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Short communication

THERMAL DEGRADATION OF FLUOROCARBON ELASTOMERS BY THERMOGRAVIMETRY

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The thermal degradation of fluorocarbon and fluorochlorocarbon polymers has been studied using dynamic thermogravimetry. The effects of silicate fillers, carbon black and the cross-linking reaction on the degradation parameters (temperatures, rates) and activation energies were found. Kinetic values were determined with the procedure of Freeman and Carroll via graphical and computer techniques.

Fluorocarbon elastomers are rubbers with specific structures and properties, especially a very good thermal stability due to the higher energy of C—C bonds with fluorine substituents [1, 2]. Their decomposition proceeds by a free radical mechanism [3, 4]. However, this process is probably more complicated in the case of fluorcarbon compounds and vulcanizates were different additives are present. The main purpose of this paper is to investigate the degradation of two types of fluorocarbons, their compounds and vulcanizates under non-isothermal conditions.

Experimental

Materials

SKF–26 (USSR): a copolymer of hexafluoropropylene with vinylidene fluoride.

SKF–32 (USSR): a copolymer of trifluorochloroethylene with vinylidene fluoride.

The pure elastomers, masticated and nonmasticated, their mixtures with fillers (silicate and carbon black) and rubber compounds (with cross-linking system: MgO, Diak–3/*NN* Dicyanamylidene-1, 6-hexamethylenediamine) and their vulcanizates were studied.

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Methods

Thermal degradation was carried out in a nitrogen atmosphere in a Perkin–Elmer TGS–1 Thermobalance at a heating rate of 5 deg/min, using 10 mg samples.

Results and discussion

The thermal degradation of fluorocarbon elastomers proceeds in one stage beginning at about T_0 = 400° (Fig. 1, Table 1).

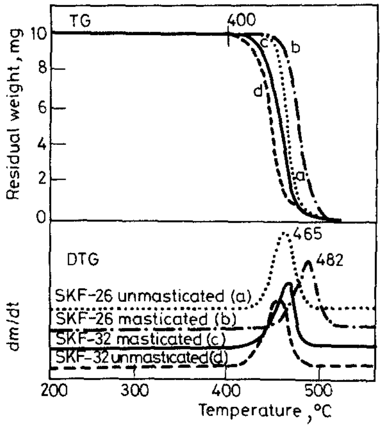

Fig. 1 TG and DTG curves of fluorocarbon elastomers SKF–26 and SKF–32

Table 1 Influence of mastication, fillers and cross-linking system on degradation temperatures of fluorocarbon rubbers

Sample	Degradation,	Temperatures, °C
	T_0	T_{DTGmax}
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

The degradation temperatures are a little lower for SKF–32 than for SKF–26. The degradation rate is also lower. This may be connected with the evolution of chlorine from SKF–32. The mastication of those rubbers does not seem to influence T_0, but causes a shift of the main degradation stage in the direction of higher temperature.

The addition of carbon black or silicate (Zeolex 25) to the masticated rubbers causes a decrease of T_0, particularly for silicate (Fig. 2). Some changes in the max. peak temperatures in the DTG curves are also observed.

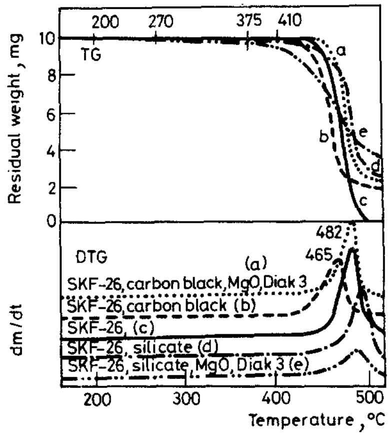

Fig. 2 TG and DTG curves of fluorocarbon elastomer SKF–26 mixtures

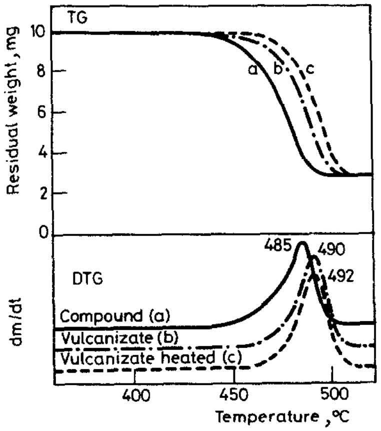

Fig. 3 TG and DTG curves of compound SKF–26 and its vulcanizates (composition: SKF–26, carbon black, MgO, Diak 3)

The cross-linking system added to SKF-26 + filler mixtures (rubber compounds) leads to a further decrease of T_0, especially for compounds with silicate (Figs 2 and 3, Table 1). The temperatures of the DTG max. of these compounds are similar to those of the pure elastomers. In the compounds with the cross-linking system, significant decreases of degradation rate (2–3 times) and activation energy are observed (Table 2).

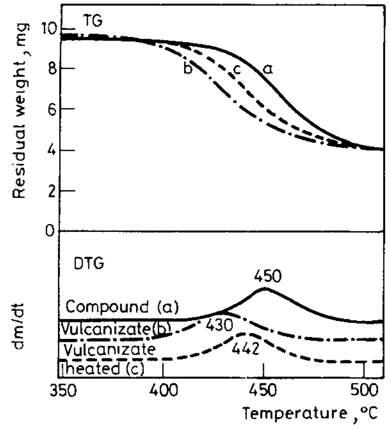

Fig. 4 TG and DTG curves of compound SKF-32 and its vulcanizates (composition: SKF-32, Zeolex 25, MgO, Diak 3)

Table 2 Degradation temperatures, maximal degradation rates and activation energies of rubbers, compound and vulcanizates

Sample	Degradation temperatures (temp., °C)		Max. degradation rate mg/min	Activation energy E, kJ/mol	
	T_0	$T_{\mathrm{DTG}max}$		Computer method	Graphical method
SKF-26 mastic.	400	482	25	567 ± 16	572
Compund SKF-26	235	485	13	415 ± 51	473
Vulcanizate (pressed)	240	490	15	502 ± 22	495
Vulcanizate (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
Vulcanizate (pressed	215	430	5.0	209 ± 31	319
Vulcanizate (heated)	280	442	5.8	432 ± 23	343

The cross-linking process (pressing and especially further heating at 200°) greatly increases the T_0 of the vulcanizates with respect to those of the compounds (Figs 3 and 4, Table 2). These temperatures, however, are lower than those for pure rubbers. This can be explained by the earlier degradation of the additives. The temperatures $T_{\mathrm{DTG}max}$ for the vulcanizates of SKF–26 are increased by about 10 deg compared to that of the compound, while in the case of SKF–32 a decrease is observed. For a full explanation of these phenomena, further study is required.

The activation energy E [5] was evaluated only for the major stage of degradation, with the results shown in Table 2. The E values can be seen to be higher for the pure masticated rubbers than for their compounds and vulcanizates. Unfortunately, the values of E involved large errors. This may be caused by the complicated mechanism of degradation of the materials studied.

References

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