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# ANTIOXIDANT TRAITS OF SOME NANOCARBON MOIETIES INTEGRATED IN POLYMER MATERIALS (A REVIEW)

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**Abstract.** This review briefly gives the status of worldwide researches in the aspect of an impact of incorporated fullerenes and carbon nanotubes (CNTs) on durability of different polymeric composites under stressful harsh therm-oxidative conditions. It has been inferred that among various nanoparticulates, fullerenes and CNTs are preferable to be used for enhancing thermal and mechanical properties of polymers. Fullerenes $C_{60}$, $C_{70}$, fullerene soot and CNTs being integrated in polymer matrix effectively prevent both their thermal and thermoxidative degradation, and photooxidation processes as well.

**Keywords:** fullerene, carbon nanotubes, polymer composite, thermooxidative degradation, radical scavenger, stabilizer.

The field of nanoscience and nanotechnology is distinguished by numerous researches to bring innovations and benefits to many areas of application. Among various nanoparticulates, clay minerals and carbon nanocompounds are more often used in enhancing physical, mechanical and thermal properties of polymer materials. Since the polymer–nanocomposites have been the staple of modern polymer industry, their degradability and durability under various environmental conditions are most essential fields of research [1].

Only for a few systems, the nanoparticulates entering the polymer as "nano-additives" serve for both purposes: degradation and stabilization of polymers. In the present article the degradation and durability processes of polymer composites with fullerenes and CNTs are reviewed.

Nanocarbon molecules have the peculiar electronic structure which makes highly possible an attack and intensive addition of nucleophilic species like electrons, free radicals, anions and hydrogen atoms [2]. Fullerenes have high values of electron affinities which are spread from 2.65 eV($C_{60}$) to 3.5 eV ($C_{84}$) [2]. The intensive addition of electrons leads to an oxidation of an adjacent substrate with simultaneous negative charge formation on the fullerene core, but the addition of free radicals results in an appearance of unpaired electron due to the fullerene double bond breakage, the first feature promotes a redox function of fullerenes the second – realizes an act of radicals chain termination with reviving free valence. The high values of fullerenes affinity allow intensive addition of electron-deficient organoradicals, such as benzyl and *tert*-butyl radicals, to the fullerenic double bounds [3-5]. The facile addition of alkyl radicals to fullerenes is also confirmed by the high addition rate constants of $10^{8\pm1}M^{-1}\cdot s^{-1}$ reported in a number of publications [6-10]. Hence the fullerenes appear to be efficient radical scavengers in chain radical processes, including thermal and theromooxidative degradation of polymers. These processes involve alkyl and peroxy radicals, and must therefore be susceptible to inhibition by compounds capable of trapping such radicals.

There is a number of publications describing thermal and thermo-oxidative degradation of polymers in the presence of fullerenes when abovementioned postulates have had the corroboration. These researches specified the stabilizing role of fullerenes $C_{60}$ and $C_{70}$ at degradation processes of many polymer materials.

The stabilizing activity of fullerene $C_{60}$ appeared to be purely comparable with the activity of the known stabilizer Irganox 1076 which has been shown both by means of model reaction of cumene initiated oxidation and in accelerated tests of polystyrene (PS) and polydimethylsiloxane rubber with the fullerene moieties [9].

The investigation was undertaken to determine the antioxdative activity of the range of fullerenes $C_{60}$ and $C_{70}$ generally manufactured in practice in order to rank them according to their comparative efficiency [7]. The model

reaction of cumene initiated (2,2'-azo-bisisobutyronitrile, AIBN) oxidation was employed herein to determine rate constants for addition of radicals to fullerenes. Kinetic measurements of oxidation rates in the presence of different fullerenes showed that the antioxidative activity as well as the mechanism and mode of inhibition were different for fullerenes $C_{60}$, $C_{70}$ and fullerene soot. All fullerenes – $C_{60}$ of gold grade, $C_{60}/C_{70}$ (93/7, mix 1), $C_{60}/C_{70}$ (80±5/20±5, mix 2) and $C_{70}$ operated in the mode of an alkyl radical acceptor, whereas fullerene soot surprisingly retarded the model reaction by a dual mode similar to that for the fullerenes and with an induction period like many of the sterically hindered phenolic and amine antioxidants. For $C_{60}$ and $C_{70}$ the oxidation rates were found to depend linearly on the reciprocal square root of the concentration over a sufficiently wide range thereby fitting the mechanism for the addition of cumyl alkyl $\dot{R}$ radicals to the fullerene core. This is consistent with the gathered literature data of the more readily and rapid addition of alkyl and alkoxy radicals to the fullerenes compared with peroxy radicals. Rate constants for the addition of cumyl $\dot{R}$ radicals to the fullerenes were determined to be $k_{(333K)} = (1.9 \pm 0.2) \cdot 10^8$ ($C_{60}$); $(2.3 \pm 0.2) \cdot 10^8$ ($C_{60}/C_{70}$, mix 1); $(2.7 \pm 0.2) \cdot 10^8$ ($C_{60}/C_{70}$, mix 2); $(3.0 \pm 0.3) \cdot 10^8$ ($C_{70}$), $M^{-1} \cdot s^{-1}$. The incremental $C_{70}$ constituent in the fullerenes leads to a respective increase in the rate constant. The fullerene soot inhibits the model reaction according to the mechanism of trapping peroxy radicals: the oxidation proceeds with a pronounced induction period and kinetic curves are linear at the semi-logarithmic coordinates. For the first time the effective concentration of inhibiting centres and inhibition rate constants for the fullerene soot have been determined to be $fn[C_{60}\text{-soot}] = (2.0 \pm 0.1) \cdot 10^{-4}$ $mol \cdot g^{-1}$ and $k_{inh.} = (6.5 \pm 1.5) \cdot 10^3 M^{-1} \cdot s^{-1}$ respectively.

It has been shown in Ref. [11] that fullerenes $C_{60}$ and $C_{70}$ are new high temperature antioxidants of polymers which are more effective than well-known inhibitors in the case of some polymers. It has been found that C-60 forms synergistic mixtures with $Ph_3Sb$ and phenyl-beta-naphthylamine (Neozone-D) in the thermo-oxidative degradation of polystyrene. These synergistic mixtures on the basis of fullerenes are new high temperature antioxidants of polystyrene (PS).

The stabilizing effect of fullerenes for thermal degradation of poly-2,6-dimethyl-1,4-phenylene oxide and its blends with 1–4 % fullerene $C_{60}$ or $C_{70}$ was studied by mass-spectrometric thermal analysis and differential scanning calorimetry (DSC). It was shown that the addition of fullerene shifts the onset of the processes of thermal degradation and the homolytic decomposition of the polymer with the formation of gaseous products to higher temperatures, thereby increasing its thermal stability. The inhibiting effect of fullerene $C_{70}$ is stronger compared to $C_{60}$ [12].

Fullerene $C_{60}$ has been studied as a thermal stabilizer and as an antioxidant of both natural rubber (*cis*-1,4-polyisoprene) and synthetic *cis*-1,4-polyisoprene [13]. The study has been conducted respectively under nitrogen flow and under 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 show that $C_{60}$ fullerene (in the 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 $C_{60}$ acts as the antioxidant for *cis*-1,4-polyisoprene, provided that the heating rate of the samples is slow (5 K/min). At higher heating rates (20 K/min) $C_{60}$ does not show any antioxidant effect. This result is extremely noteworthy. It proves that fullerene loses its antioxidative capacity in the case of the polymer intensive oxidation affording the sharp increase of macroperoxy radicals concentration, due to apparent insusceptibility towards oxygen-centred radicals.

Thermal stabilization of isotactic polypropylene (*i*-PP) in the presence of fullerene $C_{60}$, its adducts with levopimaric acid, nanocarbon and carbon black is investigated by chemiluminescence (CL) [14]. The thermal oxidation of i-PP samples was carried out in air at 443, 453 and 463 K. 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 in the following order: fullerene $C_{60}$ < nanocarbon < carbon black < < fullerene $C_{60}$ adduct.

Many works describe the influence of $C_{60}$ fullerene on the thermal and thermooxidative degradation of poly-methyl methacrylate (PMMA).

Researches were made on the effects of $C_{60}$ on the degradation of PMMA and PS in the stream of helium having 0.06 % of oxygen and in dynamic oxygen by DSC method and under oxygen at 555 and 511 K for the case of PMMA and PS, respectively, by thermogravimetry (TG) [15]. It was shown that $C_{60}$ retards the degradation of the polymers. By TG it was demonstrated that in the presence of fullerene, induction periods rise substantially on the curves showing polymers weight loss dependence on time of degradation,. By using the DSC method it was illustrated that $C_{60}$ considerably increases the temperatures of the onset of polymers degradation. Details of the degradation mechanism were considered. The suggestion was made that in the case of the thermal degradation the retarding effect of $C_{60}$ is connected with its interaction with macroradicals $\dot{R}$ under formation of less active

compounds. It was supposed that in the thermo-oxidative degradation of PMMA at elevated temperatures, the inhibiting effect of $C_{60}$ is due to its interaction with $R^{\cdot}$ and oxygen-containing radicals with the formation of less active compounds. In the case of PS the retarding influence of fullerene is mainly connected with its reaction with oxygen-containing radicals, but the interaction of $C_{60}$ with $R^{\cdot}$ must not be ruled out.

The introduction of additional MMA units (5–15 mol %) to PMMA reduces the rate of thermooxidative degradation due to the formation of anhydride rings *via* interaction between neighboring comonomer units. The $C_{60}$ additives inhibit the thermooxidative degradation of MMA copolymers with styrene, butyl acrylate, glysidyl methacrylate and hydroxyethyl methacrylate for a long time. The feasible schemes describing the reactions of $C_{60}$ fullerene with macroradicals produced as a result of the thermooxidative degradation of copolymers and explaining the inhibiting effect of $C_{60}$ fullerene are presented [16, 17].

Other authors also proposed the results of studies of thermal and oxidative degradation of a free-radical produced PMMA and the influence of fullerene $C_{60}$ on these processes [18-20]. The DSC, TG, differential thermogravimetric analysis (DTG), and mass spectrometry (MS) were involved in these investigations. It has been established that during oxidative degradation in air of PMMA, three processes occur practically simultaneously: thermal degradation, or scission of chains; oxidation, or insertion of oxygen atoms in the polymer chains and in the products of the degradation; and a sublimation of degradation products.

The introducing of small quantities of $C_{60}$ in the system results in the replacement of oxygen by fullerene or to a partial avoidance of oxidation, as a result of which, at the first stage, a smaller quantity of degradation products is formed and oxidized. The $C_{60}$ molecules are divided during oxidative degradation of PMMA into two groups: linked (similar to 20 %) and nonlinked with macroradicals of PMMA. The non-linked molecules of $C_{60}$, in turn, are subdivided into oxidized and volatilizing ones without oxidation and degradation. The inhibiting effect of $C_{60}$ on the thermal oxidative degradation reduces basically to two processes: to formation of fullerene-containing chains of PMMA and to nonchain inhibition. The matrix of PMMA has also a significant influence on the thermal behavior of $C_{60}$.

This behavior of fullerene $C_{60}$ is extended to atactic, anionic syndiotactic and isotactic forms of PMMA. It is suggested that fullerene-containing polymers produced upon the thermal and thermooxidative degradation of PMMAs together with the nonchain inhibition of PMMAs oxidation accounts for the stabilizing effect of fullerene [21].

Fullerene $C_{60}$ inhibits high-temperature oxidative degradation of PMMA and methyl methacrylate

copolymers with methacrylic acid [22]. Copolymers of methyl methacrylate with methacrylamides undergo thermal oxidative degradation less actively than PMMA. Additions of fullerene $C_{60}$ inhibit the degradation [23].

For the thermal and thermooxidative degradation in fullerene $(C_{60}, C_{70}) /$ polymer (PMMA, polystyrene) systems, concentration limits were observed for the stabilizing effect of fullerenes that depends on the solubility of fullerene in the polymer: for PS and PMMA, these values are $4 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol/kg of fullerene, respectively. Thermal and thermooxidative degradation occurred in the presence of fullerenes were also characterized by the existence of temperature limits for the effective action of inhibitors. For PS-based systems containing $C_{60}$ or $C_{70}$, the temperature limit of thermal degradation was 380 degrees C; for PMMA-based systems, this parameter amounted to 612 and 603 K for $C_{60}$ and $C_{70}$, respectively. For the thermooxidative degradation of these polymers and polycarbonate, the temperature range of 608–613 K was the highest temperature limit for fullerene $C_{60}$ acting as an antioxidant, which was much lower than 643 K, the temperature corresponding to the onset of the intense oxidation of fullerene [24].

The techniques of mass-spectrometric thermal analysis, DSC, DTG and wide-angle X-ray analysis of thermal and oxidative degradation of two types of fullerene-containing polymer systems (FCPS) were studied: i) FCPS with covalent interaction of fullerene $C_{60}$ with polymers; ii) FCPS representing mixtures of $C_{60}$ with polymers in which interaction of components is realized only by means of Van-der-Waals' forces. In both types of FCPS the electron acceptor properties of $C_{60}$ are manifested. In some systems of the first type, a great decrease in thermal stability of a polymer component was observed; in the systems of the second type the ability of fullerene $C_{60}$ to play a role of the "trap" of free radicals is especially manifested. The polymer matrix also influences the thermal behavior of fullerene $C_{60}$, In particular, fullerene can serve as a specific "probe" of chemical processes that occur during the thermal degradation of the polymer. Different PS and PMMAs containing 1–10 wt % $C_{60}$ (FCPS) were investigated [25].

Two-step investigation was made to determine the antioxidant properties of fullerenes $C_{60}/C_{70}$ and $C_{60}$ in PS [10]. The antioxidative activity of fullerene $C_{60}/C_{70}$ has been studied by a model reaction of the initiated oxidation of styrene and then in accelerated tests of $C_{60}/C_{70}$ and $C_{70}$ mixtures with PS. It was established that the initiation and oxidation rates of the model reaction is substantially reduced in the presence of $C_{60}/C_{70}$. For the first time the rate constant for the addition of styryl radicals to $C_{60}/C_{70}$ has been determined to be $k_{(333K)} = (9.0 \pm 1.5) \cdot 10^{7}$ $M^{-1} \cdot s^{-1}$. By DSC and TGA it was demonstrated that fullerenes show a stabilizing effect comparable with the influence of the 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 the formation of less active compounds and intensive addition of nucleophilic species like electrons, free radicals, anions and hydrogen atoms.

The antiradical activity of fullerene $C_{60}$ was studied for the oxidation of 1,4-dioxane and styrene initiated by azobisisobutyronitrile and benzoyl peroxide as model reactions [26]. The effective rate constants of the reaction of peroxyl radicals with fullerene $C_{60}$ ($k_7$) and the stoichiometric inhibition factor (*f*) were determined in air and pure oxygen. The rate of the liquid-phase oxidation of 1,4-dioxane does not depend on the oxygen pressure and the effective rate constant of inhibition is $k_7 = (2.4 \pm 0.2) \cdot 10^4$ $M^{-1} \cdot s^{-1}$. Chain termination in the oxidation of styrene occurs when $C_{60}$ reacts with both the peroxyl radicals ($k_7 = (1.2 \pm 0.1) \cdot 10^3$ $M^{-1} \cdot s^{-1}$), and alkyl ($k_8 = 1.07 \cdot 10^7 \, M^{-1} \cdot s^{-1}$) radicals.

The influence of fullerene $C_{60}$ additives on the thermal behavior and the thermo-degradation of poly-*n*-alkyl acrylates, from butyl to heptyl, and of corresponding polymethacrylates was investigated by thermogravimetry under dynamical conditions and pyrolysis/gas chromatography under isothermal conditions at 673–923 K [27]. Fullerene is a well-known efficient acceptor of radicals and its presence influences the thermal degradation of acrylic polymers, shifting the decomposition process from a radical pathway to a non-radical mechanism. For poly-*n*-alkyl acrylates the addition of fullerenes leads 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 recorded temperatures of maximum weight loss obtained during thermogravimetric experiments are slightly increased by the presence of fullerene. The effect of fullerene is more noticeable in the thermal behaviour of poly-*n*-alkyl methacrylates, in fact the enhancements of the temperature of maximum weight loss are 292–298 K. 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. Fullerene acts as a radical acceptor suppressing the unzipping process and favouring the non-radical side-chain reactions [27].

Carbon nanotubes (CNTs) have electron affinities similar to those of fullerenes, and might therefore also be hypothetically predicted to behave as radical traps in chain reactions such as polymerisation and thermal degradation. Because of their potential radical accepting capacity, CNTs can be expected to interrupt chain propagation, leading to the antioxidant and stabilising action in polymers.

Actually, the polymer-nanotube composites are able to carry high current densities which undoubtedly will afford Joule heating of the polymer. P. Watts *et al.* [28] observed the high heating effects (above 473 K) of the polymer on the passage of direct current through composites. It is therefore important to study how CNTs affect the stability of polymers at elevated temperatures. According to TGA and CL profiles it has been proved that CNTs act as antioxidants during thermo-oxidative degradation of composites of polystyrene, polyethylene, polypropylene and poly-vinylidene fluoride. An increase in the CNTs content beyond 5 % leads to only small increases in antioxidant efficiency. In the poly-vinylidene fluoride case it seems that the nanotubes can act as both antioxidants and halogen absorbers [28].

Sterilization of implants and other clinical accessories is an integral part of any medical application. Although many materials are used as implants, polyethylene stands unique owing to its versatility. Carbon nanotubes are being used as a filler material to enhance the properties of polyethylene. However, the role of multi-walled carbon nanotubes (MWCNTs) as an effective antioxidant and radical scavenger in resisting the deteriorating effects of sterilization is yet to be studied in detail. The work [29] was aimed to investigate the mechanical properties and oxidation stability of irradiated high density polyethylene (HDPE) reinforced by MWCNTs with various concentrations such as 0.25, 0.50, 0.75 and 1.00 wt %. The composites were exposed to $^{60}$Co source in air and irradiated at different dosage level starting from 25 to 100 kGy and then shelf aged for a period of 120 days prior to investigation. The loss in toughness, Young's modulus and ultimate strength at 100 kGy for 1 wt % MWCNTs composite were found to be 21.5, 20.3 and 19.2 %, respectively, compared to those of unirradiated composite. FT-IR and ESR studies confirmed the antioxidant and radical scavenging potentialities of MWCNTs with increased concentration and irradiation dosage. It was found that by the addition of 1 wt % MWCNTs into virgin HDPE, the oxidation index of the composite at 100 kGy was decreased by 56.2 %. It is concluded that the addition of MWCNTs into polyethylene not only limits the loss of mechanical properties but also improves its post irradiation oxidative stability.

Carbon nanotubes are extensively incorporated as reinforcement into polymeric materials due to their extraordinary properties. The antioxidant ability of CNTs in HDPE was studied [30]. Single-walled carbon nanotubes (SWCNTs), MWCNTs, and hydroxylated multi-walled carbon nanotubes (MWCNTs-OH) were involved to investigate the influence of wall number and surface functionalization of CNTs on their antioxidant behavior in HDPE. Based on measurements of the oxidation induction temperature and oxidation induction time of CNTs/HDPE composites, it is found that the

antioxidant ability of the three kinds of CNTs is in the following order: MWCNTs-OH > MWCNTs > SWCNTs. The antioxidant ability and mechanism of CNTs are further examined by electron spin resonance spectra and Raman spectra. It is observed that the antioxidant behavior of CNTs obeys a free radical scavenging mechanism. The order of the radical scavenging efficiency and the defect concentration for CNTs are in good agreement with that of their antioxidant ability in HDPE. With more walls and surface hydroxyl groups, CNTs have more structural defects and exhibit higher antioxidant ability. The study raises the possibility that CNTs can improve antioxidant properties as well as mechanical properties of polymer matrix [30].

The influence of carbon nanotubes on the photodegradation of ethylene-vinyl acetate (EVA)/carbon nanotube nanocomposites was studied by irradiation under photooxidative conditions (at $\lambda > 300$ nm, at 333 K and in the presence of oxygen). The influence of the nanotubes on both the photooxidation mechanism of EVA and the rates of oxidation of the matrix was characterized on the basis of infrared analysis. On the one hand, it was shown that CNTs act as inner filters and antioxidants, which contribute to reduction in the rate of photooxidation of the polymeric matrix. On the other hand, it was shown that light absorption could provoke an increase in the local temperature and then induce the photooxidation of the polymer. The competition between these three effects determines the global rate of photooxidation of the polymeric matrix. Several factors are involved, the concentration of the CNTs, the morphology of the nanotubes and the functionalization of the nanotube surface [31].

MWCNTs/linear low density polyethylene (LLDPE) nanocomposites were studied in order to understand the stabilisation mechanism for their thermal and oxidative degradation [32]. Thermogravimetry coupled with infrared evolved gas analysis and pyrolysis gas chromatography–mass spectrometry demonstrate that MWCNTs presence slightly delays thermal volatilization (by 15–20 degrees) without modification of thermal degradation mechanism. Whereas thermal oxidative degradation in air is delayed by about 100 K independently from MWCNTs concentration in the range used here (0.5–3.0 wt %). The stabilization due to formation of a thin protective film of MWCNTs/carbon char composite generated on the surface of the nanocomposites is shown by SEM and ATR FT-IR of degradation residues [32].

The paper [33] presents a preliminary investigation on the effects of incorporating CNTs into polyamide-6 (PA6) on mechanical, thermal properties and fire performance of woven glass reinforced CNTs/PA6 nanocomposite laminates. The samples were characterized by tensile and flexural tests, thermal gravimetric analysis (TGA), heat distortion temperature (HDT) measurements,

thermal conductivity and cone calorimeter tests. Incorporation of up to 2 wt % CNTs in CNTs/PA6/GF laminates improved the flexural stress of the laminates up to 36 %, the thermal conductivity by approximately 42 %; the ignition time and peak HRR time was delayed by approximately 31 and 118 %, respectively [33].

High energy ball milling (HEBM) was utilized, as an innovative process, to incorporate CNTs into a polyethylene (PE) matrix avoiding: high temperatures, solvents, ultrasonication, chemical modification of CNTs. Composites with 1, 2, 3, 5, and 10 wt % of CNTs were prepared. Films were obtained melting the powders in a hot press. Morphology and physical properties (thermal, mechanical, electrical properties) were evaluated [34]. The used processing conditions have allowed to obtain a satisfactory level of dispersion of CNTs into the PE matrix with a consequent improvement of the physical properties of the samples. The thermal degradation was significantly delayed already with 1–2 wt % of CNTs. The mechanical properties resulted greatly improved low filler content (up to 3 wt %). The electrical measurements showed a percolation threshold in the range of 1–3 wt % of CNTs [34].

MWCNTs were incorporated in ultrahigh molecular weight polyethylene (UHMWPE), which is a polymer used in industrial and orthopedic applications. The composites were prepared by ball milling and thermo-compression processes at concentrations up to 3 wt % and subsequently gamma irradiated at 90 kGy. Electrical conductivity measurements showed a low percolation threshold of 0.5 wt %. Electron spin resonance detection of the radiation-induced radicals proved the radical scavenger behavior of MWCNTs: when the nanotube concentration increased, the number of radicals generated by the gamma irradiation process decreased. Allyl radicals seem to be the radicals most affected by the presence of nanotubes in this polymeric matrix. Fourier transformed infrared spectroscopy measurements and an accelerated ageing protocol were performed to ascertain the influence of the irradiation on the oxidation index. The results pointed to the positive contribution of MWCNTs in increasing the oxidative stability of the composite compared to pure UHMWPE. Crosslinking density induced by gamma irradiation was obtained by swelling measurements. The findings showed that, despite the radical scavenger performance, MWCNTs are capable of maintaining the efficiency of the crosslinking density, unlike the other antioxidants, which inhibit radiation crosslinking [35].

Polymer nanocomposites with CNTs as fillers have attracted more attention than any other nanomaterials. A full development of these materials requires a deep understanding of the way they behave under the applied conditions. In the work [36], the resistance to accelerated photooxidation of syndiotactic polypropylene/MWCNTs films was compared to the photooxidation behaviour of unfilled polypropylene films with the same structural

organization. The chemical and structural modifications resulting from photooxidation have been observed when using infrared spectroscopy and diffractometric analysis. It was found that a good dispersion degree of the nano-filler, evaluated by atomic force microscopy, contributes to reduction in the rate of photooxidation and an increase in the oxidative thermal stability of the polymeric matrix. Different concomitant effects are considered to explain these results, among which morphology and structure of the nanocomposites together with the MWCNTs capacity interact with oxygen molecules making them unavailable at the first stages of photooxidation.

## Conclusions

Fullerenes – $C_{60}$, $C_{70}$, fullerene soot and carbon nanotubes (CNTs) efficiently retard thermo-photodegradable processes in different polymer matrix – polyolefine, polyacrylate, polyamide, polycarbonate, rubber and other composite materials due to active trapping of radicals. Most of publications specify the exclusive addition of carbon-centered macroradicals to fullerenes in the considered systems underlining the prevailing role of fullerenes rather as heat stabilizers than scavenger of peroxy radicals. In one case the stabilization was due to the formation of a thin protective film of MWCNTs/carbon char composite generated on the surface of the nanocomposites.

The kinetic data obtained specify the level of antioxidative activity of the used carbon nanocompounds and scope of their rational use in different composites. The results may be helpful for designing an optimal profile of composites containing fullerenes and CNTs.

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**АНТИОКИСНЮВАЛЬНІ ВЛАСТИВОСТІ ДЕЯКИХ НАНОКАРБОНОВИХ КОМПОНЕНТІВ, ІНТЕГРОВАНИХ В ПОЛІМЕРНІ МАТЕРІАЛИ (ОГЛЯД)**

*Анотація. Коротко описаний стан досліджень, які проводяться в світі, стосовно аспектів впливу фулеренів та карбонових нанотрубок (ВНТ) на міцність різних полімерних композицій за жорстких термоокиснювальних умов. Показано, що для покращення термічних та механічних властивостей полімерів найбільш доцільно використовувати фулерени та ВНТ. Фулерени $C_{60}$, $C_{70}$, фулеренова сажа та ВНТ вводять в полімерну матрицю для попередження її термічної та термоокис-нювальної деструкції, а також фотоокиснювальних процесів.*

*Ключові слова: фулерен, карбонові нанотрубки, полі-мерна композиция, термоокиснювальна деструкція, акцептор радикалів, стабілізатор.*