

실리카로 보강한 폴리디메틸실록산 탄성체의 물리적인 특성

박 보 영 · J. E. Mark

Department of Chemistry and the Polymer Research Center, University of
Cincinnati, Cincinnati, OH 45221, U. S. A

(1989년 5월 19일 접수)

Silica as Reinforcing Filler in a Polydimethylsiloxane Elastomer

B. Y. Park and J. E. Mark

Department of Chemistry and the Polymer Research Center, University of
Cincinnati, Cincinnati, OH 45221, U. S. A

(Received May 19, 1989)

요약 : 분자의 양 말단에 $-OH$ 기가 부착된 Polydimethylsiloxane(PDMS) emulsion에 silica와 sodium silicate 용액을 첨가한 탄성체의 물리적인 성질을 고찰하였다. Silica로 충전한 PDMS 탄성체는 등온 응력-신장 실험에서 물성이 크게 향상되고 있으며, 보강 효과로 인하여 변형이 큰 영역에서 모듈러스(f^*)는 고분자와 입자간의 debonding 결과 하향곡선으로 감소한다. 변형이 지속됨에 따라 PDMS 쇄의 strain-induced crystallization으로 인한 배향성은 모듈러스를 상향곡선으로 증가시키고 있다. 그리고, 이들 탄성체의 파괴에너지(E_r)는 silica 함량이 증가함에 따라 증가함으로써 탄성체의 성질은 더욱 tough하게 나타났다.

Abstract : Silica and sodium silicate solutions were blended into samples of hydroxy-terminated polydimethylsiloxane (PDMS) emulsions, which were then end linked into elastomeric networks. The equilibrium stress-strain isotherms measured in elongation show that silica greatly increased the ultimate properties of the elastomers and were thus effective reinforcing fillers. At high elongation, the reduced stress for the filled elastomer showed downturns due to debonding between polymer and filler, and upturns due to strain-induced crystallization. The energy for rupture (E_r) at high filled elastomer was higher than that of the low one.

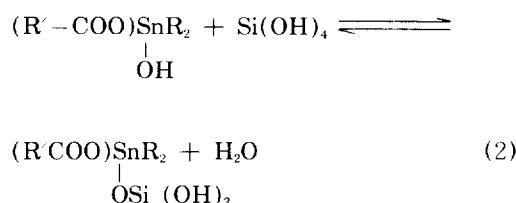
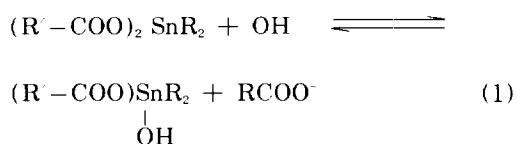
INTRODUCTION

One of the standard fillers used to reinforce elastomeric materials is silica (SiO_2).¹⁻³ It has excellent reinforcing capabilities, and there is a great deal of literature on this aspect of its behavior and on a number of its other physical

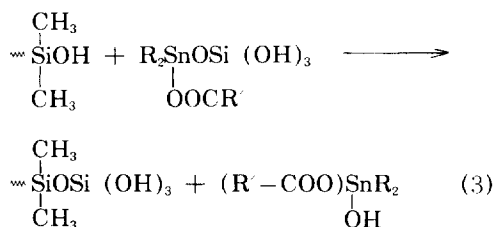
properties as well. The polymer chain ends are terminated with silanol, and the weight-average molecular weights are $2 \times 10^5 g mol^{-1}$. Weight-average particle sizes are approximately $0.3 \mu m$.^{2,4}

The dispersion is prepared by blending the PDMS emulsion with silica (aerosil 130, particle size : 16nm) and a 45% sodium silicate solution,

The organotin compound is used as curing catalyst, di-octyltin-dilaurate (DOTDL). The catalyst reacts in alkaline medium with water-soluble silicate at ambient temperature :



The formed silastannoxanes are more hydrophobic and therefore migrate to the oil-water interface, where they condense with silanol groups present on the surface of the PDMS emulsion :



It is assumed that polymers with short, i. e., monomeric or dimeric, terminal silicate groups migrate into the interior of the PDMS emulsion where they cause crosslinking with the oil phase. Polymers with longer terminated silicate groups are solvated by water thereby causing steric and ionic stabilization of PDMS particles at the interface. Vulcanization is thus already terminated prior to the evaporation of water.

The stabilizing effect is destroyed upon evaporation of water, and silica and siloxane molecules now come in close contact with each other. Hydrogen bonding is the last step in the formation of the elastomeric network.^{4,5} The

degree of reinforcement for the increasing SiO₂ filler contents is determined from equilibrium stress-strain measurements in elongation.⁶⁻⁹

EXPERIMENTAL

Materials

The PDMS emulsion was purchased (Dow Corning Corp.) as was the catalyst, di-octyltin-dilaurate (M and T Chem. Inc.), as well as the sodium silicate solution (Fisher Sci. Co.), which was used to adjust the PH. Amorphous silica used to reinforce the elastomer, was blended into PDMS emulsion.

Preparation of elastomer and filled elastomer: The unfilled elastomer of PDMS emulsion was blended with DOTDL and the sodium silicate solution was added to adjust the PH to about 11.

The filled systems were blended with silica according to above procedure. The mixture was cast into a mold and cured for a couple of days. The sheets, which were 1.5mm thick, were pressed with a hand press. After 20 days of curing, test strips approximately 3mm×50mm, were cut from the sheets.⁶⁻⁹ The compositions of the mixture used are given in Table 1.

Effect on Swelling

The weighed strips were placed into a n-heptane until swelling equilibrium was achieved, approximately 4 days. After maximum swelling, the strips were weighed carefully and then dried under vacuum to a constant weight. The volume fraction of polymer (V_f) in the swollen

Table 1. The Compositions of the Mixture

Sample	S-1	S-2	S-3	S-4	S-5
Ingredient	Wt. %				
PDMS Emulsion	99.5	94.5	89.5	84.5	79.5
DOTDL	0.5	0.5	0.5	0.5	0.5
Sodium Silicate Solution	R.Q*	R.Q	R.Q	R.Q	R.Q
Silica	—	5	10	15	20

*R.Q : Required Quantity.

filled systems was then obtained.¹⁰

Stress-Strain Measurements

Equilibrium stress-strain data were obtained in the usual manner,¹¹⁻¹³ on the unswollen samples at 25°C.

Measurements were made using a sequence of increasing values of the elongation or relative length, L of the sample, with frequent inclusions of values out of sequence to test for reversibility. Two elastomeric properties were of interest : Nominal stress, given by $f^* \cong f/A^*$, where f is the elastic force and A* the undeformed cross-sectional area, and the reduced stress or modulus^{12,13} defined by $\{f^*\} \cong f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_1$ is the elongation or relative length of sample. The measurements were carried out to the rupture points.

RESULTS AND DISCUSSION

The degree of swelling is usually expressed in terms of its reciprocal, and the volume fractions (V_f) in the filled system are shown in the second column of the Table 2. V_f values increase with increasing SiO₂ content which for a high crosslink density means a greater restraint on the network and thus results in lower swelling.¹⁰ The equilibrium stress-strain isotherms obtained on the network were represented as plots of the modulus versus reciprocal elongation, as suggested by the Mooney-Rivlin equation,^{8,14}

Table 2. Filler Concentrations and Stress-strain Results

Sample	V_f	Stress-Strain Results ^a				
		$2C_1$ (N mm ⁻²)	$2C_2$ (N mm ⁻²)	α_r	$(f/A^*)_r$ (N mm ⁻²)	$(10^9 E_r)$ (J mm ⁻³)
S-1	0.04	0.0025	--	11.0	0.06	0.30
S-2	0.08	0.035	0.032	6.0	0.23	0.70
S-3	0.11	0.074	0.062	3.5	0.28	0.40
S-4	0.14	0.08	0.19	6.0	0.63	1.85
S-5	0.17	0.13	0.18	4.5	0.75	1.76

^aMooney-Rivlin constants, ultimate properties and energy required for rupture.

$$\{f^*\} = 2C_1 + 2C_2 \alpha^{-1} \tag{4}$$

where $2C_1$ and $2C_2$ are constants independent of elongation α .

The former is an approximation to the high deformation modulus,¹¹ and the latter is a measure of the increase in nonaffineness with increase in elongation.^{12,13,15}

Typical results for the filled network systems are shown in Figure 1. The curves are approximately linear at moderate elongation. Non-linearity at low elongation is due to strong bonding between polymer and filler for higher filler concentration and at higher elongation is due to strain-induced crystallization.^{9,16,17} The upturns in $\{f^*\}$ arising from the reinforcing

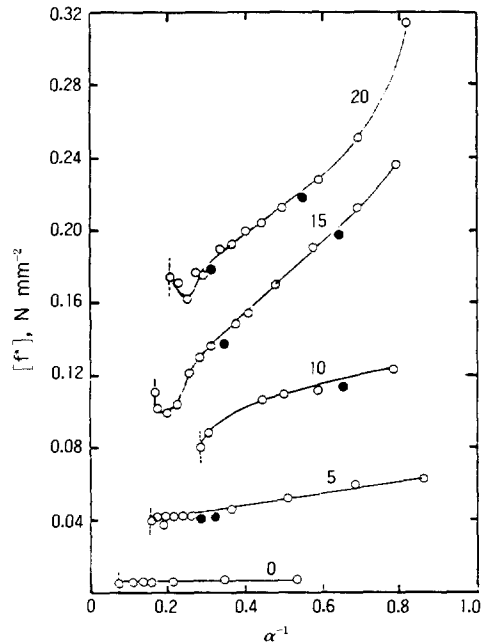


Fig. 1. Stress-strain isotherms at 25°C for the silica-filled PDMS networks, represented as the dependence of the nominal stress or modulus on reciprocal elongation. The open circles locate the results, obtained using a series of increasing values of elongation, and the filled circles the results obtained out of sequence to test for reversibility. Each curve is labelled with the wt. % filler present in the networks, and the vertical dashed lines locate the rupture points.

effects of the fillers are preceded by downturns presumably arising from the straightening and aligning of the network chains in the (oriented) crystallites. The decrease in modulus just prior to the upturns, may indicate that the debonding that is occurring between filler and polymer is complete. Values of the elongation constants $2C_1$ and $2C_2$ obtained from least-squares analysis of the linear portions of the isotherm are given in columns three through four in Table 2.

The modulus greatly increases with an increase in the silica content. For the sample having the largest SiO_2 content, the increase in modulus was 13 times larger than that of the unfilled sample. This is similar to the amount of reinforcement obtained from in-situ precipitated SiO_2 and TiO_2 .¹⁸⁻²⁰ The same equilibrium stress-strain data are shown as plots of the nominal stress versus elongation in Fig. 2.

The advantage of this representation is that the area under each curve represents the energy E_r , required for rupture,^{21,22} which is a standard measure of toughness. Values of the α_r , and

nominal stress $(f/A^*)_r$ at rupture and E_r , obtained from the isotherms, are given in the last five through seven columns in Table 2.

Although α_r is relatively constant in filled systems, both $(f/A^*)_r$ and E_r increase with increasing SiO_2 content, as expected.

CONCLUSION

The equilibrium stress-strain isotherms measured in elongation show that silica greatly increased the ultimate properties of the elastomers and were thus effective reinforcing fillers. V_f values increase with increasing SiO_2 content which for a high crosslink density means a greater restraint on the network and thus results in lower swelling in n-heptane. Non-linearity at low elongation is due to strong bonding between polymer and filler for higher filler concentration and at higher elongation is due to strain-induced crystallization. The energy for rupture (E_r) at high filled elastomer was higher than that of the low one.

Acknowledgement : It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant No. 84-15082(Polymers Program : Materials Science Division).

REFERENCES

1. E. L. Warrick, O. R. Pierce, K. E. Polmanter, and J. C. Saam, *Rubber Chem. Technol.*, **52**, 437(1979).
2. J. C. Saam, D. Graiver and M. Baile, *Rubber Chem. Technol.*, **54**, 976(1981).
3. W. J. Bobear, in "Rubber Technology", 2nd Ed., by M. Morton, Van Nostrand Reinhold, New York, 1973.
4. H. G. Elias and F. Vohwinkel, "New Commercial Polymers 2", Gordon and Breach, Science Publishers, Inc., New York, 1977.
5. C. J. Evans and S. Karpel, "Oranotin

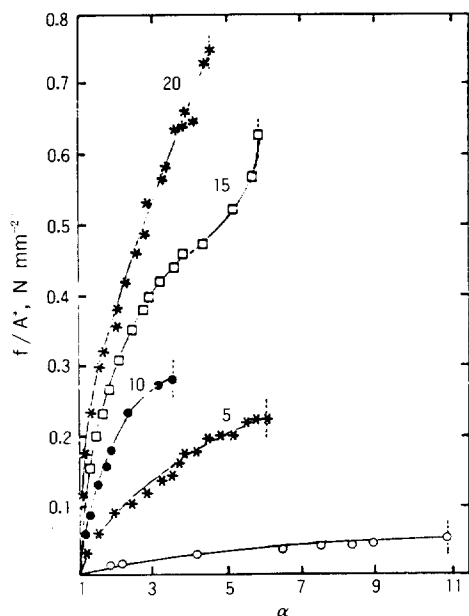


Fig. 2. The stress-strain isotherms represented as the dependence of the nominal stress on elongation. See legend to Figure 1.

Silica as Reinforcing Filler in a Polydimethylsiloxane Elastomer

- Compounds in Modern Technology", Elsevier Science Publishing Company, Inc., New York, 1985.
6. J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006. (1977).
 7. J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635(1966).
 8. J. E. Mark, *Polymer J.*, **17**, 265(1985).
 9. M. A. Sharaf and J. E. Mark, *Polym. Eng. Sci.*, **26**, 304(1986).
 10. B. B. Bonstra, *Polymer.*, **20**, 694(1979).
 11. J. E. Mark, *Rubber Chem. Technol.*, **48**, 49 5(1975).
 12. J. E. Mark, *Acc. Chem. Res.*, **18**, 202 (1985).
 13. J. P. Queslel and J. E. Mark, *Adv. Polym. Sci.*, **65**, 135(1984).
 14. L. R. G. Treloar, "The Physics of Rubber Elasticity", Oxford University Press, Clarendon, 1975.
 15. P. J. Flory, *Polym. J.*, **17**, 1(1985).
 16. J. E. Mark, *Polym. Eng. Sci.*, **19**, 409 (1979).
 17. T. K. Su and J. E. Mark, *Macromolecules*, **10**, 120(1977).
 18. J. E. Mark, *Brit. Polym. J.*, **17**, 144(1985).
 19. G. S. Sur and J. E. Mark, *Polym. Bulletin*, **20**, 131(1988).
 20. S. B. Wang and J. E. Mark, *Polym. Bulletin*, **17**, 271(1987).
 21. M. A. Llorente, A. L. Andrady, and J. E. Mark, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 621(1981).
 22. M. Y. Tang, A. Letton, and J. E. Mark, *Coll. Polym. Sci.*, **262**, 990(1984).