New Equation for the Description of the Stress-strain Properties of Elastomers

M. ZABORSKI*, A. VIDAL**, J.B. DONNET** AND M. DEBSKI***

A new relationship providing a description of the complete stress-strain curves of filled and unfilled elastomers submitted to uniaxial deformation at constant extension rate is proposed. The validity of the equation and the corresponding parameters have been determined with different samples: natural rubber filled with carbon black, poly(butadiene-b-styrene) and cis-1,4-polybutadiene unfilled or filled with polyacrylonitrile, low density polyethylene and polyvinylchloride.

Several equations have been proposed to describe the stress-strain properties of elastomeric networks. They derive from either the statistical or the phenomenological theories of rubber-like elasticity[1]. While in the former case, the theoretical models are based either on Gaussian[2-6] or on non-Gaussian statistics[3,7-11] phenomenological theories, on the other hand, if not merely descriptive, are inspired by purely mathematical considerations[12-29].

Very often, however, experimental results do not fit the curves calculated from the proposed equations. This paper proposes a new relationship providing a description of the complete stress-strain curves of filled and unfilled rubbers submitted to uniaxial deformations at constant extension rate. Derived from the phenomenological theory of elasticity the corresponding empirical equation has the following expression:

$$\sigma = A(\lambda - \lambda^{-2})^B \exp[C(\lambda^2 + 2\lambda^{-1} - 3) + D(\lambda^{-2} + 2\lambda - 3)] \qquad \ldots 1$$

where σ = tensile force per unit cross-section of the sample

λ = extension ratio

A, B, C and D = constants.

This new equation is proposed for the interpretation of the stress-strain properties of elastomeric materials. Its different parameters will be determined and its validity will be checked in the case of several filled and unfilled samples.

EXPERIMENTAL

The following samples were studied:

- Natural rubber (NR) filled with 60 p.h.r. FEF carbon black (N 550)

- Poly(butadiene-b-styrene): Cariflex TR 1101

- Cis-1,4-polybutadiene (SKD-II = PB) unfilled or filled (30% in volume) with polyacrylonitrile (PAN), low density polyethylene (PE) and polyvinylchloride (PVC).

Crosslinking resulted from the use of dicumylperoxide (PB: 0.27 p.h.r., NR: 2.7 p.h.r.) after heating at 150°C for 1 h under pressure.

Stress-strain measurements were carried out on dumbells (ASTM-W₁) using a F-1000 E

*Institute of Polymers, Technical University of Lodz, Poland

**Centre de Recherches suria Physico–Chimie des Surfaces Solides-CNRS, 24 Ave. Kennedy, 68200 Mulhouse, France

***ul Danuty 4, 61054 Poznan, Poland

TABLE 1. CARIFLEX TR 1101: STRESS-STRAIN PROPERTIES (σ = STRESS EXPERIMENTALLY MEASURED; σ_1 = STRESS CALCULATED ACCORDING TO EQUATION 1; σ_2 = STRESS CALCULATED ACCORDING TO EQUATION 5); VALUES OF THE PARAMETERS OF EQUATIONS 1 AND 5 AND OF STANDARD DEVIATIONS; T = 22°C

NR	λ	σ (MPa)	σ_1 (MPa)	$V_{\sigma 1}$ (%)	σ_2 (MPa)	$V_{\sigma 2}$ (%)
1	1.25	1.839	1.815	−1.31	1.178	−56.07
2	1.50	1.970	1.961	−0.45	1.786	−10.31
3	1.75	1.970	2.014	2.17	2.164	8.98
4	2.00	2.003	2.033	1.50	2.436	17.77
5	2.25	2.003	2.044	1.99	2.652	24.47
6	2.50	2.036	2.055	0.91	2.836	28.22
7	2.75	2.102	2.073	−1.41	3.002	29.97
8	3.00	2.135	2.101	−1.60	3.155	32.33
9	3.25	2.167	2.143	−1.11	3.301	34.35
10	3.50	2.200	2.201	0.04	3.441	36.06
11	3.75	2.299	2.276	−1.00	3.577	35.72
12	4.00	2.397	2.372	−1.04	3.710	35.39
13	4.25	2.529	2.492	−1.50	3.841	34.17
14	4.50	2.660	2.638	−0.82	3.971	33.02
15	4.75	2.824	2.816	−0.27	4.100	31.12
16	5.00	3.054	3.032	−0.73	4.227	27.76
17	5.25	3.284	3.291	0.21	4.354	24.58
18	5.50	3.612	3.603	−0.25	4.481	19.39
19	5.75	3.941	3.978	0.94	4.600	14.45
20	6.00	4.401	4.431	0.67	4.732	7.00
21	6.25	4.893	4.978	1.70	4.857	−0.74
22	6.50	5.550	5.641	1.61	4.982	−11.40
23	6.75	6.305	6.448	2.22	5.107	−23.00
24	7.00	7.356	7.436	1.07	5.231	−40.62
25	7.25	8.539	8.650	1.29	5.356	−59.44
26	7.50	10.246	10.152	−0.92	5.480	−86.98
27	7.75	12.217	12.021	−1.63	5.604	−118.01
28	7.91	13.793	13.456	−2.51	5.683	−142.69

Equation 1: A = 2.3340; B = 0.1670; C = 0.0724; D = 0.2261

Equation 5: $2C_1$ = 0.4926; $2C_2$ = 1.7990

Standard deviations: $S_{\sigma 1}$ = 0.0144; $S_{\sigma 2}$ = 0.5097

dynamometer at a cross head speed of 1000% min^{-1}

Equation 1 is converted into a linear form:

$$Ln\ \sigma\ =\ Ln\ A + B\ Ln(\lambda - \lambda^{-2})\ + \\ C(\lambda + 2\lambda^{-1} - 3) + D(\lambda + 2\lambda - 3)\ ...2$$

The parameters of this equation have been determined by a least square regression analysis.

The deviation of the calculated $(\hat{\sigma})$ from the experimental (σ) value of stress is given by:

$$V_\sigma\ =\ \frac{\hat{\sigma} - \sigma}{\sigma}\qquad ...3$$

and the standard deviation S_σ for the complete stress-strain curve between experimental and calculated values is provided by:

$$S_\sigma\ =\ \sqrt{\frac{\Sigma_{i=1}^n V_\sigma^2}{n - K - 1}}\qquad ...4$$

RESULTS AND DISCUSSION

Tables 1, 2 and *3*, give in the case of Cariflex TR 1101, natural rubber filled with N 550 and PAN filled cis-1,4-polybutadiene, respectively, the values of the stress corresponding to different elongations, either experimentally measured (σ) or calculated according to *Equation 1* (σ_1) or by use of the Mooney-Rivlin relationship (σ_2) as follows:

$$\sigma_2\ =\ (\lambda - \lambda^{-2})\ (2C_1 + 2C_2\lambda^{-1})\qquad ...5$$

The values of the different parameters of *Equation 1*, those of the two constants of the Mooney-Rivlin relationship and the standard deviations, $S_{\sigma 1}$ and $S_{\sigma 2}$ between the experimental and calculated values are also given in the tables.

It appears *(Figures 1 – 3)* that *Equation 1* fits fairly well the experimental stress-strain curves

TABLE 2. NATURAL RUBBER FILLED WITH N 550: STRESS-STRAIN PROPERTIES (σ = STRESS EXPERIMENTALLY MEASURED; σ_1 = STRESS CALCULATED ACCORDING TO EQUATION 1; σ_2 = STRESS CALCULATED ACCORDING TO EQUATION 5); VALUES OF THE PARAMETERS OF EQUATIONS 1 AND 5 AND OF STANDARD DEVIATIONS; T = 22°C

NR	λ	σ (MPa)	σ_1 (MPa)	$V_{\sigma 1}$ (%)	σ_2 (MPa)	$V_{\sigma 2}$ (%)
1	1.25	0.835	0.831	−0.48	0.311	−168.39
2	1.50	1.275	1.277	0.13	1.165	−9.46
3	1.75	1.802	1.804	0.09	2.174	17.12
4	2.00	2.373	2.450	3.16	3.230	26.52
5	2.25	3.253	3.236	−0.52	4.295	24.27
6	2.50	4.220	4.171	−1.16	5.360	21.27
7	2.75	5.363	5.260	−1.97	6.420	16.46
8	3.00	6.593	6.495	−1.51	7.475	11.79
9	3.25	7.956	7.863	−1.19	8.524	6.66
10	3.50	9.319	9.337	0.19	9.569	2.61
11	3.75	10.637	10.881	2.24	10.610	−0.25
12	4.00	12.308	12.450	1.14	11.648	−5.66
13	4.25	13.758	13.991	1.66	12.684	−8.47
14	4.50	15.429	15.445	0.11	13.717	−12.48
15	4.75	16.879	16.755	−0.74	14.748	−14.45
16	4.86	17.495	17.270	−1.30	15.201	−15.09

Equation 1: A = 1.3228; B = 0.3908; C = −0.1267; D = 0.6966

Equation 5: $2C_1$ = 4.0711; $2C_2$ = −4.4514

Standard deviations: $S_{\sigma 1}$ = 0.0154; $S_{\sigma 2}$ = 0.4933

TABLE 3. CIS-1,4-POLYBUTADIENE FILLED WITH PAN: STRESS STRAIN PROPERTIES (σ = STRESS EXPERIMENTALLY MEASURED; σ_1 = STRESS CALCULATED ACCORDING TO EQUATION 1; σ_2 = STRESS CALCULATED ACCORDING TO EQUATION 5; T = 22°C

NR	λ	σ (MPa)	σ_1 (MPa)	$V_{\sigma 1}$ (%)	σ_2 (MPa)	$V_{\sigma 2}$ (%)
1	1.25	0.651	0.655	0.68	0.542	−20.03
2	1.50	0.856	0.840	−1.89	0.894	4.25
3	1.75	1.018	1.019	0.09	1.163	12.45
4	2.00	1.195	1.209	1.13	1.390	14.02
5	2.25	1.400	1.415	1.04	1.594	12.18
6	2.50	1.641	1.640	−0.07	1.785	8.04
7	2.75	1.895	1.886	−0.48	1.966	3.62
8	3.00	2.171	2.154	−0.78	2.142	−1.34
9	3.25	2.447	2.446	−0.04	2.314	−5.74
10	3.50	2.772	2.762	−0.36	2.483	−11.62
11	3.75	3.081	3.103	0.64	2.650	−16.36

— Experimental

● Equation 10

○ Mooney-Rivlin
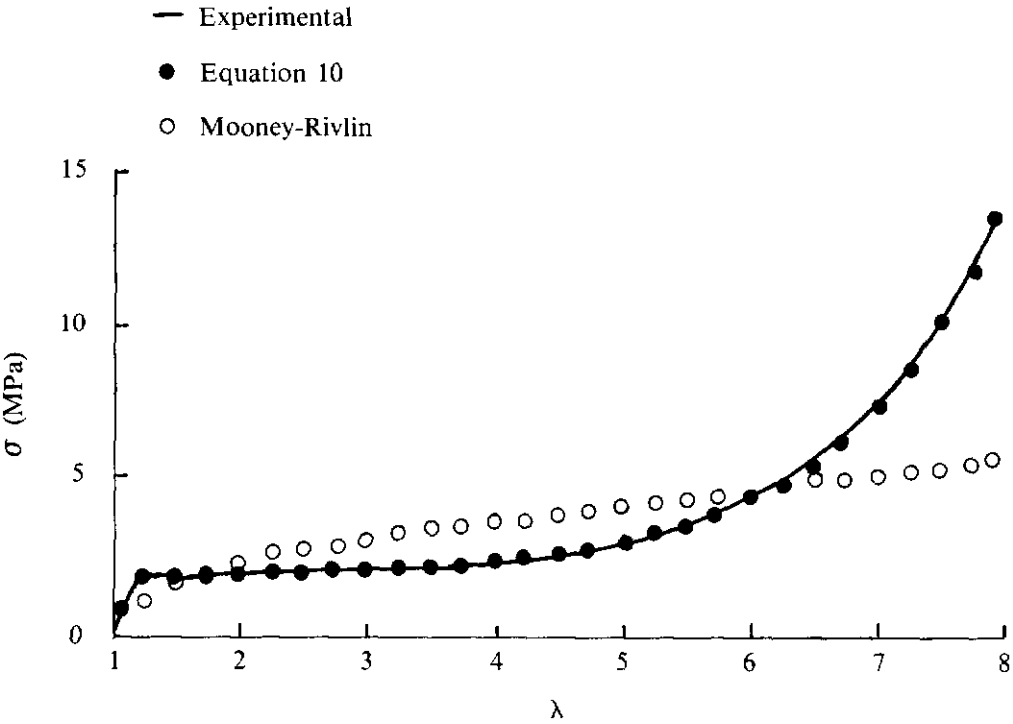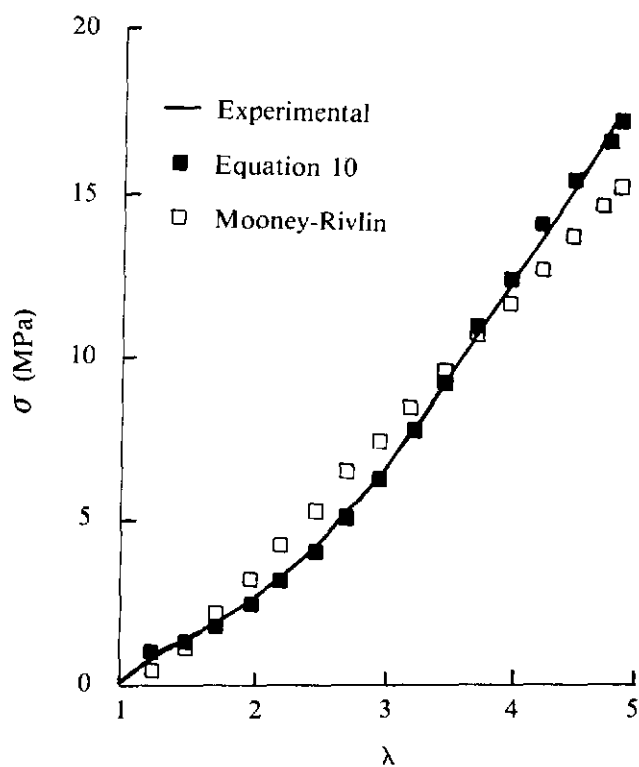
Figure 1. Stress-strain curves: Cariflex TR 1101, T = 22°C.

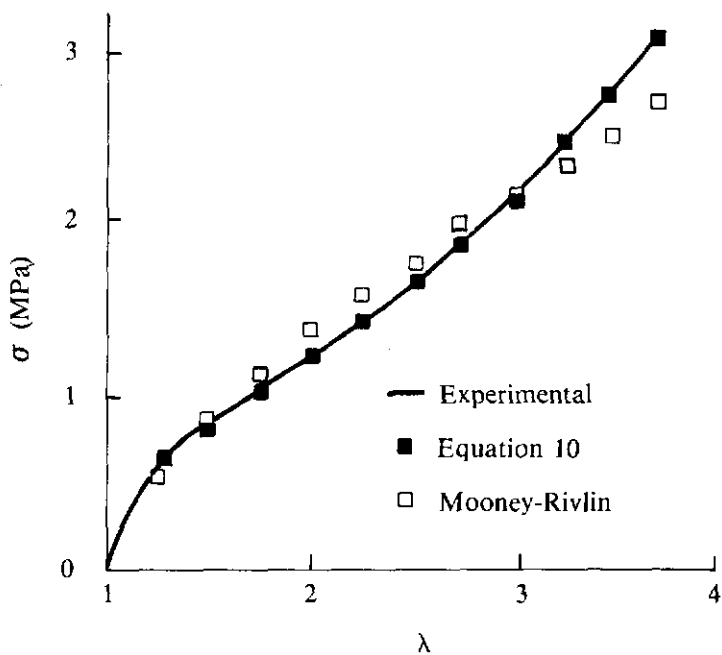*Figure 2. Stress-strain curves: natural rubber filled with N 550 carbon black, $T = 22°C$.*

Figure 3. Stress-strain curves: cis 1,4-polybutadiene filled with PAN, $T = 22°C$.

of the different samples, with a standard deviation (S_o) lower than 2%. As for the Mooney-Rivlin relationship, it appears to be providing values which are widely different from the experimental ones. In this case, the mean error can indeed be as high as 50%.

The *A* coefficient of *Equation 1* is not only proportional to the elastomer crosslinking density but is also dependent on the filler activity and loading level *(Table 4, Figure 4)*. As for coefficients *B, C* and *D,* they describe the correlation between the properties of the elastomer and those of an ideal neo-Hookian solid. For the latter, the values of *B, C* and *D* are 1, 0, and 0, respectively. (1–*B*) is thus providing an evaluation of the deviation of the system with respect to the equilibrium state. *B* coefficients for all samples appear to be in the 0.3 to 0.6 range. (1–*B*) seems to be proportional to the number of weak physical intermolecular

bonds or to elastomer/filler interfacial interactions, the concentration of which is dependent on the polymeric filler content. It is indeed observed that the parameter *B* decreases upon increase of the concentration of the thermoplastic dispersed in the elastomer *(Figure 5)*.

Upon cyclic deformation, *B* values are increased by a factor of 2, and thus are close to that of the unfilled elastomer.

Equation 1 can also be applied to the curves generated by a decrease of elongation, in this particular case it appears that *B* ~ 1.3.

C and *D* parameters are related to the flow and orientation processes of amorphous domains which occur upon deformation of the samples. They appear to be of opposite sign *(Figure 6)*. Thus for unfilled elastomers, *C* is positive and *D* negative. The reverse is observed with filled materials, but changes occur on

TABLE 4. VALUES OF THE COEFFICIENTS OF EQUATION 1 AS CALCULATED FOR DIFFERENT SAMPLES
$(\lambda_b$ = ELONGATION AT BREAK)

| Item	Sample				λ_b	S_j
	A	B	C	D		
PB(DCP)	0.56	0.53	0.033	−0.140	5.71	0.0079
PB + PE(DCP)	1.20	0.31	−0.003	0.089	6.91	0.0080
PB + PAN(DCP)	0.95	0.28	−0.051	0.350	3.84	0.0230
PB + PVC(DCP)	0.54	0.35	−0.120	0.020	7.08	0.0236
NR + N 550(DCP)	1.32	0.39	−0.130	0.696	4.86	0.0154
Cariflex TR 1101	2.33	0.17	0.072	−0.226	7.91	0.0144
Tyre tread gum	1.19	0.06	−0.054	0.500	5.00	0.0160
PB + PE(DCP)						
1 Strain	1.24	0.31	−0.002	0.08	6.64	0.0064
2 Strain	0.71	0.60	0.140	−0.37	6.21	0.0236
1 Return	0.77	1.28	0.250	−0.89	6.14	0.0482
2 Return	0.69	1.27	0.250	−0.85	6.04	0.0512
PB + PAN(DCP)						
1 Strain	0.95	0.31	−0.04	0.33	3.75	0.0354
2 Strain	0.96	0.76	0.42	−1.01	3.57	0.0289
1 Return	1.18	1.30	0.47	−1.30	3.53	0.0445
2 Return	0.85	1.13	0.50	−1.26	3.47	0.0286
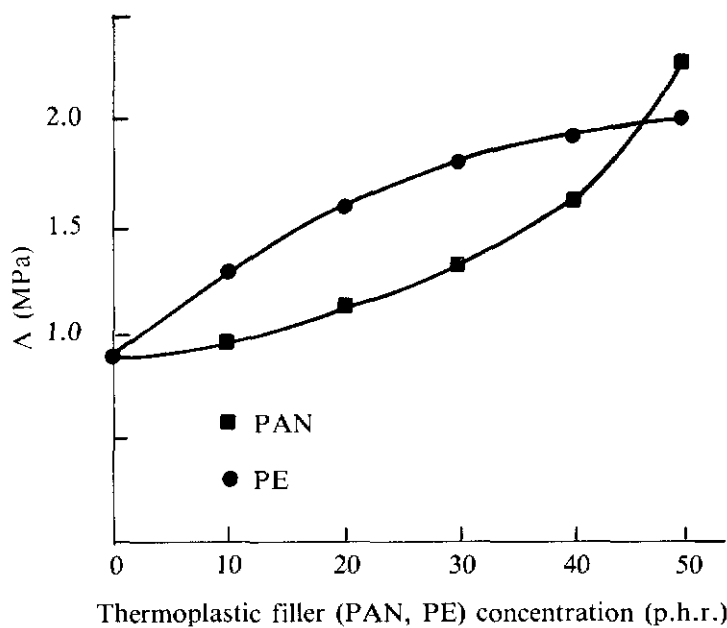
Figure 4. A versus *filler concentration: cis 1,4-polybutadiene filled with PAN or PE.*
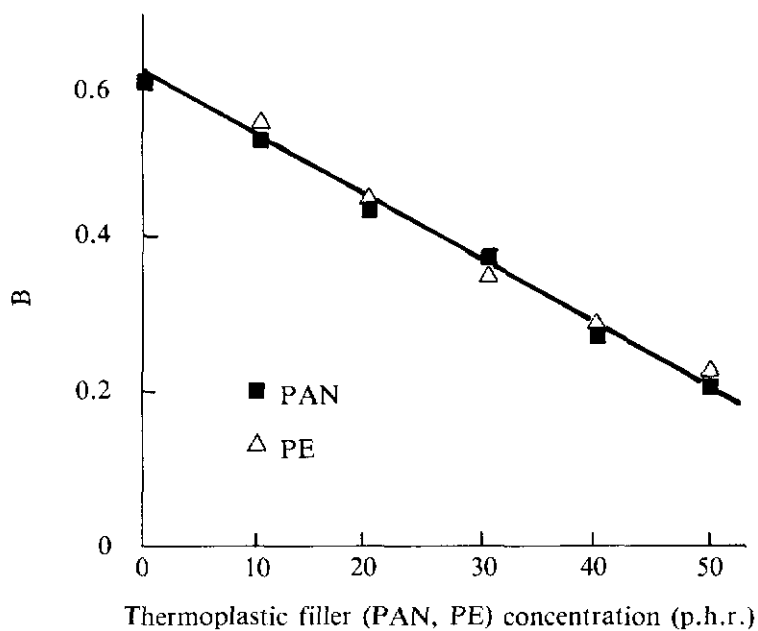

Figure 5. B versus *filler concentration: cis 1,4-polybutadiene filled with PAN or PE.*
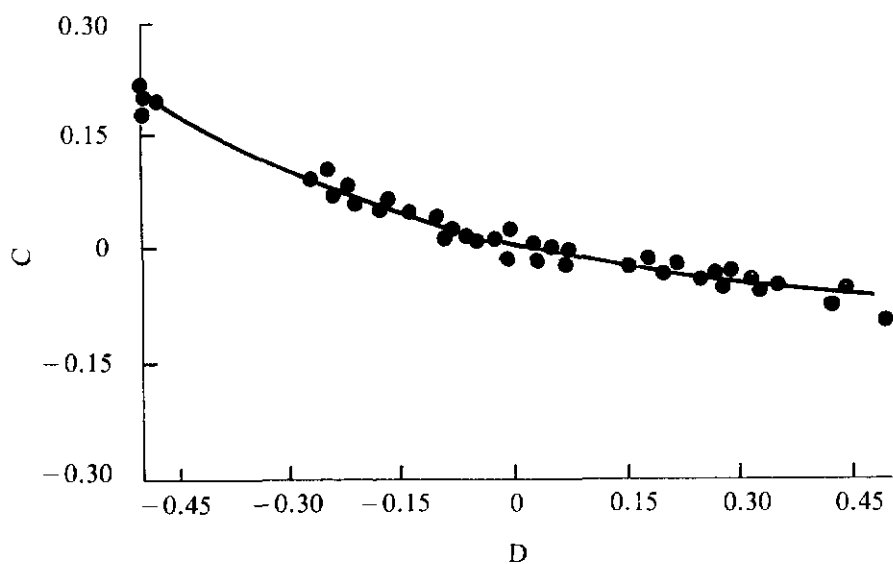
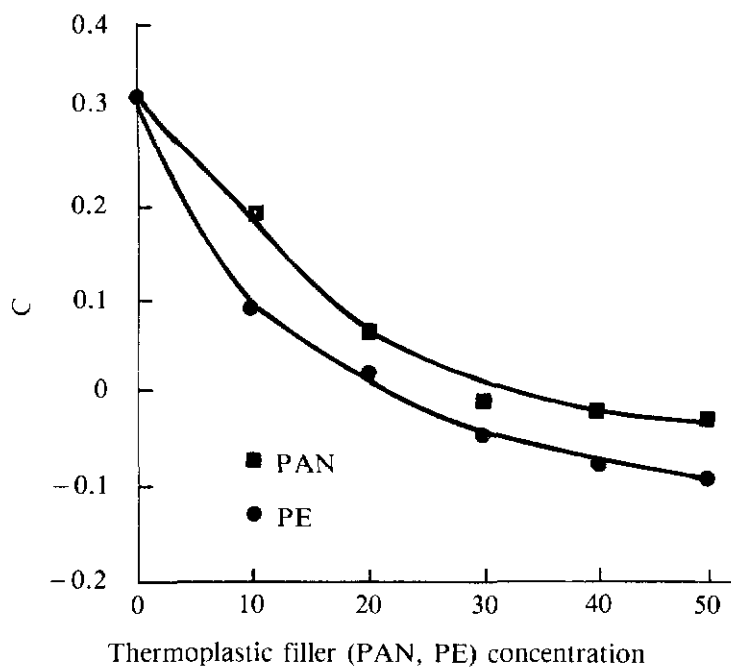*Figure 6. C* versus *D for filled and unfilled elastomers.*

Thermoplastic filler (PAN, PE) concentration

Figure 7. C versus *filler concentration: cis 1,4-polybutadiene filled with PAN or PE.*
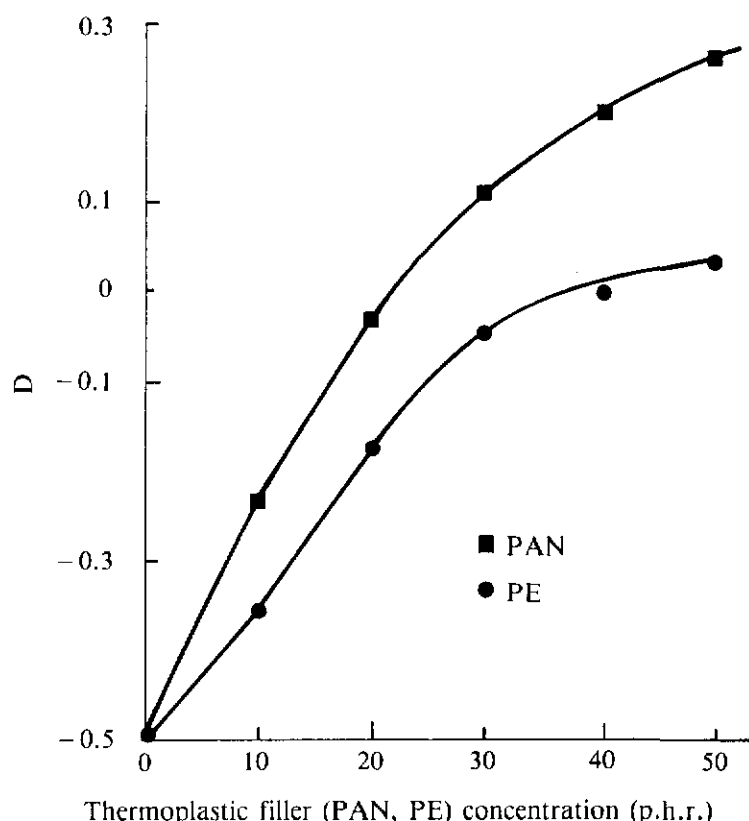
Figure 8. D versus *filler concentration; cis 1,4-polybutadiene filled with PAN or PE.*

cyclic deformation of the samples. Such results suggest that orientation of the macromolecules rather than flow processes are playing a significant role as shown in *Figures 7* and *8.*

The equation we thus propose is providing an accurate description of the stress-strain curves of elastomeric samples, on the whole range of deformations. It is valid for all types of rubbers, filled or not, amorphous or crystalline. It allows a good description of systems out of equilibrium and can be used for the description of hysteretic processes.

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