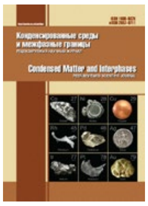

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The influence of fullerene C_{60} on the thermal stability of polyvinyl chloride

T. T. Sadykov✉, A. G. Mustafin, E. I. Kulish, R. M. Akhmetkhanov

Ufa University of Science and Technology,
32 ul. Zaki Validi, Ufa 450076, Russian Federation

Abstract

Objective: Polyvinyl chloride (PVC) is one of the most widely used industrial polymers, yet its practical application is limited by its low thermal and thermo-oxidative stability. The degradation of PVC is accompanied by the elimination of HCl and the formation of isolated and conjugated double bonds, which leads to polymer aging and deterioration of material properties. Despite the availability of numerous fundamental studies devoted to the degradation and stabilization of PVC, the mechanism of its decomposition remains under discussion, with radical, ionic, and combined pathways being considered. Therefore, the search for efficient stabilizers is still largely empirical. The aim of this work was to reveal the features of thermal and thermo-oxidative degradation of rigid and plasticized PVC in the presence of fullerene C_{60}.

Experimental: The objects of study included industrial PVC grade S-7059M, fullerene C_{60}, phenolic antioxidants (diphenylolpropane, ionol), and ester plasticizers (dioctyl phthalate, dioctyl sebacate). Thermal and thermo-oxidative dehydrochlorination was carried out at 175 °C in a bubbling-type reactor under nitrogen or oxygen flow. Stabilizing effects were evaluated by the rate of HCl release, thermal stability time (according to GOST 14041-91), and melt flow index measurements. It was shown that fullerene C_{60} significantly inhibits PVC dehydrochlorination, reducing the rate of HCl release by more than twofold. The maximum effect is achieved at a content of 0.1 mmol per mol of PVC. In plasticized PVC systems, fullerene demonstrated high antioxidative activity, comparable to or exceeding that of industrial phenolic antioxidants. An «echo-stabilization» effect was observed, attributed to the inhibition of ester plasticizer oxidation.

Conclusions: Thus, fullerene C_{60} can be considered a promising stabilizer for PVC, effectively retarding its thermal and thermo-oxidative degradation. The revealed regularities confirm the predominant role of the radical mechanism in PVC dehydrochlorination and highlight the potential of fullerene for extending the service life of PVC materials.

Keywords: Polyvinyl chloride, Fullerene C_{60}, Polymer dehydrochlorination, Ester plasticizers, Phenolic antioxidants

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✉ Timur T. Sadykov, e-mail: gttima@mail.ru

1. Introduction

It is well known that polyvinyl chloride (PVC), characterized by relatively low thermal and thermo-oxidative stability, tends to undergo chemical transformations, mainly through the elimination of HCl and the formation of isolated and conjugated C=C bonds in the macromolecules. The insufficient stability of PVC leads to its aging, accompanied by changes in the overall set of properties of materials based on this polymer. Therefore, PVC requires effective stabilization – a set of measures aimed at reducing or preventing polymer aging. However, the stabilization of PVC is associated with certain difficulties. This is largely due to the fact that insufficient attention has been paid to the mechanism of PVC degradation itself. In many monographs and reviews devoted to the stabilization and processing of polyvinyl chloride, the degradation mechanism is not discussed at all [1–8].

Although a number of monographs, long since recognized as classical works, have been published [9–13], the question of the mechanism of PVC degradation remains the subject of active debate between the proponents of radical, ionic, and combined mechanisms. As a result, the development of new stabilizing additives for PVC, as well as the creation of compositions based on them, is still carried out largely intuitively and empirically.

Accordingly, for a better understanding of the degradation mechanism of PVC, special interest lies in the study of fullerene C_{60} as a stabilizer, since it belongs to the class of inhibitors of chain radical reactions. It has been shown [14–17] that C_{60} inhibits the thermal and thermo-oxidative decomposition of several homo- and copolymers of methyl methacrylate, polyvinylpyrrolidone, and polyethylene glycol, including under high-temperature conditions.

However, no information has been found on the effect of fullerenes on the decomposition of PVC. In this regard, it appears highly relevant to study the regularities of thermal and thermo-oxidative degradation of rigid and plasticized PVC in the presence of fullerene C_{60}.

2. Experimental

Thermal and thermo-oxidative dehydrochlorination of plasticized PVC was carried out at 175 °C in a bubbling-type reactor under a nitrogen or oxygen flow (3.5 L/h). The dehydrochlorination rate was determined according to the procedure described in [18]. The thermal stability time of PVC (τ) was determined from the induction period corresponding to the color change of the Congo red indicator during HCl evolution in the course of polymer degradation (175 °C) in accordance with GOST 14041-91. The melt flow index was evaluated using an extrusion plastograph mi 2.2 ("Gutter", FRG).

Polyvinyl chloride S-7059M was purified by Soxhlet extraction with ethanol. Fullerene C_{60} (ZAO "Fullerene Center," Nizhny Novgorod, Russia; 99.0%) was used without additional purification.

Antioxidants diphenylolpropane (DPP, 99.7%) and 2,6-di-tert-butyl-4-methylphenol (ionol, 99.8%) were also used without additional purification. Ester plasticizers dioctyl phthalate (DOP) and dioctyl sebacate (DOS) were purified by filtration through a column packed with aluminum oxide.

3. Results and discussion

The study showed that under conditions of thermal and thermo-oxidative degradation of neat PVC, fullerene C_{60} significantly (by a factor of two) reduces the rate of polymer dehydrochlorination (Fig. 1). The maximum decrease in the dehydrochlorination rate is observed at a fullerene concentration of 0.1 mmol per mol of PVC.

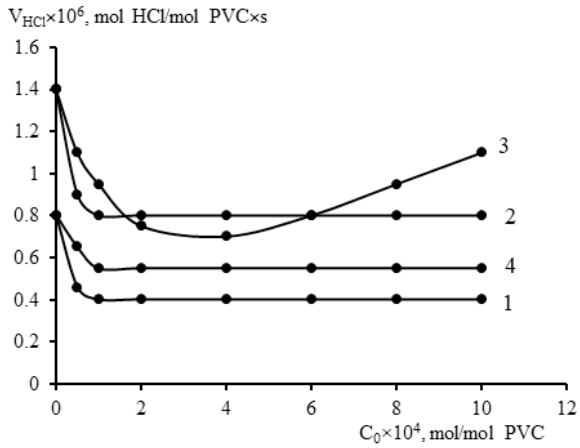

Fig. 1. Dependence of the rate of thermal (*1*, *4*) and thermo-oxidative (*2*, *3*) dehydrochlorination of PVC on the concentration of fullerene C_{60} (*1*, *2*) and diphenylolpropane (*3*, *4*)

The inhibiting effect of fullerene in the radical-chain process of purely thermal degradation is associated with its interaction with free radicals to form thermally stable diamagnetic compounds [16]:

$2R\bullet + C_{60} \rightarrow R_2C_{60}$

$2R\bullet + R_2C_{60} \leftrightarrow R_4C_{60}$

In thermo-oxidative degradation, reactions with active radicals R• and RO2•, as described in the literature [14, 16], are also possible:

$RO\bullet(R\bullet) + C_{60} \rightarrow RO(R)C_{60}$

It should also be noted that when PVC is combined with fullerene, the latter exhibits a slight acceptor effect toward HCl released during degradation, as evidenced by the thermal stability time. This may be related to the sorption of hydrogen chloride by the fullerene structure (Table 1).

Even greater stabilizing efficiency of C_{60} is observed when it is introduced into PVC plasticized with ester plasticizers (Figs. 2, 3). In terms of antioxidative activity, fullerene is practically not inferior to DPP and significantly surpasses ionol.

Obviously, under these conditions the well-known “echo-stabilization” effect occurs: fullerene C_{60} inhibits the thermal oxidation of ester plasticizers, which in turn reduces the destabilizing influence of oxidized plasticizers on PVC degradation [19].

The high stabilizing efficiency of fullerene C_{60} in relation to plasticized PVC is also confirmed by the thermal stability time. As shown by the data in Table 2, the introduction of fullerene leads to a significant increase in thermal stability in model plasticized compositions additionally containing metal-containing HCl acceptors.

The evaluation of rheological properties of model PVC plasticates with fullerene C_{60}, based on the melt flow index (MFI), demonstrated that the incorporation of fullerene C_{60} into the

Table 1. Thermal stability time of PVC in the presence of fullerene C_{60}

Component	Composition, phr (parts by mass per 100 parts by mass of PVC)					
	1	2	3	4	5	6
PVC	100	100	100	100	100	100
Fullerene C_{60}	-	0.05	0.1	0.3	0.5	1.0
τ, min (175 °C)	4	6	9	10	13	18

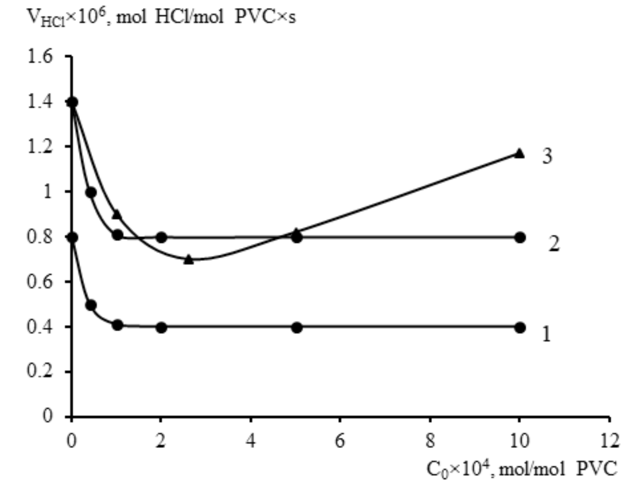

Fig. 2. Dependence of the rate of thermo-oxidative dehydrochlorination of PVC plasticized with dioctyl phthalate (40 phr) on the concentration of fullerene C_{60} (*1*), diphenylolpropane (*2*), and ionol (*3*)

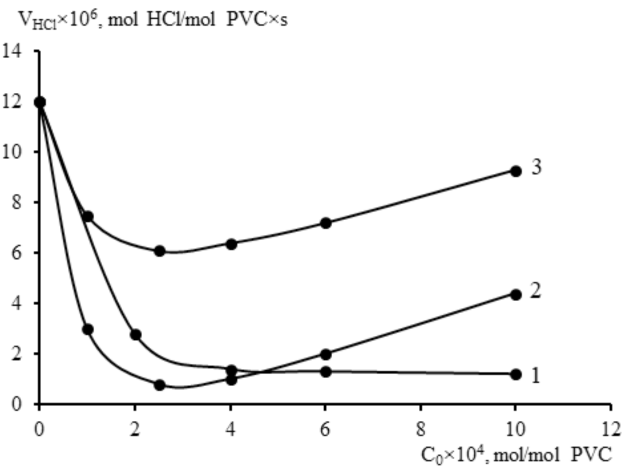

Fig. 3. Dependence of the rate of thermo-oxidative dehydrochlorination of PVC plasticized with dioctyl sebacate (40 phr) on the concentration of fullerene C_{60} (*1*), diphenylolpropane (*2*), and ionol (*3*)

Table 2. Thermal stability time of PVC compositions

Component	Composition, phr (parts per 100 parts of PVC)							
	1	2	3	4	5	6	7	8
PVC	100	100	100	100	100	100	100	100
DOP	40	40	40	40	40	40	40	40
Calcium stearate	-	-	2	2	2			
Lead sulfate (tribasic)	-	-	-	-	-	1	1	1
Fullerene C_{60}	0.5	1	-	0.5	1	-	0.5	1
τ, min (175 °C)	7	12	17	36	45	66	98	132

Table 3. Melt flow index of model PVC compositions

Component	Composition, phr (parts per 100 parts of PVC)			
	1	2	3	4
PVC	100	100	100	100
DOP	40	40	40	40
Lead sulfate (tribasic)	2	2	2	2
Fullerene C_{60}	–	0.05	0.2	1.0
MFI, g/10 min (T = 180 °C, P = 15 kg)	19.8	14.9	11.2	5.3

composition results in a regular decrease in the MFI values (Table 3).

4. Conclusions

Thus, under conditions of thermal and thermo-oxidative degradation of neat PVC, fullerene C_{60} effectively inhibits the dehydrochlorination process. The high antioxidative efficiency of C_{60}, comparable to or exceeding that of industrial phenolic antioxidants, leads to a significant reduction in the dehydrochlorination rate of PVC plasticized with esters. The strong stabilizing effect of fullerene C_{60} is also confirmed in PVC compositions by the thermal stability time. The revealed regularities of the influence of C_{60} on the thermal and thermo-oxidative degradation of both rigid and plasticized PVC support the radical mechanism of PVC degradation.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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* *Translated by author of the article*

Information about the authors

Timur T. Sadykov, Cand. Sci. (Chem.), Associate Professor at the Department of Physical Chemistry and Chemical Ecology, Ufa University of Science and Technology (Ufa, Russian Federation).

https://orcid.org/0000-0003-2042-1032
gttima@mail.ru

Akhat G. Mustafin, Dr. Sci. (Chem.), Professor, Head of the Department of Physical Chemistry and Chemical Ecology, Ufa University of Science and Technology (Ufa, Russian Federation).

https://orcid.org/0000-0002-8342-8787
agmustafin@gmail.com

Elena I. Kulish, Dr. Sci. (Chem.), Professor, Head of the Department of Macromolecular Compounds and General Chemical Technology, Ufa University of Science and Technology (Ufa, Russian Federation).

https://orcid.org/0000-0002-6240-0718
onlyalena@mail.ru

Rinat M. Akhmetkhanov, Dr. Sci. (Chem.), Associate Professor, Professor at the Department of Macromolecular Compounds and General Chemical Technology, Ufa University of Science and Technology (Ufa, Russian Federation).

https://orcid.org/0000-0003-0016-0218
rimasufa@rambler.ru

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