Polymer Bulletin 18, 33–37 (1987)

Polymer Bulletin

Precipitation of iron oxide filler particles into an elastomer

S. Liu and J. E. Mark*

Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, OH 45221, USA

Summary

Samples of peroxide-cured butyl rubber were impregnated with anhydrous $FeCl_3$, which was then hydrolyzed in a magnetic field to give ferric hydrous oxide particles. The filler thus formed in-situ was found to give good reinforcement of the elastomer. A relatively small but significant anisotropy was found for both the elongation modulus and the equilibrium degree of swelling.

Introduction

There has now been a number of studies in which filler particles are precipitated into a polymer to produce a reinforced elastomeric material (1-8). One of the advantages of this novel technique is the control it gives over the degree of agglomeration of the filler. The particles obtained thus far have been of a ceramic nature, for example silica (1-4,6,7) and titania (5,8) produced by the in-situ hydrolysis of silicates and titanates.

Another novel approach to reinforcing elastomers involves the use of magnetic particles which are dispersed into a polymer prior to its being cross linked in a magnetic field (9,10). In this case, it is possible to manipulate the particles with the field, thus producing anisotropic reinforcement even from spherical particles.

The present investigation combines these two techniques. The in-situ hydrolysis of ferric chloride (11-15) is used to precipitate ferric hydrous oxide particles into a cross-linked polyisobutylene (PIB) elastomer. It is anticipated that at least some of the particles formed will have sufficient response to a magnetic field to give anisotropy as discernible from stress-strain and swelling equilibrium measurements.

Experimental Details

The PIB sample employed was a "butyl rubber" copolymer (16) containing 2 mol % unsaturated repeat units to permit cross linking. It had a number-average molecular weight of 4.56×10^5 g mol^{-1}, and was generously provided by Dr. E. N. Kresge of the Exxon Chemical Company of

* To whom offprint requests should be sent

Linden, NJ. Benzoyl peroxide was blended into this sample (3 parts by weight to 100 parts PIB), and portions were pressed into aluminum molds which were then sealed. The first stage of the cross-linking process was carried out at 125° C for 30 min.; the samples were then removed from the molds and post cured under nitrogen at 90° C for 24 hr. Each portion was extracted with gently-stirred methyl ethyl ketone at room temperature for three days before drying. The sol fractions thus removed amounted to only 0.4 - 1.6 wt %.

Anhydrous ferric chloride ($FeCl_3$) was dissolved in toluene to give a series of solutions having nominal molarities in the range 0.2 - 0.8. Insolubles were removed by filtration. Each extracted PIB sample was swelled with one of these solutions for 4 hrs. Values of the volume fraction of polymer in these swollen samples ranged from 0.131 to 0.161. The samples were evaporated to dryness and placed into vials containing aqueous solutions of hydrochloric acid at the molarities given in the second column of Table I. Each vial was mounted between the poles of a

Table I

Preparation of Samples, Elongation Moduli, and Swelling Results

Preparation of Samples					Swelling Equilibrium[c]	
Exp	HCl Conc. (Molarity)	Wt % Filler	Axial Orientation[a]	$[f^*]$[b] ($N\ mm^{-2}$)	v_2[d]	L/L_i
1	-	0.00	-	0.164	-	-
	-	9.21[e]	-	0.170	-	-
2	0.01	8.97	-	0.341	0.450	1.21
	0.01	8.97	-	0.345	0.454	1.20
3	0.1	8.98	-	0.403	0.435	1.24
	0.1	8.98	-	0.400	0.433	1.26
4	0.1	1.55	//	0.198	0.222	1.53
	0.1	1.55	⊥	0.198	0.223	1.54
5	0.01	4.07	//	0.262	0.301	1.46
	0.01	4.07	⊥	0.242	0.311	1.38
6	0.1	4.09	//	0.306	0.286	1.65
	0.1	4.09	⊥	0.269	0.296	1.46
7	0.1	7.32	//	0.463	0.322	1.33
	0.1	7.32	⊥	0.443	0.397	1.21

[a] Long axis of sample strip relative to magnetic lines of force. [b] Reduced stress at reciprocal elongation $\alpha^{-1} = 0.7$. [c] In benzene at room temperature. [d] Volume fraction of polymer in the swollen network. [e] Unhydrolyzed $FeCl_3$ dissolved in the network.

permanent magnet having a field strength of 525 Gauss, and the entire assembly was heated to 100° C for 24 hrs. Precipitation of yellow β-FeOOH was clearly visible in each sample. The samples were removed from the vials and then dried under vacuum to constant weight. The drying temperature was kept below 50° C. Use of this relatively low temperature minimized transformation of the β-FeOOH to α-Fe_2O_3, which is very noticeable because of its dark-red color. The former oxide should respond more to a magnetic field since is probably antiferromagnetic (17) and the latter only paramagnetic (18).

Two sets of strips (~1 x 4 x 30 mm^3) were cut with their long axes parallel ($\parallel$) to what had been the magnetic lines of force, and two other sets were cut perpendicular ($\perp$). For purposes of comparison, two reference strips were cut from a sheet of unfilled polymer, and from a sheet of polymer filled with unhydrolyzed $FeCl_3$, respectively. Two pairs of additional reference strips were obtained by cutting strips in arbitrary but mutually perpendicular directions from two sheets prepared in the absence of a magnetic field. The reference strips are described in the first four columns and the first six rows of Table I, and the test strips filled in the presence of the field in the corresponding columns of the last eight rows.

Stress-strain measurements in elongation were conducted in the usual manner (19,20) on one set of the (unswollen) strips. Measurements were carried out to their rupture points. The other set was used for swelling equilibrium measurements, in benzene at room temperature.

Results and Discussion

Values of the equilibrium value f of the elastic force, the undeformed cross-sectional area A^*, and the elongation or relative length α were used to calculate the reduced stress or modulus:

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2}) \quad (1)$$

The resulting values are shown as a function of reciprocal elongation in Figure 1, and the specific values at a reciprocal elongation $\alpha^{-1} = 0.7$ are given in column five of the Table.

The first pair of experiments demonstrates that unhydrolyzed $FeCl_3$ dissolved in the network causes very little change in modulus. Both of the next two pairs of isotherms confirm the expection that precipitating the filler in the absence of a magnetic field should give a nearly mechanically isotropic system. Comparison of the results for pair two with three, and pair five with six, indicates that decrease in pH (increase in HCl molarity) has essentially no effect on the wt % filler precipitated, but does cause an increase in modulus. This may be due to the fact that low pH gives particles that are more rodlike in shape (12). In any case, experiments two through seven clearly demonstrate a strong reinforcing effect, with its magnitude increasing with increase in filler content. Also, as is shown in column five of the Table and in the Figure, the modulus is higher in the direction that was parallel to the

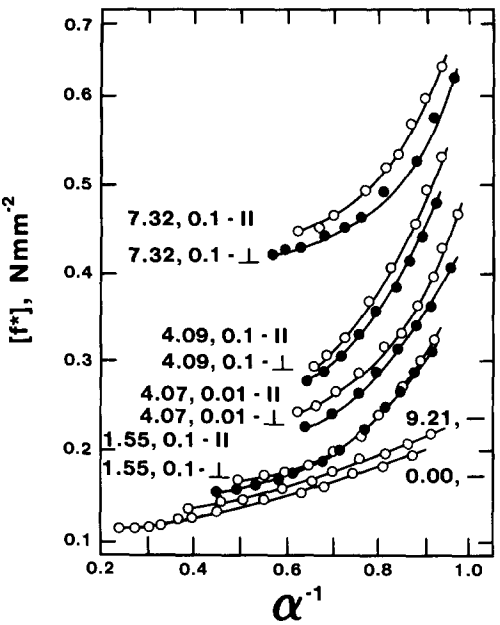

Figure 1. Representative stress-strain isotherms for the PIB networks in elongation at 25°C. The labels give the wt % filler precipitated into the elastomer, the molarity of the acid used in the $FeCl_3$ hydrolysis, and the orientation of the long axis of the sample relative to the lines of force of the magnetic field, if present. See Table I.

magnetic lines of force and the difference increases with increase in wt % filler. Some particle orientation was obviously obtained by means of the magnetic field and the conditions that maximize this effect are presently being sought.

The swelling equilibrium results are first described in terms of the volume fraction v_2 of polymer present in the network (with the volume of the filler being ignored in the present comparisons). Its values are given in column six of the Table. In general, increase in wt % filler is seen to increase v_2, as expected. Also, some anisotropy is observed in the swelling, as demonstrated by the values of v_2 and by the increases in the length of the strips reported in the final column of the Table. In particular, the increases in length are smaller (less swelling) in the perpendicular direction and the differences generally increase with increase in wt % filler. In this case the decreased swelling direction corresponds to lower modulus, in agreement with some earlier results (9), but the opposite correlation has also been observed (10).

The observed anisotropy, and its control by means of a magnetic field, could be of practical as well as fundamental importance.

Acknowledgements

It is a pleasure to acknowledge the financial support provided by the Army Research Office through Grant DAAL03-86-K-0032 (Materials Science Division) and by the Air Force Office of Scientific Research through Grant AFOSR 83-0027 (Chemical Structures Program, Division of Chemical Sciences).

References

1. J. E. Mark, Brit. Polym. J., **17**, 144 (1985), and relevant papers cited therein.
2. Y.-P. Ning and J. E. Mark, J. Appl. Polym. Sci., **30**, 3519 (1985).
3. J. E. Mark and G. S. Sur, Polym. Bulletin, **14**, 325 (1985).
4. J. E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang, and W. C. Roth, Polymer, **26**, 2069 (1985).
5. G. S. Sur and J. E. Mark, Eur. Polym. J., **21**, 1051 (1985).
6. Y.-P. Ning and J. E. Mark, Polym. Eng. Sci., **26**, 167 (1986).
7. G. S. Sur and J. E. Mark, Makromol. Chemie, **187**, 2861 (1986).
8. S.-B. Wang and J. E. Mark, Polym. Bulletin, **17**, 271 (1987).
9. Z. Rigbi and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **23**, 1267 (1985).
10. G. B. Sohoni and J. E. Mark, J. Appl. Polym. Sci., **33**, 000 (1987).
11. E. Matijević, Prog. Colloid Polym. Sci., **61**, 24 (1976).
12. E. Matijević, J. Colloid Interface Sci., **63**, 509 (1978).
13. S. Kratohvil, E. Matijević, and M. Ozaki, Colloid Polym. Sci., **262**, 804 (1984).
14. E. Matijević, Ann. Rev. Mater. Sci., **15**, 483 (1985).
15. E. Matijević, Colloid Polym. Sci., **265**, 155 (1987).
16. C. C. Sun and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **25**, 000 (1987).
17. C. H. Griffiths, M. P. O'Horo, and T. W. Smith, J. Appl. Phys., **50**, 7108 (1979).
18. H. Remy, "Treatise on Inorganic Chemistry", Vol. 2, Elsevier, New York, 1956.
19. J. E. Mark and J. L. Sullivan, J. Chem. Phys., **66**, 1006 (1977).
20. M. A. Llorente, A. L. Andrady, and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., **18**, 2263 (1980).

Accepted May 20, 1987 K