Chemical Modification of Minerals and Its Application as Silicone Rubber Reinforcing Filler

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By ultrafinecrashing and chemical modifying, the modified mineral ultrafinepowders as silicone rubber reinforcing fillers were prepared firstly, their reinforcing effect have approached to the level of silica.

Natural minerals have not been used as silicone rubber reinforcing fillers so far, though they have been used as rubber reinforcing fillers. In general, fumed silica with small size, large special surface and good aggregated structure is used as silicone rubber reinforcing filler.[1] But, because fumed silica is very expensive, the development of the silicone rubber industry is limited. If cheap natural minerals can be used as silicone rubber reinforcing fillers through some physical and chemical processing, it will promote the development of silicone rubber industry, meanwhile it will open a new field for application of natural minerals.[2]

Natural mineral is a hydrophilic substance, while the silicone rubber is a hydrophobic substance. In order to enhance the infiltration and interaction between mineral ultrafinepowder and silicone rubber matrix, the surface of mineral has to be modified. The authors have carried out researches on this area for a few years. The preliminary results are reported in this paper.

Table 1. The prescriptions and cure conditions of sample

Compounds	Pres.1	Pres.2	Pres.3
Methyl vinyl silicone rubber	120	120	120
Benzoyl peroxide	2	2	2
Diphenyl dihydroxy silicone	2.5	2.5	2.5
Fumed silica	60	40	40
Precipitated silica		40	
Minerals			40

Cure condition: time 15 min, temperature 140 ℃, pressure 10 Mpa,

Based on the works before,[3,4] talcum with flake shape and wollastonite with granular shape are chosen as raw material. After purifying, grading and preliminary grinding, the mineral powders were obtained. Using the gas steam grinder, the mineral powders were crashed into ultrafinepwders(size < 2μm and special area 100 m^2/g). Surface Chemical Modification (SCM) is a usually way for modifying. The mineral powders were put into the controlling temperature agitator, after heated to some temperature, coupling agent (wt 2%) were jet into container, the temperature was kept for 15 min, then cooled down to room temperature, the modified mineral ultrafinepowders were prepared. Mechanical Chemical Modification (MCM) is another way for modifying. The mineral powders and solid state coupling agents (wt 2%) were mixed in the agitator, then the mixtures were put into a pulverizer, the pressure and velocity were adjust suitably, the minerals were surface modified and crashed simultaneously, the modified mineral ultrafinepowders were obtained. Referring to the prescriptions and cure conditions shown in Table 1, silicone rubber samples were made using modified mineral ultrafinepowders, fumed silica and precipitated silica as filler respectively. Normal measurement methods for silicone rubber were adopted to test the physical properties of the sample. The results are shown in Table 2.

Table 2. Reinforcing effect of fillers

Filler [a]	Pres No.	Tensile kg/cm^2	100% Module kg/cm^2	Tear kg/cm	Elongation %	Hardness Shore A
T	3	51.9	42.7	15.2	153	72
T_{S1}	3	53.4	44.9	14.6	130	71
T_{S2}	3	54.1	46.4	14.8	135	73
T_B	3	57.0	36.8	17.4	213	71
W	3	46.9	41.1	13.7	123	74
W_{S1}	3	51.6	50.3	13.8	107	72
W_{S2}	3	57.2	52.3	13.2	118	73
W_B	3	53.5	30.3	16.5	237	65
FS	2	61.9	40.1	18.0	171	79
PS	1	49.6	45.0	16.0	116	79

[a] T and W express talcum and wollatonite; subscript S1, S2 and B express modification with coupling agent A-189 [HSC_3H_6-Si-$(OCH_3)_3$], A-151[$(C_2H_5O)_3$-Si-CH=CH_2] and B-5 [RO-B-$(OR')_2$]; FS and PS express fume silica and precipitated silica respectively. S1 and S2 are liquid coupling agent, surface chemical modification is used; B5 is solid coupling agent, mechanical chemical modification is used.

According to Table 2, reinforcing effects are different for two minerals though same coupling agent is used. For example, using A-151 the tensile strength is increased 4%, module is increased 9% for talcum; and tensile strength is increased 22%, modules increased 27% for wollastonite. In other words, coupling agent A-151 is more effective for wollastonite than talcum. Another phenomenon is that the reinforcing effects are different when different coupling agent are used for same mineral. As an example, for wollastonite, when A-189 is used, the tensile strength increases 10% and modules increases 22%, when A-151 is used, the tensile strength increases 22% and modules increases 27%. In other words, for wollastonite, A-151 is more effective than A-189 in reinforcing. It is obvious that there are different reinforcing effects to different minerals, coupling agents and modifying ways. The reason is that each mineral has itself structure and surface properties, and each coupling agent has itself hydrophilic and hydrophobic groups, they show different sensitive and reactive each other, and different reinforcing effects are appeared. The molecule of coupling agent contain both hydrophilic and hydrophobic groups. As the coupling agent is mixed with mineral, the hydrophilic groups would be absorbed on the surface of mineral, the

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chemical reaction takes place, leaving the hydrophobic groups around the particles, the hydrophilicity of mineral surface will drop. For example,[7] the surface energy of talcum powder is 54mJ/m^2, after modified with A-151, the surface energy is 14mJ/m^2, so that surface modified mineral can infiltrate and interact with silicone rubber matrix, and the reinforcing effect is improved. As an example, SCM mechanism of A-151 [$(CH_3CH_2O)_3$-Si-$(CHCH_2)$] is shown as follow:[5,6]

$$(CH_3CH_2O)_3Si(CHCH_2) + H_2O \rightarrow (HO)_3Si(CHCH_2) + CH_3CH_2OH \quad (1)$$

$$\text{Minerals-OH} + (HO)_3Si(CHCH_2) \rightarrow \text{Minerals-O-Si}(CHCH_2) + H_2O \quad (2)$$

$$\text{Minerals-O-Si}(CHCH_2) + SR \quad \rightarrow \quad \text{Minerals-O-SiCHCH-SR} \quad (3)$$

The filler T_B and W_B are made by MCM. The mechanism of MCM is somewhat different from SCM. According to the research by S. Wolff[8] and us,[9] the mechanism of MCM could be believed that there are more active points and electric charge on the surface of minerals produced by fractionating, shearing, colliding and other mechanical forces during the smashing process. Also, there are more defects and electric charge on the molecule of solid state coupling agent. This causes that the minerals and coupling agents interact easily at the moment of crashing. As a result, the segments of coupling agent cover on the surface of minerals, and the surface of minerals change from hydrophilicity will drop. For instance,[7] the surface energy of wollastonite powder is 36mJ/m^2, and the powder modified with B-5 is 12mJ/m^2, so that the latter can infiltrate and interact with silicone rubber matrix more easily than the former, and the reinforcing effect is enhanced.

In general, when solid coupling agent is used as modifying agent, mechanical chemical modification could be adopted; when liquid coupling agent is used as modifying agent, surface chemical modification could be adopted. According to experiment results, B-5 coupling agent is more effective to enhance tensile strength and tear strength of sample; and A-151 coupling agent is more effective to enhance tensile strength and 100% modules of sample.

From Table 1 and Table 2, it is easy to find that when 40 weight portion T_{S2} or W_{S2} replaced 20 weight portion FS or 40 weight portion PS, the 100% modules of T_{S2} sample and W_{S2} sample are superior to FS smple and PS sample, the tensile strength of T_{S2}'s and W_{S2}'s are superior to PS sample and are near to FS sample; Similarly, the tensile strength and tear strength of T_B sample and W_B sample are superior to PS sample and near to FS sample. These results show that the modified mineral ultrafinepowders can partly replace silica as a silicone rubber reinforcing filler. Morever, because modified mineral ultrafinepowders only contains $\leq$ wt 2% coupling agent, it is cheaper than silica, it has good development prospects.

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