

Effect of Coupling Agent as Integral Blend Additive on Silicone Rubber Sealant

Liu Jiesheng,^{1,2} Wu Shaopeng,² Dong E¹

¹School of Civil Engineering and Architecture, Wuhan University of Polytechnic, Wuhan 430023, China

²Key Laboratory of Silicate Materials Science and Engineering of Ministry of Education, Wuhan University of Technology, Wuhan 430070, China

Correspondence to: L. Jiesheng (E-mail: wsljs628@yahoo.com)

ABSTRACT: Silane coupling agent (SCA) plays an important role in the improvement of adhesive properties of the silicone rubber (SR) sealant. In this study, three trifunctional silane coupling agents, (γ -aminopropytriethoxysilane (APTES), (γ -Glycidoxypropyl) methyltrimethoxysilane (GDMMS), and 3-(Trimethoxysilyl)propyl methacrylate (MPS), were used as blend additive in SR, and the effect of silane coupling agents on the properties of SR was studied. The results showed that the bond strength of samples with different combination of APTES/GDMMS, GDMMS/MPS, or APTES/MPS, was significantly improved than those of single silanes. Silanes with polar group make contribution to the bond strength increase of SR sealant. The highest bond strength value (0.53 MPa) was obtained using the combination of APTES and GDMMS. The study of the samples with (APTES and GDMMS) showed that the bond strength and tensile strength of SR increase with the increasing amount of SCA. Further increase in the SCA content makes the bond strength and tensile strength of SR sealant decrease. The increase in the amount of SCAs makes the failure modes of samples convert from adhesive failure to cohesive failure. Tack-free time decreased linearly as the amount of SCA loading increased, while the hardness increased. It can be deduced that the trifunctional SCA has catalytic effect on the crosslinking action of SR sealant. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: additives; adhesives; hydrophilic polymers; interfaces; silicones

Received 23 December 2011; accepted 23 June 2012; published online

DOI: 10.1002/app.38257

INTRODUCTION

It is well-known that as a sealant, the sealing properties are basically achieved when the sealant adheres to the adjoining based materials and is also able to absorb movement of the joint without tearing away from the substrate, or without tearing apart itself.¹ For maximum effectiveness, a sealant must remain firmly attached to the substrate at all times.

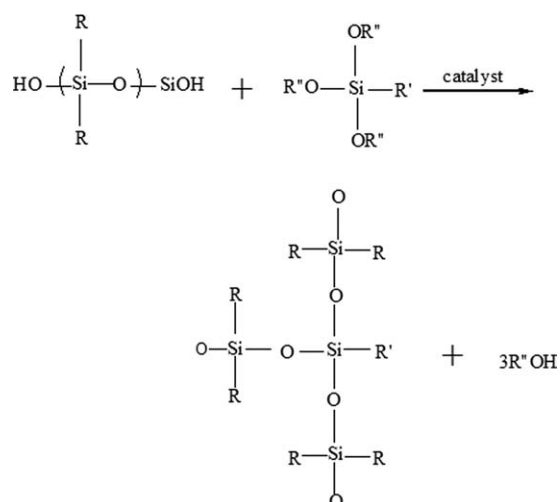
Dilute aqueous or alcohol solutions of silane coupling agents (SCA), used as primers, have been used extensively in the past few decades to improve the adhesion between the sealants and an inorganic substrate surface. It can be ascribed to the fact that the alkoxy groups of SCA can hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then active —OH groups can react with the hydroxyl groups on the substrate surface to produce a strong Si—O—Si bond. Therefore, the adhesion strength was significantly improved.^{2,3}

Using the right coupling agent, a poorly adhering paint, ink, coating, adhesive, or sealant can be converted to a material that

often maintain adhesion properties even if subjected to severe environmental conditions.^{4–6}

Many attempts have been made to study the role of SCAs in improving the adhesion properties. Unfortunately, SCA in most of the published work was used as primer,^{7–9} and little attention is given to the role of SCA added as integral blend additive. It has been reported that bifunctional SCA as additive have found broad application in polymer modification, and they have proved to be effective chain extenders for various polycondensates and reactive compatibilizers in polymer blends.¹⁰ However, the effect of trifunctional SCA used as integral blend additive on the composites is still not understood. It is therefore interesting to investigate the role of trifunctional SCA as an integral blend additive in composites.

In this study, we have prepared a two-component room temperature vulcanizing (RTV-2) silicone rubber sealant (SR) using SCA with trifunctional groups as integral blend additive, and the effect of SCAs with trifunctional groups on the SR sealant properties was investigated from the aspects of mechanical



Scheme 1. Preparation of SR.

properties, bond strength, hardness, tack-free time, failure mode of the samples and the interface.

EXPERIMENTAL

Materials

Polydimethylsiloxanes (PDMS) with a viscosity of 50,000 Pa.s, purchased from Dow Corning Company, was used. Methyltris(methylethylketoxime)silane (MOS), supplied by Hubei Huanyu Chemical, was used as the crosslinker because of its multiple functionalities. Fumed silica with the particle size less than 40 μm , obtained from Galaxy Chemical in Wuhan of China, was treated with coupling agent and added as reinforcing filler. Three trifunctional silane coupling agents, including γ -amino-propyltriethoxysilane (APTES), (γ -Glycidoxypropyl) methyl-dimethoxysilane (GDMMS), and 3-(Trimethoxysilyl)propyl methacrylate (MPS), purchased from Diamond Advanced material of Chemical Company in China, were used as adhesion promoters of SR sealant. α , ω -diolpolymethylsiloxane oil acts as a plasticizer, purchased from Dow Corning Company. No further purification of the chemicals was required.

Table I. Polymerization Recipe of the SR

Materials	Amounts of the materials (phr)
Catalyst	0.03
Silane coupling agents	0.2
	0.3
	0.4
	0.5
	0.6
PDMS	10
Filler	100
α , ω -diolpolymethylsiloxane oil	20
Crosslinker(MOS)	3.0

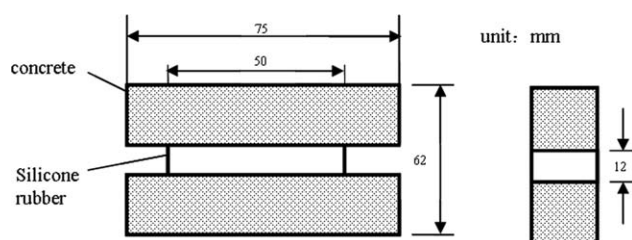


Figure 1. Test specimen.

Preparation of Silicone Rubber

The representative chemical constituents of the SR used in this study consist of crosslinker (component A) and hardener (component B) in a mixing ratio of A : B = 1 : 0.03. Modified silica added as filler and plasticizer were already added in component A. Silane coupling agents, APTES, GDMMS, and MPS, used as integral blend additives in component B. The silicone fluid (component A) underwent vulcanization at the ambient temperature for 48 h with the use of a curing agent (component B), and the required samples were allowed to cure for one week under ambient conditions. In order to compare test results conveniently, all of the samples were prepared using this condition except for changing the types and amounts of the SCAs. Thus, SR sealant was formed and the preparation mechanism was shown in Scheme 1. The polymerization recipe of the SR sealant was shown in Table I.

Characterization

The samples were manufactured as standard dumbbell pieces (gage length 60 mm \times width 12 mm \times thickness 2 mm), and the tensile tests were carried out with a Universal Testing Machine WDW-05 (Shanghai, China) at an extension rate of 200 mm/min at room temperature. Five samples were tested and an average value was obtained.

The adhesion properties of SR sealant samples with concrete substrate, as shown in Figure 1, were tested according to ASTM C719. An Instron tensile tester (Model 1011) was used and the specimens were placed in the grips of the testing machine. The specimens were then pulled at a constant velocity of 10 mm/min until the failure occurred. Hardness was measured according to ASTM D618 using 6 mm thick samples on BAREISS Shore durometer (Germany). The tack-free time of each sample was determined at room temperature using a timer in accordance with ASTM C679-87.

Scanning electron microscopic (SEM) studies of the fractured surface of lap bond strength test samples were carried out on an FEI designed Sirion 200 field-emission scanning. The accelerated voltage was 25 kV.

The crosslinking density of SR was determined by swelling method using the equation,

$$\gamma = \frac{1}{2M_c}$$

where M_c is the molecular weight between crosslinks.

$$M_c = -\frac{\rho V_0 \phi^{1/3}}{\ln(1 - \phi) + \phi + \chi \phi^2}$$

Table II. The Relative Efficiency of SCAs on the Bond Strength of SR

Coupling agent	None	KH550	KH560	KH570	KH550 KH560	KH550 KH570	KH570 KH560
Adhesion strength (MPa)	0.13	0.30	0.32	0.29	0.53	0.35	0.35

where V_0 is the molar volume of the solvent. ρ , is the density of the SR sealant. χ , the interaction parameters between the SR and the solvent (toluene), is 0.465. ϕ , the volume fraction of the swollen sample, can be determined as followed.

$$\phi = \frac{\frac{W_1}{\rho}}{\frac{W_2 - W_1}{\rho_1} + \frac{W_1}{\rho}}$$

where W_1 is the weight of SR sheet before swelling. W_2 is the weight of SR sheet after swelling. ρ_1 is the density of toluene.

RESULTS AND DISCUSSION

Effect of SCA on the Adhesion Properties of Silicone Rubber

In this study, effect of three trifunctional SCAs on the adhesive properties of SR sealant was investigated on the basis of the comparison of bond strength at identical conditions (0.03 phr catalyst, 10 phr PDMS, 100 phr Filler, 20 phr plasticizer, 3.0 phr crosslinker), as shown in Table I.

In these samples, the total amount of SCA is 0.4 phr and different classes of SCAs were designed for the SR sealant as shown in Table II. It can be seen from Table II that the bond strength was significantly improved by the trifunctional SCAs. The bond strength value (0.13 MPa) of SR sealant without SCA was obtained, and it sharply increases from 0.13 MPa to 0.32 MPa with the application of SCAs. It can be explained that SCAs are effective adhesion promoters when used as integral additives or primers for paints, inks, coatings, adhesives, and sealants.¹¹ As integral additives, they can migrate to the interface between the adhered product and the substrate, and the trifunctional SCAs function as molecular bridges at the interface of dissimilar polymer binder and substrate, resulting in the formation of chemical bonds across the interface, and the improvement of the bond strength as shown in Figure 2.¹²

Also, it can be concluded that the bond strength of samples with different combination of APTES/GDMMS, GDMMS/MPS, or APTES/MPS, was significantly improved than those of single SCA (APTES, GDMMS, MPS). A possible explanation is that

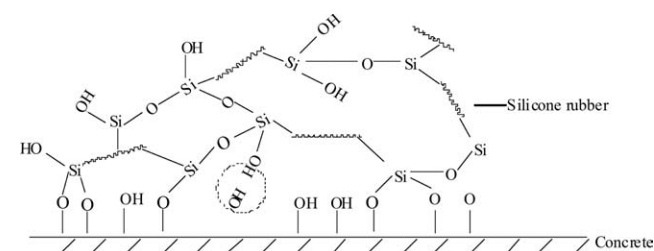
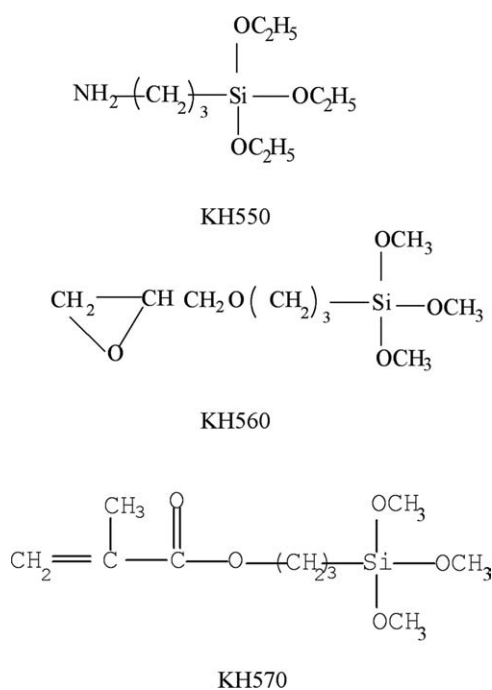


Figure 2. Mechanism of adhesion improvement with adding of coupling agent.

the selected SCA, in particular blended with other SCAs, might interact with the SR sealant system better than that of the single SCA system, and might promote chemical bonding between the SR sealant and substrate, forming stronger chemical bonding.^{13,14}

It also can be seen from Table II that the highest bond strength value (0.53 MPa) was obtained using the combination of APTES and GDMMS, which differed significantly from those of samples with the mixture of APTES+MPS, and GDMMS+MPS. The lowest bond strength value (0.35 MPa) was obtained from the sample with the mixture of APTES and MPS, and this value did not differ significantly from those of samples with GDMMS/MPS (0.35 MPa) and samples with MPS/APTES (0.36 MPa). This can be explained by the chemical reaction between the coupling agent and the substrate, and from the structure of the silane coupling agents, as shown in Scheme 2.

The trifunctional SCAs of GDMMS and APTES, migrate to the interface of the substrate, and form the chemical interactions between the SR and the substrate.¹⁵ Meanwhile, because of the polar properties with amido and epoxy groups, the mixture of GDMMS and APTES could be regarded as a “secondary chemical coupling agent.”¹⁶ It can be concluded that the samples with the mixture of GDMMS and APTES showed better bond strength than others. SCAs with polar groups make contribution to the bond strength increase of SR sealant.



Scheme 2. Molecular structure of SCA.

Table III. The Effect of Amount of SCA on the Bond Strength

SCA (phr)	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Bond strength (MPa)	0.29	0.35	0.34	0.41	0.53	0.33	0.32
Failure modes	Adhesive	Adhesive	Adhesive	Adhesive	Adhesive	Cohesive	Cohesive

A series of SR samples were prepared with different amounts of the mixture of GDMMS and APTES (0.2, 0.3, 0.4, 0.5, 0.6 phr, ratio of GDMMS to APTES 1 : 1) to investigate the relationship between the SCAs loading and the bond strength of SR sealant. Table III contains the data collected from bond strength test with different amount of SCAs. It can be noted that the bond strength of samples firstly increases from 0.29 MPa to 0.53 MPa with increasing amount of SCAs and then decreases to 0.32 MPa.

According to Plueddemann,¹⁷ the silane whether used as an additive or a primer, must concentrate on the interface and concentration of SCA has a significant influence on the bond strength of composites. SCA solution with a very low concentration may be not enough to create a coupling agent network that fully covers the surface of an inorganic material, resulting in lower bond strength.¹⁸ When the amount of SCA increases, the SR sealant can get closer contact with the concrete substrate and higher coverage rate on the surface of interface can be

obtained, which results in the increase of the bond strength. Further increase in the amount of coupling agent decreases the bond strength, probably because the higher amount of SCA may induce a multiple molecular layer on the surface of the concrete. Excess amounts of SCA play the role of impurities near interface and the wettability between the SR and substrate became worse, leading to a decrease in the bond strength. Optimum adhesion is achieved with one to three molecular layers of SCAs on the surface.³ Thus, the further increase in the amount of SCA reduces the adhesive strength of sealant.

In order to further study the effect of SCAs added as the integral blend additive on the properties of the SR sealant, the failure modes of the samples are also investigated in this study. Adhesive failure and cohesive failure are two major failure modes between the sealant and the concrete substrate. Adhesive failure occurs when the adhesive strips cleanly from the substrate, as shown in Figure 3(a). Cohesive failure is failure either side of the interface, even marginally into the bulk of the substrate or coating/glue, as shown in Figure 3(b). One can see from Table III that the increase in SCA loading makes the failure mode of the samples convert from adhesive failure to cohesive failure. It might be explained by the fact that further increase in SCA loading results in sharp decrease in mechanical strength of SR sealant. When the samples are loaded, the failure occurs within the center of the sealant.

To observe the relationship between the bond strength and interface, the research of fracture surface of interface between SR sealant and concrete substrate was conducted. After the adhesive failure of sample occurs, obvious difference of concrete substrate surface can be noticed in Figure 4. As can be seen

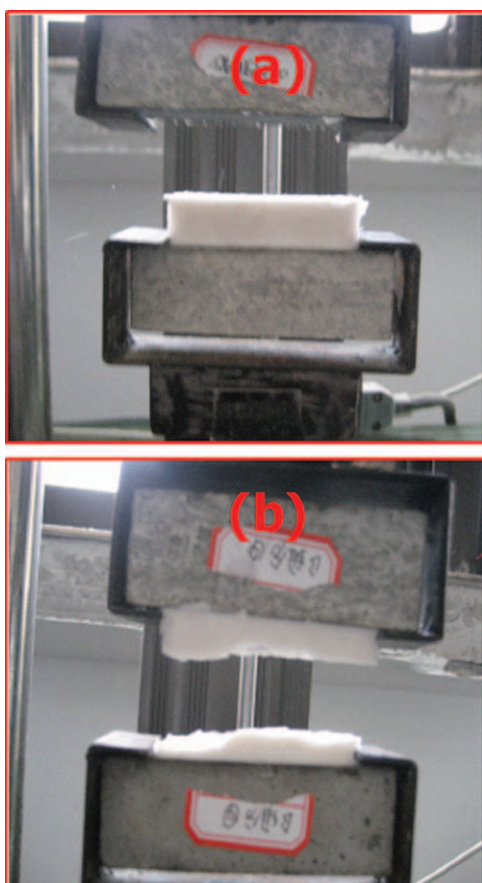


Figure 3. Failure modes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

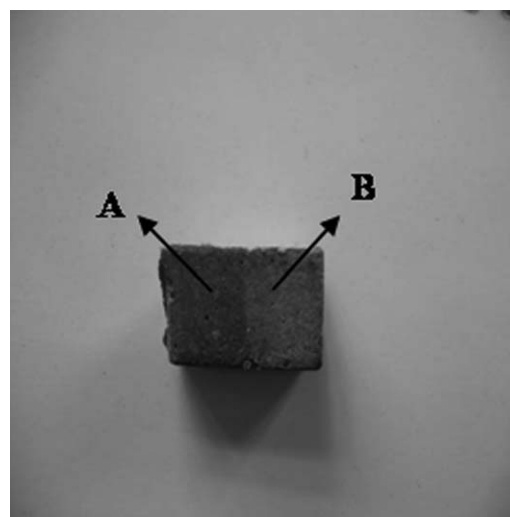


Figure 4. Photo of the surface of concrete.

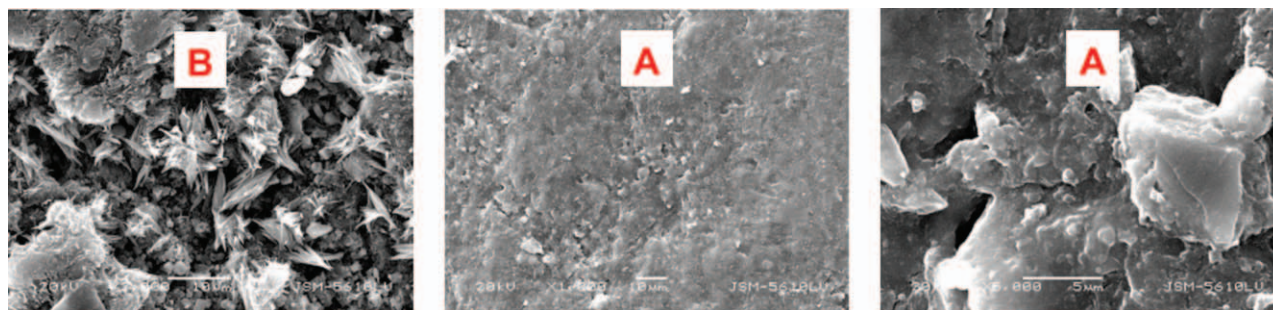


Figure 5. SEM images of surface concrete. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from Figure 4, “A” refers to the interface of the silicone sealant and concrete, and “B” part of the concrete substrate is the surface of the concrete substrate without pretreatment. The aim of the research was to gain an understanding of what takes place on the interface between the sealant and concrete substrate by comparison with the “A” and “B” part of the concrete substrate. SEM was used for the research of the interface and the chief difference can be obtained from Figure 5. It is observed from SEM image of “B” part of concrete substrate that the surface of the concrete substrate contain cement hydration products with larger crystals of $\text{Ca}(\text{OH})_2$ and ettringite, while the SEM image of “A” part of the concrete substrate, shows that the residual SR sealant covered on the surface of the concrete substrate firmly, even if the failure of the samples occurs after the tensile tests. On the basis of the results as stated above, one can conclude that the SR sealant shows good bond property with the concrete substrate, which further proved the adhesion improvement by integral blend adding of SCA.

Effect of SCA on the Mechanical Properties of Silicone Rubber

The SR sealants were prepared with different content of 0.2, 0.3, 0.4, 0.5, 0.6 phr of GDMMS and APTES in order to investigate the effect of different amount of trifunctional SCA on the mechanical properties of SR sealant. The results as shown in Figure 6 indicated that the tensile strength linearly increases with the increase of the SCA first, and further increase in SCA content

makes the tensile strength decrease. The tensile strength of SR was found to drop from polycondensation, the highest value of 1.01 MPa down to 0.78 MPa. This might be attributed to the fact that the trifunctional SCA plays the role of crosslinking agent in SR sealant. As shown in Figure 7, the increase in the SCA content results in the increase of crosslinking density of SR, which makes the mechanical properties of the sealant present uptrend. The decrease in the tensile strength at higher SCA amount may be caused by a self-condensation reaction of the hydrolyzed and polycondensation. There exist mainly two possible reactions of SCAs in SR sealant composites: homofunctional polycondensation of SCA and heterofunctional polycondensation reaction between SCA and active polysiloxane.¹⁹ As the amount of SCA increases, SCA are inclined to be homofunctional polycondensation reaction because of their good hydrolysable property. The probability of homofunctional polycondensation rises with the increasing in the amount of SCA, which weakens the interaction among the molecules of SR sealant and decrease the tensile strength of SR.

It is indicated from the results that the amount of the SCA strongly influences the crosslinking density and the mechanical properties of SR.

Effect of SCA on the Hardness of Silicone Rubber

To further assess the relationship between SCAs and SR sealant, the hardness of the SR was conducted by Shore A hardness. The results are summarized in Table IV. As seen from Table IV, one

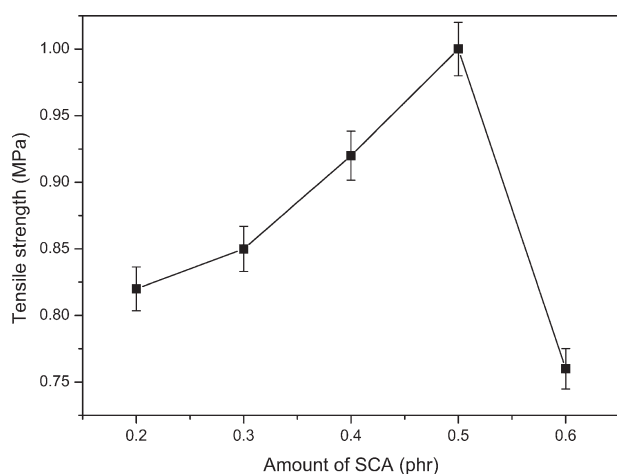


Figure 6. Effect of SCA on the mechanical properties of SR.

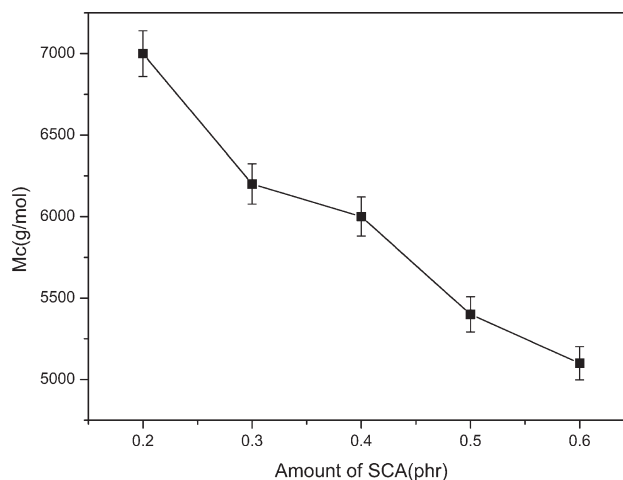


Figure 7. Effect of SCA on the crosslinking density of SR.

Table IV. Effect of Silane Coupling Agent on the Hardness of SR

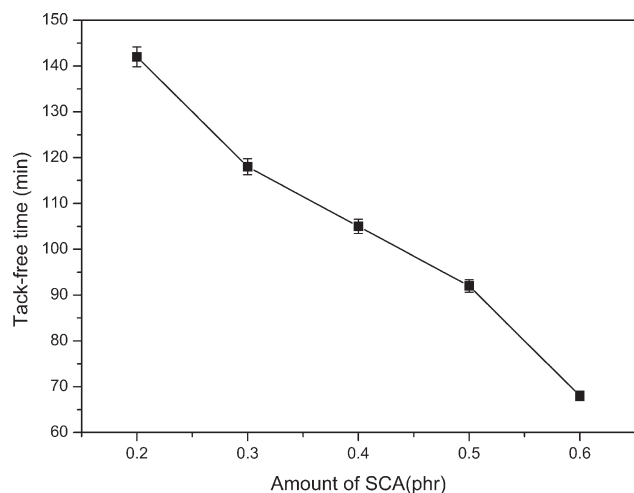
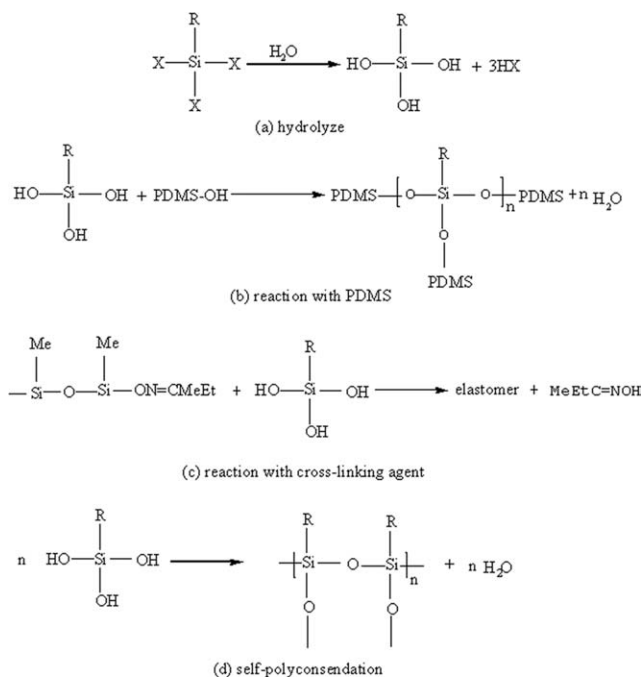
Silane coupling agent (phr)	0.2	0.3	0.4	0.5	0.6
Shore A	61	72	76	80	87

can conclude that the increase content of SCA makes the increase in the hardness of SR sealant. This can be explained that the increase of SCA makes the crosslinking density of SR sealant increase as mentioned in Figure 7, which causes the hardness of SR presents uptrend.

Effect of Silane Coupling Agent on the Tack-Free Time of Silicone Rubber

Tack-free time is the time period during which a sealant that is molded in the field remains tacky and is not yet fully serviceable. It is important for assessing sealant performance and used in identifications, classification, and quality control of products. In this study, tack-free time of SR sealant is carried out by the dry-to-touch method. The results obtained from dry-to-touch method in Figure 8, show that a significant variation in the tack-free time occurs when the amount of SCA increases from 0.2 phr to 0.6 phr. As seen in Figure 8, the tack-free time of SR sealant decreases from 160 min to 65 min with the increasing amount of SCA. This may be explained by the reactions in the SR matrix. The hydrolytic polycondensation of alkoxy-silanes which are well-known for their use in preparing composite materials is a multistep and complicated process. Several reactions in which the occurrence of trifunctional SCA hydrolyzes to active centers (SiOH) are carried out firstly in the presence of water and then the active centers undergo polycondensation with other active centers. The trifunctional SCA molecules with active SiOH can polycondensed with PDMS-OH, and crosslinking agent (MOS) in SR matrix as shown in Scheme 3(b) and (c). As the amount of SCA increase, the self-polycondensation of SCA occurred, as shown in Scheme 3(d).

From the reactions in Scheme 3, it can be concluded that the increase content of trifunctional SCA gives rise to the high number of active centers, which enhances the crosslinking reac-

**Figure 8.** Effect of silane coupling agent on the tack-free time of SR.**Scheme 3.** Reactions of SCA in the SR matrix.

tion of SR and the tack-free time decreases. Thus, it may be deduced that the trifunctional SCA has catalytic effect on the crosslinking action of SR sealant.

CONCLUSIONS

The trifunctional SCA was used as an integral blend additive in the SR sealant and the effects of SCA on the properties of SR was investigated. The results showed that the bond strength of samples first increases with increasing amount of coupling agent and then decreases from 0.53 Mpa to 0.32 Mpa. Different blends of SCAs, were significantly improved than those of single SCA, and SCAs with polar group makes contribution to the bond strength increase of SR. The increase in SCA loading makes the failure modes of samples convert from adhesive failure to cohesive failure mode. The tensile strength of SR sealant linearly increases with the increase of the SCA first, and further increase in the amount of the SCA makes the tensile strength of SR sealant decrease. The increase in trifunctional SCA content makes the increase of the crosslinking density of SR sealant and it can be concluded that the trifunctional SCA plays the role of crosslinking agent in SR sealant. Hardness of the composites increased with the increase amount of SCA. The tack-free time of SR decreased linearly as the amount of SCA loading increases. It may be deduced that the SCA has catalytic effect on the crosslinking action of SR.

ACKNOWLEDGMENTS

This work has been supported by the Key Projects in the National Science & Technology Pillar Program during the Eleventh Five-Year Plan Period in China, (2006BAB04A05), and the authors express their great appreciation for funding provided by the National Natural Science Foundation of China (11002102).

REFERENCES

1. Kim, E. S.; Kim, H. S.; Jung, S. H.; Yoon, J. S. *J. Appl. Polym. Sci.* **2007**, *103*, 2782.
2. Buyl, F. *Int. J. Adhes. Adhes.* **2001**, *21*, 411.
3. Hutchinson, A. R.; Iglauer, S. *Int. J. Adhes. Adhes.* **2006**, *26*, 555.
4. Momayez, A.; Ehsani, M. R.; Ramezaniapour, A. A.; Rajaie, H. *Cement Concr. Res.* **2005**, *35*, 748.
5. Andrzej, G.; Luc, C.; Katarzyna, K. *Mater. Charact.* **2006**, *56*, 281.
6. Kuo, K. H.; Chiu, W. Y.; Hsieh, K. H. *Mater. Chem. Phys.* **2009**, *113*, 941.
7. Teresa, V. P.; José Miguel, M. M. *Int. J. Adhes. Adhes.* **2005**, *25*, 320.
8. Lech, C.; Andrzej, G.; Mikolaj, K. *Cement Concr. Comp.* **2006**, *28*, 360.
9. Jan, R.; Victoria, A.; Mirko, N.; Cornelia, B. *Langmuir* **2008**, *24*, 12603.
10. Böhme, F.; Jakisch, L.; Komber, H.; Wursche, R. *Polym. Degrad. Stabil.* **2007**, *92*, 2270.
11. Moon, J. H.; Shul, Y. G.; Hong, S. Y.; Choi, Y. S.; Kim, H. T. *Int. J. Adhes. Adhes.* **2005**, *6*, 534.
12. Golaz, B.; Michaud, V.; Manson, J. A. E. *Int. J. Adhes. Adhes.* **2011**, *31*, 805.
13. Matinlinna, J. P.; Lassila, L. V. J.; Vallittu, P. K. *J. Dent.* **2006**, *34*, 740.
14. Chotirat, L.; Caochanchaikul, K.; Sombatsompop, N. *Int. J. Adhes. Adhes.* **2007**, *27*, 669.
15. Sathyanarayana, M. N.; Yaseen, M. *Prog. Org. Coat.* **1995**, *26*, 275.
16. Mallakpour, S.; Barati, A. *Prog. Org. Coat.* **2011**, *4*, 391.
17. Plueddemann, E. P. *J. Adhes.* **1970**, *2*, 184.
18. Xiong, G. J.; Luo, B. Y.; Wu, X.; Li, G. Y.; Chen, L. Q. *Cement Concr. Comp.* **2006**, *28*, 97.
19. Comyn, J.; Day, J.; Shaw, S. J. *Int. J. Adhes. Adhes.* **2000**, *20*, 77.