 335-340 °C was the highest temperature limit for the action of fullerene C_{60} acting as an antioxidant. This limit is lower than the temperature (370-400 °C) of oxidation of the fullerene itself [28].

MS thermal analysis, DSC, DTG and broadband X-ray diffraction analysis were used to study the thermal and oxidative degradation of two types of fullerene-containing polymer systems (FCPS): 1) FCPS with covalently bonded fullerene C_{60}; 2) FCPS is a mixture of C_{60} with polymers, where the interaction is carried out only by means of the Van der Waals forces. The fullerene property to accept electrons and radicals is manifested in both types of FCPC. In the first type systems, a significant decrease of thermal stability of the polymer component was observed; in the second type systems, the ability of fullerene C_{60} to play the role of a «trap» of free radicals is especially pronounced. The polymer matrix also affects the thermal behavior of fullerene C_{60}. In particular, fullerene can serve as a specific «probe» of chemical processes that is occured during the thermal decomposition of a polymer. Various PS and PMMA containing 1-10 wt.% C_{60} (FCPS) had been studied [29].

A two-stage study was conducted to determine the antioxidant properties of fullerenes C_{60}/C_{70} and C_{60} in PS [12]. The antioxidant activity of the C_{60}/C_{70} was studied by aid of a model reaction of the initiated oxidation of styrene, and then in accelerated tests of mixtures of C_{60}/C_{70} and C_{70} with PS. It was found that the rates of initiation and oxidation of the model reaction significantly decrease in the presence of C_{60}/C_{70}. The rate constant for adding styryl radicals to C_{60}/C_{70} was determined for the first time $k_{(333K)} = (9.0 \pm 1.5) \cdot 10^7$ $M^{-1}s^{-1}$. It was demonstrated that fullerenes exhibit a stabilizing effect comparable to that of sterically hindered phenols (ca. Irganox 1010) and secondary aromatic amines (ca. Agerite White). It was suggested that fullerenes inhibitory effect is associated with its interaction with the $R^{\bullet}$ macroradicals leading to the formation of inactive particles that are not capable more to develop the chain oxidation process.

The antiradical activity of fullerene C_{60} was studied in the case of oxidation of 1,4-dioxane and styrene initiated by azobisisobutyronitrile and benzoyl peroxide [30]. The effective rate constants of interaction of peroxide radicals with fullerene C_{60} (k_7) and also the stoichiometric inhibition index (f) were determined for aerobic oxidation and oxidation with pure oxygen. The effective inhibition rate constant was found as $k_7 = (2.4 \pm 0.2) \cdot 10^4$ $M^{-1}s^{-1}$. Chain termination during styrene oxidation occurs both during the interaction of C_{60} with peroxide ($k_7 = (1.2 \pm 0.1) \cdot 10^3$ $M^{-1}s^{-1}$) and alkyl ($k_8 = 1.07 \cdot 10^7$ $M^{-1}s^{-1}$) radicals.

The effect of C_{60} fullerene additives on the thermal degradation of poly-n-alkyl acrylates and polymethacrylates was studied using thermogravimetry under dynamic conditions and pyrolysis/gas chromatography in isothermal mode at 400-650 °C range [31]. Fullerene is well-known effective radical scavenger and its presence really affects the thermal decomposition of acrylic polymers, shifting the decomposition process from a radical path to a non-radical mechanism. This was confirmed by repeated experiments and there is no doubt about it.

For poly-n-alkyl acrylates, the addition of fullerenes leads to an increase in the yield of olefin and alcohol, – the products of the polymer decomposition occuring along a non-radical path. At the same time, the yields of other pyrolysis products, such as monomer, dimer, saturated diester, trimer, corresponding acetate and methacrylate are reduced. The recorded maximum weight loss temperatures fixed by TG experiments increase slightly in the presence of fullerene. The effect is more pronounced for the thermal behavior of poly-n-alkyl methacrylates: the increase in maximum weight loss temperature is 19-25 °C. Mixtures containing fullerene lead to a noticeable decrease in the yield of monomer and, at the same time, an increase in the number of olefins and methacrylic acid. Fullerene acts as an acceptor of radicals, inhibiting the ramification of the oxidation chains and contributing to the occurrence of non-radical side reactions [31].

Carbon nanotubes (CNTs) have electron affinity that is similar or even greater than fullerenes, and therefore it can be assumed their acting as powerful radical traps in chain reactions such as polymerization and thermal decomposition. It can be expected that due to their potential ability to accept radicals CNTs integrated in a polymer matrix will be excellent terminators of chain oxidation processes, leading, in particular, to the antioxidant stabilizing effects.

It was recorded that polymer-nanotube composites with significant electrical conductivity and capable to carrying high current densities are very heat up during a passage of electric current. Actually, authors Ref. [32] observed high heating effects (above 200 °C) of the polymer while the direct current passed through the composites. Therefore, it was important to study how CNTs affect the stability of polymers at elevated temperatures. In the article, it has been shown according to the TGA and CL profiles that CNTs act as antioxidants during strong calefaction of polystyrene, polyethylene, polypropylene and polyvinylidene fluoride compositions. The dosage of CNTs over 5% leads only to small increase in the antioxidant efficiency. In the case of polyvinylidene fluoride, there is data that nanotubes can act simultaneously as antioxidants and halogen absorbents [32].

Sterilization of implants and other clinical supplies is an integral part of any medical application. Although many materials are used as implants, polyethylene materials are unique due to their versatility. It is proposed to use CNTs as a filler to improve the properties of such polyethylene composites. The goal was to study the role of multi-walled CNTs (MWCNTs) as effective antioxidant and radical scavenger to improve the sterilization effect. The work [33] was undertaken to study mechanical properties and oxidation stability of irradiated high density polyethylene (HDPE) reinforced with 0.25%, 0.50%, 0.75%, and 1.00 wt. % MWCNTs. The composites were exposed to radioactive ^{60}Co in air and irradiated at various dosages, ranging from 25 to 100 kGy, and then aged for 120 days before the main experiments. It was found that the loss in toughness, Young's modulus and limit strength at 100 kGy for a composite with 1 wt.% MWCNTs is 21.5%, 20.3%, and 19.2% of the wastages in the composites without MWCNTs. FTIR and ESR studies have also confirmed the higher antioxidant and radical abilities of MWCNTs of more dosages. It was found that adding 1 wt.% MWCNTs to pure HDPE the oxidation index of the composite at 100 kGy decreases by 56.2%. Thus, finally was concluded that introduction of MWCNTs to polyethylene matrix leads to not only to improvement of mechanical properties, but also to increasing oxidation resistance of the composite material upon the irradiation [33].

Carbon nanotubes are widely used as reinforcements in polymeric materials due to their exceptional properties. The antioxidant ability of CNTs in HDPE was studied in the Ref. [34]. Single-walled carbon nanotubes (SWCNTs), MWCNTs, and hydroxylated multi-walled carbon nanotubes (MWCNTs-OH) were involved in this study to determine the effect of the walls number and surface functionalization on their antioxidant behavior. Based on measured temperature and time of induction of oxidation of CNTs / HDPE composites the detected antioxidant efficiency of CNTs may be ordered as: MWCNTs-OH > MWCNTs > SWCNT. It was defined by means of ESR and Raman techniques the free radical quenching mechanism. The extent of radical capture efficiency and number of defects in CNTs are in good agreement with their antioxidant ability. CNTs having more number of walls and surface hydroxyl groups contain more structural defects and exhibit a higher antioxidant activity. The study gives concrete and real recommendations on how to improve the antioxidant properties of CNTs, as well as the mechanical properties of polymers [34].

The effect of carbon nanotubes on photodegradation of ethylene-vinyl acetate (EVA)/carbon nanotube nanocomposites was studied. The nanocomposites were photooxidized in oxygen atmosphere under irradiation with wavelength $\lambda > 300$ nm, and temperature 60 °C. The effect of nanotubes on both the EVA photooxidation mechanism and the oxidation rate of the polymer matrix were determined. It was shown that CNTs act simultaneously as internal filters and as antioxidants, which contributes to a sharp decrease in the rate of the polymer matrix photooxidation. It was also shown that the light absorption can cause an increase in local temperature and entail photooxidation of the polymer. The competition between these three effects makes up the overall rate of the photooxidation. Several influencing factors were investigated: varied concentrations, morphology and degree of functionalization of CNTs surface [35].

MWCNTs/linear low density polyethylene (LLDPE) nanocomposites have been studied to understand stabilization mechanism of their thermal and oxidative degradation [36]. Thermogravimetry combined with infrared analysis of the evolved gas and gas chromatography-mass spectrometry combined with pyrolysis gas chromatography showed that the MWCNTs slightly delays thermal volatilization (by 15-20 °C) without changing the mechanism of thermal decomposition. While thermo-oxidative degradation in air is delayed by about 100 °C regardless MWCNTS concentrations used (0.5-3.0 wt.%). The stabilization occurs due to formation of a thin protective film of MWCNTs (the carbon generated on the surface of nanocomposites), which was shown using SEM and ATR FTIR of residual degradation products [36].

Results of investigation on the influence of CNTs additions in polyamide-6 (PA6) on mechanical, thermal properties and fire resistance of nanocomposite layered materials made from fiberglass-reinforced CNT/PA6 are presented in Ref. [37]. The samples were characterized by tensile and bending tests, TGA, thermal distortion temperature (HDT) measurements, thermal conductivity tests and a cone calorimeter. The additions of up to 2 wt.% CNTs in CNT/PA6/GF laminates improves the bending stress of the laminates by 36%, thermal conductivity by about 42%, and the ignition and heat release times were slowed by about 31% and 118%, respectively [37].

The high energy grinding process was used (HEBM) as a new approach for incorporating CNTs into a polyethylene (PE) matrix. This approach allows avoiding high temperatures, solvents, ultrasonic exposure and chemical treatment of CNTs usually used in preparation of composites. Films containing 1, 2, 3, 5, and 10 wt.% of CNTs were prepared by hot pressing of the composite powders. The morphological and thermal, mechanical, and electrical properties of the films were determined [38]. The processing conditions used allowed to obtain a satisfactory level of CNTs dispersion in the PE matrix that is obligatory to have the reproducible results. The thermal degradation was significantly suppressed already with 1-2% wt of CNTs. The mechanical properties are significantly improved for low filler content (up to 3 wt. %). The electrical measurements showed a percolation threshold for compositions containing CNTs within the range 1-3 wt % [38].

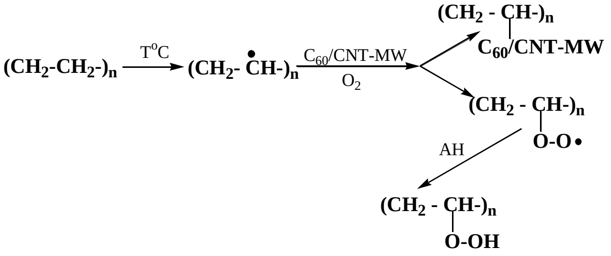
MWCNTs have been incorporated into ultra-high molecular weight polyethylene (UHMWPE). This type of polyethylene is used in orthopedics and in industry for special purposes. The compositions were obtained by ball grinding and thermal compression processes in concentrations of MWCNTs up to 3 wt.% and then subjected to gamma radiation at 90 kGy. Conductivity measurements have shown fairly low percolation threshold for nanocomposites with 0.5 wt.% of CNTs. The electron-spin resonance of the detection of radicals induced by radiation proved the pronounced ability of MWCNTs to accept radicals: i.e. with increasing the concentration of nanotubes in the composites, the number of free radicals generated during gamma irradiation decreased sharply. Allyl radicals are apparently the most active types of radicals in the process of attachment to nanotubes in this polymer matrix. In order to establish the effect of irradiation on the oxidation index, infrared spectroscopy methods with Fourier transform and accelerated ageing methods were used. The results showed that MWCNTs additives uniquely increase the thermo-oxidative stability of the composites as compared to the control samples. At the same time, despite the ability to quench radicals, MWCNTs do not affect the crosslink density – this is unlike other antioxidants that inhibit the processes of radiation crosslinking in polymers [39].

Polymer nanocomposites containing CNTs as fillers have attracted much more attention than any other nanomaterials. Therefore, the detailed elaboration of the materials requires a deep understanding of how they behave under operating conditions. In Ref. [40], the resistance to accelerated photooxidation of the syndiotactic polypropylene/MWCNTs composite films was compared with behavior of unfilled polypropylene films with the same structural morphology. Chemical and structural changes resulting from photooxidation were monitored using infrared spectroscopy and diffractometry analysis. It was found that good degree of dispersion of the nanofiller, estimated by atomic force microscopy, reduces the rate of photooxidation and increases the oxidative thermal stability of the polymer matrix. To explain these results, various concomitant effects were considered in the work, including morphology and structure of nanocomposites, as well as the ability of MWCNTs to interact with oxygen [40].

A chapter was published in a book that summarizes many of the latest technological advances in the field of carbon fillers for elastomers such as carbon black, carbon nanotubes, and fullerenes. Their characteristics, influence, and level of their load on the thermal properties of rubbers such as natural rubber, styrene butadiene rubber, ethylene propylene diene monomer, and acrylonitrile butadiene rubber (NBR) are discussed in light of recent published data. In addition to the literature review, this chapter provides valuable information related to methods of thermal analysis of polymer compositions – differential scanning calorimetry, thermogravimetric, and thermomechanical analysis [41, 42].

Results of thermooxidative degradation of composites of low density polyethylene (LDPE) containing fullerene C_{60}/C_{70} and purified multi-walled carbon nanotubes (CNT-MW-Ib) are described [43]. TG and DTA analysis of the composites showed that carbon nanocompounds (CNC) exhibit high stabilizing activity comparable to the action of strong commercial basis antioxidants. The mechanism of stabilizing action is reduced mainly to the breakage of alkyl macroradicals on the CNC frameworks.

A set of reactions ensuring the effective stabilization of a polymer matrix may be represented as follows:



CONCLUSIONS

According to the inherent property to quench free radicals the carbon nano-compounds (CNC) – fullerenes and carbon nanotubes are able to effectively retard and terminate the chain oxidation processes of polymers thermal and thermo-photooxidative degradation. As shown in many investigations, this feature is spread both to the carbon-chain and hetero-chain polymer composites.

A solid polymeric environment implying the restricted oxygen diffusion is the most suitable for CNC to manifest the anti-oxidative activity as it rules by the scavenging carbon-centered radicals

The anti-oxidative efficiency of CNC is very high and comparable with that of strongest commercial polymer thermal stabilizers.

There are other approaches to improve the stability of polymer composites: e.g. to improve interfacial compatibility between the polymer matrix and nanocarbon additives or to replace carbon atoms in the CNC structure with heteroatoms, etc.

REFERENCES
ЛИТЕРАТУРА

1. **Kumar A.P., Depan D., Tomer N.S., Singh R.P.** Nanoscale particles for polymer degradation and stabilization—trends and future perspectives. *Prog. Polym. Sci.* 2009. V. 34. N 6. P. 479-515.
2. **Aloyev V.Z., Zhirikova Z.M., Tarchokova M.A.** Effectiveness of use of nano fillers of different types in polymeric composites. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim Tekhnol [Russ. J. Chem. Chem. Tech]*. 2020. V. 63. N 4. P. 81-85 (in Russian). DOI: 10.6060/ivkkt.20206304.6158. **Алоев В.З., Жирикова З.М., Тарчокова М.А.** Эффективность использования нанонаполнителей разных типовв полимерных композитах. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 4. С. 81-85. DOI: 10.6060/ivkkt.20206304.6158.
3. **Jineesh A.G., Mohapatra S.** Thermal properties of polymer–carbon nanocomposites. In Carbon-Containing Polymer Composites. Singapore: Springer. 2019. P. 235-270.
4. **Cioslowski J.** Electronic Structure Calculations on Fullerenes and Their Derivatives. New York: Oxford University Press. 1995. Ch. 3-5. 281 p.
5. **Krusic P.J., Wasserman E., Keizer P.N., Morton J.R., Preston K.F.** Radical reactions of C60. *Science*. 1991. V. 254. N 5035. P. 1183-1185.
6. **Krusic P.J., Wasserman E., Parkinson B.A., Malone B., Holler Jr, E.R., Keizer P.N., Preston K.F.** Electron spin resonance study of the radical reactivity of C60. *J. Am. Chem. Soc.* 1991. V. 113. N 16. P. 6274-6275.
7. **McEwen C.N., McKay R.G., Larsen B.S.** C60 as a radical sponge. *J. Am. Chem. Soc.* 1992. V. 114. N 11. P. 4412-4414.
8. **Walbiner M., Fischer H.** Rate constants for the addition of the benzyl radical to fullerene C60 in solution. *J. Phys. Chem.* 1993. V. 97. N 19. P. 4880-4881.
9. **Zeynalov E.B., Allen N.S., Salmanova N.I.** Radical scavenging efficiency of different fullerenes C60, C70 and fullerene soot. *Polym. Degrad. Stabil.* 2009. V. 94. N 8. P. 1183-1189.
10. **Dimitrijevic N.M., Kamat P.V., Fessenden R.W.** Radical adducts of fullerenes C60 and C70 studied by laser flash photolysis and pulse radiolysis. *J. Phys. Chem.* 1993. V. 97. N 3. P. 615-618.
11. **Zeinalov E.B., Koβmehl G.** Fullerene C60 as an antioxidant for polymers. *Polym. Degrad. Stabil.* 2001. V. 71. N 2. P. 197-202.
12. **Zeynalov E.B., Magerramova M.Ya., Ishenko N.Ya.** Fullerenes C60/C70 and C70 as antioxidants for polystyrene. *Iran. Polym. J.* 2004. V. 13. N 2. P. 143-148.
13. **Troitskii B.B., Troitskaya L.S., Dmitriev A.A., Anikina L.I., Novikova M.A., Denisova V.N., Khokhlova L.V.** Fullerenes and synergistic mixtures on their basis as high-temperature antioxidants of polymers. *Molec. Mater.* 2000. V. 13. N 1-4. P. 209-212.
14. **Nekoei A. R., Haghgoo S.** DFT investigation on some nitrogen-doped fullerenes with more antiradical and antioxidant activities than C 60. *Struct. Chem.* 2019. 30. P. 1737-1748. DOI: 10.1007/s11224-019-01311-2.
15. **Tam J., Liu J., Yao Z.** Effect of microstructure on the antioxidant properties of fullerene polymer solutions. *RSC Advances*. 2013. V. 3. N 4. P. 4622-4627.
16. **Shibaev L.A., Egorov V.M., Zgonnik V.N., Antonova T.A., Vinogradova L.V., Melenevskaya E.Y., Bershtein V.A.** An enhanced thermal stability of poly (2, 6-dimethyl-1,4-phenylene oxide) in the presence of small additives of C60 and C70 fullerenes. *Polym. Sci. Ser. A. Chem., Phys.* 2001. V. 43. N 2. P. 101-105.
17. **Cataldo F.** On the reactivity of C60 fullerene with diene rubber macroradicals. I. The case of natural and synthetic cis-1, 4-polyisoprene under anaerobic and thermooxidative degradation conditions. *Fullerene Sci. Technol.* 2001. V. 9. N 4. P. 497-513.
18. **Jipa S., Zaharescu T., Santos C., Gigante B., Setnescu R., Setnescu T., Olteanu R.L.** The antioxidant effect of some carbon materials in polypropylene. *Mater. Plastice*. 2002. V. 39. N 1. P. 67-72.
19. **Troitskii B.B., Troitskaya L.S., Dmitriev A.A., Yakhnov A.S.** Inhibition of thermo-oxidative degradation of poly(methyl methacrylate) and polystyrene by C60. *Europ. Polym. J.* 2000. V. 36. N 5. P. 1073-1084.

20. **Troitskii B.B., Domrachev G.A., Khokhlova L.V., Anikina L.I.** Thermooxidative degradation of poly (methyl methacrylate) in the presence of C60 Fullerene. *Polym. Sci. Ser. A, Chem., Phys.* 2001. V. 43. N 9. P. 964-969.
21. **Troitskii B.B., Domrachev G.A., Semchikov Y.D., Khokhlova L.V., Anikina L.I., Denisova V.N., Yashchuk L.M.** Fullerene-C60, a new effective inhibitor of high-temperature thermooxidative degradation of methyl methacrylate copolymers. *Russ. J. Gen. Chem.* 2002. V. 72. N 8. P. 1276-1281.
22. **Ginzburg B.M., Ugolkov V.L., Shibaev L.A., Bulatov V.P.** The effect of fullerene C60 on the thermooxidative degradation of a free-radical PMMA studied by thermogravimetry and calorimetry. *Techn. Phys. Lett.* 2001. V. 27. N 10. P. 806-809.
23. **Ginzburg B.M., Shibaev L.A., Ugolkov V.L.** Effect of fullerene C60 on thermal oxidative degradation of polymethyl methacrylate prepared by radical polymerization. *Russ. J. Appl. Chem.* 2001. V. 74. N 8. P. 1329-1337.
24. **Ginzburg B.M., Shibaev L.A., Ugolkov V.L., Bulatov V.P.** Influence of C60 fullerene on the oxidative degradation of a free radical poly (methyl methacrylate). *J. Macromolec. Sci., Pt. B.* 2003. V. 42. N 1. P. 139-166.
25. **Shibaev L.A., Ginzburg B.M., Antonova T.A., Ugolkov V.L., Melenevskaya E. Y., Vinogradova L.V., Zgonnik V.N.** Thermal and thermooxidative degradation of poly (methyl methacrylate) in the presence of fullerene. *Polym. Sci. Ser. A, Chem., Phys.* 2002. V. 44. N 5. P. 502-509.
26. **Troitskii B.B., Domrachev G.A., Khokhlova L.V., Yashchuk L.E., Denisova V. N., Novikova M.A., Dorofeeva Y.A.** Effect of fullerene C60 and other antioxidants on high-temperature oxidative degradation of poly (methyl methacrylate) and methyl methacrylate copolymers with methacrylic acid. *Russ. J. Gen. Chem.* 2003. V. 73. N 7. P. 1091-1094.
27. **Troitskii B.B., Domrachev G.A., Khokhlova L.V., Yashchuk L.E., Denisova V. N., Novikova M.A., Khorshev S.Y.** Inhibiting effect of fullerene C60 and other antioxidants on thermal oxidative degradation of copolymers of methyl methacrylate with methacrylamides. *Russ. J. Gen. Chem.* 2003. V. 73. N 12. P. 1904-1908.
28. **Troitskii B.B., Khokhlova L.V., Konev A.N., Denisova V.N., Novikova M.A., Lopatin M.A.** Temperature and concentrations limits for fullerenes C60 and C70 as polymer degradation inhibitors. *Polym. Sci. Ser. A, Chem., Phys.* 2004. V. 46. N 9. P. 951-956.
29. **Ginzburg B.M., Shibaev L.A., Melenevskaja E.Y., Pozdnjakov A.O., Pozdnjakov O.F., Ugolkov V.L., Leksovskii A.M.** Thermal and tribological properties of fullerene-containing composite systems. Part 1. Thermal stability of fullerene-polymer systems. *J. Macromolec. Sci., Pt. B.* 2004. V. 43. N 6. P. 1193-1230.
30. **Yumagulova R.K., Medvedeva N.A., Yakupova L.R., Kolesov S.V., Safiullin R.L.** Free-radical chain oxidation of 1,4-dioxane and styrene in the presence of fullerene C60. *Kinet. Catal.* 2013. V. 54. N 6. P. 709-715.
31. **Zuev V.V., Bertini F., Audisio G.** Fullerene C60 as stabiliser for acrylic polymers. *Polym. Degradat. Stability.* 2005. V. 90. N 1. P. 28-33.
32. **Watts P.C.P., Fearon P.K., Hsu W.K., Billingham N.C., Kroto H.W., Walton D.R.M.** Carbon nanotubes as polymer antioxidants. *J. Mater. Chem.* 2003. V. 13. N 3. P. 491-495.
33. **Sreekanth P.R., Kumar N.N., Kanagaraj S.** Improving post irradiation stability of high density polyethylene by multi walled carbon nanotubes. *Composit. Sci. Technol.* 2012. V. 72. N 3. P. 390-396.
34. **Shi X., Jiang B., Wang J., Yang Y.** Influence of wall number and surface functionalization of carbon nanotubes on their antioxidant behavior in high density polyethylene. *Carbon*. 2012. V. 50. N 3. P. 1005-1013.
35. **Morlat-Therias S., Fanton E., Gardette J.L., Peeterbroeck S., Alexandre M., Dubois P.** Polymer/carbon nanotube nanocomposites: influence of carbon nanotubes on EVA photodegradation. *Polym. Degradat. Stability*. 2007. V. 92. N 10. P. 1873-1882.
36. **Bocchini S., Frache A., Camino G., Claes M.** Polyethylene thermal oxidative stabilisation in carbon nanotubes based nanocomposites. *Eur. Polym. J.* 2007. V. 43. N 8. P. 3222-3235.
37. **Shen Z., Bateman S., Wu D.Y., McMahon P., Dell'Olio M., Gotama J.** The effects of carbon nanotubes on mechanical and thermal properties of woven glass fibre reinforced polyamide-6 nanocomposites. *Composit. Sci. Technol*. 2009. V. 69. N 2. P. 239-244.
38. **Gorrasi G., Sarno M., Di Bartolomeo A., Sannino D., Ciambelli P., Vittoria V.** Incorporation of carbon nanotubes into polyethylene by high energy ball milling: morphology and physical properties. *J. Polym. Sci. Pt. B: Polym. Phys.* 2007. V. 45. N 5. P. 597-606.
39. **Martinez-Morlanes M.J., Castell P., Alonso P.J., Martinez M.T., Puertolas J.A.** Multi-walled carbon nanotubes acting as free radical scavengers in gamma-irradiated ultrahigh molecular weight polyethylene composites. *Carbon*. 2012. V. 50. N 7. P. 2442-2452.
40. **Guadagno L., Naddeo C., Raimondo M., Gorrasi G., Vittoria V.** Effect of carbon nanotubes on the photo-oxidative durability of syndiotactic polypropylene. *Polym. Degradat. Stability*. 2010. V. 95. N 9. P. 1614-1626.
41. **Kodal M., Karakaya N., Wis A.A., Ozkoc G.** Thermal Properties (DSC, TMA, TGA, DTA) of Rubber Nanocomposites Containing Carbon Nanofillers. In: Carbon-Based Nanofiller and Their Rubber Nanocomposites. Elsevier. 2019. P. 325-366. DOI: 10.1016/B978-0-12-817342-8.00011-1.
42. **Atlukhanova L.B., Kozlov G.V., Rumyantsev E.V., Dolbin I.V.** Analysis of temperature dependence of catalytic activity of carbon nanotubes at epoxy polymers curing within frameworks of fractal analysis. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 3. P. 64-69 (in Russian). DOI: 10.6060/ivkkt201962fp.5841. **Атлуханова Л.Б., Козлов Г.В., Румянцев Е.В., Долбин И.В.** Анализ температурной зависимости каталитической способности углеродных нанотрубок при сшивании эпоксиполимеров в рамках фрактального анализа. *Изв. вузов. Химия и хим. технология.* 2019. Т. 62. Вып. 3. С. 64-69. DOI: 10.6060/ivkkt201962fp.5841.
43. **Aghahuseynova M.M., Salmanova N.I., Zeynalov E.B.** Study of polymer composites, containing Carbon nanotubes, properties. 20th Gavin Conferences. World Congress on Chemistry. Dubai, UAE. Proceedings of the conference: E-posters. Supporting Journal: Current Research in Bioorganic & Organic Chemistry. 2019. V. 3. P. 50-51.

Поступила в редакцию 07.02.2020
Принята к опубликованию 14.09.2020

Received 07.02.2020
Accepted 14.09.2020