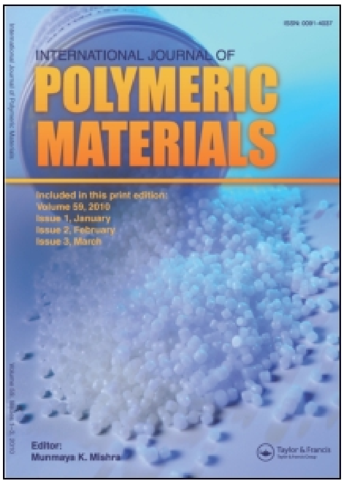

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Investigation of Fullerenes as High Temperature Stabilizers of Poly(methyl methacrylate) and Polystyrene

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Investigation of Fullerenes as High Temperature Stabilizers of Poly(methyl methacrylate) and Polystyrene

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Investigation has been made on the effects of fullerenes C_{60} and C_{70} on the degradation of PMMA and PS under helium and oxygen by a DSC method. The dependences of the temperature of the onset of the thermal and thermo-oxidative degradation of the polymers on concentration of C_{60} and C_{70} have been obtained. The temperature limits of effective inhibition of the polymers by fullerenes have been determined. The temperature limit depends on the chemical structure of polymer, namely it is considerably greater in the degradation of more stable polymer. In the thermo-oxidative degradation of the polymers with addition of fullerenes, the temperature limit of inhibition of less stable PS is much less and of more stable PMMA is considerably greater than that in the presence of well-known antioxidants. It was concluded that fullerenes are more effective high temperature inhibitors of the thermo-oxidative degradation of PMMA than well-known antioxidants. The suggestion was made that the thermo-oxidative degradation of polymers initiates the oxidation of fullerenes.

Keywords: Fullerenes; stabilizers; polystyrene; poly(methyl methacrylate)

1. INTRODUCTION

Recently it has been shown that fullerene C_{60} retards the thermal degradation of poly(methyl methacrylate) (PMMA) [1 – 3], polystyrene

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(PS) [3] and the autocatalytic thermal dehydrochlorination of poly (vinyl chloride) [1] at elevated temperatures. It is well known [4, 5] that C_{60} reacts easily with low molecular weight alkyl radicals with formation of remarkable persistent products R_nC_{60} (where $n = 1, 2, 3, \ldots$). The suggestion was made that the inhibiting influence of C_{60} on the thermal degradation of PMMA, PS and poly(vinyl chloride) is connected with its interaction with macroradicals generating in the thermal aging of these polymers with formation of less active compounds [1 – 3]. In the case of poly(vinyl chloride), there is the probability of interaction of C_{60} with chlorine atoms also [1].

The most important factor in causing instability in polymers is the presence of oxygen during processing and use. The thermo-oxidative degradation of polymers is the branched chain reaction with the degenerated branching of chain [6 – 8]. Radicals containing oxygen, such as $RO^{\bullet}$, $RO^{\bullet}_2$ and $^{\bullet}OH$ are of principal importance in this process. It is known [4, 5] that fullerenes interact with oxygen-containing radicals too. Recently [3] it has been shown that C_{60} is inhibitor of the thermo-oxidative degradation of PMMA and PS at elevated temperatures. It was supposed that in the case of PMMA, the inhibiting effect of fullerene is due to its interaction with macroradicals $R^{\bullet}$ and oxygen-containing radicals with formation of more stable compounds. In the case of PS, the retarding effect of C_{60} is connected with its interaction mainly with oxygen-containing radicals, but the interaction of fullerene with macroradicals $R^{\bullet}$ must not be ruled out.

In this study, the thermal and thermo-oxidative degradation of PMMA and PS has been investigated in the presence of different concentrations of fullerenes C_{60} and C_{70}. It is very important to know temperature limit of effective inhibition of degradation of polymers by stabilizers. This study deals with the determination of temperature limit of inhibition of the thermal and thermo-oxidative degradation of PMMA and PS by fullerenes.

In recent years thermal analysis methods such as differential thermal analysis and differential scanning calorimetry (DSC) are applied in the study of thermal and thermo-oxidative degradation and stabilization of polymers. It is ability of these methods to detect the thermal consequences of the onset of degradation which makes them useful techniques for polymers showing exothermic or endothermic degradation.

We have used a DSC method for studying the effects of fullerenes on the degradation of polymers.

2. EXPERIMENTAL

2.1. Materials

The method of preparation and purification of C_{60} was described previously [1]. The purity of C_{60} was $\geq 99.9\%$. C_{70} was prepared and purified by the same method. The purity of C_{70} was 98%.

PMMA and PS were prepared by bulk polymerization as described before [1, 3].

2.2. Methods

The degradation of PMMA and PS films was carried out by a DSC method in the stream of helium (20 ml/min) and in dynamic oxygen (40 ml/min) at 100 – 500°C with scanning rate of 5°C/min. A charge of $1.0 \times 10^{-6} - 3.0 \times 10^{-6}$ kg of PMMA or PS was used for each experiment. A DSC-7 Perkin-Elmer instrument was used.

Films of PMMA and PS without additives and with addition of C_{60} or C_{70} were prepared as described previously [1, 3].

The degradations of C_{60} and C_{70} were investigated by a DSC method in helium and in oxygen at 100 – 500°C with scanning rate of 5°C/min. A charge of 1.0×10^{-6} kg of compound was used for each experiment.

3. RESULTS AND DISCUSSION

DSC curves of the degradation of PS and PMMA in dynamic oxygen have been represented previously [3]. They have exotherms for polymer oxidation process. The DSC curves show that the temperature of the onset of intensive degradation of polymer, T_0, is 220°C and 275°C for PS and PMMA, respectively. In degradation of the polymers in an inert gas, no appreciable changes in baseline are seen in the DSC curves up to 368°C and 320°C for PS and PMMA, respectively. It follows that in the degradation of the polymers under oxygen, the onset of degradation at 220°C for PS and 275°C for PMMA is due to the branched chain nature of the oxidation reaction process.

In the papers [10, 11] the thermo-oxidative aging of PS over a temperature range from 249°C to 300°C has been studied. In has been shown that water is the main volatile product. In the thermo-oxidative degradation of PS at elevated temperatures, the mechanism of oxidation of hydrocarbons in the liquid phase is believed to be operative [10, 11]. It seems to be generally agreed that initiation of the oxidative process is due to abstraction of hydrogen atoms near the tertiary carbon atoms [10, 11].

The thermo-oxidative degradation of PMMA has been investigated up to 320°C [12, 13]. It has been shown that at elevated temperatures (>200°C) the major low molecular weight product of this process is methyl methacrylate (>90%) and the main reaction is the reaction of depropagation initiated owing to oxidation of the main chain. In PMMA thermo-oxidative degradation at elevated temperatures apart from the monomer, the following compounds are generated in significant amounts: 2-methyl-oxirane carbonic acid methyl ester, methyl pyruvate, dimethyl itaconate and acetaldehyde [12].

It is well known [6] that in the thermo-oxidative degradation, PS is much less stable than PMMA due to the presence of fragments with hydrogen atoms near the tertiary carbon atoms in PS macromolecules which have less energy of C—H bonds than C—H bonds in PMMA. As mentioned above, the value of T_0 for PMMA is higher by 55°C than that for PS.

From the aforesaid, it appears that the thermo-oxidative stability and the thermo-oxidative degradation of PS differ considerably from those of PMMA.

Figures 1 and 2 illustrate characteristic DSC curves of the thermo-oxidative degradation of PS (Fig. 1) and PMMA (Fig. 2) in the presence of fullurene C_{70}. It is seen that C_{70} retards the thermo-oxidative degradation of the polymers. In its presence, the values of T_0 for PS and PMMA are more than those in the absence of C_{70}. As already noted, recently [3] it has been shown that C_{60} is inhibitor of the thermo-oxidative degradation of PMMA and PS at elevated temperatures. The

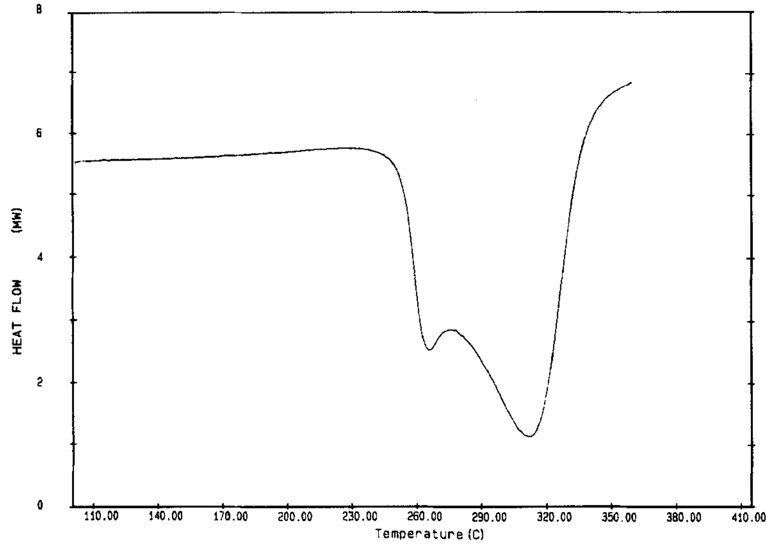

FIGURE 1 DSC curve in oxygen for PS with addition of 5×10^{-3} mol/kg C_{70}.

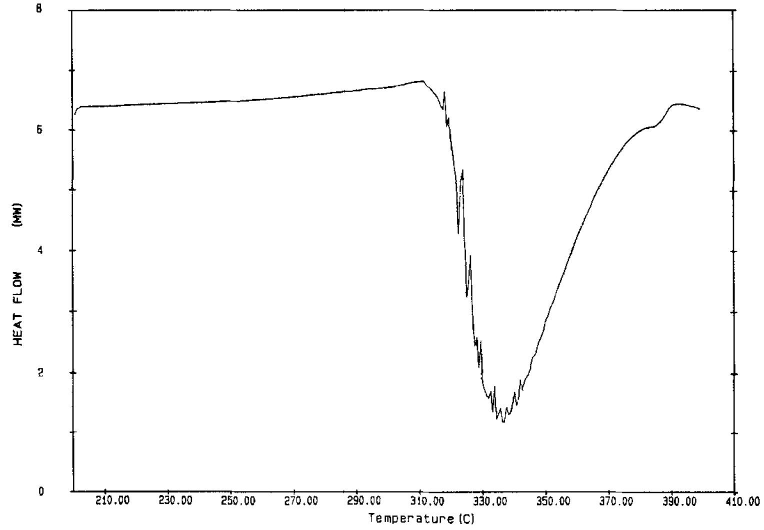

FIGURE 2 DSC curve in oxygen for PMMA with addition of 2.5×10^{-3} mol/kg C_{70}.

results obtained indicate that not only C_{60} but also C_{70} retards the thermo-oxidative aging of these polymers.

Figures 3 and 4 show the dependences of T_0 on concentration of C_{60} and C_{70} in the thermo-oxidative degradation of PMMA (Fig. 3) and PS (Fig. 4). Beginning with definite concentration of an additive ($\sim 7 \times 10^{-3} - 10 \times 10^{-3}$ mol/kg), the maximum value of T_0, T_0^{max}, is observed. The values of T_0^{max} changes slightly with further increase in fullerene concentration. The value of T_0^{max} for PMMA is equal to 309°C and 317°C in the case of C_{60} and C_{70}, respectively (Fig. 3). The value of T_0^{max} for PS is 248°C in the case of C_{60} and C_{70} (Fig. 4). From the results obtained, it follows that the value of T_0^{max} is temperature limit of effective inhibition of the thermo-oxidative degradation of

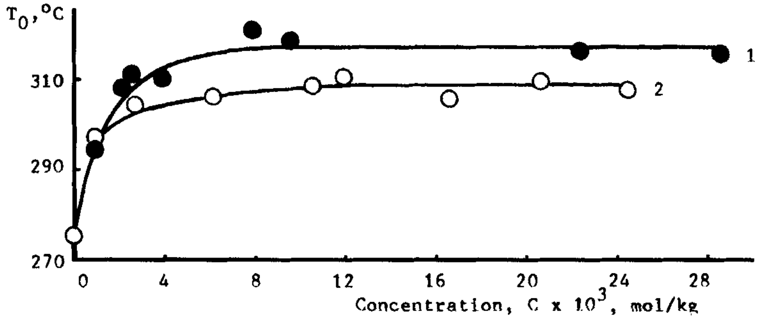

FIGURE 3 Dependences of T_0 on concentration of C_{70} (1) and C_{60} (2) in the thermo-oxidative degradation of PMMA.

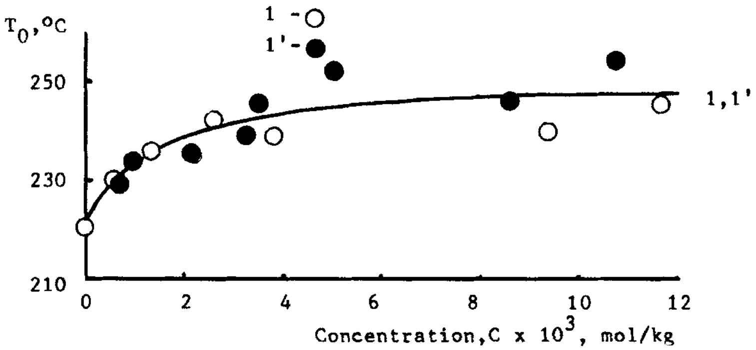

FIGURE 4 Dependences of T_0 on concentration of C_{60} (1) and C_{70} (1′) in the thermo-oxidative degradation of PS.

polymer by a stabilizer. Thus, in the case of fullerenes, the temperature limit of effective inhibition is about 310–320°C and about 250°C in the thermo-oxidative degradation of PMMA and PS, respectively.

It is known [14, 15] that C_{60} exposed to pure oxygen is oxidized to a mixture of CO and CO_2 at high temperatures, ~400°C. The thermal stability of C_{60} in oxygen has been investigated by differential scanning calorimetry also [14]. We studied the decomposition of fullerenes themselves by the DSC method in oxygen under conditions identical to those employed in the degradation of the polymers. The DSC curves for C_{60} and C_{70} are represented in Figures 5 and 6. The DSC curves show well defined exotherms for oxidation process. Figures 5 and 6 illustrate that no appreciable changes in baseline are seen in the DSC curves up to the onset of intensive oxidation of fullerenes, T_0^{stab}. The values of T_0^{stab} are equal to 447°C and 353°C for C_{60} and C_{70}, respectively. It is seen that the value of T_0^{stab} for C_{60} is greater than that for C_{70}. One can conclude that the oxidative stability of C_{60} is considerably greater than C_{70}.

The results obtained show that the values of T_0^{stab} are much more than the values of $T_0^{\max}$ for PS and PMMA in the thermo-oxidative degradation of the polymers in the presence of fullerenes.

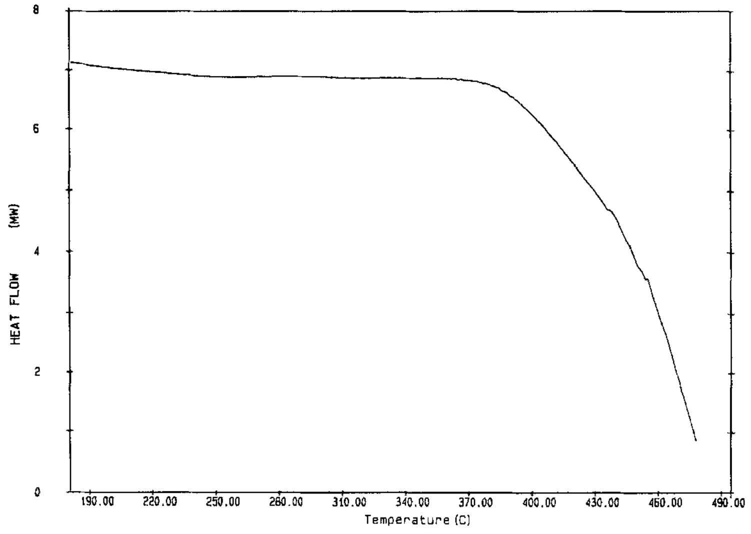

FIGURE 5 DSC curve in oxygen for C_{60}.

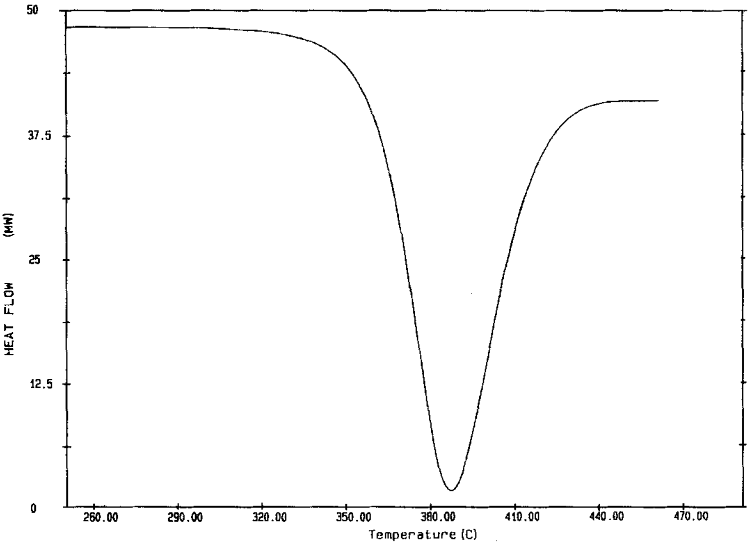

FIGURE 6 DSC curve in oxygen for C_{70}.

Recently [16], we have studied the thermo-oxidative stability of well-known antioxidants, such as aromatic and sterically hindered amines, sterically hindered phenols, S- and P-containing compounds by a DSC method under experimental conditions identical to those employed in the decomposition of fullerenes. It has been show [16] that the values of T_0^{stab} for well-known antioxidants are in the range from 210°C to 270°C. These values are much less than those for fullerenes. It may be concluded that in comparison with well-known antioxidants, fullerenes have considerable advantage as high temperature stabilizers for polymers.

Previously [7, 16, 17], data obtained by the use of different techniques, such as oxygen absorption technique [7, 17] and the DSC method [16] show that the upper temperature limit of inhibition of the thermo-oxidative degradation of polyethylene, polypropylene [7, 17], PS and PMMA [16] by well-known effective antioxidants is in the range from 280°C to 295°C. It does not depend on mechanism of inhibiting influence of antioxidant on the thermo-oxidative degradation of the polymers and depends insignificantly on the chemical structure of polymer. The suggestion was made that the value of the temperature limit of inhibition of the thermo-oxidative degradation of polymers depends to a great extent on intensive oxidative decomposition of antioxidant itself [16].

In the thermo-oxidative degradation of polymers in the presence of fullerenes, behaviour of these latter has some perculiarities. In the case of fullerenes, the temperature limit of effective inhibition depends on the chemical structure of polymer: the values of T_0^{stab} for less stable polymer, PS, are less by 60–70°C than those for more stable polymer, PMMA (Figs. 3 and 4). It should be noted that in the case of fullerenes, the value of $T_0^{\max}$ for less stable PS is much less [$T_0^{\max}$ is about 250°C (Fig. 4)] than that in the case of well-known antioxidants ($T_0^{\max}$ is in a range of 280–295°C [16]) but in the presence of fullerenes, the value of $T_0^{\max}$ for more stable PMMA is considerably greater [$T_0^{\max} \cong 310-320$°C (Fig. 3)] than that in the presence of well-known inhibitors ($T_0^{\max} \cong 285-295$°C [16]). Thus, one can conclude that fullerenes are more effective high temperature inhibitors of the thermo-oxidative degradation of PMMA than known antioxidants.

It may be assumed that peculiarities of behaviour of fullerenes by comparison to well-known antioxidants are connected with mechanism of inhibiting influence of fullerenes on the thermo-oxidative degradation of polymers. As mentioned above, in the paper [3] the suggestion has been made that the inhibiting effect of fullerene C_{60} is due to their interaction with oxygen-containing radicals as well as macroradicals $R^{\bullet}$ in the case of PMMA and due to their interaction mainly with oxygen-containing radicals in the case of PS.

$$ROO^{\bullet}(R^{\bullet}) + C_{60} \rightarrow ROO\dot{C}_{60}(R\dot{C}_{60}) \tag{1}$$

More stable fullerene-containing radicals formed may react with oxygen, with other ROO or R radicals:

$$ROO\dot{C}_{60}(R\dot{C}_{60}) + O_2 \rightarrow ROOC_{60}OO^{\bullet}(RC_{60}OO^{\bullet}) \tag{2}$$

$$ROO\dot{C}_{60}(\dot{C}_{60}) + ROO^{\bullet} \rightarrow (ROO)_2C_{60}(RC_{60}OOR) \tag{3}$$

$$ROO\dot{C}_{60}(R\dot{C}_{60}) + R^{\bullet} \rightarrow ROOC_{60}R(R_2C_{60}) \tag{4}$$

$$ROOC_{60}OO^{\bullet}(RC_{60}OO^{\bullet}) + R^{\bullet} \rightarrow (ROO)_2C_{60}(RC_{60}OOR) \tag{5}$$

From Eqs. (1)–(5), it is seen that in the thermo-oxidative degradation of polymers in the presence of fullerenes, the formation of fullerene-containing peroxides may occur. At elevated temperatures, these latter may decompose with formation of free radicals which may cause the additional initiation of polymer degradation. As a result, a rapid decrease in a concentration of fullerene takes place and on the curves of dependence of T_0 on fullerene concentrations, $T_0^{\max}$ are observed (Figs. 3 and 4). Thus, it may be assumed that the thermo-oxidative degradation of polymers initiates the oxidation of fullerenes. The less the value of T_0 in the thermo-oxidative degradation of polymer itself [for example, in the case of PS, $T_0 = 220°\mathrm{C}$ (Fig. 4)], the less is the value of $T_0^{\max}$ in the aging of this polymer in the presence of fullerenes [for the case of PS, $T_0^{\max} \cong 250°\mathrm{C}$ (Fig. 4)]. The greater the value of T_0 in the thermo-oxidative degradation of polymer without additives [for the case of PMMA, $T_0 = 275°\mathrm{C}$ (Fig. 3)], the greater is the value of $T_0^{\max}$ in the aging of this polymer in the presence of fullerenes [in the case of PMMA $T_0^{\max} \cong 310–320°\mathrm{C}$ (Fig. 3)]. It is interesting to note that in the thermo-oxidative degradation of the polymers in the presence of fullerenes, the difference between $T_0^{\max}$ for PMMA and PS ($\Delta T_0^{\max}$ is about 60–70°C) is reasonably close to that between T_0 for PMMA and PS in the thermo-oxidative aging of the polymers without additives ($\Delta T_0 = 55°\mathrm{C}$). It should be noted once again that fullerenes themselves begin to oxidize at temperatures which are much more than values of $T_0^{\max}$ for PS and PMMA in the thermo-oxidative degradation of the polymers in the presence of fullerenes. As indicate above, T_0^{stab} is equal to 447°C and 353°C for C_{60} and C_{70}, respectively (Figs. 5 and 6).

It is of interest to investigate the thermal degradation of PS and PMMA in the presence of fullerenes at different concentrations.

It is known [6] that the thermal degradation of PMMA and PS is the chain radical reaction. The thermal stability of PS is greater than PMMA [6]. As stated above, the DSC curves of the degradation of the polymers under the inert gas show that the values of T_0 are 368°C and 320°C for PS and PMMA, respectively, *i.e.*, the value of T_0 for PS is 48°C higher.

Figures 7 and 8 illustrate the dependences of T_0 on concentration of C_{60} and C_{70} in the thermal degradation of PMMA (Fig. 7) and PS (Fig. 8). As already pointed out, recently [1–3] it has been shown that

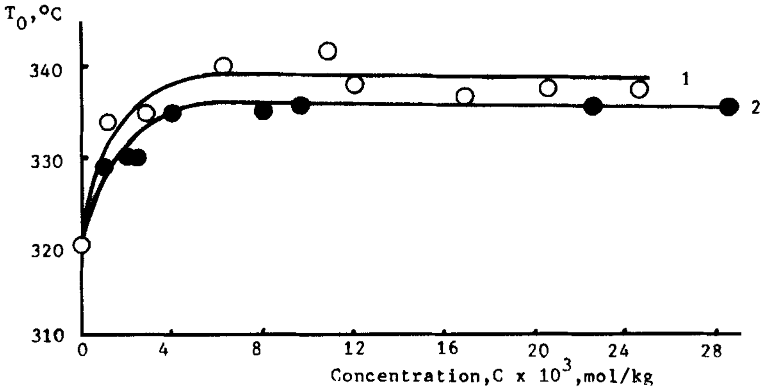

FIGURE 7 Dependences of T_0 on concentration of C_{60} (1) and C_{70} (2) in the thermal degradation of PMMA.

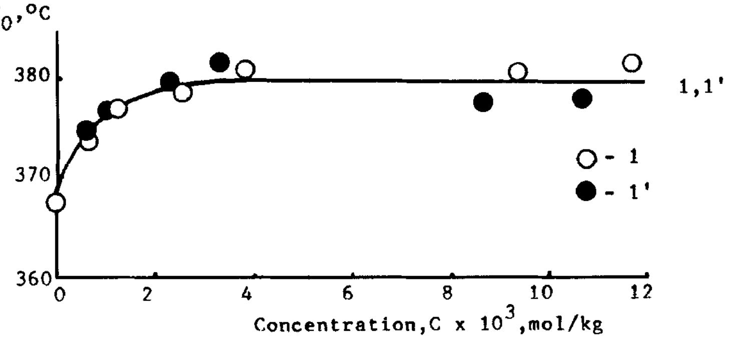

FIGURE 8 Dependences of T_0 on concentration of C_{60} (1) and C_{70} (1′) in the thermal degradation of PS.

fullerene C_{60} retards the thermal degradation of PMMA and PS. The results obtained (Figs. 7 and 8) indicate that not only C_{60} but also C_{70} is inhibitor of the thermal aging of these polymers at elevated temperatures.

As can be seen from Figures 7 and 8, in the thermal degradation of PMMA and PS in the presence of fullerenes, T_0^{max} are observed on the curves of the dependence of T_0 on fullerene concentration, as in the thermo-oxidative aging of the polymers. The value of T_0^{max} for PMMA is 336°C and 339°C, in the case of C_{70} and C_{60}, respectively. The value of T_0^{max} for PS is 380°C in the case of C_{60} and C_{70}.

Thus, for the case of fullerenes, the temperature limit of effective inhibition is about 335–340°C and 380°C in the thermal degradation of PMMA and PS, respectively. It is seen that the value of T_0^{max} for more stable PS is greater than for less stable PMMA. It may be concluded that in the thermal degradation of polymers in the presence of fullerenes, the temperature limit of effective inhibition depends on the chemical structure of polymer, as in the thermo-oxidative aging of polymers. It should be noted that in the thermal degradation of the polymers in the presence of fullerenes, the difference between T_0^{max} for PS and PMMA ($\Delta T_0^{max} \cong$ 40–45°C) is close to that between T_0 for PS and PMMA in the thermal aging of the polymers without additives ($\Delta T_0 = 48°C$).

It is known [14, 15] that C_{60} is stable at high temperatures of up to 900°C in an inert atmosphere. We studied the degradation of C_{60} and C_{70} by the DSC method in an inert gas. No appreciable changes in baseline are seen in the DSC curves up to the upper temperature limit of heating of samples of fullerenes, 500°C.

As mentioned above, the suggestion was made that the inhibiting influence of fullerene C_{60} on the thermal degradation of PMMA and PS is connected with its interaction with macroradicals $R^{\bullet}$ generating in the thermal aging of these polymers, with formation of less active compounds [1–3]. It may be proposed that at elevated temperatures ($>300°C$) reactions of macroradicals R with fullerenes have an equilibrium character:

$$R^{\bullet} + C_{60}(C_{70}) \rightleftharpoons R\dot{C}_{60}(R\dot{C}_{70}) \qquad (6)$$

$$R\dot{C}_{60}(R\dot{C}_{70}) + R^{\bullet} \rightleftharpoons RC_{60}R(RC_{70}R) \qquad (7)$$

With increasing temperature, equilibriums are shifted to the left. This leads to a decrease in inhibiting efficiency of fullerenes. At temperatures equal to T_0^{max}, fullerenes do not effectively retard the thermal degradation of polymers.

4. CONCLUSION

The results obtained illustrate that not only fullerene C_{60} but also fullerene C_{70} is the high temperature inhibitor of the thermal and thermo-oxidative degradation of PMMA and PS. It has been shown that the thermal decomposition of fullerenes themselves does not occur up to at least 500°C. Under oxygen, C_{60} and C_{70} begin to oxidize at 447°C and 353°C, respectively. These temperatures are much more than those for well-known antioxidants. It was concluded that in comparison with well-known antioxidants, fullerenes have considerable advantage as high temperature stabilizers for polymers.

The dependences of the temperature of the onset of the thermal and thermo-oxidative degradation of PMMA and PS on concentration of C_{60} and C_{70} have been obtained. The temperature limits of effective inhibition of the polymers by fullerenes have been determined.

In the thermo-oxidative degradation of polymers, behaviour of fullerenes has some perculiarities as compared with well-known antioxidants. For the case of fullerenes, the temperature limit of effective inhibition depends on the chemical structure of polymer. The temperature limit of inhibition by fullerenes is much less in aging of less stable PS and is considerably greater in the degradation of more stable PMMA than that by well-known antioxidants. It was concluded that fullerenes are more effective high temperature inhibitors of the thermo-oxidative degradation of PMMA than known antioxidants. The suggestion was made that perculiarities of behaviour of fullerenes by comparison to known antioxidants are connected with mechanism of fullerenes inhibiting influence on the thermo-oxidative degradation of polymers. It has been proposed that the thermo-oxidative aging of polymers initiates the oxidation of fullerenes.

It has been shown that in the thermal degradation of polymers in the presence of fullerenes, the temperature limit of effective inhibition depends on the chemical structure of a polymer, as in the thermo-oxidative aging of polymers.

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