

# EFFECTS OF SOME PHENYLETHYNYL-SILICON COMPOUNDS ON HEAT-CURABLE SILICONE RUBBER

## III 1,1,3,3-TETRAMETHYL-1,3-DIPHENYLETHYNYL-DISILOXANE\*

FENG Shengyu(冯圣玉) YU Shuqi(于淑岐)

LI Shijun(李世军) ZHANG Shengyou(张圣有)

CHEN Jianhua(陈剑华) and DU Zuodong(杜作栋)

(*Institute of New Materials, Shandong University, Jinan 250100*)

### ABSTRACT

We have shown that some phenylethynylsilicon compounds are good cure crosslinkers of heat-curable silicone rubber (HCSR). In this paper the effects of 1,1,3,3-tetramethyl-1,3-diphenylethynyl-disiloxane (TMDPDS) as a crosslinker on HCSR were studied. The vulcanizates with fine mechanical properties could be obtained with suitable amounts of TMDPDS. Sol fractions, and crosslinking density of vulcanizates and vulcanization retardation effect of TMDPDS on hydrosilation curing silicone rubber were also discussed.

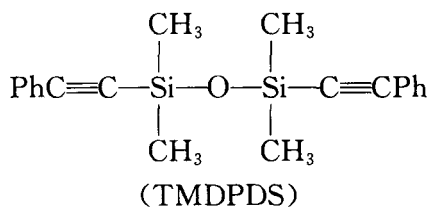
### INTRODUCTION

Since silicone rubber has many excellent properties, it has become a kind of indispensable new materials for many application fields<sup>[1,2]</sup>. As it is well known, vinylsilanes or polyvinylsiloxanes are usually used as crosslinkers of silicone rubber, but the rubber obtained therefrom is still

\* For parts I and II, see refs. 3 and 4

Received January 31, 1994

relatively poor in strength. In order to develop new kinds of silicone rubber, we chose silicon compounds containing phenylethynyl groups instead of the usual vinyl groups as crosslinkers. In our attempt of using 1, 3-bis (methylphenylethynylvinyl) disiloxane (TDSI) and phenylethynylvinyl-diethoxysilane (PVDES) as crosslinking agents of heat-curable silicone rubber (HCSR)<sup>[3,4]</sup>, we have found that the properties of the silicone rubber can be improved. Both TDSI and PVDES have vinyl and phenylethynyl groups. Then, what will be the result of using the silicon compounds with only phenylethynyl groups? For this reason, in this paper we wish to report the effects of 1, 1, 3, 3-tetramethyl-1, 3-diphenylethynyldisiloxane (TMDPDS), as a crosslinker on HCSR. The experimental results indicate that TMDPDS is also a good crosslinker. The tensile strength and the tear strength of some vulcanizates can reach as high as 14.1 MPa and 65.0 kN/m, respectively. But unlike TDSI and PVDES, in the test range, the amounts of TMDPDS used have little effect on the properties of the silicone rubber. The crosslinking state of vulcanizates and the vulcanization retardation effect of TMDPDS on hydrosilation curing silicone rubber were also analysed.



## EXPERIMENTAL

### 1. Materials

Silicone gum ( $\bar{M}_n$ ,  $6.5 \times 10^5$  and vinyl group content, 0.15 mol%), octamethylcyclotetrasilazane ( $D_4^N$ ), polyvinylsilicone oil (C gum) (vinyl group content, 9.0 mol% and viscosity, 92.2 cP) and hydric silicone oil (H-oil) (hydrogen content, 1.23 wt%) were provided by the Forth Petrochemical Works of Jinan. Fumed silica (specific surface area, 176 m<sup>2</sup>/g) was made in the Shenyang Chemical Works. They were all industrial products and were used without further purification. Pt-catalyst (Pt-cat) was prepared as Ref. [3]. TMDPDS was prepared according to the method introduced in the Ref. [5].

## 2. Preparation of HCSR

The formulae of HCSR are given in Table 1. Compounding and vulcanizing of stocks proceeded according to the reference [6]. Vulcanization conditions: the first stage of the vulcanization at 170°C for 30 min under the pressure of 29.4 MPa; the second stage of the vulcanization (postcure) at 200°C for 3h under atmosphere.

**Table 1** Formulae of HCSR

| Materials                   | PCV <sup>a</sup> (wt. parts) | HCV <sup>b</sup> (wt. parts) |
|-----------------------------|------------------------------|------------------------------|
| Silicone gum                | 100                          | 100                          |
| Fumed silica                | 57                           | 57                           |
| D <sub>4</sub> <sup>N</sup> | 8                            | 8                            |
| C gum <sup>c</sup>          | 2 or 0                       | 2 or 0                       |
| TMDPDS                      | 0—0.24                       | 0—0.24                       |
| H-oil                       | 0                            | 1.15                         |
| Pt-cat                      | 0                            | 0.2                          |
| DCBP <sup>d</sup>           | 1                            | 0                            |

a PCV=Peroxide-curing vulcanizate

b HCV=Hydrosilation curing vulcanizate

c Without TMDPDS, C gum is 2; otherwise C gum is zero

d DCBP=2,4,2',4'-tetrachlorobenzoyl peroxide

## 3. Mechanical properties of vulcanizates

The mechanical properties of every vulcanizate were measured on DL-250 Rubber Test Instrument. Sol fraction (*S*) and average molecular weight (*M<sub>c</sub>*) of effective chains between crosslinks were determined by benzene extract and toluene-swelling methods, respectively, and full details are in ref. [3]. Vulcanization retardation effect of TMDPDS on hydrosilation curing silicone rubber stocks was observed at room temperature.

# RESULTS AND DISCUSSION

## 1. Effects of TMDPDS on mechanical properties of HCSR

The formulae without TMDPDS, which are classic formulae using C gum as a crosslinker, were chosen for a basis. In the experiments, various

amounts of TMDPDS were used instead of C gum to investigate the effects of TMDPDS on mechanical properties of HCSR. The results (see Table 2) show that mechanical properties of the silicone rubber, especially tear strength, can be greatly improved by using TMDPDS instead of C gum as a crosslinker. For example, the tensile strength and the tear strength of sample V-3 are up to 14.1 MPa and 65.0 kN/m, respectively. For sample VI-4, not only its tensile strength and tear strength are high but also elastic modulus is large (4.01 MPa). With an increase in the amounts of TMDPDS used from 0.04 to 0.24 part, there are no obvious changes in the tensile and tear strength of the peroxide-curing vulcanizates (PCV), but the elongation of vulcanizates rises and hardness decreases slightly, showing that the crosslinking density of the vulcanizates turns to decline. The reason of decreasing of crosslinking density other than "crispness" of the vulcanizates with the increasing amounts of TMDPDS is probably that phenyl groups stabilize a part of radicals produced by decomposition of peroxide catalyst (DCBP) to make these radicals lose catalytic activity. Because of the relative increasing of phenyl groups, their stabilization on radicals is strengthened enough to counter-balance the increase of crosslinking density caused by increasing the amounts of the crosslinker used.

**Table 2** Effects of TMDPDS on heat-curable silicone rubber

| Type | Sample No. | TMDPDS (wt. part) | Tensile strength (MPa) | Tear strength (kN/m) | Modulus at 100% extension (MPa) | Elongation at break (%) | Hardness (Sh A) | Permanent deformation (%) |
|------|------------|-------------------|------------------------|----------------------|---------------------------------|-------------------------|-----------------|---------------------------|
| PCV  | V-0        | 0                 | 12.4                   | 51.7                 | 3.06                            | 304                     | 62              | 2.0                       |
|      | V-1        | 0.04              | 12.2                   | 63.8                 | 3.17                            | 339                     | 63              | 2.8                       |
|      | V-2        | 0.08              | 11.7                   | 64.8                 | 2.82                            | 362                     | 62              | 3.2                       |
|      | V-3        | 0.12              | 14.1                   | 65.0                 | 2.73                            | 399                     | 61              | 5.0                       |
|      | V-4        | 0.16              | 12.0                   | 64.2                 | 2.70                            | 434                     | 59              | 4.0                       |
|      | V-5        | 0.24              | 12.6                   | 68.1                 | 2.74                            | 404                     | 60              | 4.0                       |
| HCV  | VI-0       | 0                 | 11.7                   | 24.5                 | 4.95                            | 347                     | 65              | 3.0                       |
|      | VI-1       | 0.04              | 13.5                   | 27.4                 | 5.38                            | 342                     | 68              | 2.8                       |
|      | VI-2       | 0.08              | 12.7                   | 48.5                 | 4.48                            | 346                     | 65              | 3.6                       |
|      | VI-3       | 0.12              | 13.4                   | 60.9                 | 3.87                            | 428                     | 65              | 4.0                       |
|      | VI-4       | 0.16              | 14.1                   | 60.3                 | 4.01                            | 456                     | 65              | 2.4                       |
|      | VI-5       | 0.24              | 13.9                   | 60.9                 | 4.27                            | 512                     | 64              | 7.6                       |

For hydrosilation curing vulcanizate (HCV), when amount of TMDPDS used is 0.04 part, the crosslinking density of the vulcanizate W-1 is high, being indicated by low tear strength and high elastic modulus at 100% extension. This also agrees with its low elongation and high hardness. With an increase in the amounts of TMDPDS used, the tear strength of the vulcanizates enhances and their comprehensive properties become better. When the amounts of TMDPDS used are more than 0.12 part, the mechanical properties of the vulcanizates have little changes. Similarly as to PCV, with an increase in the amounts of TMDPDS used, elongation of vulcanizates becomes a little higher and the hardness lower, indicating that crosslinking density of the vulcanizates decrease. However, this should be ascribed to vulcanization retardation effect of phenylethynyl groups on HCV stock<sup>[7]</sup>. In fact, TMDPDS plays the roles of both a crosslinker and a vulcanization retarder. The gradual decrease in the crosslinking density of the vulcanizates with the increase of the amounts of TMDPDS used (or the increase of phenylethynyl groups) shows that vulcanization retardation of TMDPDS is somewhat dominant over crosslinking.

In addition, unlike TDSI<sup>[3]</sup> and PVDES<sup>[4]</sup>, no extreme value in the mechanical properties of the vulcanizates appears with the change of the amounts of TMDPDS used. This is probably because both TDSI and PVDES contain phenylethynyl and vinyl groups, and TMDPDS only contains phenylethynyl groups.

## *2. Sol fraction ( $S$ ) and average molecular weight ( $M_c$ ) of effective chains between crosslinks of vulcanizates*

In order to evaluate the crosslinking state of vulcanizates, their  $S$  and  $M_c$  were measured, respectively. The results are listed in Table 3. The data show that the amounts of TMDPDS used have little effect on the  $S$  of the vulcanizates. To sum up,  $S$  of every vulcanizate is low, showing its good curing state. In the meantime, amounts of TMDPDS used also have only a little effect on the  $M_c$  of the vulcanizates. This is coincident with that on the mechanical properties of the vulcanizates (see Table 2). But with an increase in the amounts of TMDPDS used,  $M_c$  goes up a little higher, showing that crosslinking density of the vulcanizates decreases somewhat. From the data in Table 3, we can also find that  $M_c$ s of PCV are larger than those of HCV, similar to the regularity reported in the literatures<sup>[3,4]</sup>. This differs with regard to the type of curing.

Table 3 S and  $M_c$  of vulcanizates

| Sample No. | S (%) | $M_c (\times 10^{-3})$ | Sample No. | S (%) | $M_c (\times 10^{-3})$ |
|------------|-------|------------------------|------------|-------|------------------------|
| V-0        | 1.84  | 3.94                   | VI-0       | 1.84  | 3.57                   |
| V-1        | 2.01  | 5.42                   | VI-1       | 1.82  | 3.69                   |
| V-2        | 2.02  | 5.48                   | VI-2       | 1.85  | 3.67                   |
| V-3        | 2.03  | 5.40                   | VI-3       | 1.82  | 4.37                   |
| V-4        | 2.08  | 5.98                   | VI-4       | 1.82  | 4.43                   |
| V-5        | 2.21  | 6.30                   | VI-5       | 1.93  | 5.09                   |

### 3. On "concentrative crosslinking"

The curing of HCSR stocks is caused by the reaction of crosslinkers with functional groups (vinyl or  $\equiv\text{Si}-\text{H}$  groups) of polysiloxane under certain conditions. According to the conception "concentrative crosslinking of the extension spring type", heptamethyl [(trivinylsilyl) ethyl] cyclotetrasiloxane was used as inner concentrative crosslinker to copolymerize with octamethylcyclotetrasiloxane to produce a new type of vinylsilicone rubber. Therefore, high modulus and high strength silicone rubber ST-4600<sup>[9,10]</sup> with excellent properties could be obtained. This is mainly because "concentrative crosslinking" occurs when stocks cure. A molecule of TMDPDS contains two phenylethynyl groups, which can react four times with functional groups of polysiloxane. Therefore TMDPDS should be a good concentrative crosslinker. Summarizing data in Tables 2 and 3, we can find that vulcanizates using TMDPDS as a crosslinker have larger  $M_c$  and better properties. This not only shows concentrative crosslinking in curing of stocks but also supports the viewpoint that concentrative crosslinking can improve properties of silicone rubber<sup>[11]</sup>.

### 4. Vulcanization retardation effect of TMDPDS on hydrosilation curing silicone rubber

TMDPDS containing two phenylethynyl groups can be used not only as a crosslinker of HCSR but also as a vulcanization retarder of hydrosilation curing silicone rubber to prolong shelf time of the stocks under room temperature (see Table 4). Vulcanizate stocks using TMDPDS as a crosslinker did not cure for 50 days at room temperature, undepending on the amounts of TMDPDS used. The behavior of TMDPDS is also somewhat different from that of TDSI and PVDES containing both vinyl and phenylethynyl groups.

**Table 4** Vulcanization retardation effect of TMDPDS on HCV ( $20 \pm 1^\circ\text{C}$ )

| Sample No. | Shelf time (days) |
|------------|-------------------|
| VI-0       | 0.7               |
| VI-1       | >50               |
| VI-2       | >50               |
| VI-3       | >50               |
| VI-4       | >50               |
| VI-5       | >50               |

## CONCLUSIONS

TMDPDS can be used not only as a good concentrative crosslinker of HCSR, but also as a good vulcanization retarder of hydrosilation curing silicone rubber. When adding certain amounts of TMDPDS in the stocks, mechanical properties of the vulcanizates could be improved, and shelf time of hydrosilation curing silicone rubber stocks could be prolonged. Different from TDSI and PVDES, the used amounts of TMDPDS only containing phenylethynyl groups have a little effect on the properties of HCSR.

### Keywords:

Silicone rubber; 1, 1, 3, 3-Tetramethyl-1, 3-diphenylethynyl disiloxane; Vulcanization retardation effect; Heat cure

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