

In-Situ Generation에 의한 Polydimethylsiloxane Networks의 강화

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In-Situ Generation of Reinforcement in Polydimethylsiloxane Networks

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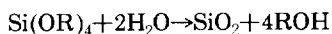
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요약 : Amino group을 함유하고 있는 사전-경화된 Polydimethylsiloxane networks에 silica를 filling시키는 새로운 방법인 in-situ generation에 관한 연구로, tetraethoxysilane (TEOS)의 가수분해를 시키는데 필요한 무기 및 유기염 촉매 효과에 관하여 검토하였다. 즉, 상온에서 침전된 silica의 양으로 촉매의 효과를 비교하였으며, 강화의 정도는 stress-strain isotherms 측정에서 upturns현상을 비교하여 판단하였다. 이와같은 관점에서, ethylamine이 가장 효과적 이었으며, 기타 다른 화합물은 ethylamine 보다는 덜 효과적 이었지만 상당한 효과가 있음이 관찰되었다.

Abstract : The catalytic effect of inorganic and organic bases was studied for the hydrolysis of tetraethoxysilane (TEOS). The reaction employed for the precipitation within already-cured polydimethylsiloxane networks containing amino groups. These substances were compared with regard to the amount of silica precipitated at room temperature, and the extent of reinforcement was judged by the upturns in the stress-strain isotherms at high elongations. From this point of view, ethylamine was the most effective and all the other compounds have similar effects but less than that.

INTRODUCTION

The chemical reactions used in the sol-gel technology^{1,2} for preparing ceramics are illustrated by the hydrolysis of an alkoxy silane.



The process first gives a swollen gel which is then dried, fired, and densified into the final, monolithic piece of silica. There have now been a number of additional studies using essentially the same reactions, but in a very different context.³⁻¹²

Specifically, the hydrolysis reactions are carried out within a polymeric matrix, with the silica generated in the form of very small, well-dispersed particles. When the matrix is an elastomer these particles provide the same highly desirable reinforcing effects obtained by the usual blending of a filler (such as carbon black) into polymers (such as natural rubber) prior to their being crosslinked or cured into tough elastomers of commercial importance.

The reactions were typically carried out at

room temperature within a tetraethoxysilane (TEOS)-swollen network of polydimethylsiloxane (PDMS) without any typical functional group. The reinforcing effects of these fillers have been clearly demonstrated by the measurements of stress-strain isotherms in elongations. According to the recent studies of catalysts for the hydrolysis of TEOS, acids were the least effective, and the salts and bases the most effective. Even though the PDMS network without any typical functional group has been studied, that containing basic functional group was studied rarely through the same in-situ techniques. The present study addressed this issue, using the PDMS network containing 3-aminopropyl or N,N-dimethyl-3-aminopropyl group. The amount of silica precipitated and the ultimate properties of the filled PDMS networks

in elongation were used to evaluate the relative effectiveness of catalysts.

EXPERIMENTAL

Preparation of Elastomers

Hydroxyl-terminated PDMS ($M_n: 18,000 \text{ g mol}^{-1}$) was crosslinked with 3-aminopropyltriethoxysilane or N,N-dimethyl-3-aminopropyltrimethoxysilane, in the undiluted state and the usual manner.¹³⁻¹⁶

The resulting network sheets with 1 mm thick, were extracted using tetrahydrofuran and methanol. Test strips cut from the sheets were 4 mm wide and 50 mm long.

Preparation of Catalyst Solutions

The five reagents employed for this purpose were given in Table 1.

They were each dissolved in water to a concentration of 5 wt %.

Table 1. Precipitation Reactants, Amount of Filler Precipitated, and Ultimate Properties of the Filled Network

Network	Crosslinking Agent	Precipitation Catalyst	Wt % SiO ₂ Precipitated	α_r	$(f/A^*)_r^a$ Nmm ⁻²	$10^3 E_r^b$ Jmm ⁻³
1	APTES ^c	None	0.00	3.40	0.25	0.28
2	APTES	THAMC	6.2	1.47	0.28	0.15
3	APTES	EDTA(3Na) ^d	5.7	1.59	0.32	0.23
4	APTES	EDTA(2Na) ^e	5.9	2.10	0.47	0.68
5	APTES	KH ₂ PO ₄	5.9	2.00	0.46	0.55
6	APTES	DEA ^f	75.51	—	—	—
7	DAPTS ^h	None	0.00	3.30	0.24	0.27
8	DAPTS	EDTA(2Na)	6.15	1.65	0.46	0.32
9	DAPTS	H ₂ O	6.86	2.14	0.56	0.70
10	DAPTS	THAM	6.77	1.95	0.12	0.12
11	DAPTS	EDTA(3Na)	6.85	2.77	0.78	0.69
12	DAPTS	KH ₂ PO ₄	7.50	2.15	0.58	0.82
13	DAPTS	DEA	32.77	—	—	—

^{a)} Ultimate strength as represented by the nominal stress at rupture.

^{b)} Energy required for rupture.

^{c)} Tris(hydroxymethyl)aminomethane.

^{d)} Trisodium salt of ethylenediaminetetraacetic acid.

^{e)} Disodium salt of ethylenediaminetetraacetic acid.

^{f)} Diethylamine.

^{g)} 3-aminopropyltriethoxysilane.

^{h)} (N,N-dimethyl-3-amino) propyltrimethoxysilane.

Precipitation of Silica

The extracted PDMS network strips were weighed and then placed into TEOS until swollen to equilibrium.

Each swollen strip was then immersed in one of the aqueous solutions for 24 hrs. The strips, which generally turned cloudy because of the precipitated SiO₂, were dried first in air for 24 hrs. and then under vacuum to constant weight. The increase in dry weight gave the amount of SiO₂ precipitated as shown in Table 1.

Stress-Strain Measurements

Equilibrium stress-strain data were obtained in elongation in the usual manner^{13,15} on the unswollen samples at 25°C. The nominal stress f^* was given by $f^* = f/A^*$, where f is the elastic force and A^* the undeformed cross-sectional area, and the reduced stress or modulus by $\{f^*\} = f^*/(\alpha - \alpha^{-2})$, where α is the elongation or relative length of the sample defined by $\alpha = L/L_i$. L_i is the length for zero stress.

RESULTS AND DISCUSSION

All the substances investigated showed significant capabilities as the catalysts for the hydrolysis reaction in PDMS network without any typical group. On the other hand, PDMS networks having basic groups showed the different catalytic effect as can be seen from the amounts of precipitated SiO₂ (given in the fourth column of the Table 1). On this point of view, the compounds with the stronger basicity, e. g. ethylamine, than 3-aminopropyl or N, N-dimethyl-3-aminopropyl group were more efficient. And all other compounds which were less basic than 3-aminopropyl or N, N-dimethyl-3-aminopropyl group were similar.

The stress-strain isotherms obtained on the filled networks were first represented as plots

of the modulus against reciprocal elongation, as suggested by the Mooney-Rivlin equation.¹⁷⁻²²

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

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

Typical isotherms, for networks chosen from the various classes of catalysts, are shown in Fig.1. In in-situ filled networks were shown to have values of the modulus which were higher than those of the corresponding unfilled network. Furthermore, the upturns in $\{f^*\}$ observed at higher elongations demonstrate the desired reinforcing effects. The values of the ultimate, specifically the ultimate strength and maximum extensibility, were given in the last two columns of the Table 1.

Fig. 2 shows the data of Fig.1 plotted in such a way that the area under each stress-strain curve

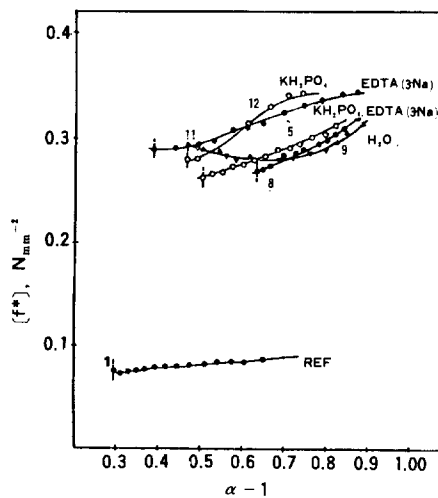


Fig. 1. The reduced stress shown as a function of reciprocal elongation for the SiO₂-filled PDMS networks at 25°C. Each curves was identified by the designation given in the Table 1 and the vertical dashed lines locate the rupture points.

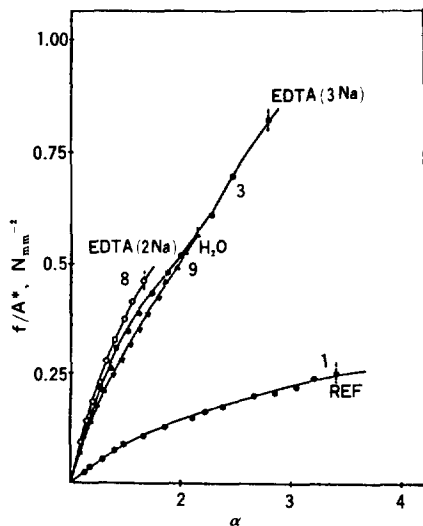


Fig. 2. The nominal stress shown as a function of elongation for the networks characterized in Fig. 1. In this representation the area under each curve corresponds to the energy required for network rupture.

corresponds to the energy E_r of rupture,¹⁴ which was the standard measure of elastomer toughness. The values of E_r for the curves showed the range from 0.28 Jmm^{-3} to 1.68 Jmm^{-3} . Thus, the in-situ reinforcement technique could easily bring about a nearly six-fold increase in elastomer toughness with relatively rapid and simple manner.

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