BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LVIII No. 2/2006	25 - 28	Seria Tehnică

Study of Thermo-Oxidative Stabilisation of *cis* - 1,4 Polyisoprenic Rubber Modified with Maleic Anhydride

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Abstract

It has been studied the preventive effect of di-lauroylthiopropionate (DLTDP), regarding the thermo-oxidative stabilisation of synthetic polyisoprenic rubber cis - 1,4 modified with maleic anhydride, using polymer samples additivated with an antioxidant content of 0.5 %, 1 % and 2 %, compared to sample of non-additivated polymer sample. Samples were laid as films on spectral windows of KBr and thermal treatment were made at 96 ^{0}C, in the presence of the air. Thermo-oxidative stabilisation of synthetic rubber depends on the antioxidant DLTDP content and the optimal concentration was between 1 - 2 % in polymer.

Key words: *thermo-oxidative stabilisation, cis -1,4 polyisoprenic rubber modified with maleic anhydride.*

Introduction

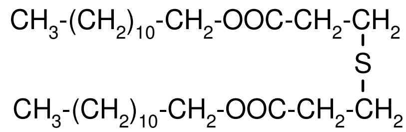
Plastics material under the influence of heat, light, and in the presence of atmospheric oxygen are subjected to degradation, both in processing processes and during their storage and using. *cis* -1,4 Polyisoprenic rubber modified with maleic anhydride undergoes faster transformations in structure under the influence of heat, in the presence of atmospheric oxygen, comparing to unmodified *cis* -1,4 polyisoprenic rubber.

Delaying of thermo-oxidative reactions in polymers is achieved by adding some substances known as antioxidants [1]. Inhibition action of oxidation reaction is achieved by:

- interrupting of propagation for kinetic chain of oxidation with new reactions of antioxidants;
- decomposing of hydroxides in non-radicalic compounds.

The process of thermo-oxidative ageing can be delayed to rubber modified with maleic anhydride, by introducing of some antioxidants from sulphur compounds class in its mass. The action of stabilisation for these compounds is presented in literature [2-7], mentioning that they can be used in association with phenolic antioxidants.

In this paper it was studied the effect of di-lauroyl-thio-dipropionate (DLTDP) antioxidant:



to synthetic *cis* -1,4 polyisoprenic rubber modified with maleic anhydride.

Experimental Part

To analyse the obtaining of samples, there were prepared 2 solutions in toluene: 2 % solution synthetic *cis* -1,4 polyisoprenic rubber modified with maleic anhydride and 0.1 % solution antioxidant DLTDP. *cis* -1,4 Polyisoprenic rubber modified with maleic anhydride used for experiments had a content of 2 % maleic anhydride. By mixing the two solutions in computed quantities there were obtained 3 samples of polymer with an antioxidant content of 0.5 %, 1.0 % and 2.0 %.

The study was made as compared to non-additivated rubber sample. The 4 samples of polymer were deposited as films on spectral windows of KBr and were heated at 96 ^{0}C in an oven, in the presence of atmospheric oxygen.

Thermal treatment was made at different time periods. At intervals of 30 minutes, there were registered molecular absorption spectra from IR domain, by taking the samples from oven for 5 minutes. IR spectra were recorded with a spectrophotometer SPECORD IR 75.

Results and Discussions

In table 1 there are presented experimental results regarding quantitative evolution of carbonyl groups in function of thermal treatment time for the 4 studied samples. In this table there are also written values for absorbance (A) at 1725 cm^{-1} and thickness of each film (d) of recorded spectra. In figure 1 there is illustrated the variation of carbonyl groups content in function of the studied rubber samples time exposure.

From the experimental data presented in table 1 and from figure 1 there can be observed the positive effect of the DLTDP antioxidant upon delaying of thermo-oxidative ageing. Thus, it is represented that the delaying of the thermo-oxidative ageing depends on the content of the antioxidant in rubber, and the induction time of reactions is not proportional with the percentage of the antioxidant.

In figure 2, it is represented the variation of the carbonyl groups as a function of DLTDP concentration, after 5 hours of thermal exposing at 96 ^{0}C, of samples of *cis*-1,4 polyisoprenic rubber modified with 2 % maleic anhydride.

For the sample which contains 0.5 % DLTDP, the content of carbonyl group decreases to 3.2 % compared to 5.2 % for not additivated rubber, which represents a diminution of the carbonyl groups content of 2.1 %. For the sample additivated with 1 % DLTDP, the carbonyl groups content is of 2.3 %, corresponding to a 2.9 % diminution compared to non additivated polymer and a diminution of 0.9 % comparing to additivated polymer with 0.5 % antioxidant used in this study. The rubber sample additivated with 2 % DLTDP presents a carbonyl groups content of 1.4 %, corresponding to a diminution of 1 % comparing to the sample with 1 % additive.

It is observed that for a content of 0.5 % additive the diminution of carbonyl groups content is of 2 %, and the increasing of additive content to 1 % and respectively to 2 % produces a smaller decreasing of carbonyl groups content. This demonstrates that adding antioxidants more than 2 % has a smaller contribution upon the diminution of the thermo oxidative ageing.

Table 1. The evolution of the thermo-oxidative ageing process of samples of *cis* –1,4 polyisoprenic rubber modified with maleic anhydride, non additivated and additivated with different quantities of antioxidant additive DLTDP

Non additivated sample			**Additivated sample with 0.5 % DLTDP**		
A, 1725 cm^{-1}	$d \cdot 10^4$, mm	% >C=O	*A*, 1725 cm^{-1}	$d \cdot 10^4$, mm	% >C=O
0	8,4	0	0	13,3	0
0,006	8,2	0,14	0,007	12,3	0,11
0,012	7,1	0,29	0,011	12,1	0,17
0,029	7,8	0,70	0,015	12,1	0,24
0,059	8,2	1,37	0,030	11,8	0,48
0,089	8,1	2,09	0,041	11,8	0,66
0,116	8,2	2,70	0,060	11,7	0,98
0,141	8,1	3,31	0,076	10,3	1,40
0,180	8,3	4,13	0,120	11,8	1,94
0,207	8,3	4,75	0,160	12,0	2,54
0,224	8,3	5,16	0,197	11,8	3,19
Additivated sample with 1 % DLTDP			**Additivated sample with 2 % DLTDP**		
A, 1725 cm^{-1}	$d \cdot 10^4$, mm	% >C=O	*A*, 1725 cm^{-1}	$d \cdot 10^4$, mm	% >C=O
0	12,0	0	0	10,8	0
0,005	11,8	0,08	0,001	12,3	0,02
0,006	1,0	0,10	0,003	10,5	0,05
0,009	11,8	0,14	0,004	10,6	0,08
0,009	11,8	0,15	0,006	11,8	0,10
0,021	11,9	0,33	0,010	10,7	0,17
0,031	12,0	0,49	0,017	11,6	0,28
0,048	12,0	0,76	0,027	11,5	0,45
0,069	11,8	1,11	0,040	10,9	0,70
0,103	12,0	1,63	0,053	11,0	0,92
0,139	11,8	2,25	0,079	11,2	1,35

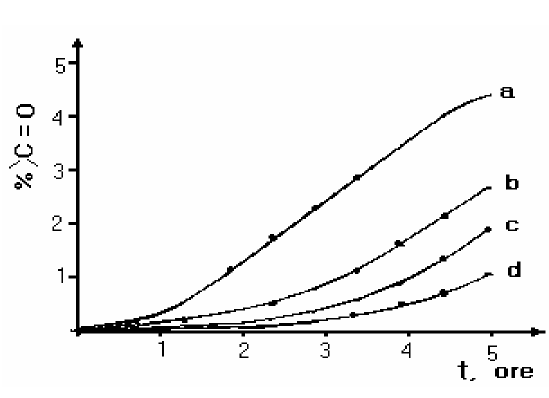


Fig. 1. The evolution of carbonyl groups in function of thermal exposing at 96 ^{0}C for non additivated rubber (a) and for additivated rubber with 0,5% (b), 1,0 % (c) and 2 % DLTDP (d)

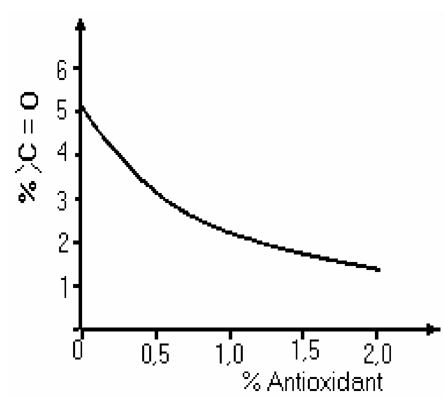


Fig. 2. The evolution of carbonyl groups content in function of DLTDP antioxidant additive content from rubber, after 5 hours of treating at 96 ^{0}C

Conclusions

In this paper it has been studied the effect of di-lauroyl-thio-dipropionate (DLTDP) antioxidant upon *cis* -1,4 polyisoprenic rubber modified with 2 % maleic anhydride.

Experimental data demonstrated that *cis* -1,4 polyisoprenic rubber modified with 2 % maleic anhydride can be thermally protected by additivation with di-lauroyl-thio-dipropionate (DLTDP) antioxidant.

The optimal concentration of antioxidant agent in the studied rubber is between 1 and 2 %.

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Studiu privind stabilizarea termooxidativă a cauciucului sintetic poliizoprenic *cis* - 1,4 modificat cu anhidridă maleică

Rezumat

S-a studiat efectul preventiv al dilauroiltiopropionaului (DLTDP) privind stabilizarea termooxidativă a cauciucului sintetic poliiziprenic cis 1-4 modificat cu anhidridă maleică, utilizând probe de polimer aditivate cu un conţinut de antioxidant de 0,5%, 1% şi respectiv 2% , comparativ cu proba de polimer neaditivată . Probele au fost depuse sub formă de pelicule pe ferestre spectrale de KBr , iar tratamentul termic s-a efectuat la temperatura de 96 ^{0}C, în prezenţa aerului. Stabilizarea termooxidativă a cauciucului sintetic este funcţie de conţinutul de antioxidant DLTDP, iar concentraţia optimă este cuprinsă între 1-2% în polimer.