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Polymers

CALORIMETRIC INVESTIGATION OF THE VULCANIZATION OF FACTICE

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Sulphur factice is produced from a mixture of a vegetable oil and sulphur at temperatures between 130 and 160°C. The slow exothermal vulcanization results in rubber-like elastomers. We have developed an isothermal calorimeter for measurements both in the liquid and the solid state and simulated the production process at the laboratory scale. The compensating calorimeter consists of a hot plate equipped with thin aluminium rods descending into a Dewar vessel. Besides optimization of the temperature control, remarkable savings of time were achieved by previous elaidinization of the oil using hydrosulphide.

Introduction

Rubber-like factices are widely used in mixtures with caoutchouc to affect characteristic features of the product and to improve its quality [1]. Sulphur factice is produced from a mixture of a vegetable oil, e.g. rape-seed oil, and sulphur or a sulphur compound for linkage. To start vulcanization, the mixture is heated to temperatures between 130 and 150°. Within hours or days the temperature increases to about 160° and the product adopts the required elastomeric consistence. Both, the addition of sulphur to glycerides of unsaturated aliphatic acids and the polymerization of the primarily formed compounds are heat-releasing processes. As oils and factices are poor heat conductors, the resultant heat is dissipated very slowly and local overheating can occur, which results in spoiled products. To investigate the

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production process, and to shorten and optimize the reaction, the temperature development was simulated in laboratory-scale experiments and the kinetics of the energy turnover was measured.

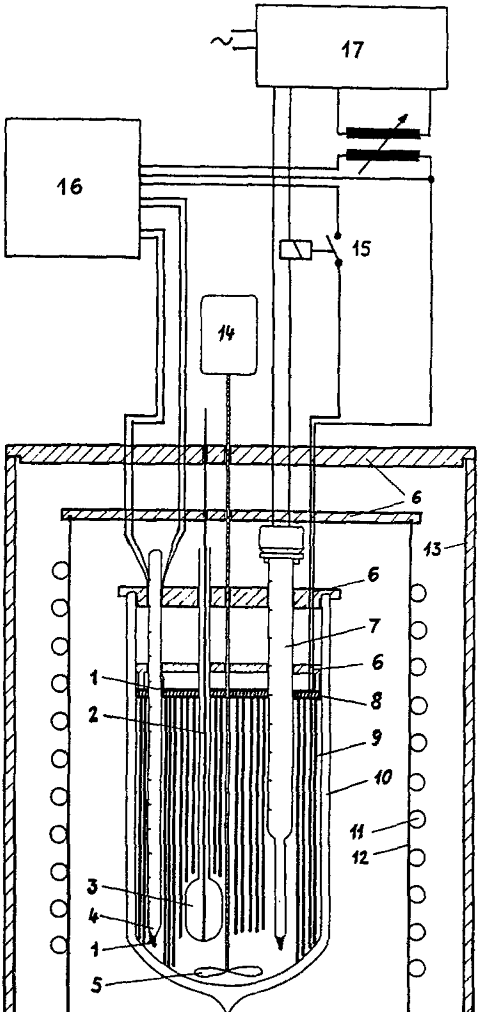

Fig. 1 Isothermal calorimeter; 1 thermocouples, 2 glass rod, 3 glass vessel with sulphur, 4 thermometer, 5 stirrer, 6 heat insulating cover, 7 contact thermometer, 8 heater, 9 aluminium rods (spider), 10 Dewar vessel, 11 hose for thermostated water, 12 metal vat, 13 heat insulating container, 14 stirrer motor, 15 relais, 16 recorder and calculator, 17 power control

The calorimeter

In order to investigate the reaction kinetics of the entire vulcanization process, the calorimeter must allow measurement of the mixture in both, the liquid and the solid state. The reaction proceeds very slowly, the differential heat developed in faint and it dissipation is hindered by poor conduction. As the resulting product is firmly adherent, we foresaw to replace parts of the instrument after each experiment. Commercially available calorimeters were found to be unsuitable [2, 3].

As the mixture had to be heated to different elevated temperatures, we constructed an electric compensating isothermal calorimeter [4]. It consists of a hot plate in which 80 aluminium rods, 3 mm in diameter, descend into a 3 l Dewar vessel (Fig. 1). In case efficient cleaning is impossible the aluminium rods can be cut off by means of side nippers, and replaced. A thin-walled glass container for sulphur, temperature sensors in the hot plate and in the mixture, and a contact thermometer are provided in addition. The calorimeter is equipped with a stirrer which was operated until the liquid sulphur was completely dissolved. The calorimeter was arranged in a vat thermostated at 30°, the stirrer motor being placed outside.

Elaidinization

Vulcanization can be speeded up by elaidinizing of the rape-seed oil in advance. Using hydrosulphide as a catalyst at ambient pressure and temperatures between 120 and 300° a part of the oleic acid is converted to its transform elaidic acid within a period of up to 10 h. By infrared spectroscopy the absorption of the trans-compounds was compared with that of the CH_2 groups. Mostly dimere and trimere compounds were developed and the formation of chain compounds was favoured, whereas more cyclic compounds are produced during direct vulcanization using sulphur. At 300° 75 per cent elaidinized within 0.5 h and at its optimum at 250°, up to 84 per cent were eladinized within 3 h.

Results

Figure 2 shows the typical curves of the integrated reaction heat as a function of time within the first ten hours, and Fig. 3 shows the differentiated reaction power of factice vulcanization with liquid sulphur using the untreated oil and after elaidinization. After that the reaction heat curve becomes constant and the reaction power consequently declines exponentially to zero within another 20 or 30 hours.

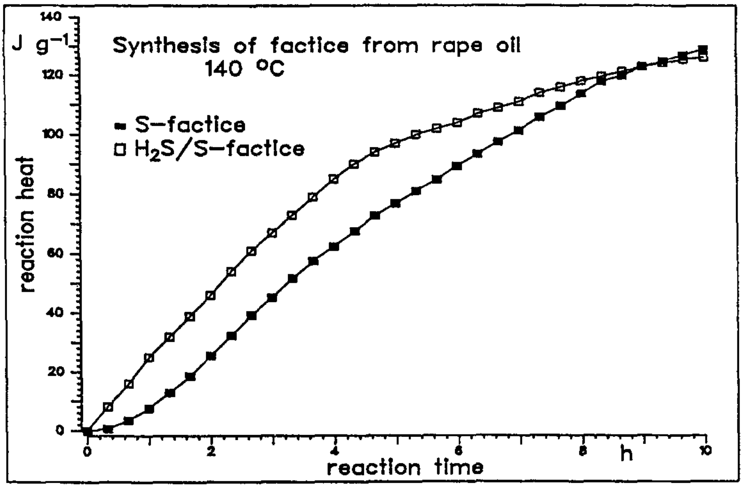

Fig. 2 Integral reaction heat of factice synthesis

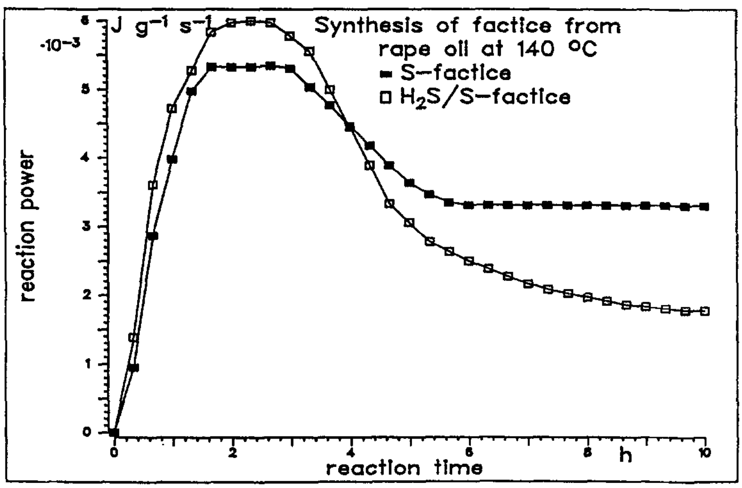

Fig. 3 Reaction power of factice synthesis

In all cases the elaidinized samples exhibited a more rapid heat release, the maximum of which and the termination of the whole reaction taking place earlier. Disregarding that there should be considerable differences in the type of compounds, our S- and H_2S/S-factices were very similar both in quality and dark colour. Taking into account the expenditure for the additional elaidinization process, the total production time could be remarkably reduced with similar energy consumption.

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Zusammenfassung – Schwefeffaktis wird aus einer Mischung von pflanzlichem Öl und Schwefel bei Temperaturen zwischen 130 und 160°C hergestellt. Ein langsamer, exothermer Vulkanisierungsprozess führt zu gummiähnlichen Elastomeren. Es wurde ein isothermes Kalorimeter entwickelt für Messungen sowohl im flüssigen als auch festen Zustand und damit der Herstellungsprozess im Laboratoriumsmaßstab simuliert. Das Kompensations-Kalorimeter besteht aus einer heizbaren Platte, die mit dünnen, sich in ein Dewargefäß erstreckenden Aluminiumstäben versehen ist. Neben einer Optimierung der Temperaturkontrolle ließen sich beträchtliche Zeiteinsparungen erzielen, indem das Öl zuvor durch Behandlung mit Schwefelwasserstoff bei Temperaturen zwischen 120 und 300°C elaidiniert wurde.