

SCANNING ELECTRON MICROSCOPY STUDY OF FILLED SILICONE RUBBER

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ABSTRACT

The fracture surfaces of a number of silicone vulcanizates were investigated by the use of scanning electron microscopy (SEM). It was found that the difference in the presence and absence of filler, the variation of its surface modification as well as the history of thermal aging of the vulcanizates, all of these factors made difference in surface morphology of the fractured surface. This was correlated with the strength of the vulcanizates. The reinforcing effect of filler and the process of fracture were discussed.

As the interaction between polymeric chains of silicone rubber is weak, the strength of its vulcanizate is very low. It can be increased tremendously, however, by incorporation of silica. The size, structure and surface properties of filler affect the vulcanizate very much. In the previous papers the authors have studied the interaction of silica with polyorganosiloxanes^[1]. Special attention was paid to the effect of filler surface modification on reinforcement and thermal stability of the vulcanizate^[2,3]. It was pointed out that the modification with hexamethyldisilazane (HMDS) or diphenyldihydroxysilane (DDS) gave better result^[4].

SEM is able to make direct observation on morphology of surface to estimate particle size and its distribution. However, only a few works on SEM touched the filled silicone rubber, mainly dealing with the state of dispersion before and after mixing on roller^[5] and with the effect of crosslink density^[6]. This work will discuss the SEM micrograph of the fracture surface of silicone vulcanizate and correlate it with the reinforcing effect of filler.

EXPERIMENTAL

1. Sample composition

- A. unmodified silica
- B. silica modified with hexamethyldisilazane
- C. silicone gum mol. wt. 4×10^5
- D. gum, 100, diphenyldihydroxysilane (DDS), 10
- E. gum, 100, ground silica 40
- F. gum, 100, unmodified silica 40, Fe_2O_3 , 3
- G. gum, 100, silica modified with silicone oil, 40
- H. gum, 100, silica modified with HMDS, 60, Fe_2O_3 , 3
- I. gum, 100, silica unmodified 40, DDS, 10, Fe_2O_3 , 3
- J. gum, 100, silica unmodified 40, DDS, 10

2. Specimen preparation

Specimen A was made from dispersion of unmodified silica in chloroform containing 1% silicone gum; specimen B was from the dispersion of HMDS modified silica in the same solvent. The addition of small amount of gum will fix the particulate in position when they were sputtercoated with gold.

Specimen C to J were made from the corresponding composites by mixing separately with 1% di-tert butyl peroxide on roller for 10 min, vulcanized at 170°C for 14 min in press, stabilized at 200°C for 24 h. Specimen I and J were thermal aged at 300°C for 72 h in addition. They were cut into dumbbell form with cross section of 2 × 3mm, stretched at a speed of 50cm/min up to break. The fracture surface was sputter-coated with gold and micrograph was taken with SEM DX-3 at typical region.

RESULTS AND DISCUSSION

Some physical properties of a number of typical vulcanizates are shown in Tab. 1. Both the tensile strength and elongation at break of the gum vulcanizate are very low. They increase greatly after incorporation of silica. The best results were obtained from the vulcanizates filled with HMDS or DDS modified silica. As is also shown thermal aging do not effect the strength of vulcanizate so severely in the presence of antioxidant, Y-ferric oxide, than in the absence of it.

Table 1 Filler effect on strength and thermal stability of silicone rubber

Sample	Tensile strength (kg/cm ²)	Elongation at break (%)	Tensile strength (kg/cm ²)	Elongation at break (%)
	(after 24 h at 200°C)		(after 72 h at 300°C)	
C	6	160	----	----
F	65	238	45	200
H	110	478	54	120
I	114	560	68	304
J	111	550	51	190

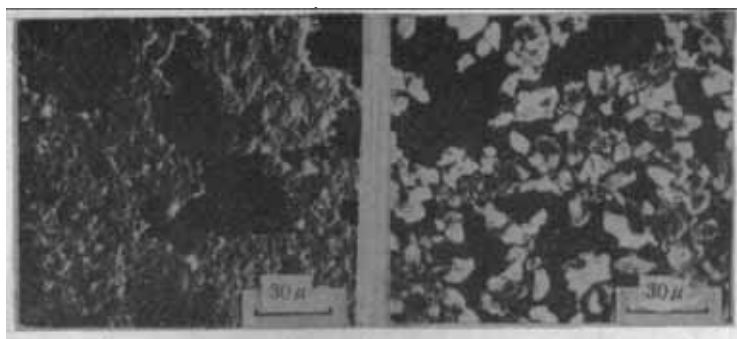


Fig. 1 Silica unmodified

Fig. 2 Silica modified with HMDS

The following description can be ascribed to the SEM micrograph:

- (1) Sample A is cotton like (as shown in Fig. 1); sample B looks globular (Fig. 2).
- (2) For specimen C there exist stripes with ridges on fracture surface (Fig. 3a) which is smooth even at higher magnification (3b).



Fig. 3a Gum vulcanizate

Fig. 3b Gum vulcanizate

Similar micrographs were obtained from specimen D and E (Fig. 4, 5).



Fig. 4 Vulcanizate with DDS

Fig. 5 Vulcanizate with ground silica

- (3) For specimen F the fracture surface is rough with irregular waves; filler particles are hardly visible (Fig. 6a, 6b).

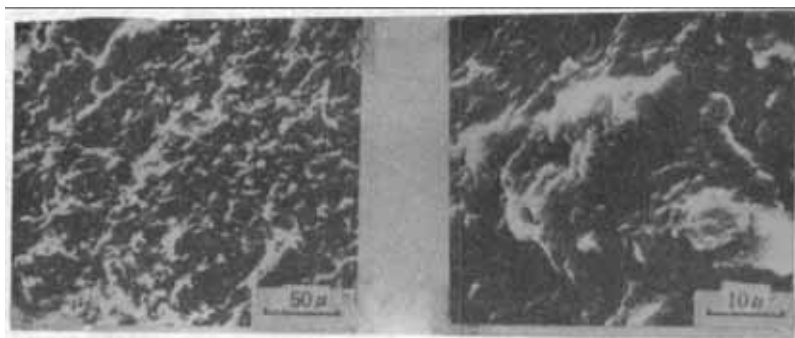


Fig. 6a Vulcanizate with silica unmodified

Fig. 6b Vulcanizate with silica unmodified

- (4) Specimen G, H, I and J, all show smooth background scattering with filler particles. Dimension of them are mostly in the range of several microns. A few big ones lie in ten or twenty microns (Fig. 7,

8 and 9). There are cracks on these surfaces that change direction or bifurcate on passing by the particles, as seen in Fig. 9a and 9b.



Fig. 7 Vulcanizate with silica modified with silicone oil

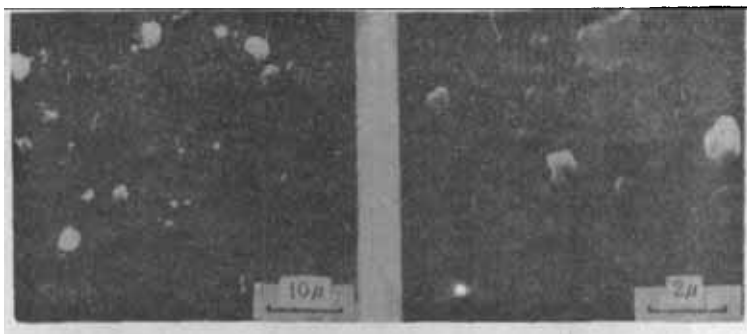


Fig. 8a Vulcanizate with silica
modified with HMDS

Fig. 8b Vulcanizate with silica
modified with HMDS

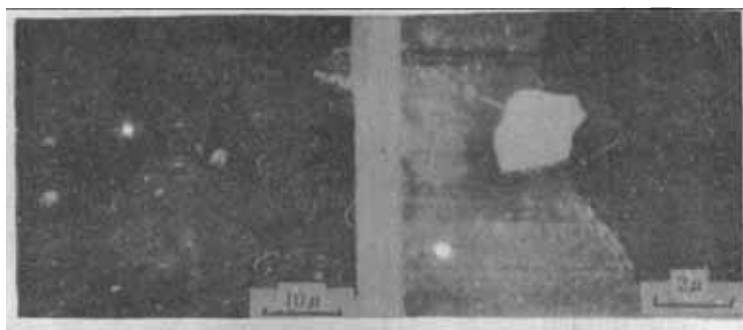


Fig. 9a Vulcanizate with silica
modified with DDS

Fig. 9b Vulcanizate with silica
modified with DDS

(5) The fracture surface morphology of specimen I containing antioxidant did not change significantly after thermal aging (Fig. 10), but it turned rough when antioxidant was omitted (Fig. 11).

In the light of reinforcement and fracture theory^[7,8] of polymer and with reference to the results of SEM of filled rubber from the other publications we are trying to elucidate the above phenomena.



Fig. 10 Vulcanizate with anti-oxidant after thermal aging

Fig. 11 Vulcanizate without anti-oxidant after thermal aging

In Fig. 1 the original state of fumed silica is depicted. Hydroxy groups on the surface ($3.6/100\text{\AA}^2$) forming strong hydrogen bond, make the particulates to agglomerate like cotton. Fig. 2 is the picture of HMDS modified silica with residual hydroxy groups of $0.84/100\text{\AA}^2$, since bulk of them has been replaced by OSiMe_3 group. Cotton-like state could not be maintained any more; they agglomerate yet into granules under the action of added gum.

Initiation and extension of microcracks are usually considered as the main course of polymer fracture. If the crack is not impeded by obstacles such as crystals of filler it will extend straight forward up to the fracture of material. Silicone gum vulcanizate has only very weak interaction among the chains, contains no crystallization either. The crack extension would meet only slight impedance so that the fracture can result from initiation of a few microcracks. That is why only stripes and big lumps with smooth surface are seen in Fig. 3a and 3b. Addition of ground silica to the gum did not change the situation very much, as shown in Fig. 5. This is obviously due to its big size and its weak interaction with rubber chain.

The cotton-like structure of unmodified silica is so strong that is hard to disintegrate thoroughly during compounding with gum. Its dispersion is not very good. However, once its surface comes to close contact with polymer, the hydroxy group will form hydrogen bond of medium strength with oxygen atom of siloxane chain. The crack extension is impeded. The failure can be resulted only from rupture of numerous strong bonds, producing irregular rough surface accordingly (Fig. 6a, 6b). Filler particles are scarcely visible over there. This may be a result of unhomogeneous dispersion and retardation of boundary cleavage.

The filler modified with HMDS, DDS or hydroxysilicone oil are apt to wet by siloxane chains. They disperse easily and evenly in polymer. Innumerable dipole-dipole interactions occur on the boundary, although the amount of hydrogen bonds has been reduced. This kind of interaction should be stronger than that between carbon black and organic polymer. The stress applied will be dispersed evenly throughout the particles such that the crack extension is impeded effectively. Fracture becomes possible only by initiation of a great number of bond cleavages. Thus we see smooth background, no more waves remains (Fig 7, 8 and 9). Since boundary interaction of filler is somewhat weakened due to surface modification, probability of interface rupture increases; filler particles left on the fractured surface, as seen in these figures. The size of them is consistent with the other observation. Question may arises whether these particles are brought in from DDS added on compounding. We have mixed purposely this compound to silicone gum, see Fig. 4, but no particles like that in Fig. 8, 9 were observed. Moreover, the presence of crack on the fracture surfaces that

change of direction or bifurcate is an unanimous evidence illustrating the role of filler on dispersion of stress and impedance of crack extension.

The addition of Y-ferric oxide will retard the oxidation. The fracture surface changes very little after thermal aging in the presence of the antioxidant; it becomes rough in its absence. The strength reduction is less severe in the former case, too.

De Vries^[9] has determined by EPR the radicals produced by cryogenic fracture of filled polyisoprene. A correlation between the radical concentration and filler effect was reported. No detectable production of free radical was observed when the sample was filled with filler providing very weak interaction with the matrix. The fracture surface looks very uneven. An easily detectable concentration of radical produced in the sample with filler of intermediate interaction. An order of magnitude more radicals was observed in the sample with filler of strong interaction, the fracture surface appears smooth with a few particles of filler on it. This experiment illustrated the relationship between the amount of cleaved chains and the effect of filler polymer interaction. Surface roughness can be used as another criterion. They are consistent with the result of our work. De^[10] made a study on the fracture surface of filled natural and EPM rubber with SEM. He found also the effect of surface modification on morphology of fractured cross section which was similar to our result.

SUMMARY

The fracture surfaces of a number of silicone rubbers were studied with SEM. Different morphologies were found in three categories of vulcanizates: (1) Vulcanizate of pure gum, vulcanizates with the addition of ground silica or DDS additive are of low strength. The cross section of them are composed of big stripes and lumps. (2) Vulcanizate filled with fumed silica is much more strong; it has a rough surface with irregular waves. (3) Vulcanizates filled with HMDS or DDS modified silica is very high in strength, have surface with smooth background on which filler particles and microcracks are clearly visible. These results were discussed in connection with the filler effect and mechanism.

Keywords:

Scanning electron microscopy, Silicone rubber, Filler effect, Silica, Fracture of polymer.

REFERENCES

- [1] 李玉福、夏永侠、徐东鹏、李光亮, *J. Polym. Sci., Chem. Ed.* **1981** 19, 3069.
- [2] 胡春野、李光亮, 第一次全国橡胶会议论文选 (Selected Papers from the Chinese First Symposium on Rubber Chemistry and Technology), **1979**, 74.
- [3] 王天用、李光亮, 特种橡胶制品 (*Processing of Specialty Rubber*), **1981**, (5) 10.
- [4] 李玉福、徐东鹏、李光亮, 特种橡胶制品 (*Processing of Specialty Rubber*), **1982**, (5) 1.
- [5] Boonstra B.B.; Cochrane H. and Dannenberg E. M., *Rubber Chem. Techn.*, **1975** 48, 579.
- [6] Magman K. G. and Berstrand G. L., *Intern. J. Polym. Mater.*, **1977** 5, 231.
- [7] Smith T. L., *Polym. Eng. Sci.*, **1977** 17 129.
- [8] Voet A., *J. Polym. Sci., Macromol. Rev.*, **1980** 15, 328.
- [9] De Vries K. L., *Rubber Chem. Techn.*, **1975** 48, 457.
- [10] Pal P. L.; Chakraverty S. N. and De S. K., *J. Appl. Polym. Sci.*, **1983**, 28, 659.