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THERMAL DEGRADATION OF FLUOROCARBON ELASTOMERS BY THERMOGRAVIMETRY

Danuta Jaroszyńska, Teresa Kleps[x]
Institute of Rubber Industry, Piastów/Warsaw, POLAND

ABSTRACT

The thermal degradation of fluorocarbon and fluorochlorocarbon polymers has been studied using a dynamic thermogravimetry method. It has been found the effect of silicate fillers and carbon black as well as the crosslinking reaction on the parametres of degradation/temperatures, rates/ and activation energies. Kinetic values have been determined emploing procedure of Freeman and Carroll by graphical and computer techniques.

INTRODUCTION

Fluorocarbon elastomers belong to rubbers with speciphic structure and properties especially a very good thermal stability due to the higher energy of C-C bonds with fluorine substituents /1-2/. The thermal degradation of elastomers containing only fluorine substituents proceeds by free radical mechanism /3,4/. However, this process is probably more complicated in the case of fluorocarbon compounds and vulkanizates where different additions are present. The main purpose of this paper is the investigation of degradation of two type of fluorocarbons, their compounds and vulkanizates carried out in non-izothermal conditios.

EXPERIMENTAL

Materials.

SKF-26/USSR/:copolymer of hexafluoropropylene with vinylidene fluoride

SKF-32/USSR/:copolymer of trifluorochloroethylene with vinylidene fluoride

The pure elastomers masticated and nonmasticated, their mixtures with fillers /silicate and carbon black/ and rubber compounds /with crosslinking system:MgO,Diak-3/NN Dicynamylidene-1,6hexamethylenediamine/as well their vulkanizates were studied.

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Measurements.

Thermal degradation was carried out in nitrogen atmosphere in a Perkin-Elmer TGS-1 Thermobalance at a heating rate 5^{o}/min, using 10 mg samples.

RESULTS AND DISCUSSION

The thermal degradation of fluorocarbon elastomers proceeds by one stage begining at about T_0=400°C/Fig.1,Table 1/.The degradation temperatures are a little lower for SKF-32 in comparison with SKF-26. The degradation rate is also lower, it can be connected with the evolution of chlorine from SKF-32. The mastication of those rubbers does not seem to influence on T_0 but causes the shift of the main degradation stage in the direction of the higher temperature.

The additions of carbon black or silicate /Zeolex 25/ to the masticated rubbers cause the decrease of T_0, largely for silicate/Fig.2/ Some changes in the max. peak temperatures in the DTG curves are also observed.

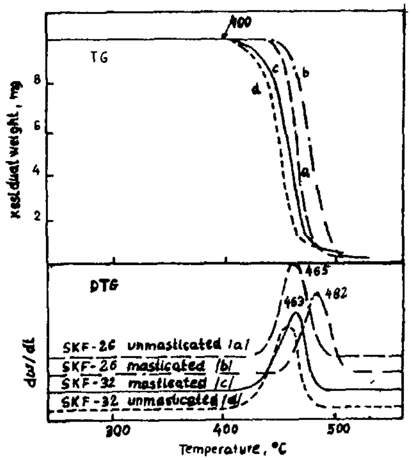

Fig.1.TG and DTG curves of the fluorocarbon elastomers SKF-26 and SKF-32

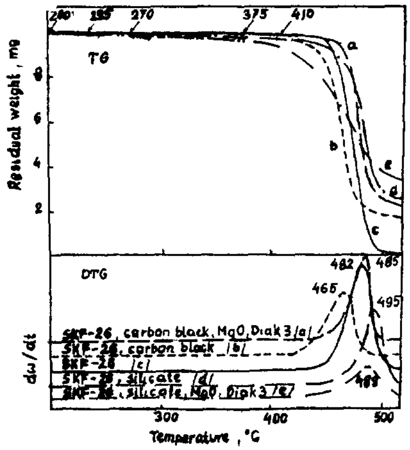

Fig.2.TG and DTG curves of the fluorocarbon elastomer SKF-26 mixtures

The cross-linking system additied to SKF-26-fillers mixtures (rubber compounds) leads to farther decrease of T_0, especially for compounds with silicate /Fig.2,3and 4,Table 1/. Temperatures of the DTG max. of this compounds are similar to those of pure elastomers. In the compounds with the cross-linking system a significant decrease of degradation rate /2-3 times/ and activation energy is observed /Table 2/.

TABLE 1

Influence of the mastication, the fillers and cross-linking system on the degradation temperatures of fluorocarbon rubbers

Type of sample	Degradation temperatures, ^{o}C T_0	 $T_{DTG\ max}$
SKF-26 unmasticated	400	465
SKF-26 masticated	400	482
SKF-32 unmasticated	380	458
SKF-32 masticated	380	463
SKF-26 mixed with carbon black/5:1/	375	465
SKF-26 mixed with Zeolex 25 /5:1/	270	495
SKF-26 mixed with carbon black and cross-linking system	235	485
SKF-26 mixed with Zeolex 25 and cross-linking system	200	489

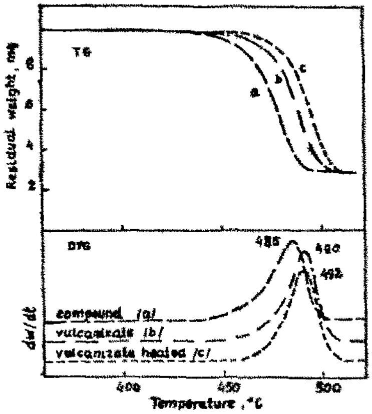

Fig.3.TG and DTG curves of the compound and vulkanizates of the SKF-26 /composition: SKF-26,carbon black,MgO,Diak3/

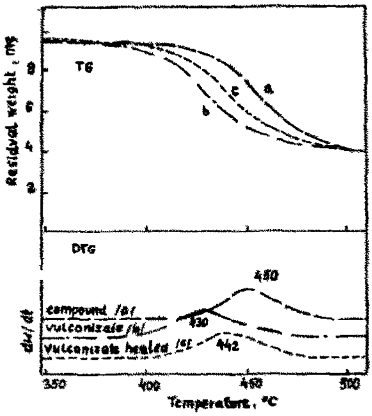

Fig.4.TG and DTG curves of the compound and vulkanizates of the SKF-32 /composition: SKF-32,Zeolex25,MgO,Diak3/

The cross-linking process:/pressing and especially farther heating in 200°C/,has greatly increased of T_o of the vulkanizates with respect to the compounds/Fig.3,4 Table 2/. These temperatures, however, are lower than those for pure rubber, it can be explained by the earlier degradation of additivers. The temperature $T_{DTG\ max}$ for the vulkanizates of SKF-26 increases about 10°C compare to compound, while in the case of SKF-32 a decrease is observed. For the full explanation of this phenomena farther study are required.

TABLE 2

Degradation temperatures, maximal degradation rate and activation energy of rubbers, compounds and vulkanizates

Type of sample	Degradation /temp.°C/		Max.degradation rate	Activation Energy/kJ/mol/ Comp.meth.	Graph.met.
	T_o	T_{DTGmax}	mg/min	E	E
SKS-26 mastic.	400	482	25	567±16	572
Compound	235	485	13	415±51	473
Vulkanizate /pressed/	240	490	15	502±22	495
Vulkanizate /heated/	340	492	16	561±41	570
SKF-32 mastic.	380	463	18.5	450±50	429
Compound SKF-32	150	450	5.5	371±22	391
Vulkanizate /pressed/	215	430	5.0	209±31	319
Vulkanizate /heated/	280	442	5.8	432±23	343

The activation energy E[5] was only evaluated to the major stage of degradation, with the results shown in Table 2.As can be seen the E values are higher for pure masticated rubbers in comparison with their compounds and vulkanizates. Unfortunate the values of the E, in our findings were connected with large errors. This may be caused by the complicated mechanism of degradation of materials have been studied.

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