TESTING FULLERENE SOOT AS ANTI-OXIDATIVE AGENT FOR POLYDIMETHYLSILOXANE RUBBER

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Abstract. Fullerenes have intrinsic high electron affinity and they are therefore capable of acting as radical traps in free radical chain reactions, including polymerization and the thermo-oxidative degradation of polymers. Reactivity of fullerene particles in polymer mediums is governed by diffusion and promotes active termination of oxidation chains on macro-R• radicals. Radical accepting capacity of fullerenes is comparable with that for well-known commercial primary stabilizers. Therefore, cheap fullerene matters even unpurified samples could be used for stabilization of polymer materials. To check this postulate, the anti-oxidative activity of fullerene soot has been studied as agents preventing thermo-oxidative disruption of siloxane rubbers. Polydimethylsiloxane (PDMS) – C_{60} (soot) composites was prepared and tested on thermo-oxidative stability. The fullerene soot additives increase all temperature points of the degradation and can serve as effective anti-oxidative agents for the rubbers.

Keywords: fullerene soot, thermooxidative degradation of polymer materials, radical scavenging reactivity of fullerenes, stabilizers of polymers, siloxane rubber.

Introduction (short literature review)

Fullerene family is considered as a classical engineered material with potential application in drug delivery, energy sphere, polymer chemistry and cosmetic products. Production of fullerenes and their use in consumer products is expected to increase in future [1].

In particular, Fullerenes have gained considerable attention due to their anti-oxidant and radical scavenging properties. It is because of the fullerenes peculiar electronic structure making attack and intensive addition of nucleophilic particles like electrons, free radicals, anions, hydrogen atoms highly possible [2]. The intensive addition of electrons leads to an oxidation of an adjacent molecule 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=$10^{8\pm1}M^{-1}s^{-1}$ reported in a number of publications

[6-10]. Thus, the fullerenes may display the radical scavenger properties in chain radical processes and can prevent disrupting impact of heat and aggressive agents.

There are a number of publications describing thermal and thermos-oxidative degradation of polymers in the presence of fullerenes. These researches specified the stabilizing role of the 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 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 a 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 the 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 cumylalkyl 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 R· radicals to the fullerenes were determined to be $k_{(333K)} = (1.9 \pm 0.2) \times 10^8$ (C_{60}); $(2.3 \pm 0.2) \times 10^8$ (C_{60}/C_{70}, mix 1); $(2.7 \pm 0.2) \times 10^8$ (C_{60}/C_{70}, mix 2); $(3.0 \pm 0.3) \times 10^8$ (C_{70}), $M^{-1} s^{-1}$. 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 of 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}-soot] $= (2.0 \pm 0.1) \times 10^{-4}$ mol g^{-1} and $k_{inh} = (6.5 \pm 1.5) \times 10^3 M^{-1} s^{-1}$ respectively.

It has been shown in the 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 thermal stabilizer and as 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 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 an antioxidant for cis-1,4- polyisoprene, provided that the heating rate of the samples is slow (5° C /min). At higher heating rates (20° C/min) C_{60} does not show any antioxidant effect. This result established 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 macroperoxy radicals concentration, due to apparent insusceptibility towards oxygen-centred radicals.

Thermal stabilisation 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 temperatures 170, 180 and 190^oC. 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 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 282° C and 238° C 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 on the curves of dependence of weight loss of polymers on time of degradation, rise substantially. 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 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· and oxygen-containing radicals with formation of less active compounds. In the case of PS the retarding influence of the fullerene is mainly connected with its reaction with oxygen-containing radicals, but the interaction of C_{60} with R· must not be ruled out.

The introduction of additional MMA units (5-15mol.%) 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 copolymers of MMA 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].

Others authors also proposed the results of studies of thermal and oxidative degradation of a free-radical produced PMMA and the influence of a 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 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 a 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 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 non-chain inhibition. The matrix of PMMA also has a significant influence on the thermal behavior of C_{60}.

This behaviour of fullerene C_{60} is extended to atactic, anionic syndiotactic and isotactic forms of the 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 depend on the solubility of the fullerene in a polymer: for PS and PMMA, these values are 4×10^{-3} and 8×10^{-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 339° C and 336° C for C_{60} and C_{70}, respectively. For the thermooxidative degradation of these polymers and a polycarbonate, the temperature range of 335°C- 340°C was the highest temperature limit for fullerene C_{60} acting as an antioxidant, which was much lower than 370°C, 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: 1) FCPS with covalent interaction of fullerene C_{60} with polymers; 2) 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 systems of the second type the ability of fullerene C_{60} to

play a role of "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 a 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 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 $k_{(333K)} = (9.0\pm1.5)\times10^7$ $M^{-1}s^{-1}$. 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 $R\cdot$ leading to formation of less active compounds an intensive addition of nucleophilic species like electrons, free radicals, anions, 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, and the effective rate constant of inhibition is $k_7 = (2.4\pm0.2)\times10^4$ $M^{-1}s^{-1}$. Chain termination in the oxidation of styrene occurs when C_{60} reacts with both the peroxyl radicals ($k_7 = (1.2\pm0.1)\times10^3$ $M^{-1}s^{-1}$), and alkyl ($k_8 = 1.07\times10^7$ $M^{-1}s^{-1}$) 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 in isothermal conditions at 400° C–650 °C [27].

The 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 19° C–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 [27].

Thus, there are many experimental facts proved a stabilizing role of fullerenes integrated in different polymer materials. However, there are some restrictions for widespread application of fullerenes as polymer stabilizers. One of them is high cost of pure fullerene samples. Therefore,

we undertook the experiments with fullerene soot, which is cheapest among fullerenes and could display applicability for effective protection of a polymer matrix against disruptive agents.

We have already the ground for such claim, when have shown the high antioxidative activity of fullerene soot in the model oxidation reaction [28]. It has been found that the fullerene soot inhibits the model reaction according to the mechanism of trapping of peroxy radicals with rate constants $k_{inh.} = (6.5 \pm 1.5) \times 10^3 \, M^{-1} \, s^{-1}$.

Experimental

The fullerene soot and PDMS rubber used were commercial samples provided by "Aldrich".

The defined portion of PDMS was dissolved in benzene. After complete dissolution of PDMS, a measured amount of C_{60} soot was added to the polymer solution, after which the solvent was slowly evaporated at room temperature to a constant fixed weight of the polymer composite.The composites thermal stability was studied using Q-1500 D derivatograph (MOM, Hungary). The tests were carried out in air in a dynamic mode when the sample was heated to 5° C per min from 20° C to 500° C using a 100 mg sample and the sensitivity of the channels set at TG-100 mV.

Thermogravimetric analysis of the PDMS-C_{60} soot composite samples

The thermal stability of the nanocompostes studied was assessed from the TG curves of the weight loss at the temperature points T_{10}, T_{20} and T_{50}, as well as from the half-life time of degradation $\tau_{1/2}$ (Table**1**).

It is found that the fullerene soot inclusions increase the T_{50} temperature point from 380°C to 400°C, $\tau_{1/2}$ parameter is increased from 63.2 to 79.8 min.

Table 1. Thermal properties of the PDMS-C60 soot nanocomposite samples

Composites (wt. %)	T_{10}, °C	T_{20}, °C	T_{50} ,°C	$\tau_{1/2}$, min
PDMS (100)	340	370	400	76
PDMS /C60 soot (100/1.0)	370	390	430	88

Conclusion

The effect of C_{60} fullerene soot on the properties of polydimetylsiloxane rubber (PDMS) composites has been studied. It has been established that these additives improve thermo-oxidative stability of the nanocomposites acting both as radical scavenger and reinforced agent.

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