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Polyfluoroalkyl –tert-butylperoxicarbonates as effective initiators for fluoropolymers structurization

N.A.Rakhimova[1], L.A. Butkovskaya[1], A.I. Rakhimov[1,2]

[1]Volgograd State Technical University, 400131, Russia, Volgograd, Lenin prospect, 28
e-mail: organic@vstu.ru

[2]Institute of Chemical problems of Ecology ANS RF, 400066, Volgograd PO box 127,
e-mail: rakhimov@sprint-v.com.ru

***Abstract**: The effect of polyfluooroalkyl –tert butylperoxicarbonates as structural agents on process of vulcanization of fluorocaoutchoucs SKF-32 and SKF-26 and on improvement of properties, obtaining by vulcanization is shown.*

***Keywords:** Polyfluooroalkyl –tert butylperoxicarbonates, initiators for fluoropolymer structurization, structure films SKF-32 and SKF-26*

Introduction

The development of methods doping of polyfluoro- groups into macromolecular systems is an actual task, since it lets to improve considerably physical and mechanical properties of polymer composite materials. [1-11]

Fluorocaoutchoucs have special position in technology, and are characterized with high resistance to strong oxidizing agents and aggressive environment, nonflammability, thermal resistance and necessary stability characteristics. [12,13]

The aim of this work is to consider a possibility of vulcanization of fluorocaoutchoucs with polyfluoro –tert-butylperoxialkyl carbonates. Fluorocaoutchoucs SKF-32 ans SKF-26, which are commercially produced, contain large quantity of CH2 groups, and though indistinct liability of CH_2 groups in f fluorocaoutchoucs to homolytical reactions, the complex of these groups and double bonds (which are formed in the structure of polymer by high temperatures in the presence of halogen hydrides acceptors) provides fluorocaoutchoucs an ability to vulcanize with peroxides. [13]

Discussion of results

It is necessary mention, that peroxides, which are used by structurization of fluoropolymers, such as benzoyl -, cumyl -, tert–butyl peroxide, have some technical disadvantages: cumyl peroxide forms highly toxic acetophenone by decomposition; benzoyl peroxide is explosive, di- tert.- butyl peroxide is volatile.

Esters of percarbonic acid have one of the most important place among highly effective initiators of peroxide type.

Polyfluoro–tert Butylperoxialkyl carbonates (PFTBPK) show the highest termal resistance [4-11].

Fluorinated peroxialkylcarbonates are obtained on the basis of polyfluoroalkyl esters of chlorocarbonic acid (PFECK) [7].

The synthesis of PFTBPK is carried out by interaction of corresponding chlorformate with mixture of tert-butylhydroperoxide and aqueous solution of sodium hydroxide in the presence of organic solvent by temperature 0° C. After blending of reagents, the temperature rises to room temperature and reaction ends in 2 hours.

X(CF2)n CH2 OC(O)Cl + (CH3)3 COOH → X(CF2)nCH2OC(O)OOC(CH3)3

Where X= H or F, n = 1,2,4,6,8

Physico-chemical properties of polyfluorinated tert.-butylperoxialkylcarbonates are presented in the table 1.

Table 1. Physico-chemical properties polyfluorinated tert.-butylperoxialkylcarbonates X(CF2)nCH2OC(O)OOC(CH3)3

#	Compound		Yield %	B point , °C. (p=133Па)	n_D^{20}	d_4^{20}	Gross - formula	Compo
								Found,⁹
	X	n						C
1	F	1	73.7	31	1.3772	1.2159	$C_7H_{11}O_4F_3$	38.81
2	H	2	80.0	46	1.3737	1.2678	$C_8H_{12}O_4F_4$	38.67
3	H	4	75.4	55-56	1.3600	1.4061	$C_{10}H_{12}O_4F_8$	34.31
4	F	6	70.8	73-75	1.3512	1.4946	$C_{12}H_{12}O_4F_{12}$	32.02

5	H	6	74.5	51	1.3488	1.5401	$C_{12}H_{11}O_4F_{13}$	30.79
6	H	8	65.5	113	1.3460	1.5801	$C_{14}H_{12}O_4F_{16}$	30.63

These are liquid substances with high density, which increases with growth of perfluorocarbon chain to d_4^{20} = 1,5801 g/cm^3 for tert.-butylperoxi 1,1,9-trihydroperfluorononanilcarbonate , $H(CF_2)_8CH_2OC(O)OOC(CH_3)_3$.

The obtained polyfluoro- tert-butylperoxialkylcarbinates were used as structuring agents of fluorocaoutchoucs (SKF-32 and SKF-26)

For this aim a resin mixture with equal molar content of peroxide was prepared. (PFTBPK, unlike benzoyl peroxide, is good mixable with fluorocaoutchoucs, thereby resin mixtures are not prevulcanised) . Peroxide was introduced by the end of component’s blending and its full allocation in resin mixture was observed. (5-10 minutes)

The structurization of samples was conducted in hydraulic press with electric heating and automatic temperature control of ranges under pressure of 10 MPa. Thereby, the speed of temperature increase was optimal (10 minutes by 180 ° for SKF-32 and 30 minutes by 160°C for SKF-26) After vulcanization the temperature of sample under pressure was gradually decreased to 60 °C (to avoid pore-formation in vulcanizate). The heat aging of obtained vulcanizates was conducted during 72 hours by 150°C and 24 hours by 200 °C.

The results are presented in tables 2 and 3. On the basis of obtained data, we can make a conclusion that structuring ability of used peroxides depends on structure, and therefore on their thermal resistance. The introduction of fluorine atom results in decreasing speed of thermal decay of peroxide and decreasing speed of structurization, which increase the density of vulcanization network. Moreover, the high structuring activity of PFTBPK is caused by formation of more active in the hydrogen-atom abstraction reaction polyfluoroalkoxil radicals.

Preparation of films from fluorocaoutchoucs by milling was conducted on laboratory rolling mills with intensive cooling of rolls. The temperature of rolls while mixing was held between 20 -25 °C. Peroxide was introduced to the end of mixing until its full allocation in resin mixture (5- 10 minutes), The vulcanization of samples was conducted after keeping for 6 hours by room temperature in hydraulic press with electric heating and automatic temperature control of ranges under pressure of 10 MPa. The speed of increasing temperature was not more then 2 %/ minute. After vulcanization the temperature of sample was gradually decreased to 60 °C , which is necessary to avoid pore-forming in vulcanizate.

The thermal resistance of obtained films (table 2,3) was tested by method of thermal differential analysis and it was found out that usage of PFTBPK results in increasing of onset temperature of vulcanizates till 280 °C (the onset temperature for unsubstituted films 225 °C).

Table 2. Physical and mechanical properties of structured films on basis of SKF-32

Peroxide	Mode of structurization °C in Min.	Module 300 %,	Tensile strength MPa	Extension coefficient,%	Persisten %

		MPa			
Benzoyl peroxide	180x10	7,7	16,8	440	12
$H(CF_2)_2CH_2OC(O)OOC(CH_3)_3$	180 x 10	7,9	18,7	510	8
$H(CF_2)_4CH_2OC(O)OOC(CH_3)_3$	180 x 10	8,0	17,5	430	12

After thermal aging

Benzoyl peroxide	150 x 72 200 x 24	- -	12,5 15,0	430 400	- -	-	- -
$H(CF_2)_2CH_2OC(O)OOC(CH_3)_3$	200 x 24	-	15,6	405	-	-	-
$H(CF_2)_4CH_2OC(O)OOC(CH_3)_3$	150 x 72	-	13,0	380	-	-	-

Table 3. Physical-chemical properties of structuring films on basis of SKF-26

Composition of mixture (weight.part) for 100 w.p.of resin	Peroxide initiator $H(CF_2)_nCH_2OC(O)OOC(CH_3)_3$ n=2	n=4	Peroximon F-40 (samples for comparison)
Peroxide	6	8	4
Technical carbon T-900	30	30	30
Calcium oxide	5	5	5
Magnesium oxide	10	10	10
Properties			
Density, MPa	21,6	23,5	21,2
Extension coefficient,%316	316	310	204
Persistent extension, %	5,8	3,5	2,5
Module 100 %, MPa	6,9	8,1	7,1
Elasticity, %	70	71	72
Viscosity 100 ^{0}C	150	151	149
Hardness after keeping by 200 ^{0}C during 24 h,MPa	22,5	-	20,3
Extension coefficient,%	178	-	170
Persistent extension, %	4	-	-
Hardness after keeping by 200 ^{0}C during 72 h,MPa	21,0	21,2	20,0
Extension coefficient,%	200	200	210
Persistent extension, %	2,5	-	2,5

Peroximon F-40 -ditret.-butylperoxide

Moreover, it is necessary to mention a considerable improvement in complex of physical and mechanical properties of obtained films for tert.-butylperoxitetrafluoropropylcarbonate: tensile strength for structuring films on the basis of SKF-32 is 18.7 MPa by high values of rebound elasticity (10 %).

A high efficiency of polyfluoroalkyl – tert –butyl peroxicarbonates as initiators for structurization of films for such fluoropolymers as SKF-32 and SKF-26 was determined.

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