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Mechanical Properties of Silicone Rubber Using Carbosilane Dendrimers as the Cross-linker

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Abstract: Peroxide-cured high-temperature vulcanized (HTV) silicone rubber was prepared by using allyl-capped carbosilane dendrimers, in which the core molecule is $Si(CH_2CH=CH_2)_4$, as the cross-linker. It showed that this kind of allyl-capped carbosilane dendrimer improved the mechanical properties of silicone rubber.

Keywords: Carbosilane dendrimers, cross-linker, silicone rubber, mechanical properties.

It is necessary to get a high-strength silicone rubber because of its low strength compared with organic rubbers. A great deal of investigations showed that the use of concentrative crosslinker is one of the effective methods to improve mechanical properties of silicone rubber[1]. Dendrimers are perfectly branched, highly symmetrical tree-like macromolecules with many potential applications, used as catalyst[2], molecular device[3], or as chemo-delivery in biology[4]. Therefore, dendrimers with characteristically designed structure and densely peripheral functionalities could be used as a new kind of concentrative crosslinker for silicone rubber. The aim of this paper is to use the kinetically and thermodynamically stable carbosilane dendrimers with peripheral allyl groups as the crosslinker of high temperature vulcanizied (HTV) silicone rubber and investigate mechanical properties of HTV.

The silicone gum ($Mn = 5.5\times10^5$), polymethylvinylsiloxane (PMVS, $Mn = 1.5 \times 10^4$), fumed silica (BET surface areas = 176 m^2g^{-1}), and 2,5-bis (*tert*-butyl peroxy)-2.5-dimethyl hexane (DBPMH) were commercially available products. The dendrimers used $Si(CH_2CH=CH_2)_4$ as core molecule were synthesized by alternative hydrosilylation and alkenylation as follows:

$$Si(CH_2CH=CH_2)_4 + MeSiHCl_2 \xrightarrow{\text{cat.}} Si(CH_2CH_2CH_2SiMeCl_2)_4$$

$$Si(CH_2CH_2CH_2SiMeCl_2)_4 + CH_2=CHCH_2MgCl \longrightarrow$$

$$Si(CH_2CH_2CH_2SiMe(CH_2CH=CH_2)_2)_4 SiG_{1\,(Allyl)\,8}$$

Herein, $SiG_{1(Allyl)8}$ represents the first generation of dendrimer. The structures of the

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second and the third generation of dendrimers are as follows:

$Si(CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe(CH_2CH{=}CH_2)_2)_2)_4$ $SiG_{2(Allyl)16}$
$Si(CH_2CH_2CH_2SiMe(CH_2CH_2CH_2SiMe(CH_2CH{=}CH_2SiMe(CH_2CH{=}CH_2)_2)_2)_2)_4$ $SiG_{3(Allyl)32}$

Preparation of HTV

Following the formula of high-strength silicone rubber, HTVs were prepared using $SiG_{n(Allyl)}$ (n = 1,2,3) or PMVS as cross-linker (see **Table 1**). The mechanical properties of vulcanizates were measured[5] on an XLD rubber test instrument.

Effects of amount of $SiG_{n(Allyl)}$ on mechanical properties of HTV

The optimum mechanical properties of vulcanizates cured with different amount of $SiG_{1(Allyl)8}$, $SiG_{2(Allyl)16}$, $SiG_{3(Allyl)32}$ are shown in **Table 2**.

Table 1 Formulations of HTV using dendrimer crosslinker (wt. parts)

Silicone Gum	Fumed SiO_2	DBPMH	PMVS	$SiG_{1(Allyl)8}$	$SiG_{2(Allyl)16}$	$SiG_{3(Allyl)32}$
100	55	1.0	2.0	-	-	-
100	55	1.0	-	012 - 0.32	-	-
100	55	1.0	-	-	0.20 - 0.36	-
100	55	1.0	-	-	-	0.20-0.36

Table 2 Effects of dendrimers of different generations on mechanical properties of HTV

Sample No.	Wt. Part of dendrimer	Hardness (SHA)	Tensile strength (MPa)	Tearing strength (kN/m)	Modulus at 100% (MPa)	Elongation at break (%)
No.1[a]	0	57	8.4	27.5	1.3	400
PSA1-1[b]	0.20 g SiG_1	57	8.9	30.0	1.2	420
PSA1-2[b]	0.24 g SiG_1	58	9.6	27.9	1.3	410
PSA2	0.32 g SiG_2	59	8.9	31.0	1.4	410
PSA3-1[b]	0.24 g SiG_3	58	8.8	29.5	1.1	440
PSA3-2[b]	0.28 g SiG_3	58	9.3	28.9	1.2	440

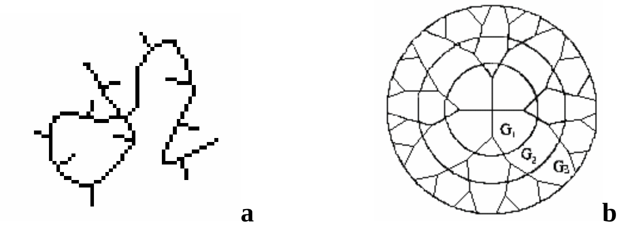
[a] 2.0 g of PMVS was used as the cross-linker.
[b] PSA1, PSA2 and PSA3 represent the HTV cured by using the first, second, and third generation of dendrimer, respectively; the last number in PSA1-1 and PSA1-2 indicate different amount of $SiG_{1(Allyl)8}$ were used, so do PSA3-1 and PSA3-2.

Herein, PSA was the abbreviation of vulcanized specimen, representing the HTV cross-linked by dendrimers. In PSA the first character indicates peroxide-cured silicone rubber (Abbrev. P), the second one means the type of dendrimers' core molecule is $Si(CH_2CH{=}CH_2)_4$ (S), and the third represents the peripheral allyl groups (A). Dendritic cross-linkers of different generations display different effects on strength of vulcanizates because these dendrimers differ in the number, density of allyl groups, and molecular weight. The optimum tensile strength of vulcanizates using $SiG_{1(Allyl)8}$ or $SiG_{3(Allyl)32}$ as crosslinker is 9.6 and 9.3 MPa, respectively. The optimum tearing strength of vulcanizates crosslinked with $SiG_{2(Allyl)16}$ reached 31.0 kN/m, much higher than that of using $SiG_{1(Allyl)8}$ or $SiG_{3(Allyl)32}$ as crosslinker. So there is little difference in tensile strengths of vulcanzates when using different generations of dendritic crosslinkers. The crosslinkers of different generations showed more obvious effects on tearing strength than on tensile strength of vulcanizates.

Comparison of allyl-capped carbosilane dendrimers and PMVS used as the crosslinker

It also can be seen from **Table 2** that both the tensile strength and tearing strength of vulcanizates cured with dendritic cross-linkers are higher than that of using PMVS as crosslinker. And the effects on tearing strength are higher than that of tensile strength. This is attributed to the concentrative cross-linking effect of dendritic crosslinkers. The dendrimers (See **Figure 1a**) should offer better concentrative cross-linking on silicone rubber than PMVS (See **Figure 1b**) does for their perfect, regular global structure with plentiful and densely peripheral functional groups. The results on mechanical properties of vulcanizates prepared using dendrimers were coincident with the prediction. On one hand, the densely vinyl groups in dendrimers can cause more concentrative cross-linking than PMVS does. On the other hand, the dendrimers with internal high cross-link density may be regarded as nano-scale reinforcing filler dispersed in the rubber matrix and which can improve the strength of vulcanizates.

Figure 1 Structures of PMVS (**a**) and dendrimer (**b**)



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