

Investigation of Allyl-Capped Carbosilane Dendrimers Used as Crosslinker for Silicone Rubber

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ABSTRACT: High-temperature vulcanized silicone rubber was prepared by using allyl-capped carbosilane dendrimers, in which the core molecules were $\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ and $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ as crosslinker and nanoscale reinforcing filler, respectively. Allyl-capped carbosilane dendrimers improved the mechanical properties of silicone rubber. The optimum tensile strength and tear strength were 9.6 MPa and 31.0

kN/m, respectively, when using $\text{SiG}_{n(\text{allyl})m}$ as the crosslinker and 10.1 MPa and 32.0 kN/m, respectively, when using $\text{Ph}_2\text{SiG}_{n(\text{allyl})m}$ as the crosslinker. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1772–1775, 2006

Key words: dendrimers; crosslinking; silicone rubber; mechanical properties; nanoscale reinforcing filler

INTRODUCTION

Silicone elastomer is a kind of high molecular weight polydiorganosiloxane. High-temperature vulcanized silicone rubber (HTV) is usually cured by peroxide or a platinum complex. Silicone rubbers are important engineering materials because of their distinguished flexibility, low toxicity, good thermal stability, and electrical insulation. They also have consistent properties over a wide temperature range, which leads to a large operating temperature range (e.g., -100 to 250°C), and excellent resistance to oxygen, ozone, and sunlight. In addition, the vulcanized rubbers have some disadvantages, such as poor tensile and tear properties.

Some investigations showed that the use of concentrative crosslinking was one of the effective methods to improve the strength of silicone rubber; and the new crosslinkers include 1,3-bis(methylphenylethynyl)vinyl) disiloxane, phenylethynylvinyl diethoxysilane, 1,1,3,3-tetramethyl-1,3-diphenylethynyl disiloxane, tetraphenylethynylsilane, polysiloxanes containing phenylethynyl groups, vinyl-containing silicone resin, hydrogen-containing silicone resin, and so forth.^{1–7} Dendrimers^{8–10} are perfectly branched, highly symmetrical, treelike macromolecules with many potential applications, for example, as catalysts,¹¹ molecular devices,^{12–14} and chemod-

elivery in biology.¹⁵ Therefore, dendrimers with characteristically designed structures could be approached for scientific purposes as a new kind of concentrative crosslinker for silicone rubber. Carbosilane dendrimers with Si atoms as branching points are one of the important families of dendritic macromolecules.^{16–21} The carbosilane dendrimers with peripheral allyl groups are kinetically and thermodynamically stable molecules, which is due to the high dissociation energy of the Si—C bond (306 kJ mol^{-1} , similar to the C—C bonds, 345 kJ mol^{-1}) and the low polarity of the Si—C bond. These characteristics imply that this kind of dendrimer is a potential good crosslinker for silicone rubber.

In this investigation, carbosilane dendrimers with $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ (abbreviated as P) or $\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ (abbreviated as S) as core molecules of different generations were employed as crosslinkers for silicone rubber. The effects on the comprehensive mechanical properties of peroxide-cured silicone rubber were examined, including the tensile strength, tear strength, and elongation at break. Herein, the vulcanized specimens PSA and PPA represent the HTV crosslinked by dendrimers with a $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ core or an $\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ core, respectively. In PSA and PPA the first character indicates peroxide-cured silicone rubber (P), the second means the type of dendrimer core (P or S), and the third represents the peripheral allyl groups (A).

EXPERIMENTAL

Materials

Silicone gum (number-average molecular weight = 5.5×10^5 , vinyl group content = 0.15 mol %), C gum

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TABLE I
Formulations of HTV Using Dendrimer Crosslinker (Wt. Parts)

Gum	Fumed SiO ₂	DBPMH	C gum	SiG ₁	SiG ₂	SiG ₃	Ph ₂ SiG _{n(allyl)}
100	55	1.0	2.0	—	—	—	—
100	55	1.0	—	0.12–0.32	—	—	—
100	55	1.0	—	—	0.20–0.36	—	—
100	55	1.0	—	—	—	0.20–0.36	—
100	55	1.0	—	—	—	—	0.24–0.44

(vinyl group content = 10.2 mol %), octamethylcyclotetrasilazane (D₄^N), 4[#] fumed silica (specific surface area = 176 m²/g), and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane are all industrial products. Carbosilane dendrimers using Ph₂Si(CH₂CH=CH₂)₂ and Si(CH₂CH=CH₂)₄ as the core molecules were synthesized by alternative hydrosilylation using dichloromethylsilane and alkenylation with allylmagnesium chloride divergently.

Preparation of HTV

Following the formula of high-strength silicone rubber, HTVs were prepared using PSA, PPA, or C gum as the crosslinker. Referring to the related literature,²² stocks were compounded and vulcanized. The first stage of cure was 160°C for 30 min under a pressure of 15 MPa; the second stage of cure (postcure) was 180°C for 2 h in hot air. The formulations of HTVs using SiG_{n(allyl)}_m and Ph₂SiG_{n(allyl)}_m as crosslinkers are listed in Table I.

C gum is mostly used as the crosslinker for peroxide-cured silicone rubber. We used 2.0 weight parts of C gum and different amounts of allyl-capped carbosilane dendrimers (SiG_{n(allyl)}_m or Ph₂SiG_{n(allyl)}_m), whose core molecule is tetraallylsilane or diphenyldiallylsi-

lane, from the first to the third generations as the crosslinker for HTVs.

Measurement of mechanical properties of vulcanizates

The mechanical properties of the vulcanizates were measured²³ on an XLD rubber test instrument.

RESULTS AND DISCUSSION

Effects of amount of SiG_{n(allyl)}_m and Ph₂SiG_{n(allyl)}_m on mechanical properties of HTVs

The mechanical properties of the vulcanizates using SiG_{1(allyl)}₈, SiG_{2(allyl)}₁₆, SiG_{3(allyl)}₃₂, Ph₂SiG_{1(allyl)}₄, Ph₂SiG_{2(allyl)}₈, and Ph₂SiG_{3(allyl)}₁₆ as crosslinkers are shown in Table II.

Although dendritic crosslinkers possess the same kind of peripheral functional groups and similar structures, dendritic crosslinkers of different generations display different effects on the mechanical properties of vulcanizates because these dendrimers differ in both the number and density of allyl groups and in molecular weights. The optimum tensile strengths of vulcanizates using SiG_{1(allyl)}₈ or SiG_{3(allyl)}₃₂ as a cross-

TABLE II
Effects of Dendrimers of Different Generations on Mechanical Properties of HTV

Sample no.	Wt. part of dendrimer	Hardness (Shore A)	Tensile strength (MPa)	Tear strength (kN/m)	Modulus at 100% (MPa)	Elongation at break (%)
No. 1 ^a	0	57	8.4	27.5	1.3	400
S1-3 ^b	0.20 SiG ₁	57	8.9	30.0	1.2	420
S1-4 ^b	0.24 SiG ₁	58	9.6	27.9	1.3	410
S2-4 ^b	0.32 SiG ₂	59	8.9	31.0	1.4	410
S3-2 ^b	0.24 SiG ₃	58	8.8	29.5	1.1	440
S3-3 ^b	0.28 SiG ₃	58	9.3	28.9	1.2	440
P1-2 ^c	0.24 Ph ₂ SiG ₁	59	8.7	30.0	1.1	480
P1-3 ^c	0.28 Ph ₂ SiG ₁	59	10.1	28.1	1.1	470
P2-2 ^c	0.28 Ph ₂ SiG ₂	58	9.4	28.2	1.1	480
P2-5 ^c	4.0 Ph ₂ SiG ₂	60	9.8	27.6	1.3	430
P3-2 ^c	0.32 Ph ₂ SiG ₃	59	9.5	32.0	1.2	480
P3-4 ^c	0.40 Ph ₂ SiG ₃	60	10.1	28.8	1.3	450

^a 2.0 g C gum was used as the crosslinker.

^b S1, S2, and S3 represent the dendrimer Ph₂SiG_{n(allyl)}_m in which n = 1, 2 and 3, respectively.

^c P1, P2, and P3 represent the dendrimer SiG_{n(allyl)}_m in which n = 1, 2 and 3, respectively.

linker are 9.6 and 9.3 MPa, respectively, and those using $\text{Ph}_2\text{SiG}_{1(\text{allyl})4}$, $\text{Ph}_2\text{SiG}_{2(\text{allyl})8}$, or $\text{Ph}_2\text{SiG}_{3(\text{allyl})16}$ as crosslinkers are 10.1, 9.8, and 10.1 MPa, respectively. The optimum tear strength of vulcanizates crosslinked with $\text{SiG}_{2(\text{allyl})16}$ reached 31.0 kN/m, which is much higher than that using $\text{SiG}_{1(\text{allyl})8}$ or $\text{SiG}_{3(\text{allyl})32}$ as the crosslinker; and the value using $\text{Ph}_2\text{SiG}_{3(\text{allyl})16}$ is much higher than using $\text{Ph}_2\text{SiG}_{1(\text{allyl})4}$ or $\text{Ph}_2\text{SiG}_{2(\text{allyl})8}$. Thus, there is little difference in the tensile strengths of vulcanizates when using different generations of dendritic crosslinkers. The different generation crosslinkers showed more obvious effects on the tear strength than on the tensile strength of vulcanizates.

Comparison of allyl-capped carbosilane dendrimers and C gum as crosslinkers

It can be seen from Table II that both the tensile strength and tear strength of vulcanizates cured with dendritic crosslinkers are higher than when using C gum as the crosslinker. The effects on the tear strength are also higher than on the tensile strength. This is attributed to the concentrative crosslinking effect of dendritic crosslinkers.

Many experiments showed that the rupture of cured rubber is caused by the breakage of chemical bonds in the main chains.²⁴ The type of crosslinking network of vulcanizates shows obvious effects if there are the same kinds of chemical bonds in different crosslink networks. Theoretically, the concentrative crosslinks can disperse applied forces to all the molecular chains connected with them via the densely crosslinked bonds of the concentrative crosslinks⁶ in vulcanizates. Thus, concentrative crosslinking can enhance the mechanical properties of silicone rubber.¹⁻⁷ The comprehensive mechanical properties can be improved if the concentrative crosslinking is achieved using crosslinkers without weak chemical bonds in their molecules.

Dendrimers should offer better concentrative crosslinking on silicone rubber than C gum because of their perfect, regular global structure with plentiful and densely peripheral functional groups. The results of the mechanical properties of vulcanizates prepared using C gum and dendrimers were coincident with the prediction. On the one hand, the dense vinyl groups in dendrimers can cause more concentrative crosslinking than C gum. On the other hand, a reinforcing filler is a particulate material that is able to increase the end-use performance of the rubber compound, including the tensile strength, tear strength, and so on. The dendrimers with internal high crosslink density may be regarded as nanoscale reinforcing fillers dispersed in the rubber matrix and then can improve the strength of vulcanizates. Thermodynamically, the conformation of the linear C gum molecule is inclined to form a random coil. Thus, parts of



Figure 1 The structures of (a) C gum and (b) dendrimer.

the vinyl groups of C gum are wrapped inside [see Fig. 1(a)]. The *peripheral* vinyl or allyl groups of dendrimers [see Fig. 1(b)] can react more completely than that of C gum, in which parts of the vinyl groups are *inside* the molecule chain, in the cure reaction with polysiloxane gum rubber.

Effects of branching density and phenyl group in dendrimer crosslinker

The discriminations between the two series of dendritic crosslinkers used in this study are the branching density and the phenyl group because of their different core molecules. Thus, the optimum tensile strength and tear strength of vulcanizates appear when different generations of dendrimers were used. The data in Table II show that the samples with optimum comprehensive mechanical properties were the vulcanizates using $\text{SiG}_{2(\text{allyl})16}$ and $\text{Ph}_2\text{SiG}_{3(\text{allyl})16}$ as crosslinkers, indicating that a suitable number of allyl groups of dendritic crosslinkers is needed; in the case discussed, it is 16.

There are both methyl and vinyl groups attached to the main chain of the silicone gum molecule, and the vinyl group content of our silicone gum is 0.15 mol %. It is mainly the vinyl groups, not the methyl groups, of polysiloxane that react with the allyl groups of the dendrimer in the peroxide-cured silicone rubber when dendritic crosslinkers are used if the stocks are well mixed, because the vinyl group is more active than the methyl group. The crosslinking between vinyl groups attached to polysiloxane main chains definitely cannot be avoided. Concentrative crosslinking cannot be formed if there are few allyl groups in a dendritic crosslinker. In addition, dendrimers are much smaller in size and more densely functionalized than C gum, which is a linear molecule, for their regular and highly branched three-dimensional structures. There must be too many polysiloxane macromolecules or segments that group together and crowd around the crosslinker to conduct the crosslinking reaction whereas the dendrimer crosslinker has too many allyl groups. Then, the concentrative crosslinking could not be achieved because it was impossible for too many vinyl groups of polysiloxane macromolecules to carry out the crosslinking reaction with all the peripheral allyl groups of a dendrimer crosslinker. As a result, to obtain the optimum mechanical properties, an appro-

appropriate generation with an appropriate number of peripheral allyl groups is needed if the dendrimer crosslinkers are used. Considering the dendritic crosslinkers used in this study, which use $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ or $\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ as the core molecules, the former has fewer and less densely peripheral allyl groups than the latter, so the optimum mechanical properties are displayed in the third and second generations, respectively.

To fulfill the crosslinking of vulcanizates and to decompose the unreacted peroxide, generally a postcure in hot air was performed after the first molding cure. The vulcanizates using $\text{Ph}_2\text{SiG}_{n(\text{allyl})m}$, in which the phenyl group links to the Si atom in the core molecule, as crosslinker showed better mechanical properties than the one without the phenyl group because phenyl groups can stabilize free radicals and minimize the oxidation crosslinking reaction in the postcure stage. Thus, from Table II we can see that the optimum mechanical properties such as the tensile strength, tear strength, and elongation at break of vulcanizates using $\text{Ph}_2\text{SiG}_{n(\text{allyl})m}$ as the crosslinker are 10.1 MPa, 32.0 kN/m, and 480%, respectively, whereas using $\text{SiG}_{n(\text{allyl})m}$ as the crosslinker they are 9.6 MPa, 31.0 kN/m, and 440%, respectively.

CONCLUSIONS

Compared to C gum, the perfectly branched, highly symmetrical, treelike carbosilane dendrimers are good crosslinkers for peroxide-cured HTV silicone rubber because of better concentrative crosslinking effects and nanoscale reinforcement of the dendrimer crosslinkers. The crosslinkers with different generations showed more obvious effects on the tear strength than on the tensile strength of vulcanizates. The vulcanizates using dendrimers with a phenyl-containing core as crosslinkers displayed better mechanical properties than the one without a phenyl group. The optimum mechanical property tensile strength, tear strength, and elongation at break of the vulcanizates cured by $\text{Ph}_2\text{SiG}_{n(\text{allyl})m}$ are 10.1 MPa, 32.0 kN/m, and

480%, respectively, and those cured by $\text{SiG}_{n(\text{allyl})m}$ are 9.6 MPa, 31.0 kN/m, and 440%, respectively.

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