

EFFECT OF MINERAL FILLERS ON THERMAL PROPERTIES AND FLAMMABILITY OF *CIS*-1,4-POLYISOPRENE VULCANIZATES

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Abstract

The effect of mineral fillers such as Ultrasil VN-3, Ze-O-Sil P-45, Aerosil 200, Frantex 8, Kaolin and precipitated calcium carbonate on the thermal properties sulphur vulcanizates of *cis*-1,4-polyisoprene were studied by means of thermal analysis. It was found that the addition of a mineral filler did not change the nature of the thermal processes in isoprene vulcanizates essentially, but it distinctly affected the positions of the peaks recorded in the DTA curves. The mineral fillers affected the temperatures and rates of degradation and destruction of polyisoprene cross-linked with sulphur. The presence of a mineral filler brought about a decrease in the flammability of *cis*-1,4-polyisoprene sulphur vulcanizates.

Keywords: decomposition, degradation, destruction, flammability

Introduction

In the thermal spectrum of an elastomer, the following reaction can be recognized: degradation, depolymerization, destruction, isomerization, cross-linking and modification of macromolecules. Because of the oxygen deficiency, even if the decomposition proceeds in air atmosphere, at temperatures above 500°C carbonaceous products are formed, which then undergo graphitization and oxidize slowly. At about 700°C, these processes are completed within approximately 20 min [1]. Addition of a filler complicates the mechanism of thermal transitions [1-9]. We previously published results of investigations concerning the effects of carbon black on the thermal decomposition and flammability of *cis*-1,4-polyisoprene vulcanizates [1]. In the present work, we consider this problem with regard to mineral fillers.

Experimental

Materials

The objects of our investigations were sulphur vulcanizates of synthetic *cis*-1,4-polyisoprene (Cariflex IR-307, Shell Chem. Co.) containing mineral fill-

ers, the characteristics of which are given in Tables 1 and 2. The components of the rubber mixtures are listed in Table 3.

Table 1 Physical properties of applied fillers [10, 13]

| Filler | Producer | Specific surface /m ² ·g ⁻¹ | Diameter of particles/ nm | Density / g·cm ⁻³ |
|--------------------------------|--------------------------|---|---------------------------|------------------------------|
| Ultrasil VN-3 | Degussa K. G. Germany | 234 | 16 | 1.95 |
| Ze-O-Sil P-45 | Sifrance France | 200 | 17 | 2.00 |
| Aerosil 200 | Degussa K. G. Germany | 200 | 10-40 | 1.45 |
| Frantex B | Franterre Soc. France | 46 | 100 | 2.45 |
| Kaolin | Poland | - | < 5000/75% | 2.60 |
| Precipitated calcium carbonate | Poland | 5 | 2500 | 2.62 |

Table 2 Chemical compositions and properties of applied fillers [10, 13]

| | Chemical composition/ | | | | Other components | Mass loss at 105°C / % | pH* |
|--------------------------------|-----------------------|--------------------------------|--------------------------------|-------------------|---|------------------------|------|
| | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CaCO ₃ | | | |
| Ultrasil VN-3 | 87 | 0.04 | 0.3 | | MnO, CuO < 0.0001 | 6 | 6 |
| Ze-O-Sil P-45 | 95 | < 0.07 | | | MnO, CuO < 0.0001 | < 5 | 7 |
| Aerosil 200 | 98 | < 0.003 | 0.3-1.5 | | TiO ₂ < 0.03 | < 1.5 | 4 |
| Frantex B | 45 | 0.8 | 38 | | Cu, Mn 0.8 | 2-4 | < 9 |
| Kaolin | 47 | < 0.35 | 39 | | Fe ₂ O ₃ 0.4-2.0 CaO+MgO < 1.5 TiO ₂ < 2.0 Na ₂ O+K ₂ O < 1.3 | 11-14 | 5-7 |
| Precipitated calcium carbonate | - | < 0.1 | - | 98 | Cu, Mn < 0.01 | 0 | < 10 |

*pH of water extract

Table 3 Formulation of rubber compounds

| Component | Content /phr | | | | | | |
|--|--------------|-------|-------|-------|-------|-------|-------|
| | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| <i>cis</i> -1,4-Polyisoprene | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Polyglycol 600 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| N-Cyclohexylbenzo- thiazyl sulphenamide | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| 2,6-Di-III <i>o</i> -butyl- <i>p</i> -cresol | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Filler | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
| Total | 112.7 | 122.7 | 132.7 | 142.7 | 152.7 | 162.7 | 172.7 |

Methods

The rubber compounds were vulcanized in an electrical press at 150°C. The optimum vulcanization time, τ_{09} , was determined rheometrically with a Monsanto rheometer.

The thermal analyses were carried out with a derivatograph, under the following conditions: atmosphere air, standard substance Al₂O₃, temperature range 25–800°C, sample mass 90 mg, heating rate 7.9 deg·min⁻¹, sensitivity: TG 100. The measurements were performed on previously disintegrated samples.

The flammability of *cis*-1,4-polyisoprene vulcanizates was determined by the Oxygen Index (OI) method, according to Polish standard PN-75/C-89020.

Results and discussion

Figure 1 shows TG, DTG and DTA curves of non-filled *cis*-1,4-polyisoprene vulcanizate. The chemical transitions of polyisoprene cross-linked with sulphur start at 200°C [9, 12]. The first exothermic peak is a symptom of thermooxidative reactions, scission accompanied by cross-linking of the elastomer. Two endothermic peaks, at 370 and 400°C, are connected with destruction of the sample. A small residue of about 3.3 wt. % burns out at 490°C.

Mineral fillers are thermally much more stable than the polyisoprene vulcanizate (Fig. 2). Below the rubber destruction temperature, only the dehydration of silica could be observed. Heating of the silica Aerosil 200 results in the evaporation water in the temperature range 90–150°C, and then dehydroxylation [14–16]. The thermogravimetric curves of the applied mineral fillers exhibit the transitions listed in Table 4.

The mineral fillers demonstrate high stability in the range of thermal transitions of the elastomers. This is particularly so for precipitated calcium carbon-

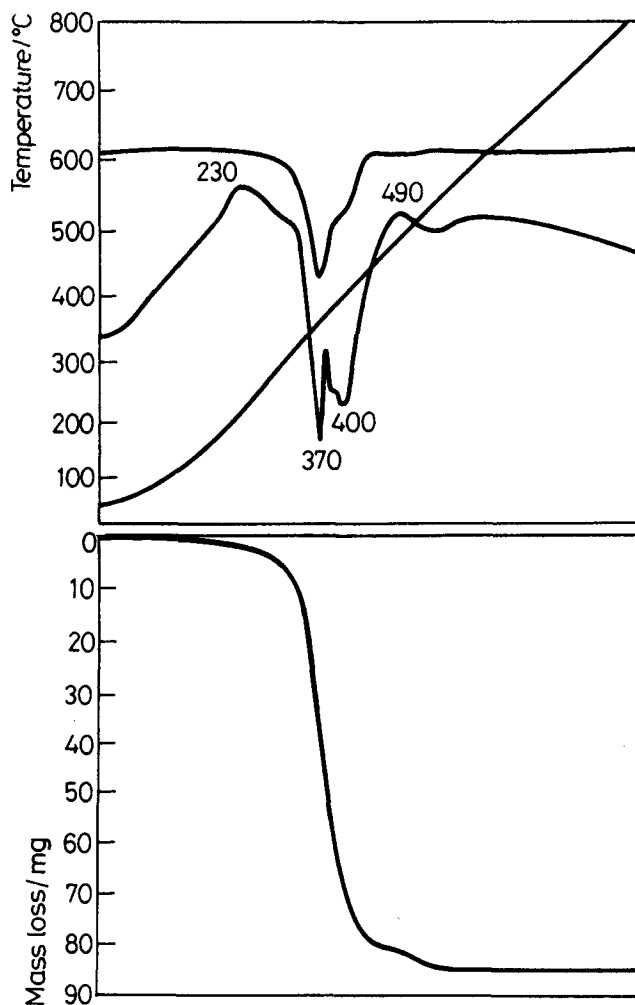


Fig. 1 Thermoanalytical curves of *cis*-1,4-polyisoprene sulphur vulcanizate

ate and Aerosil 200. Though a partial thermal decomposition of precipitated calcium carbonate is observed at 700°C, it takes place well above the combustion temperature of the small residue remaining after polyisoprene destruction (Figs 1 and 3).

Addition of the mineral fillers in small amounts to the rubber compound does not influence the *cis*-1,4-polyisoprene vulcanizate thermal transitions significantly. However, at higher contents of Aerosil 200, Ze-O-Sil P-45, Ultrasil VN-3 or precipitated calcium carbonate, increases in the onset and maximum temperatures of the first exothermic transition are observed

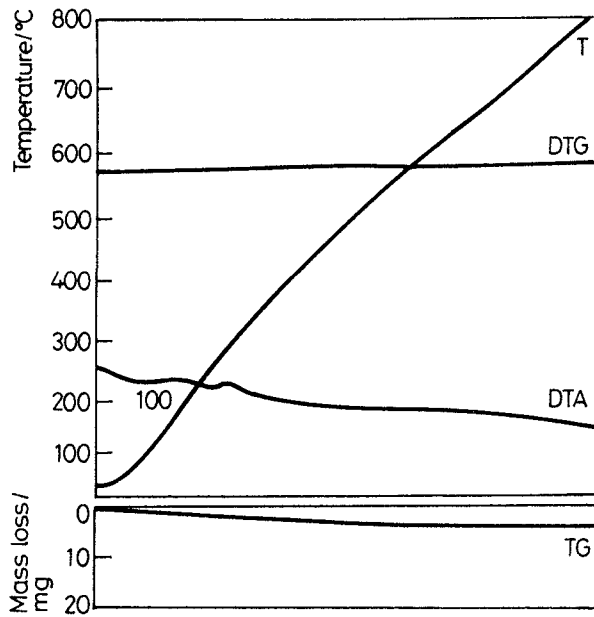


Fig. 2 Thermoanalytical curves of silica Aerosil 200

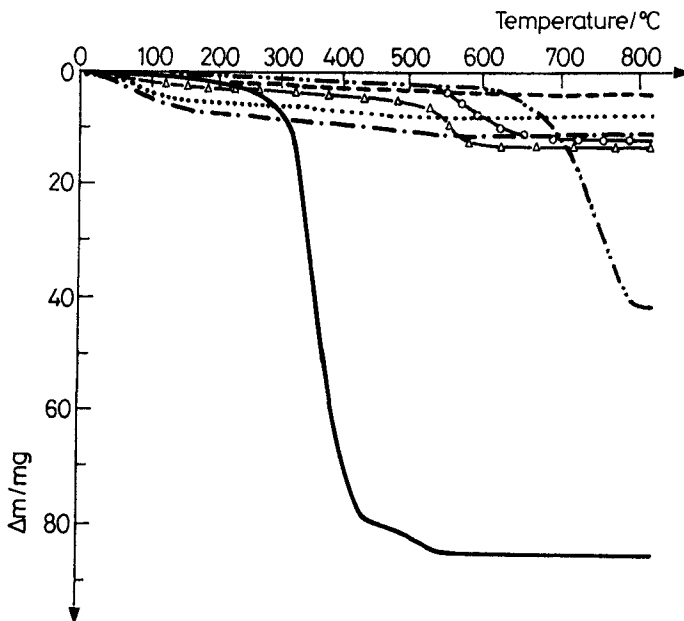
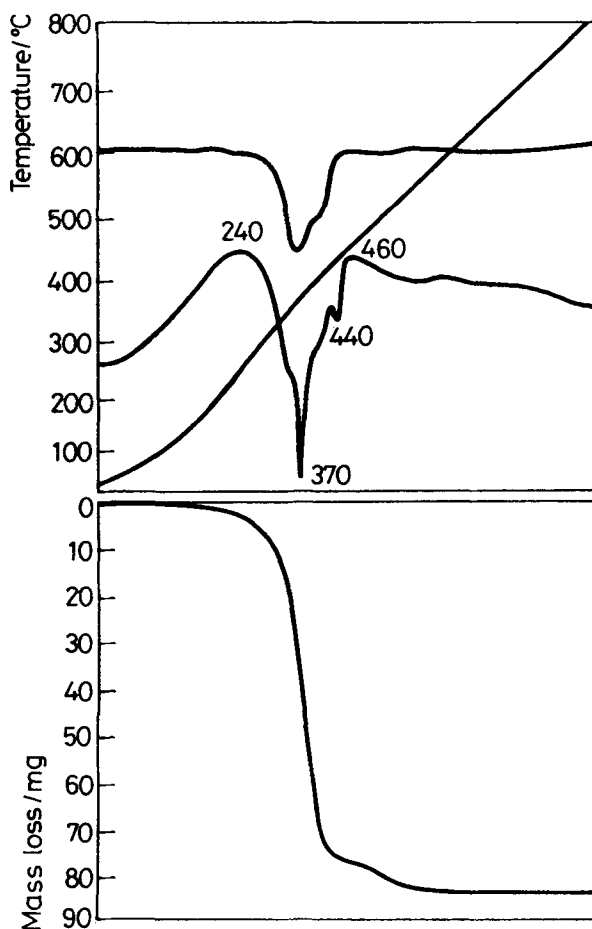


Fig. 3 TG curves of *cis*-1,4-polyisoprene vulcanizate and mineral fillers; — vulcanizate, --- Aerosil 200, ··· Ultrasil VN-3, -·-·- Ze-O-Sil P-45, - - - calcium carbonate, -o-o- kaolin, -Δ-Δ- Frantex B

Table 4 Results of thermogravimetric analysis of mineral fillers

| Filler | Temperature/°C | | Mass loss at 800°C/% |
|-----------------------------------|-----------------------------|------------------------------|-------------------------|
| | $T_{5\% \text{ mass loss}}$ | $T_{10\% \text{ mass loss}}$ | |
| Ultrasil VN-3 | 140 | – | 7.8 |
| Ze-O-Sil P-45 | 100 | 430 | 11.1 |
| Aerosil 200 | – | – | 3.3 |
| Frantex B | 430 | 510 | 13.3 |
| Kaolin | 520 | 570 | 12.2 |
| Precipitated calcium carbonate | 650 | 690 | 41.7 |

**Fig. 4** Thermoanalytical curves of *cis*-1,4-polyisoprene sulphur vulcanizate filled with

(Figs 4–6). These fillers also cause the elastomer decomposition rate to decrease, which facilitates oxygen diffusion into the reaction zone, and as a consequence the final stage of polymer destruction is exothermic (Figs 5 and 7).

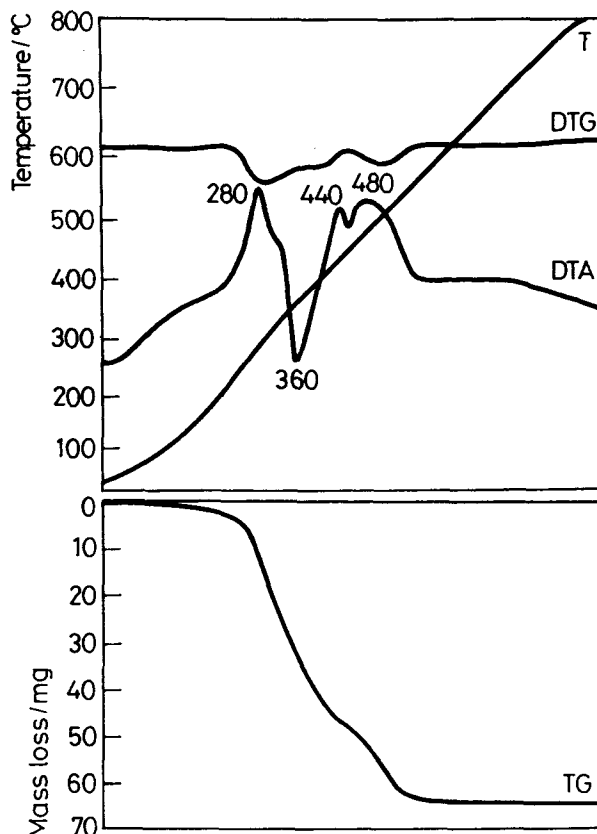


Fig. 5 Thermoanalytical curves of *cis*-1,4-polyisoprene sulphur vulcanizate filled with Aerosil 200, 50 phr

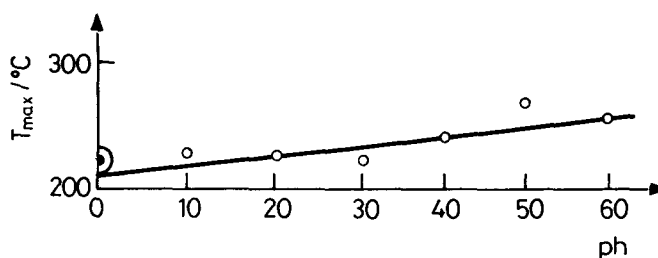


Fig. 6 Effect of Ultrasil VN-3 content on T_{\max} of the first exothermic transition of *cis*-1,4-polyisoprene sulphur vulcanizates. \odot unfilled vulcanizate

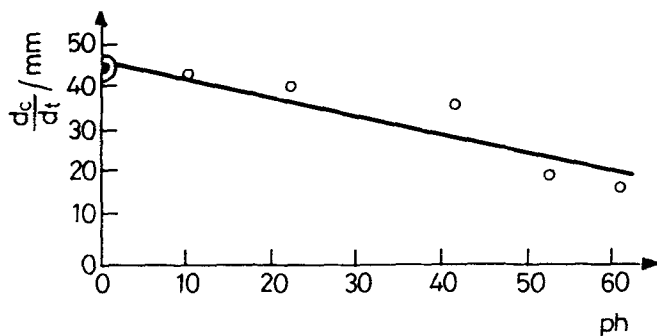


Fig. 7 Effect of Ultrasil VN-3 on *cis*-1,4-polyisoprene sulphur vulcanizate decomposition rate. \odot unfilled vulcanizate

In our opinion, two phenomena are responsible for the rather insignificant effects of the mineral fillers on the thermal stability of elastomers. First, the adsorption and immobilization of macromolecules on a solid surface, diminishing the amplitude of their thermal oscillations, should be taken into consideration. This effect is positive and is the stronger, the higher the activity of the filler. Secondly, the amount of oxygen present in capillaries and cracks is proportional to the specific surface area of the filler, determined via adsorption, e.g. by the BET method. At elevated temperature, the oxygen is desorbed and its concentration in the close vicinity of the immobilized macromolecules of elastomer

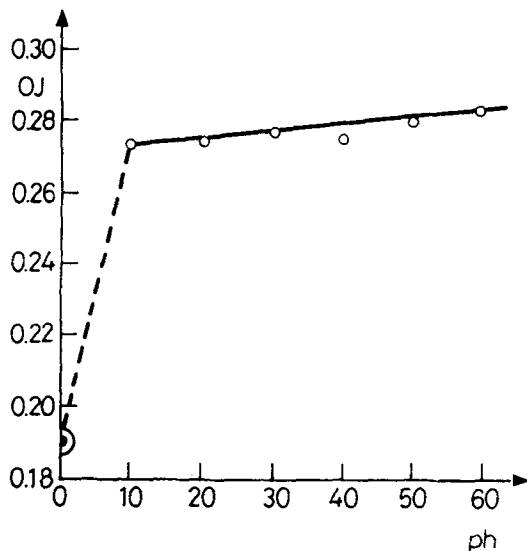


Fig. 8 Effect of Ultrasil VN-3 on *cis*-1,4-polyisoprene sulphur vulcanizate oxygen index, (OI) \odot unfilled vulcanizate

temporarily increases, which favours oxidative chain reactions of a radical character. The first positive effect is therefore balanced. In contrast with carbon blacks, mineral fillers do not act as free radical scavengers.

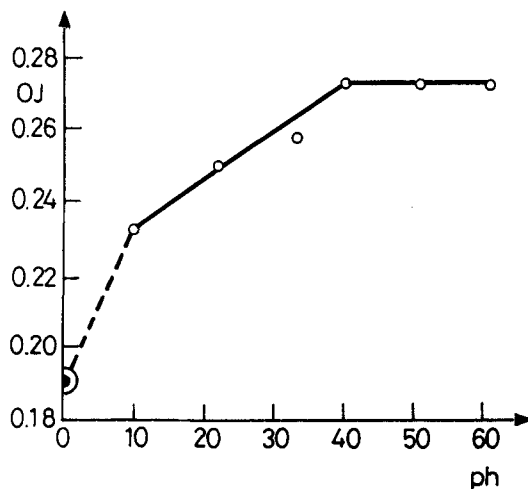


Fig. 9 Effect of Frantex B content on *cis*-1,4-polyisoprene sulphur vulcanizate oxygen index, (OI) ● unfilled vulcanizate

The addition of a mineral filler also affects the flammability of polyisoprene (Figs 8 and 9). This effect is connected with the inhibition of destruction, which means that less volatile flammable substances are formed in the presence of fillers, as shown by the results of derivatographic measurements. If a mix contains active fillers with a high specific surface of fractal character, a certain amount of destruction products is adsorbed even at high temperature. The added mineral fillers also change the structure of the boundary layer between the sample and the flame. In the case of unfilled polyisoprene, the boundary layer, which is the pathway for mass and energy transport, is composed of strongly degraded macromolecules and liquid products of their decomposition [12]. In the presence of the filler, the boundary layer is formed of thermally stable and non-flammable substance. Moreover, the heat of combustion of the filled vulcanizate is smaller than that of the unfilled one. The addition of a mineral filler can decrease the heat emission, the quantity of which is insufficient to maintain elastomer destruction with the demanded efficiency, and the burning comes to an end.

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Zusammenfassung — Mittels Thermoanalyse wurde der Einfluß von Mineralfüllstoffen wie zum Beispiel VN-3, Ze-O-Sil P-45, Aerosil 20, Frantex 8, Kaolin und gefälltem Calciumkarbonat auf die thermischen Eigenschaften der Schwefelvulkanisate von *cis*-1,4-Polyisopren untersucht. Man fand, daß die Natur der thermischen Vorgänge in Isoprenvulkanisaten durch die Zugabe von Mineralfüllstoffen nicht wesentlich verändert wird, die Lage der Peaks in der DTA-Kurve jedoch klar beeinflusst. Die Mineralfüllstoffe beeinflussen die Temperatur und Geschwindigkeit von Abbau und Zerstörung des mit Schwefel vernetzten Polyisoprenes. Die Gegenwart von Mineralfüllstoffen bringt darüber hinaus eine reduzierte Entzündbarkeit der *cis*-1,4-Polyisopren-Schwefelvulkanisate mit sich.