

INFLUENCE OF FILLERS ON THE THERMAL STABILITY OF ELASTOMERS. THERMOGRAVIMETRIC STUDY

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The thermal degradation of hydrocarbon elastomers and polychloroprene in the presence of silica, clay, precipitated calcium carbonate and carbon black has been studied using dynamic thermogravimetry. The influence of fillers on degradation parameters of elastomers and activation energy was discussed.

In the literature there are only a few informations about influence of fillers on thermal characteristic of elastomers and they concern above all carbon black. Most attention should be done to the publications of Brazier [1] and Sircar [2] concerning some general purpose rubbers and vulcanisates.

Janowska, Slusarski and co. [3] studied the influence of particle size of carbon black and specific area on thermal properties of polyisoprene.

Recently Walter [4] described the influence of reactive mineral filler CaCO_3 on the degradation of blend PVC/NBR.

Our earlier papers contained the study of activity of mineral fillers and carbon black in thermal stability of vulcanized rubbers containing chlorine [5] and silicone elastomer [6].

In this work the influence of some mineral fillers and carbon black on thermal parameters of hydrocarbon elastomers and polychloroprene has been studied.

Experimental

Materials and investigation method

The subject of investigation were hydrocarbon rubbers: synthetic polyisoprene (IR)-SKI-3, polybutadiene (BR)-SKD, copolymer of butadiene

and styrene (SBR)-Ker 1500, terpolymer (EPDM)-Dutral 535 and polychloroprene (CR) - Skrypren B-30, and fillers: silica (Aerosil 200, specific area $S = 180 \text{ m}^2/\text{g}$), precipitated calcium carbonate ($S = 3.7 \text{ m}^2/\text{g}$), clay ($S = 7.4 \text{ m}^2/\text{g}$) and carbon black (HAF, $S = 75.5 \text{ m}^2/\text{g}$).

Measurements were carried out in a nitrogen atmosphere in a Perkin Elmer TGS-1 Thermobalance at a heating rate of 10 deg/min. TG and DTG curves were recorded and analysed.

Results and discussion

Hydrocarbon elastomers

The addition of mineral fillers of carbon black type HAF to the hydrocarbon elastomers cause only small changes in their stability and thermal parameters, does not change at all the characteristic of degradation. Figure 1 presents as an example the curves TG/DTG of polyisoprene and fillers blends.

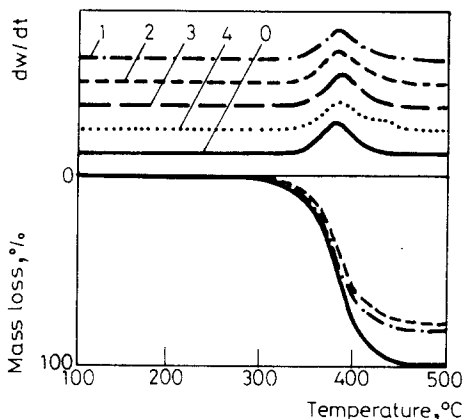


Fig. 1 TG and DTG curves of polyisoprene (0) and blends with fillers: silica (1), clay (2), calcium carbonate (3) and carbon black (4)

The results from Table 1 show that in presence of mineral fillers as well as carbon black thermal stability (T_5) of elastomers increases from a few to above twenty degrees and the best effects in the case of SBR an IR was obtained. In spite of different chemical structure and very various specific area no substantial differences in influence of studied fillers has been observed.

Table 1 Parameters of thermal stability of elastomers

Type of sample	T_5 , °C	T_{max} , °C	E_A kJ/mol
IR	330	380	156.6
IR/silica	340	382	173.9
IR/clay	345	380	182.9
IR/calc.carb.	340	380	192.4
IR/carbon black	340	382	182.3
BR	370	473	263.4
BR/silica	373	470	266.7
BR/clay	375	470	285.2
BR/calc.carb.	375	475	299.4
BR/carbon black	375	480	239.3
SBR	275	460	253.6
SBR/silica	285	470	255.0
SBR/clay	300	460	271.3
SBR/calc.carb.	303	460	275.0
SBR/carbon black	300	462	280.8
EPDM	290	471	214.0
EPDM/silica	292	480	258.6
EPDM/clay	295	478	278.2
EPDM/calc.carb.	295	470	272.0
EPDM/carbon black	298	486	328.3

Comparison a parameters of the thermal degradation does not show distinct influence of fillers on the temperature of maximal rate of degradation (T_{max}) and rate of degradation. In most cases however the substantial increase of activation energy (E_A) up to tens kJ/mol has been observed.

These data as well as in some degree T_5 show, that the thermal stability of hydrocarbon elastomers in the presence of mineral fillers and carbon black is higher. This can be explained by blocking reaction in mechanical way of degradation of elastomers or as has been stated earlier in the case of IR/carbon black [3] mixture interaction between fillers and polymer macromolecules.

Polychloroprene

The presence of carbon black increases a little the thermal stability of polychloroprene, on the other hand, contrary to changes in hydrocarbon elastomers mineral fillers have tendency to decrease the thermal stability of CR.

Table 2 Parameters of thermal stability of polychloroprene

Type of sample	T_5 , °C	T_{max} , °C		E_A kJ/mol		Carbon residue, %
CR	300	376	452	202.6	94.5	20.2
CR/silica	290	365	460	201.7	116.2	15.5
CR/clay	290	355	455	191.3	104.9	17.9
CR/calcium carbonate	300	360	450	159.0	90.9	20.4
CR/carbon black	312	373	460	211.9	104.6	17.9

In the stage of intense elimination of hydrogen chloride decreases T_{max} , rate of degradation and activation energy, excluding E_A of blend CR/carbon black. No meaningful changes were obtained in the stage of main chain destruction, only insignificant increases E_A . On the other hand with exception of blend CR/whiting significant decrease of carbon residue after destruction has been observed.

No differences in the presence of calcium carbonate can be connected with compensating reaction CaCl_2 formed in reaction $\text{HCl} + \text{CaCO}_3$, which remains in the solid products of degradation (higher molecular mass) instead of carbonate.

The results show, that the presence of mineral fillers in CR increases the rate of thermal degradation and carbon black acts as stabilizer.

References

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Zusammenfassung — Mittels DTG wurde der thermische Abbau von Kohlenwasserstoffelastomeren und Polychloropren in Gegenwart von Siliziumdioxid, Tonerde, gefälltem Calciumcarbonat und Ruß untersucht. Weiterhin wurde der Einfluß der Streckmittel auf den Abbau der Elastomere und auf die Aktivierungsenergie besprochen.