

Influences of Branched Vinyl Silicone Oil on the Physical and Ultraviolet Transparent Properties of Silicone Rubber

YINGLE YIN*, XINTAI CHEN*, JIE LU* AND XUHUANG CHEN**#

Ultraviolet transparent silicone rubber with different content of branched vinyl silicone oil was prepared by heat curing method. Curing process, mechanical and optical properties of modified silicone rubber were investigated by rotational rheometer, differential scanning calorimeter, electronic creep testing machine as well as ultraviolet and visible spectrophotometer. Crosslink density of silicone rubber was determined by the toluene-swelling method. Experimental results show that silicone rubber can form an effect of concentrative crosslinking in the presence of branched vinyl silicone oil. When adding certain amount (2 wt%) of branched vinyl silicone oil, the silicone rubber exhibited good mechanical properties (tensile strength 6.51MPa, elongation at break 229.8%). Gel time and crosslink density of silicone rubber increased with the increase of branched vinyl silicone oil, while the UV transmittance of silicone rubber decreased as the loading of branched vinyl silicone oil increased. In conclusion, silicone rubber has excellent mechanical and optical properties (UV transmittance can be up to 92% and 89% at 350 nm and 300 nm, respectively), when the content of branched vinyl silicone oil is 2 wt%.

Keywords: Branched vinyl silicone oil; storage modulus; gel time; UV transmittance; tensile strength

Silicone rubber has been widely used in many areas because of its excellent properties including biocompatibility, oxidation resistance, thermal stability, climate resistance, low surface tension and unique high permeability^{1–10}. However, silicone rubber has weak interaction forces among the polymer chains, as the Si–O bond has larger bond length and less alkyl groups than C–C bond. Therefore, silicone rubber has lower mechanical strength¹¹. In order

to resolve the problem of lower mechanical strength of silicone rubber, a lot of work have been done by researchers. Concentrative crosslinking^{7,12–18} is an effective method employed to improve mechanical properties of silicone rubber and has been widely used by many researchers. It is a phenomenon whereby a highly crosslinked point is present in silicone rubber. Crosslinkages in silicone rubber could distribute stress well without the problem of weak interface. Researchers

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found that concentrative crosslinking could be presented in silicone rubber by adding phenylethynylsilicon compounds¹²⁻¹⁷ or organosilicone compounds with multiple vinyl groups¹⁸. Du¹⁶ used 1,3-bis(methylphenylethynylvinyl) disiloxane as modifier to determine whether it could cause effects of concentrative crosslinking and inhibit the curing process of silicone rubber. Experimental results showed that integrated mechanical performances can be largely improved by adding suitable amount of 1,3-bis(methylphenylethynylvinyl) disiloxane. Furthermore, it is also an excellent curing retarder for silicone rubber. Zhao¹⁸ used several kinds of vinyl-containing silicone resin as modifier and found that silicone rubber modified with suitable amount of vinyl-containing silicone resin exhibited excellent mechanical properties, especially the tearing strength. The more $\text{SiO}_{1.5}$ units in the vinyl-containing silicone resin, the higher the strength of the modified silicone rubber will be. From above studies, organosilicone compounds that contained multiple active groups including vinyl, phenylethynyl or ethynyl groups are excellent modifiers for silicone rubber as they can cause the concentrative crosslinking during the curing process of silicone rubber.

Theoretically, branched vinyl silicone oil is also a good modifier as it contains multiple vinyl groups. Compared with other modifiers containing multiple phenyl and/or ethynyl groups, there are little or no unsaturated groups in fully cured silicone rubber modified with branched vinyl silicone oil. In addition, the curing process of silicone rubber modified with branched vinyl silicone oil can be easily controlled¹⁹. These advantages will contribute to decrease the UV absorption and to obtain highly ultraviolet transparent silicone rubber. However, there is little research about branched vinyl silicone oil and its influences on optical properties of silicone rubber. In this study, we report experimental results of

branched vinyl silicone oil as the modifier for silicone rubber where mechanical and optical properties of silicone rubber were measured.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane RH-502 (cross-linking agent, hydrogen content 0.75 wt%, viscosity 60 mpa·s), vinyl silicone oil RH-304 (base gum, vinyl content 0.16 wt%, viscosity 5000 mpa·s), branched vinyl silicone oil RH-Vi306 (modifying agent, vinyl content 2.25 wt%, viscosity 1000 mpa·s), vinyl-MQ silicone resin RH-0826 (reinforcing agent, vinyl content 1.2 wt%, M/Q=1, viscosity 6000 mpa·s) and platinum (catalyser, 400 ppm) were purchased from Runhe Chemical Co. Ltd. (Zhejiang, China). 1-Ethynylcyclohexanol (inhibitor) was obtained from Jiaying Sicheng Chemical Co. Ltd. (Jiaying, China). Methylbenzene was purchased from Tianda Chemical Regent Factory (Tianjin, China). Molecular structures of vinyl silicone oil, polymethylhydrosiloxane and branched vinyl silicone oil were shown in *Figure 1*. All the above reagents were industrial grades and used as received.

Preparation of Silicone Rubber

Silicone rubbers with different content of branched vinyl silicone oil were prepared according to formulations in *Table 1*. Firstly, vinyl silicone oil, vinyl-MQ silicone resin, branched vinyl silicone oil, platinum and 1-Ethynylcyclohexanol were injected into the round-bottom flask at room temperature. The mixtures were continuously stirred to homogenous solution. Subsequently, certain amount of polymethylhydrosiloxane was added into the solution, followed by

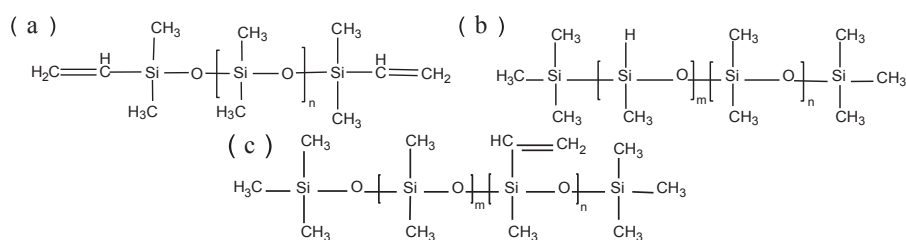


Figure 1. Molecular structures of (a) Vinyl silicone oil, (b) Polymethylhydrosiloxane and (c) Branched vinyl silicone oil.

TABLE 1. COMPOSITIONS OF THE SILICONE RUBBER

Materials	1	2	3	4	5
Vinyl silicone oil/g	20	20	20	20	20
Vinyl-MQ silicone resin/g	80	80	80	80	80
Branched vinyl silicone oil/g	0.5	1	2	3	4
Platinum/g	0.5	0.5	0.5	0.5	0.5
1-Ethynylcyclohexanol/g	0.04	0.04	0.04	0.04	0.04
Polymethylhydrosiloxane/g	7.93	8.01	8.19	8.37	8.54

continuous stirring for 20 minutes. The content of polymethylhydrosiloxane in silicone rubber with different content of branched vinyl silicone oil was calculated using Equation 1. The solution was then transferred into vacuum at room temperature to remove air bubbles. Next, the blend solution was poured into a special mould (depth 1mm of mould cavity) and cured in an oven at 100°C for about 15 minutes.

$$W = \frac{A(W_1 \times a\% + W_2 \times b\% + W_3 \times c\%)}{(H\% \times 27)} \dots 1$$

Where W , W_1 , W_2 and W_3 are the weight of polymethylhydrosiloxane, vinyl silicone oil, vinyl-MQ silicone resin and branched vinyl silicone oil, respectively; $H\%$ is the mass fraction of hydrogen in polymethylhydrosiloxane; $a\%$, $b\%$ and $c\%$ are the mass fraction of vinyl in vinyl silicone oil, vinyl-MQ silicone resin and branched vinyl

silicone oil, respectively. A is the mole ratio of Si-H and Si-Vi at 1.6.

The basis of Equation 1 is the hydrosilylation of silicone rubber. Mechanism of hydrosilylation (Figure 2) is that three-dimensional reticulated silicone rubber will be obtained by the reaction between vinyl groups ($\text{Si}-\text{CH}_2=\text{CH}_2$ or $\text{Si}-\text{Vi}$) and hydrogen groups ($\text{Si}-\text{H}$) in the presence of catalyser. Theoretically, the mole ratio (A) of Si-H and Si-Vi should be 1. However, the occurrence of side reaction will wear out a part of the hydrogen groups. In order to obtain good mechanical and highly ultraviolet transparent properties of silicone rubber, the mole fraction of hydrogen group ($\text{Si}-\text{H}$) should be slightly more than the vinyl group in uncured silicone rubber. Silicone rubber with excellent comprehensive properties will be obtained when the mole ratio (A) of Si-H and Si-Vi is 1.6.

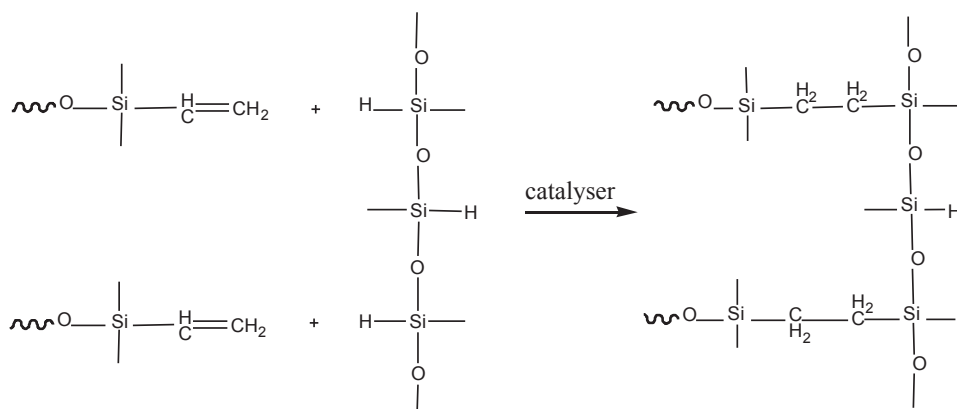


Figure 2. Mechanism of hydrosilylation.

Characterisation of Silicone Rubber

Gel time and storage modulus of silicone rubber were measured by rotational rheometer (TA R2000EX) at oscillation mode (frequency 1Hz, temperature 90°C, strain 0.5%). The curing process of silicone rubber with different content of branched vinyl silicone oil were analysed by differential scanning calorimeter (PE, DSC8000) at a heating rate of 10°C/min in the range of 30–140°C. Tensile strength, tensile modulus and elongation at break of silicone rubber were determined by electronic creep testing machine (Xinsansi Material Testing Co. Ltd., Shenzhen, China, CMT-4204) at a tensile rate of 20 mm/min. Shore durometer was used to evaluate the hardness of silicone rubber. UV transmittance of the silicone rubber was measured by ultraviolet and visible spectrophotometer (Hitachi U-3900) in wavelength coverage of 200–800 nm (thickness of sample 1 mm).

The average molecular weight (M_c) of effective chains implies the crosslinking degree of silicone rubber as well as physical and chemical actions of additives with additives, main links with main links and additives with main links¹⁸. The crosslink

density of silicone rubber was determined by the toluene-swelling method^{20,21}. The process of this experiment is as follows. A silicone rubber disk (diameter 10mm, thickness 1mm) was immersed into excess anhydrous toluene in a sealed vessel at 25.0±0.1°C. After seven days being immersed in toluene, the sample was taken out and weighed immediately before being immersed in the toluene again. The sample was then weighed every 3h until the weight become constant. This is called the swelling equilibrium of the sample. The crosslink density (V_e) of silicone rubber was then calculated by the Flory Rehner Equation²² (Equation 2).

$$V_e = \frac{\rho}{M_c} = -\frac{[\ln(1-\phi) + \phi + X_1\phi^2]}{(V_0\phi^{1/3})} \quad \dots 2$$

Where V_e is the crosslink density (mol/cm³) of silicone rubber; M_c is the average molecular weight (g/mol) between crosslinking points in silicone rubber; ϕ is the volume fraction of vulcanisate in the swelling body and can be calculated using Equation 3; X_1 is the interaction efficiency between macromolecule and solvent, here 0.465; V_0 is the mole volume of the solvent (106.54×10⁻³ L/mol, toluene); ρ is the density (g/cm³) of silicone rubber.

$$\varphi = (W_i/\rho) / [(W_s - W_i) / \rho_1 + W_i/\rho] \quad \dots 3$$

Where W_i and W_s are the weight of the initial sample and swollen weight (g), respectively; ρ_1 is the density (g/cm³) of toluene.

RESULTS AND DISCUSSION

Curing Process of Silicone Rubber

Gel point (GP) is the time whereby the extent of critical reaction will be produced by gelation. After the presence of gelation, the solution viscosity of uncured silicone rubber will increase causing difficulty in removing the bubbles. Gel point was measured by the crossover point of loss and storage modulus²³⁻²⁶, as determined during the cross-linking reaction of silicone rubber by rotational rheometer. The time before the presence of gel point is called gel time. The gel time is an important parameter for silicone rubber preparation, mainly because uncured solution of silicone rubber needs time to blend and to remove air bubbles. Feng^{12,16} elaborated the influences of the amount of 1,3-bis(methylphenylethynylvinyl) disiloxane (BMPVDS) and 1,3-diphenylethynylsiloxane (TMDPDS) on the shelf life of uncured silicone rubber under room temperature, respectively. Results imply that both BMPVDS and TMDPDS can prolong the shelf life of uncured silicone rubber. From this phenomenon, Feng concluded that both BMPVDS and TMDPDS can inhibit the curing process of silicone rubber. The influence of branched vinyl silicone oil on the curing process of silicone rubber is shown in *Figure 3*. The gel time of silicone rubber increased with the increase of branched vinyl silicone oil content in the silicone rubber. When the content of branched vinyl silicone oil was 0.5 wt%, the gel time of silicone rubber was 105.2 seconds. When the content was 4 wt%, the gel time increased to 216.1 seconds. The above phenomenon clearly proved that branched

vinyl silicone oil can inhibit the curing process of silicone rubber.

The curing process of silicone rubber with different content of branched vinyl silicone oil at 90°C is shown in *Figure 4*. The storage modulus of silicone rubber initially increases with increasing content of branched vinyl silicone oil and obtains the maximum value at 2 wt%, then gradually decreases in the high content range. Thus, it is concluded that the cured silicone rubber with appropriate amount of branched vinyl silicone oil will obtain the maximum value of storage modulus. In addition, it was observed that the initial point of curing curve of silicone rubber moved right with the increase of branched vinyl silicone oil. This implied that branched vinyl silicone oil has an inhibiting action on the curing process of silicone rubber.

Figure 5 showed the curing curve of silicone rubber with different contents of branched vinyl silicone oil tested by DSC. From *Figure 5(a)*, it is obvious that exothermic peak of silicone rubber moved towards high temperature with increasing content of branched vinyl silicone oil. These changes of exothermic peak proved that branched vinyl silicone oil has some inhibiting actions on curing process of silicone rubber. The same conclusion was also obtained from *Figure 5(b)* and *Table 2*. From *Figure 5(b)* and *Table 2*, it can be seen that the beginning and ending of curing temperature increased with increase content of branched vinyl silicone oil in silicone rubber. A proposed hypothesis to explain these changes is that the relatively low viscosity and the relatively high vinyl content of branched vinyl silicone oil could be the main reason. If this hypothesis is correct, branched vinyl silicone oil will have the priority to react with polymethylhydrosiloxane, whereas vinyl silicone oil and vinyl-MQ silicone resin will not react with polymethylhydrosiloxane until the wear-out of branched vinyl silicone

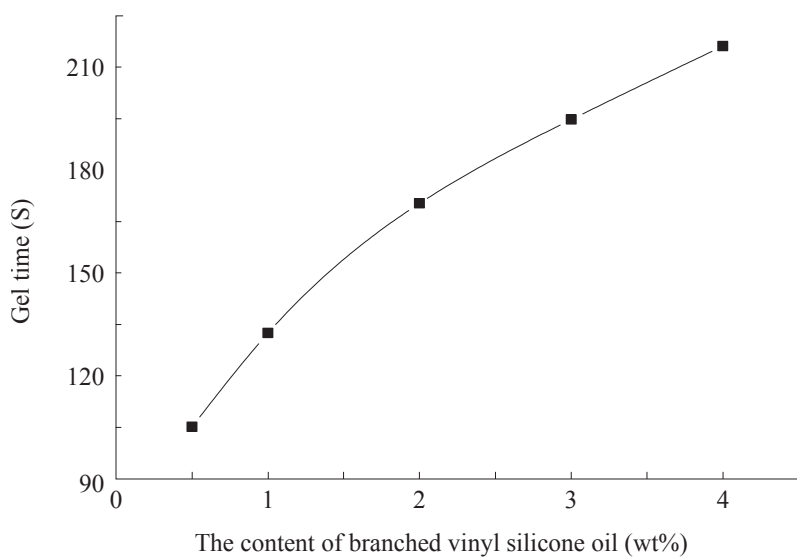


Figure 3. Influence of branched vinyl silicone oil on gel time of silicone rubber at 90°C.

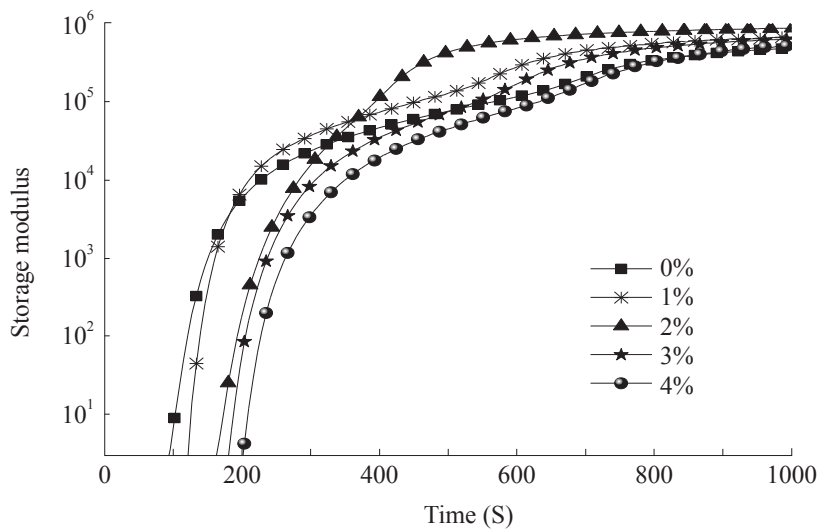


Figure 4. Variations of storage modulus of the silicone rubber for different amounts of branched vinyl silicone oil.

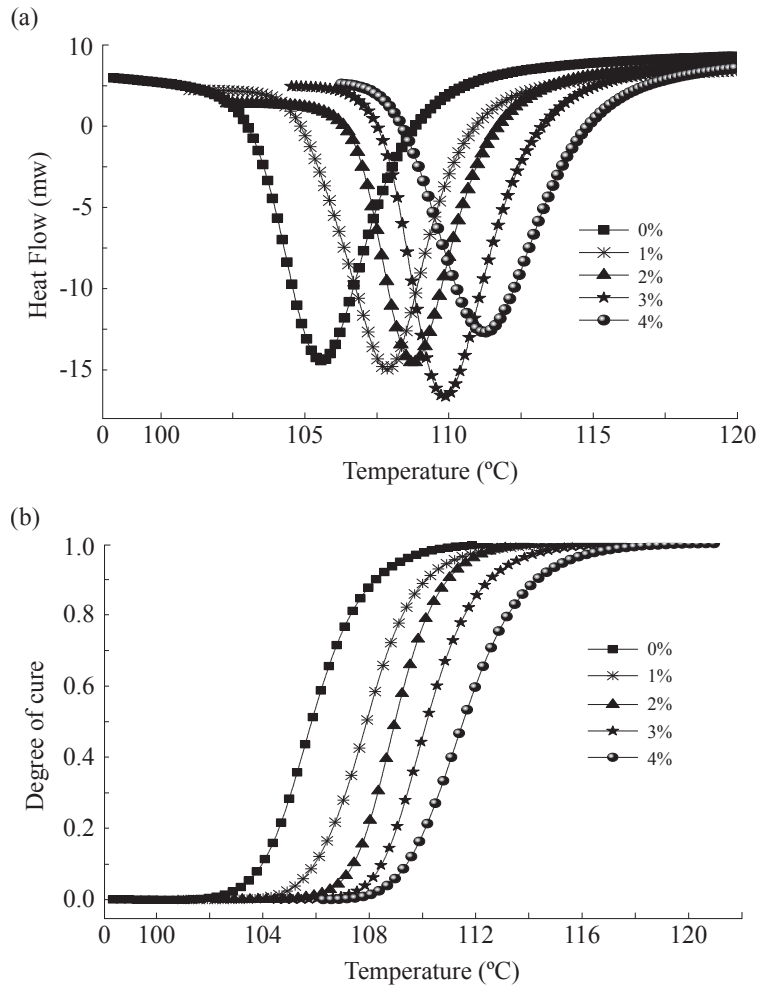


Figure 5. DSC curves of silicone rubber with different amount of branched vinyl silicone oil at a heating rate of 10°C/min. (a) Curing curve of the sample; (b) Curing degree of the sample.

TABLE 2. DSC DATA OF SILICONE RUBBER USING DIFFERENT AMOUNT OF BRANCHED VINYL SILICONE OIL

Characteristics of silicone rubber	Content of branched vinyl silicone oil/wt%					Error
	0	1	2	3	4	
T_i (°C)	99.08	101.90	103.96	105.40	106.36	±1.6%
T_p (°C)	105.66	107.91	108.78	109.92	116.32	±1.9%
T_f (°C)	114.35	116.46	117.53	119.38	124.95	±1.3%

T_i is the initial curing temperature, T_p is the peak temperature of DSC curve, T_f is the ending curing temperature.

oil. However, the accuracy of this hypothesis needs further study.

Mechanical Properties of Silicone Rubber

Figure 6 presents the influence of branched vinyl silicone oil on the mechanical properties of silicone rubber. With increasing content of branched vinyl silicone oil, tensile strength and elongation at break of silicone rubber increased initially and obtained peak value (6.51 MPa and 229.8%, respectively) at 2 wt%, then decreased in the high content range. It was found that tensile strength and elongation at break will reach the maximum values at appropriate content of branched vinyl silicone oil. From experimental results as shown in Table 3, the branched vinyl silicone oil can also improve the hardness of silicone rubber. Concentrative crosslinking will be generated at the stage of curing when the branched vinyl silicone oil was added. It can dramatically enhance the crosslink density of the silicone rubber. In addition, highly crosslinked points

will be obtained in silicone rubber with the presence of concentrative crosslinking. In other words, the interaction force between macromolecules will be enhanced in the presence of concentrative crosslinking, which could distribute stress well in the silicone rubber. This is the main reason for the excellent mechanical properties of silicone rubber modified with appropriate amount of branched vinyl silicone oil. However, if the content of branched vinyl silicone oil continues to increase, it will cause excessive crosslinking, resulting in silicone rubber with a tendency of embrittlement where the mechanical properties is poor.

Optical Properties of Silicone Rubber

The result of UV transmittance of silicone rubber with different content of branched vinyl silicone oil is shown in Figure 7. It is clear that UV transmittance of silicone rubber decreased as the loading of branched vinyl silicone oil increases. Table 3 showed

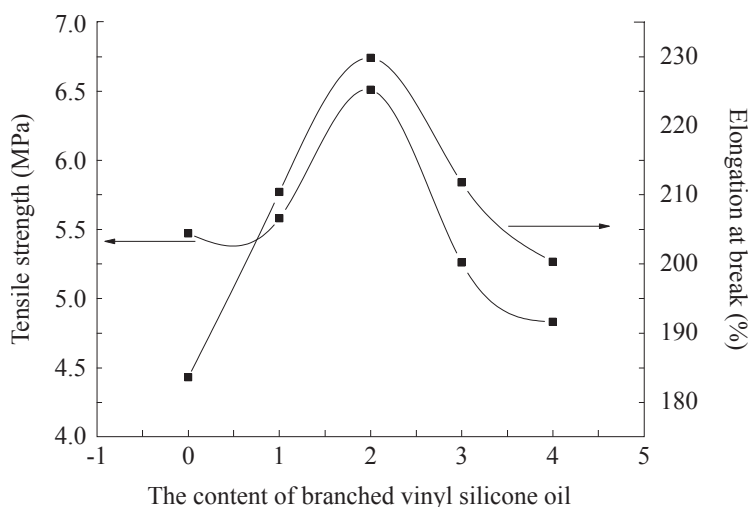


Figure 6. Influences of branched vinyl silicone oil to tensile properties of silicone rubber.

TABLE 3. INFLUENCES OF BRANCHED VINYL SILICONE OIL TO MECHANICAL PROPERTIES OF SILICONE RUBBER

Characteristics of silicone rubber	Content of branched vinyl silicone oil/wt%					Error
	0	1	2	3	4	
Shore hardness (HA)	58	61	63	62	62	$\pm 2.7\%$
Tensile modulus (MPa)	1.35	3.19	4.01	3.25	2.3	$\pm 5.9\%$
M_c (g/mol)	2097.3	1876.5	1837.6	1787.8	1579.1	$\pm 5.0\%$
$V_e \times 10^{-4}$ (mol/cm ³)	5.72	6.39	6.53	6.71	7.60	$\pm 5.1\%$

V_e is the crosslink density of silicone rubber, M_c is the average molecular weight between crosslinking points in silicone rubber.

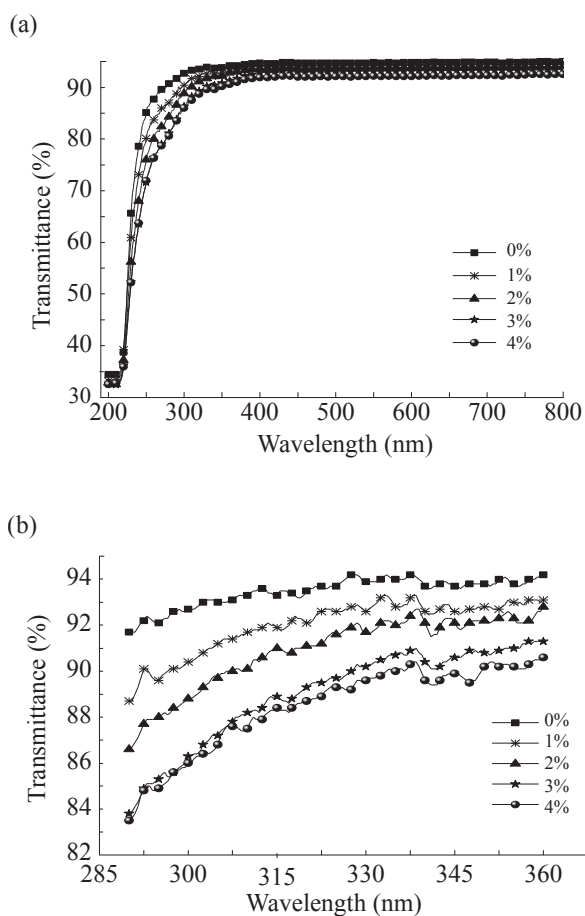


Figure 7. (a) Influence of branched vinyl silicone oil to UV transmittance of silicone rubber; (b) The enlarged spectrogram of (a) from 290 nm to 360 nm.

that crosslink density (V_c) of silicone rubber increases with the increased content of branched vinyl silicone oil which also increases the interaction force between macromolecules in the silicone rubber. Thus, this shortened the distance between the macromolecules. That could be the main reason to explain the decreasing of UV transmittance of silicone rubber with increasing content of branched vinyl silicone oil²⁷⁻²⁸. However, the UV transmittance of silicone rubber with 2 wt% of branched vinyl silicone oil will reach 92% and 89% at the 350 nm and 300 nm, respectively.

CONCLUSIONS

The branched vinyl silicone oil was found to be an excellent modifier for ultraviolet transparent silicone rubber in this study. It has an inhibiting action on the curing process of silicone rubber and also provided time for the uncured silicone rubber to be well blended and to remove air bubbles. The UV transmittance of silicone rubber exhibited the contrary tendency because the distance between the macromolecules of silicone rubber decreased as the branched vinyl silicone oil increased. Storage modulus, tensile strength and elongation at break reached the peak value at 2 wt% of branched vinyl silicone oil. The use of this amount of branched vinyl silicone oil in the silicone rubber can effectively avoid the presence of excessive crosslinking. In conclusion, the ultraviolet transparent silicone rubber has good integrated properties including mechanical and optical properties, when the content of branched vinyl silicone oil is 2 wt%.

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REFERENCES

1. ZHANG, J. AND FENG, S.Y. (2003) Effect of Crosslinking on the Conductivity of Conductive Silicone Rubber. *J. Appl. Polym. Sci.*, **89**(13), 3471–3475.
2. TANG, Y. AND TSING, R. (1999) Rheological, Extractive and Thermal Studies of the Room Temperature Vulcanized Polydimethylsiloxane. *Polym.*, **40**(22), 6135–6146.
3. HEINER, J., STENBERG, B. AND PERSSON, M. (2003) Crosslinking of Siloxane Elastomers. *Polym. Test.*, **22**(3), 253–257.
4. CHEN, L., LU, L., WU, D.J. AND CHEN, G.H. (2007) Silicone Rubber/Graphite Nanosheet Electrically Conducting Nanocomposite with a low Percolation Threshold. *Polym. Composite*, **28**(4), 493–498.
5. MEUNIER, L., CHAGNON, G., FAVIER, D., ORGEAS, L. AND VACHER, P. (2008) Mechanical Experimental Characterisation and Numerical Modelling of an Unfilled Silicone Rubber. *Polym. Test.*, **27**(6), 765–777.
6. PARK, E.S. (2007) Mechanical Properties and Processibility of Glass-fiber, Wollastonite and Fluoro-rubber-reinforced Silicone Rubber Composites. *J. Appl. Polym. Sci.*, **105**(2), 460–468.
7. HAN, Y.M., ZHANG, J.Y., YANG, Q.Y., SHI, L., QI, S.C. AND JIN, R.G. (2008) Novel Polymethoxysiloxane-based Crosslinking Reagent and its In-situ Improvement for Thermal and Mechanical Properties of

- Siloxane Elastomer. *J. Appl. Polym. Sci.*, **107**(6), 3788–3795.
8. PARK, E.S. (2008) Processibility and Mechanical Properties of Micronized Poly-tetrafluoroethylene Reinforced Silicone Rubber Composites. *J. Appl. Polym. Sci.*, **107**(1), 372–381.
9. LIU, P.B., LIU, D.L., ZOU, H.W., FAN, P. AND XU, W. (2009) Structure and Properties of Closed-cell Foam Prepared from Irradiation Crosslinked Silicone Rubber. *J. Appl. Polym. Sci.*, **113**(6), 3590–3595.
10. PARK, E.S. (2008) Mechanical Properties and Antibacterial Activity of Peroxide-cured Silicone Rubber Foams. *J. Appl. Polym. Sci.*, **110**(3), 1723–1729.
11. XU, Q., PANG, M.L., ZHU, L.X., ZHANG, Y.Y. AND FENG, S.Y. (2010) Mechanical Properties of Silicone Rubber Composed of Diverse Vinyl Content Silicone Gums Blending. *Mater. Design*, **31**(9), 4083–4087.
12. FENG, S.Y., YU, S.Q., LI, S.J., ZHANG, S.Y., CHEN, J.H. AND DU, Z.D. (1995) Effects of Some Phenylethynyl-silicon Compounds on Heat-curable Silicone Rubber III 1,1,3,3-tetramethyl- 1,3-diphenylethynyl-disiloxane. *Chinese J. Polym. Sci.*, **13**(3), 228–234.
13. FENG, S.Y., JIANG, P., YU, S.Q., ZHANG, S.Y., CHEN, J.H. AND DU, Z.D. (1995) Effects of Some Phenylethynylsilicon Compounds on Heat-curable Silicone Rubber—IV. Tetraphenylethynylsilane. *Eur. J. Polym.*, **31**(3), 309–311.
14. HU, X.W., ZHENG, Z.M. AND XU, C.H. (2007) Synthesis of New 1,3-bis(phenylethynyl)disilazanes. *Chinese Chem. Lett.*, **18**(11), 1351–1352.
15. XU, C.H. AND FENG, S.Y. (2000) Investigation of Polysiloxanes Containing Phenylethynyl Groups as Cross-linkers of Heat-curable Silicone Rubber. *J. Appl. Polym. Sci.*, **76**(10), 1154–1157.
16. FENG, S.Y. AND DU, Z.D. (1991) Effects of Some Phenylethynylsilicon Compounds on Heat Curable Silicone Rubber. I. 1,3-bis (methylphenylethynylvinyl)disiloxane. *J. Appl. Polym. Sci.*, **43**(7), 1323–1326.
17. YU, S.Q., FENG, S.Y., LI, S.J., CHEN, J.H. AND DU, Z.D. (1992) Effects of Phenylethynylsilicon Compounds on Heat-curable Silicone Rubber. Part 2. Phenylethynylvinyl-diethoxysilane. *J. Mater. Chem.*, **2**(5), 529–531.
18. ZHAO, S.G. AND FENG, S.Y. (2002) Vinyl-containing Silicone Resin as the Crosslinking Agent of Heat-curable Silicone Rubber. *J. Appl. Polym. Sci.*, **83**(14), 3123–3127.
19. LI, G.L. (1998) Polymer Chemistry of Organosilicone. Beijing: Science Press (in Chinese).
20. DAI, L.N., ZHANG, Z.J., ZHAO, Y.F., LIU, H.M. AND XIE, Z.M. (2009) Effects of Polymeric Curing Agent Modified with Silazanes on the Mechanical Properties of Silicone Rubber. *J. Appl. Polym. Sci.*, **111**(2), 1057–1062.
21. XU, Q., PANG, M., ZHU, L.X., ZHANG, Y.Y. AND FENG, S.Y. (2010) Mechanical Properties of Silicone Rubber Composed of Diverse Vinyl Content Silicone Gums Blending. *Mater. Design*, **31**(9), 4083–4087.
22. FLORY, P.J. AND REHNER, J. (1943) Statistical Mechanics of Cross-linked Polymer Networks (I) Rubberlike Elasticity. *J. Chem. Phys.*, **11**(11), 512–520.
23. CHAMBON, F. AND WINTER, H.H. (1987) Linear Viscoelasticity at the Gel Point of a Crosslinking PDMS with Imbalanced Stoichiometry. *J. Rheol.*, **31**(8), 683–697.

24. TUNG, C.Y.M. AND DYNES, P.J. (1982) Relationship between Viscoelastic Properties and Gelation in Thermosetting Systems. *J. Appl. Polym. Sci.*, **27(2)**, 569–574.
25. JARUCHATTADA, J., FUONGFUCHAT, A. AND PATTAMAPROM, C. (2012) Rheological Investigation of Cure Kinetics and Adhesive Strength of Polyurethane Acrylate Adhesive. *J. Appl. Polym. Sci.*, **123(4)**, 2344–2350.
26. SUN, X.W., ZHU, W., DU, Z.J., DU, Q.L., LI, M. AND ZHANG, C. (2013) Rheological Properties of Polyurethane Adhesive in Curing Process. *Polym. Mater. Sci. Eng.*, **29(3)**, 31–34(in Chinese).
27. SADAVARTE, N.V., HALHALLI, M.R., AVADHANI, C.V. AND WADGAONKAR, P.P. (2009) Synthesis and Characterization of New Polyimides Containing Pendent Pentadecyl Chains. *Eur. Polym. J.*, **45(2)**, 582–589.
28. JANG, W., SHIN, D., CHOI, S., PARK, S. AND HAN, H. (2007) Effects of Internal Linkage Groups of Fluorinated Diamine on the Optical and Dielectric Properties of Polyimide Thin Films. *Polymer*, **48(7)**, 2130–2143.