Thermochimica Acta, 160 (1990) 29-32
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

COMPENSATING ISOTHERMAL CALORIMETER TO INVESTIGATE THE VULCANIZATION OF FACTICE

E. ROBENS[1], G. SANDSTEDE[2]

[1] Institut für Anorganische und Analytische Chemie der Johannes-Gutenberg-Universität, Postfach 3980, D-6500 Mainz (F.R.G.)

[2] Battelle-Institut e.V., Postfach 900160, D-6000 Frankfurt am Main (Federal Republic of Germany)

SUMMARY

Sulphur factice is produced from a mixture of a vegetable oil and sulphur for linkage. To start vulcanization, the mixture is heated to temperatures between 130 and 150 °C. Within hours or days the temperature increases to about 160 °C and the product solidifies. To investigate the production process and to optimize the reaction, the temperature development was simulated in laboratory-scale experiments and the heat released was measured. In order to investigate the reaction kinetics of the entire vulcanization process, the calorimeter must allow the measurement of the mixture in liquid and solid state. The developed compensating calorimeter consists of a hot plate equipped with thin aluminium rods descending into a Dewar vessel with a sulphur container and temperature sensor. A stirrer was used as long as the mixture was liquid.

INTRODUCTION

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 °C. Within hours or days the temperature increases to about 160 °C because of the released reaction heat and the product takes on the required elastomeric consistence (ref. 1). 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 developed heat is dissipated very slowly and local overheating can occur, which results in spoiled products. To investigate the production process and to optimize the reaction, the temperature development was simulated in laboratory-scale experiments and the kinetics of the energy turnover was measured.

0040-6031/90/$03.50

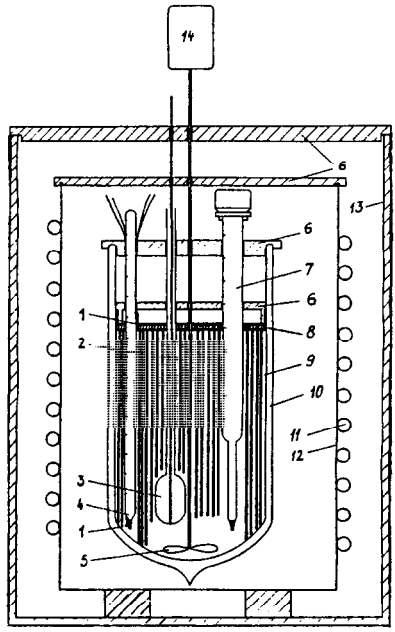


Fig. 1:
Isothermal calorimeter, 1 thermocouples, 2 glass rod, 3 glass vessel with sulphur, 4 thermometer, 5 stirrer, 6 heat insulating cover, 7 contact thermometer, 8 heater, 9 aluminium rods (spider), 10 Dewar vessel, 11 hose for thermostated water, 12 metal vat, 13 heat insulating container.

SELECTION OF THE CALORIMETERS

Most favourably, the factice reaction is investigated using a compensating isothermal calorimeter (refs. 2,3) in which the production process is closely simulated. Then, the resultant reaction power as a function of time at actual temperature can be directly used to optimize practical operation. A variety of calorimeters is available on the market (refs. 4,5). In this special case, however, there are several difficulties:

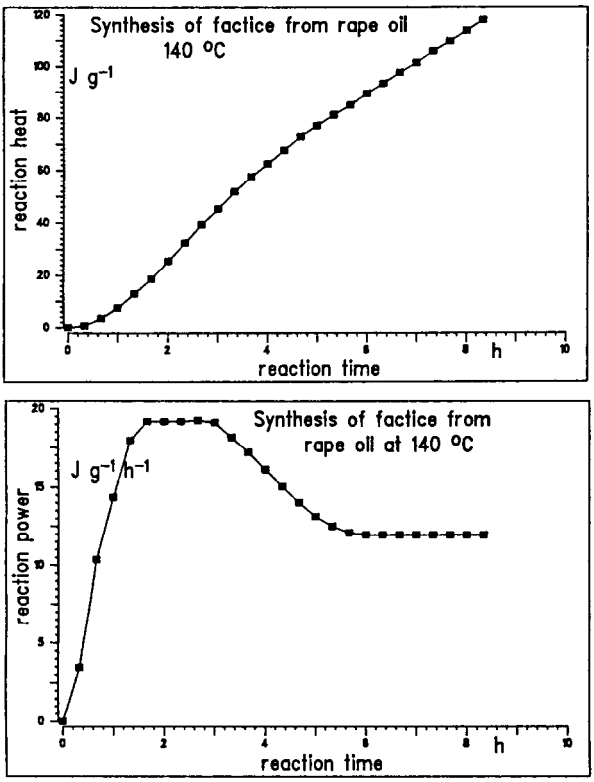
- The reaction proceeds very slowly and the differential heat developed is faint.
- During the formation of factice the initial liquid mixture of oil and cross linking agents becomes viscous and finally forms a solid.
- The product is strongly adhering.

Commercially available calorimeters were found to be unsuitable for this investigation.

CALORIMETER FOR THE LIQUID PHASE

Since it was doubtful whether the total process could be observed by means of calorimetry, we started first measuring the reaction in the liquid state. A simple isothermal calorimeter was built, consisting of a 1 l Dewar vessel with stirrer, heater,

thermometer and contact thermometer. The liquidized sulphur was stored in a thin-walled glass bulb and added to the oil by breaking the bulb with a glass rod. The measurements were extended as long as the mixture could be stirred. The power that had to be added to maintain the reaction temperature was about 11 W. Since the stirring power was about 3 W, an increase in stirrer power to compensate for the increase in viscosity of the mixture would create major disturbances. After one hour, however, the dissolution of the liquid sulphur was complete, and the stirrer could be switched off. The results provided the basis for developing a calorimeter that is suitable for investigating the total reaction.



Figs. 2 + 3: Integral reaction heat and the reaction power of factice synthesis.

CALORIMETER FOR THE LIQUID AND SOLID PHASES

In order to investigate the reaction kinetics of the entire vulcanization process, the calorimeter must allow the measurement of the mixture in both, the liquid and the solid state. With such an instrument problems will arise concerning the distribution of the added heat, removal of the vulcanized product and cleaning. As the resulting product was firmly adherent, we foresaw to replace parts of the instrument after each experiment. As the mixture had to be heated to different elevated temperatures, we constructed an electric compensating isothermal calorimeter (Fig. 1).

It consists of a hot plate in which 80 aluminium rods, 3 mm in diameter, descend into a 3 l Dewar vessel. In case efficient cleaning is impossible the aluminium rods can be cut off by means

of side nippers, and replaced. Furthermore, a thin-walled glass container for sulphur, temperature sensors in the hot plate and in the mixture, and a contact thermometer are provided. 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 °C, the stirrer motor being placed outside.

RESULTS

The calorimeter is a kind of thermostat, the heat loss being compensated by electrical heating with constant power, discontinuously controlled by a contact thermometer. The heating periods are recorded on-line and integrated. Fig. 2 shows the typical curve of the resulting integrated reaction heat as a function of time, and Fig. 3 the differentiated reaction power of a factice synthesizing process.

ACKNOWLEDGEMENT

The investigation was performed at Battelle-Institute e.V. Frankfurt am Main. The authors highly acknowledge valuable discussions with Dr. Lohmann (D.O.G.) and Dipl.-Ing. R. Nowack (Battelle). We are indebted to the D.O.G. Deutsche Ölfabrik Ges. f. chem. Erz. mbH & Co., Hamburg, for financial support.

REFERENCES

1 Faktis. Kontakt 27, D.O.G. Deutsche Ölfabrik Ges. f. chem. Erz. mbH & Co., Postfach 11 19 29, D-2000 Hamburg 11.
2 F. Becker: Thermisch-Kalorische Meßverfahren. In: Ullmanns Encyclopädie der technischen Chemie, 4. ed., vol. 5, Verlag Chemie, Weinheim 1980, pp. 779-796.
3 F. Becker: Kalorimetrie - eine vielseitige Methode für energetische Messungen in Physik, Chemie und Biologie. Jahresbericht des Physikalischen Vereins Frankfurt am Main, 159 (1984), pp. 153-177.
4 W. Hemminger, G. Hoehne: Grundlagen der Kalorimetrie. Verlag Chemie, Weinheim 1979.
5 R.Sh. Mikhail, E. Robens: Microstructure and Thermal Analysis of Solid Surfaces. Wiley, Chichester 1983, pp. 113-118.