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Grafting of polymer onto filler particles used to reinforce an elastomer

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SUMMARY

The in-situ hydrolysis technique developed to precipitate reinforcing filler into an elastomer was extended so as to produce silica-type particles containing methacryloxy groups. Methyl methacrylate absorbed into these filled networks was then radically polymerized to give poly(methyl methacrylate) (PMMA) most of which is unextractable and therefore presumably grafted onto the particles. The PMMA thus introduced was found to further increase the ultimate strength of the networks.

INTRODUCTION

A number of previous studies (1-4) have demonstrated that elastomeric networks of poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]_x$ can be greatly reinforced by an in-situ precipitation technique. Generally the networks are swollen with tetraethoxysilane (TEOS), which is then hydrolyzed to a silica-type filler at room temperature in the acid- or base-catalyzed reaction

$$Si(OC_2H_5)_4 + 2\ H_2O \longrightarrow SiO_2 + 4\ C_2H_5OH \qquad (1)$$

These studies have focused on PDMS as the polymer to be reinforced because of the inherent weakness of its unfilled networks and the extent to which these networks can be swollen with the structurally very similar TEOS. The presence of filler particles has been demonstrated by electron microscopy and scattering techniques (1,3), and their reinforcing effects by stress-strain measurements (1-4).

In a modification of this technique, silanes having the structure $RSi(OR')_3$ where hydrolyzed, where R is an alkyl or aryl group (5,6). The goal in these studies was to introduce some deformability into the filler particles through the non-hydrolyzable R groups, thereby possibly making the filled elastomers even tougher.

The present study is an extension of this modified technique, in which the R is the unsaturated group $CH_2{=}C(CH_3)COO(CH_2)_3-$. Specifically, mixtures of 3-methylacryloxypropyl trimethoxysilane (MOTMS) and TEOS are hydrolyzed in-situ to give reinforcing particles in

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** Permanent address: Department of Chemical Engineering, Yeungnam University, Daegu 632, Korea networks of PDMS. Methyl methacrylate monomer [$CH_2=C(CH_3)COOCH_3$] is then absorbed into the networks and polymerized in-situ (7,8). The extent to which the resulting glassy poly(methyl methacrylate) (PMMA) is grafted onto the modified filler particles is gauged by extraction measurements. The degree of reinforcement obtained for the various networks is determined from stress-strain measurements in elongation.

EXPERIMENTAL DETAILS

Materials

The MMA monomer and the free-radical initiator, benzoyl peroxide, were purified just prior to use by standard procedures. TEOS, MOTMS, and hydroxyl-terminated PDMS of number-average molecular weight 18.0 x 10^3 g mol^{-1} were purchased from Petrarch Systems and used as received.

Preparation of Elastomer

The hydroxyl-terminated PDMS was endlinked with TEOS, in the undiluted state, in the usual manner (9,10). The resulting network sheet, which was approximately 1 mm thick, was weighed and then extracted, first using tetrahydrofuran and then methanol. The soluble fraction thus removed amounted to only a few wt %. Test strips cut from the sheet were approximately 4 mm wide and 50 mm long.

In-Situ Precipitation of Functionalized Silica

The weighed, extracted PDMS strips were placed into a mixture of MOTMS and TEOS until swollen to equilibrium. The compositions of the mixtures used are given in the first column of Table I. Each swollen strip was then immersed in a 3 wt % aqueous solution of hydrogen chloride or diethylamine for 12 hrs, as described in the following column. The strips, which generally turned cloudy because of the precipitated silica, were dried in air for 24 hr, extracted in tetrahydrofuran for three days, and then redried under vacuum to constant weight. Values of the weight percent filler thus incorporated were obtained from the increased weights of the dried strips.

Table I. Hydrolysis conditions and amounts of filler precipitated

Wt % MOTMS[a]	Catalyst	Wt % Filler
0.0	HCl	15.8
20.4		8.3
44.1		7.5
85.9		2.2
100.0		1.6
45.4	$(C_2H_5)_2NH$	18.6

[a] Methacryloxypropyl trimethoxysilane.

In-Situ Polymerization of Methyl Methacrylate

Sufficient benzoyl peroxide was dissolved in methyl methacrylate monomer to give a 1 wt % solution. Known amounts of the solution were then added to portions of the PDMS network prepared using the diethylamine catalyst. The samples were then refrigerated for three days to assure uniform swelling of the samples. After that, the polymerization reaction (7,8) was carried out at 70 °C for 24 hrs, under a nitrogen atmosphere. After completion of the polymerization, the samples were held under a vacuum for 12 hrs to remove unreacted monomer. Removable PMMA was extracted using tetrahydrofuran at room temperature for 24 hrs. The extracted soluble material was checked by means of IR spectroscopy to assure that it was PMMA.

Stress-Strain Measurements

Equilibrium stress-strain data were obtained in the usual manner (9-11), on the unswollen samples at 25 °C. The nominal stress was given by $f^* \equiv f/A^*$, 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 $\alpha = L/L_i$ is the elongation or relative length of the sample (4,11,12). The measurements were carried out to the rupture points.

RESULTS AND DISCUSSION

The amounts of precipitated filler in the various networks are listed in the last column of Table I. The amount decreases with increase in wt % MOTMS in the silane mixture. This is presumably due to a decreased degree of network swelling in the MOTMS, and a lower rate of hydrolysis. In any case, the basic catalyst was more effective than the acidic one, in agreement with previous results (13).

The wt % PMMA introduced into the networks is given in the second column of Table II. Comparisons of the FG-1E sample with the FG-1, and the FG-2E with the FG-2, show that very little of the PMMA is extractable. This was also found for another pair of samples, not further studied, for which extraction decreased the wt % PMMA only from 32.2 to 30.3 wt %. These results suggest that most of the polymer was successfully grafted onto the filler particles through the methacryloxy groups.

The stress-strain isotherms obtained on the networks were represented as plots of the modulus against reciprocal elongation, as suggested by the Mooney-Rivlin equation (4,12,14)

$$[f] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

where $2C_1$ and $2C_2$ are constants independent of elongation. Of interest here are the magnitudes of $[f^*]$ itself, and upturns in $[f^*]$ at high values of α (15). The results for the unfilled, filled, and filled and grafted networks are shown in Figure 1. The filled network is seen to have much higher values of the modulus, thus demonstrating good reinforcement from the in-situ precipitation. Furthermore, the two

Table II. Grafting and extration results, and the ultimate properties of the resulting networks

Grafting and Extraction Results		Ultimate Properties		
Network[a]	Wt % PMMA[b]	f_r^{*}[c] (N mm^{-2})	α_r[d]	$10^3 E_r$[e] (J mm^{-3})
U	0.0	0.19	3.5	0.28
F	0.0	1.07	2.3	0.76
FG-1	23.8	1.24	2.1	0.67
FG-1E	21.4	1.17	2.1	0.64
FG-2	33.1	1.47	1.9	0.70
FG-2E	32.4	1.34	2.0	0.67

[a] Unfilled, filled, filled and grafted, and filled and grafted and extracted.

[b] Poly(methyl methacrylate).

[c] Nominal stress at rupture.

[d] Elongation at rupture.

[e] Energy required for rupture.

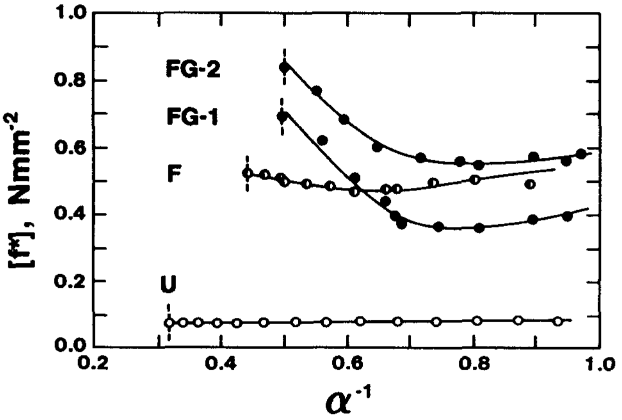

Fig. 1. The reduced stress shown as a function of reciprocal elongation at 25°C for poly(dimethylsiloxane) networks that are unfilled (U), filled with methacryloxy-modified silica particles (F), and filled with these particles with poly(methyl methacrylate) (PMMA) grafted onto them (FG-1 and FG-2). The vertical dashed lines locate the rupture points of the network

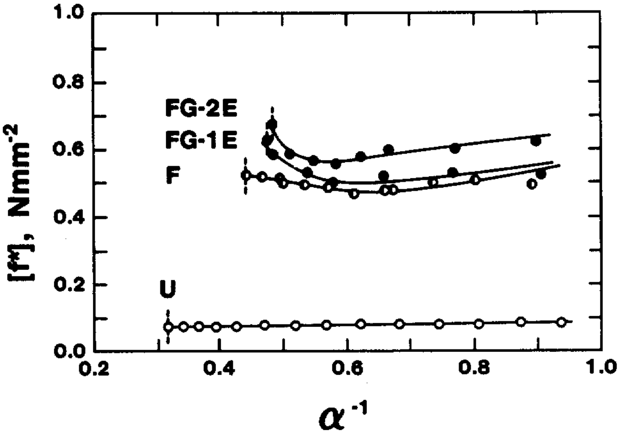

Fig. 2. Results on the networks described in Fig. 1, but now after removal of extractable PMMA (FG-1E and FG-2E)

filled networks into which PMMA was introduced show large upturns in [f*], with correspondingly higher values at rupture.

The results for the filled and grafted networks after extraction, again compared with the results for the unfilled and filled networks, are shown in Figure 2. The upturns in [f*] are significantly diminished, indicating that both the grafted and extractable PMMA can contribute to the improvement in mechanical properties.

Representation of the isotherms as plots of nominal stress against elongation gave the values of the ultimate strength, maximum extensibility, and energy of rupture (16) given in the last three columns of Table II. The basic conclusion reached is that adding in-situ polymerization to in-situ precipitation can increase the ultimate strength of an elastomer. There is an accompanying decrease in extensibility, however, and as a result there is not much change in the energy required for rupture. It may be possible to find conditions under which all three of these ultimate properties are improved.

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REFERENCES

1. J. E. Mark, Brit. Polym. J., **17**, 144 (1985).

2. S. J. Clarson and J. E. Mark, Polym. Comm., **28**, 249 (1987).

3. J. E. Mark, in Ultrastructure Processing of Ceramics, Glasses, and Composites, ed. by J. D. MacKenzie and D. R. Ulrich, Wiley, New York, 1988.

4. J. E. Mark and B. Erman, Rubberlike Elasticity. A Molecular Primer, Wiley-Interscience, New York, 1988.

5. Y.-P. Ning, Z. Rigbi, and J. E. Mark, Polym. Bulletin, **13**, 155 (1985).

6. J. E. Mark and G. S. Sur, Polym. Bulletin, **14**, 325 (1985).

7. F.-S. Fu and J. E. Mark, ms. submitted to J. Polym. Sci., Polym. Phys. Ed.

8. F.-S. Fu and J. E. Mark, ms. submitted to J. Appl. Polym. Sci.

9. J. E. Mark and J. L. Sullivan, J. Chem. Phys., **66**, 1006 (1977).

10. J. E. Mark, Adv. Polym. Sci., **44**, 1 (1982).

11. J. E. Mark and P. J. Flory, J. Appl. Phys., **37**, 4635 (1966).

12. L. R. G. Treloar, The Physics of Rubber Elasticity, 3rd Ed., Clarendon Press, Oxford, 1975.

13. G. S. Sur and J. E. Mark, Makromol. Chemie, **187**, 2861 (1986).

14. J. E. Mark, Rubber Chem. Technol., **48**, 495 (1975).

15. J. E. Mark, Polym. Eng. Sci., **19**, 254, 409 (1979).

16. M. A. Llorente, A. L. Andrady, and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **19**, 621 (1981).

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