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Abstract

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CATALYTIC CURING OF POLYDIMETHYLSILOXANE AT ROOM TEMPERATURE

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As is known, the process of converting linear or branched alkylpolysiloxanes into an infusible and insoluble state proceeds at 200–250° and requires a long time. The necessity of such heat treatment complicates the technology of obtaining materials based on organosilicon polymers and, to a considerable extent, limits the range of their application.

Despite the importance of the problem of curing liquid and rubber-like organosilicon polymers at room temperature, no ways of solving it had been proposed up to the present time. In the literature there were only brief communications of an advertising character, indicating that in the USA an organosilicon rubber of cold curing (Silastic RTV) had been developed ([1],[2]). We considered it possible, for the formation of three-dimensional alkylpolysiloxanes, to use the interaction of hydroxyl groups of linear polydimethylsiloxanes with alkoxy groups of polyfunctional organosilicon monomers.

This method of forming transverse siloxane bonds is more advantageous from the energetic point of view than the cleavage of hydrogen or an alkyl radical from the polymer chain, on which the principle of the usual thermal vulcanization of polydimethylsiloxane rubber is based, and could therefore be carried out at considerably lower temperatures.

In order to find effective accelerators of vulcanization, we carried out a study of the catalytic activity of certain esters of orthotitanic acid (ethyl, propyl, and butyl), as well as a number of organotin compounds, the greater part of which belong to the group of dialkyltin salts, with the general formula $R_2\mathrm{Sn(OCOR_1)_2}$, where R is an ethyl or butyl radical, and $\mathrm{OCOR_1}$ is acetyl, capryl, or stearyl.

Caprylates or stearates were synthesized for the first time; moreover, the former did not represent an individual product, since they were obtained from fractions of technical caprylic acid.

In all cases an effect of cold vulcanization of liquid and rubber-like polydimethylsiloxanes was found, which was expressed in a gradual increase in the viscosity

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

and shear stress of the polymer, an increase in its elastic properties, and a decrease in solubility. Figures 1 and 2 show curves characterizing the change in shear stress (P) and elasticity (recovery) of the polymer under the influence of organotin and organotitanium compounds, and Table 1 gives some properties of the vulcanizates.

For measuring the shear stress and elasticity of the polymers, we used a laboratory instrument—a rotational plastometer, specially developed for characterizing the plastic properties of organosilicon—

organic rubber (^{4}). The data obtained show that the character of the vulcanization process changes sharply depending on the type of organometallic compound used. Esters of orthotitanic acid cause a rapid change in the properties of the polymer at the initial stage of the reaction, after which the rate of the process drops sharply, while the polymer formed as a result,

Fig. 1. Change in shear stress during vulcanization of a silicon-organic polymer under the influence of: **1** —an organotin compound (0.7%), **2** —butyl titanate (3%)

Fig. 2. Change in elastic properties (recovery) during vulcanization of a silicon-organic polymer under the influence of: **1** —an organotin compound (0.7%), **2** —butyl titanate (3%)

as is evident from the data in Table 1, has low shear-stress values and an increased content of soluble fraction.

Table 1

Properties of vulcanizates obtained at 20° (after 24 hours)

Accelerator in vulcanization	Amount of accelerator, %	Shear stress, g/cm^2	Elasticity	Content of soluble fractions, %
Butyl titanate	3.0	190	0.95	31.5
Organotin compound	0.7	560	1.00	27.8

It should be noted that esters of orthotitanic acid, unlike organotin compounds,

Fig. 3

Figure 3: Fig. 3

are capable of causing vulcanization of polydimethylsiloxanes in the absence of tetraethoxysilane, which merely promotes a somewhat more complete course of the vulcanization process without changing its character. This fact indicates that esters of orthotitanic acid are not catalysts, but components of the vulcanization reaction of polydimethylsiloxanes, directly participating in the formation of cross-links. This, in our opinion, also explains the feature of the curve characterizing the vulcanization process shown in Fig. 1: the high initial rate of the reaction is associated with the vigorous development of branching and crosslinking processes of the polydimethylsiloxane macromolecules as a result of their interaction with the hydroxyl groups formed during hydrolysis of the orthotitanic acid ester, while the subsequent slowing of the reaction is the natural consequence of the decrease in mobility of the macromolecules as the number of cross-links increases.

The vulcanization process caused by organotin compounds is of an entirely different character. It is characterized by the presence of a definite induction period, followed by a period of sharp increase in the reaction rate, during which the vulcanization process is practically completed. The duration of the induction period and the rate of the vulcanization process depend, as our experiments showed, on the nature of the catalyst and its dosage, as well as on the molecular weight of the polymer.

Figure 3 presents curves for the change in shear stress of liquid polydimethylsiloxanes, which show that, as the decrease in

of the molecular weight of the polymer the reaction rate decreases, and the induction period increases. As a study of the strength and relative elongation of filled vulcanizates (rubbers) has shown, in the molecular-weight range from 40,000 to 100,000 the mechanical properties of the vulcanizates are practically independent of the molecular weight; however, on going to high polymers of the SKT rubber type (mol. wt. 300,000–500,000), a considerable increase in strength is observed. The following data may be cited as an example:

Molecular weight of polymer	Tensile strength of vulcanizate, kg/cm^2	Relative elongation, %
70,000	21.8	180
400,000	37.6	350

Fig. 3. Dependence of the vulcanization rate on the molecular weight of the polymer.
1 –mol. wt. 48,000; 2 –mol. wt. 63,000; 3 –mol. wt. 77,000.

Fig. 4

Figure 4: Fig. 4

Interesting data were obtained in studying the effect of the structure of organotin compounds on their catalytic activity. Fig. 4 gives the results of a series of experiments on determining the change in the shear stress of polydimethylsiloxane (mol. wt. 60,000) in the presence of equimolecular dosages of organotin compounds differing in the nature of the alkyl and acyl radicals entering into their composition*.

Fig. 4. Effect of the nature of the catalyst on the vulcanization rate.
1 –dibutyltin diacetate; 2 –dibutyltin dicaprylate; 3 –dibutyltin distearate; 4 –diethyltin dicaprylate; 5 –diethyltin distearate.

If one compares in Fig. 4 the curves relating to dialkyl derivatives of the same type (for example, 1, 2, and 3 or 4 and 5) and the curves corresponding to organotin compounds with identical acyl groups but different alkyl radicals (for example, 2 and 4 or 3 and 5), it may be concluded that, as the size of the organic radicals entering into the stannates increases, their catalytic activity decreases, which is manifested in an increase in the induction period of the reaction and a decrease in its rate. It is very interesting that an increase in the alkyl radical affects the decrease in the activity of the catalyst much more strongly than an increase in the acyl group (as can be seen, for example, from comparing curves 1 and 2 with 4 and 2).

The observed regularities, as well as the mechanism of the catalytic action of organotin compounds, can, in our opinion, be explained on the basis of the assumption of the formation of an active complex according to the scheme (see the scheme on p. 606).

The larger the alkyl radical, the greater the degree of saturation of the tin with electrons, the less the –OH and OR groups are polarized and, consequently, the more difficult it is for them to react with one another. The same, but to a lesser extent,

* The curve corresponding to diethyltin diacetate could not be obtained under the conditions of this experiment, since, in view of the excessively high activity of this catalyst, its introduction into the polymer caused structuring and partial vulcanization of polydimethylsiloxane.

$$\mathrm{O{-}Si(R_1)_2{-}O\cdots H\cdots O{-}Sn(R_1)_2(OAc)_2 \leftarrow R_1 \quad {-}O{-}Si(OR)_2{-}O{-} \quad Sn(R_1)_2(OAc)_2 \leftarrow R_1\cdots O\cdots H{-}O{-}Si(R}$$

$$\sim \mathrm{O{-}Si(R)(R_1){-}O{-}Si(O{-})(O{-}){-}O{-}Si(R_1)_2} \sim + \ \mathrm{Sn(R_1)_2(OAc)_2} \quad \text{(complex with alcohol)}$$

refers to the influence of the acyl groups. However, because of the displacement of π-electrons toward oxygen, the positive inductive effect caused by an increase in the alkyl radical will be manifested to a lesser degree. As we see, the proposed mechanism is fully confirmed by the experimental facts and provides a basis for establishing the relation between the structure of the catalyst and its activity.

After our work had already been completed, a brief communication appeared on the vulcanization of polydimethylsiloxane using dibutyltin dilaurate and tetraethoxysilane (^{4}), in which views analogous to ours are expressed concerning the role of tetraethoxysilane in the vulcanization process, but no explanation is given of the mechanism of action of the catalysts.

Table 2

Mechanical properties of organosilicon rubbers obtained by different methods

Vulcanizing agent	Vulcanization conditions: temperature, °C	Vulcanization conditions: duration, h	Tensile strength, kg/cm^2	Relative elongation, %	Shore hardness
Benzoyl peroxide	150	0.5	20–25	180–250	40–50
Benzoyl peroxide	200	12	20–25	180–250	40–50
Organotin compound	20	24	35–47	250–350	45–55

The developed method of "cold" vulcanization of liquid and rubber-like polydimethylsiloxane polymers can be used to obtain various rubber materials, casting compositions, rubberized fabrics, coatings, and compounds that cure at room temperature.

Organosilicon rubbers obtained by this method possess $1\frac{1}{2}$–2 times higher strength than rubbers of the same composition obtained by the ordinary method of two-stage vulcanization at 150–200° in the presence of benzoyl peroxide. Table 2 gives comparative characteristics of rubbers filled with zinc oxide and obtained by the methods of "cold" and "hot" vulcanization. The duration of vulcanization, depending on the composition of the catalyst, can be varied from several minutes to several days. The rubbers obtained have high heat resistance—they retain elasticity and mechanical strength for a long time under the action of temperatures of 200–250°.

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Note: Figure translations are in progress. See original paper for figures.

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