Polymer Bulletin 6, 381–387 (1981)

Polymer Bulletin

Rubber Elasticity at Very Large Elongation

Junji Furukawa, Yukio Onouchi, Shinji Inagaki and Hiroshi Okamoto

Department of Applied Chemistry, Aichi Institute of Technology,
Yakusa-cho, Toyota 470-03, Japan

Summary

The rubber elasticity increases in general at very large elongation and sometimes it is ascribed to the strain-induced crystallization. However, the authors found that a steep increase takes place in an ordinary Mooney-Rivlin plot not only for natural rubber but also for non-crystallizable rubbers such as SBR, NBR, EPDM and polyurethane, and the upturn for non-crystallizable rubbers disappears if data are examined with the theoretical equation derived taking the limited extensibility of chains into consideration. In the ordinary Mooney-Rivlin plot the elongation inducing the stress upturn due to the limited extensibility of chains increases with decreasing degree of vulcanization and sometimes it does not appear before the upturn of the rubber of low degree of vulcanization. The strain-induced crystallization can bring about the steep increase of elastic force, but it is not always adequate to ascribe the upturn to the strain-induced crystallization. The upturn also occurs due to the limitation of extensibility of chains.

Introduction

The rubber elastic force f is given by the following theoretical equation in terms of the elongation ratio α[1]

$$f = \nu kTA(\alpha - 1/\alpha^2) \qquad (1)$$

where ν and A are the number of chains in a unit volume (1 cm^3) and the initial cross-sectional area (1 cm^2), respectively. The equation implies that f is proportional to α at a very large elongation, but actually there is a steep increase at a large elongation giving an inverse S-shaped curve in a stress-strain re-

0170-0839/82/0006/0381/$01.40

lation. A so-called Mooney-Rivlin equation (2) containing two constants, C_1 and C_2, is available in practical cases[2].

$$f = 2(C_1 + C_2/\alpha)(\alpha - 1/\alpha^2) \qquad (2)$$

However, it does not explain the steep increase at a large elongation. A linear relationship between $f/(\alpha - 1/\alpha^2)$ and $1/\alpha$ holds only at a small elongation and an upturn in the stress occurs at a large elongation or a small reciprocal elongation less than 0.5 usually. It is believed in the literature that the upturn in the stress is mostly ascribed to the limitation of extensibility of the chain, but sometimes the strain-induced crystallization is taken to be the origin of the upturn.

Recently, J.E. Mark[3] claimed the strain-induced crystallization in his experiments on natural rubber (NR) and cis-polybutadiene. He pointed out that a crystallizable rubber like NR shows an upturn at a large elongation in the Mooney-Rivlin plot, whereas non-crystallizable one such as polydimethylsiloxane or atactic polyethyl acrylate does not. He emphasized that the strain-induced crystallization is the origin of the upturn in the modulus, and the wide-spread interpretation of this upturn in terms of limited chain extensibility is incorrect. He also found that the polybutadiene of 98.5% cis-1,4-content vulcanized by γ-irradiation shows a stress-strain curve characteristic to the strain-induced crystallization such as a down turn due to crystallization followed by an upturn. Crystallization is confirmed by the X-ray analysis[4]. Consequently, it is true that the strain-induced crystallization brings about the upturn for the crystallizable rubber. However, the theory of elasticity based on the limited chain extensibility suggests also the upturn for the rubber of low degree of vulcanization occurs at very large extension, and the degree of vulcanization of polydimethylsiloxane and atactic polyethyl acrylate employed by J.E. Mark as non-crystallizable rubbers are too low estimated from thier elastic modulus to exhibit the upturn and the rupture seems to take place before the ultimate elongation. In fact, our experiment with styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), ethylene-propylene rubber (EPDM) and urethane rubber (PU) shows clearly the upturn in

spite of thier non-crystallizable nature. This paper describes the data and the discussion, how the vulcanization affects the upturn.

Theoretical

For the examination of the strain-induced crystallization, the equations (1) and (2) are not suitable, because they are derived under the conditions of enough small elongation. In order to eliminate the effect of the limited chain extensibility it is proposed to employ the equations of James-Guth[5] or authors. The James-Guth equation is expressed as an inverse Langevin function of the fractional elongation α/α_m, α_m being a maximum elongation ratio.

$$f = \left(\frac{\nu kT\alpha_m}{3}\right)\left\{L^{-1}(\alpha/\alpha_m^{1/2}) - (1/\alpha^{3/2})\, L^{-1}(1/\alpha^{1/2}\cdot\alpha_m^{1/2})\right\}$$

$$\simeq \left(\alpha + \frac{3}{5}\frac{\alpha^3}{\alpha_m^2} + \frac{99}{175}\frac{\alpha^5}{\alpha_m^4} + \cdots\cdots\cdots - 1/\alpha^2\right) \qquad (3)$$

The authors[6] proposed a simple equation (4) or (5) based on the assumption of uniform stress unlike the usual assumption of uniform strain.

$$f = \nu kTF(\alpha) \qquad (4)$$

$$f = 2(C_1 + C_2/\alpha)F(\alpha) \qquad (5)$$

where

$$F(\alpha) = \frac{\alpha_m}{2}\ln\frac{1 + \alpha/\alpha_m}{1 - \alpha/\alpha_m} - 1/\alpha^{3/2}\ln\frac{1 + 1/\alpha^{1/2}\,\alpha_m}{1 - 1/\alpha^{1/2}\,\alpha_m} \qquad (6)$$

This equation (4) was found to be valid even for a very large elongation in most cases, since a linear relation holds in a plot between f and $F(\alpha)$ without any upturn at a large elongation. A linear relation also holds in a modified Mooney-Rivlin plot between $f/F(\alpha)$ and $1/\alpha$ without any upturn. From equation (6) the upturn at the ordinary Mooney-Rivlin plot is to be much affected by C_1- and C_2-values. Equation (6) is expanded to

$$F(\alpha) = \alpha - \frac{1}{\alpha^2} + \frac{\alpha_m}{3}\cdot\left(\frac{\alpha}{\alpha_m}\right)^3 + \cdots\cdots$$

to give an equation (7)

$$\frac{f}{\alpha - 1/\alpha^2} \cong 2(C_1 + C_2/\alpha)\left(1 + \frac{1}{3}\frac{\alpha^2}{\alpha_m^2}\right) \qquad (7)$$

which possesses a maximum at a condition of

$df/(\alpha - 1/\alpha^2)/d\alpha = 0$, or

$$\frac{4}{3}\frac{C_1}{\alpha_m^2}\alpha^3 = 2C_1 - \frac{2C_2}{3}\left(\frac{\alpha}{\alpha_m}\right)^2$$

So far as $\alpha \ll \alpha_m$, the second term in the right side is neglected and the upturn $(1/\alpha)_{up}$ is given by

$$(1/\alpha)_{up}^3 = \frac{2}{3}\frac{1}{\alpha_m^2}\frac{C_1}{C_2} \qquad (8)$$

Since $1/\alpha_m^2$ runs parallel to C_1, the position of the upturn is much dependent on the C_1-value or the modulus of the rubber vulcanizate. At an elevated temperature, α_m is given by the square of the chain length and hence,

$$\alpha_m \propto (1/C_1)^{1/2} \qquad (9)^*$$

and

$$(1/\alpha)_{up} \propto (C_1^2/C_2)^{1/3} \qquad (10)$$

Equation (10) implies that the upturn is much affected by the C_1-values and the vulcanizates of low modulus possess the upturn at the very large elongation. The C_1-value or the degree of vulcanization of polydimethylsiloxane and atactic polyethyl acrylate in the Mark's experiment seem to be too low to exhibit the upturn and the rupture would take place before occuring the upturn. The authors examined the vulcanizates of SBR, NBR, EPDM and PU, and found that they indicate upturns in spite of thier non-crystallizable structure. NR gives, of course, an rupture but in this case most of upturns are ascribed to the limited extensibility, because there is no discrepancy from the linear plots if the modified equation based on the limited extensibility is employed.

Experiment

The compounding recipes and the curing conditions of vulcanized rubber samples were listed in Table 1.

Stress-strain measurement of these vulcanizates were carried out for the dumbell type specimen employing Tensilon tensile tester.

---

*If C_2/α is assumed to be the effect of the secondary crosslinks, equation (9) is written to be

$$\alpha_m \propto \left\{\frac{1}{C_1 + C_2/\alpha_m}\right\}^2 \qquad (11)$$

and applicable to the case at low temperature, when the effect of the secondary crosslinks is significant

Table 1 Compounding recipes and Vulcanization

Rubber	NR-#1	SBR-1502	NBR-230S	EPDM-24	PU
	100	100	100	100	100
Stearic acid	-	1.0	1.0	1.0	-
Zinc oxide	-	5.0	5.0	5.0	-
Accelerator*	-	CBS 0.5	MBTS 0.25	TMTD 0.5	-
Sulfur	-	1.0	1.0	1.0	-
DCP**	0.25∼3.0	-	-	-	1.2∼2.8
Carbon black	-	0 ∼ 50	-	-	-
DOP***	-	-	0 ∼ 30	-	-
Vulcanization					
Temp.(°C)	160	160	160	160	140
Time (min.)	20	20	20	20	30

* CBS ; N-Cyclohexyl 2-benzothiazole sulfenamide, MBTS ; Dibenzothiazyl disulfide, TMTD ; Tetramethyl thiuram disulfide
** DCP ; Dicumyl peroxide, ***DOP ; Dioctyl phtalate

Results and discussion

The stress-strain relation was measured at 20°C at an elongation ratio of 100 mm/min. It was found that all cases fit to equation (5) as shown in figures.

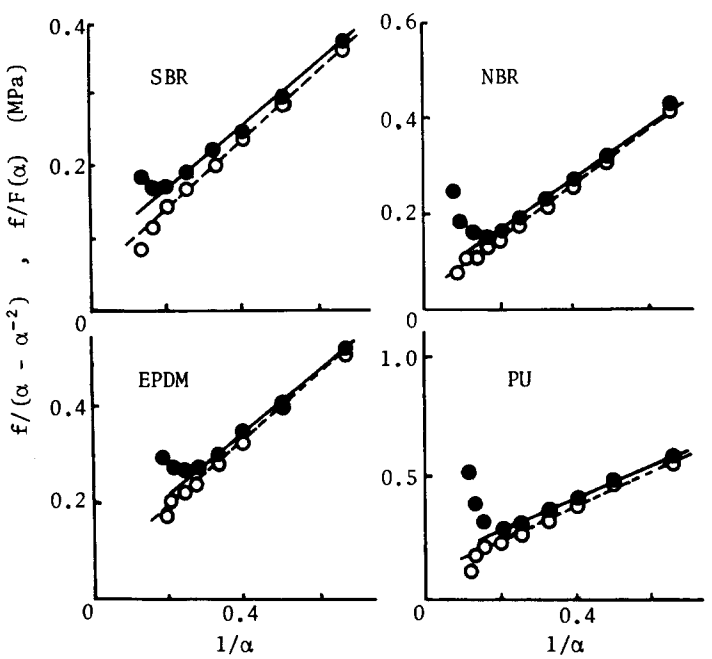

Figure Plots of equations (2) and (5) for various vulcanizates.
●; eqn.(2) , ○; eqn.(5)

The reciprocal elongation ($1/\alpha$) inducing the upturn in the Mooney-Rivlin plot is measured and compared with values calculated from equation (10). It was found that there is a parallity between them in most cases except for the case with large content of carbon black as follows. In cases with large content of carbon black there may be the effect of the orientation enhanced by the active filler.

Table 2 DCP-cured NR and PU (pure gum stocks)

Rubber	DCP (phr)	C_1 (MPa)	C_2 (MPa)	$(C_1^2/C_2)^{1/3}$	$(1/\alpha)_{up}$
NR	0.25	0.023	0.041	0.23	0.21
	0.50	0.046	0.059	0.33	0.29
	0.75	0.076	0.052	0.48	0.30
	1.00	0.121	0.054	0.65	0.33
	3.00	0.250	0.172	0.71	0.46
PU	1.20	0.081	0.360	0.26	0.20
	2.00	0.197	0.169	0.62	0.25
	2.80	0.331	0.101	1.03	0.33

Table 3 Carbon black loaded SBR

C.B. (phr)	C_1 (MPa)	C_2 (MPa)	$(C_1^2/C_2)^{1/3}$	$(1/\alpha)_{up}$
0	0.026	0.24	0.14	0.14
5	0.031	0.28	0.16	0.23
10	0.034	0.31	0.15	0.27
15	0.054	0.31	0.21	0.31
20	0.055	0.32	0.21	0.31
30	0.064	0.42	0.21	0.40
40	0.137	0.43	0.35	0.44
50	0.282	0.27	0.66	0.44

Table 4 DOP-mixed NBR

DOP (phr)	C_1 (MPa)	C_2 (MPa)	$(C_1^2/C_2)^{1/3}$	$(1/\alpha)_{up}$
0	0.052	0.343	0.20	0.16
5	0.037	0.306	0.16	0.15
10	0.033	0.233	0.17	0.15
20	0.031	0.204	0.17	0.14
30	0.022	0.147	0.15	0.13

Conclusion

It was found that non-crystallizable rubbers are also capable of exhibiting a steep increase of elastic force due to the limited extensibility if the rupture is avoided. The strain-induced

crystallization, if possible, may induce the upturn in elastic force before the ultimate elongation, but it is not always necessary for the upturn. For the examination of the abnormal increase of the elastic force due to the crystallization or the enhanced orientation, the modified equation derived taking the limited extensibility into consideration is more useful than ordinary Mooney-Rivlin equation.

References

1) P.J.FLORY, "Principles of Polymer Chemistry", Cornell Univ. Press, 1953

2) M.MOONEY, J. Appl. Phys., 11, 582(1940); S.GUMBELL, L.MULLINS and R.S.RIVLIN, Trans. Faraday Soc., 49, 1945(1953); R.S.RIVLIN and D.W.SAUNDERS, Phil. Trans. Royal Soc., A-243, 251(1951)

3) J.E.MARK, Polymer Eng. & Sci., 19, 254(1979)

4) M.SHARAF, J.E.MARK, B.GUNESIN-MINARD, D.N.SCHULZ, S.CESCA, Ph. TEYSSIE and M.JULEMONT, Paper presented at ACS Rubber Div. (Cleveland) Oct. 1979

5) E.GUTH and H.M.JAMES, J. Chem. Phys., 11, 455(1943)

6) J.FURUKAWA, H.OKAMOTO and S.INAGAKI, Kautschuk u. Gummi Kunststoffe, 29, 744(1976)

Received December 19, 1981
Accepted January 4, 1982