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Analytic nonlinear elasto-viscosity of two types of BN and PI rubbers at large deformations

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In this work, in analytical form, are derived instantaneous stress-strain and vice-versa relations using the Neo-Hookean and the Mooney-Rivlin models. These relations are obtained resolving algebraic equations of third and fourth degree respectively. The above mentioned analytical solutions are incorporated in the hereditary integral equations of Volterra to predict the creep and relaxation of such as materials at large deformations. One takes into account the non-linearity of the viscous behaviour in the presence of similarity in the isochrone stress-strain curves. Our theoretical results are compared with experimental data for two kinds of rubbers and demonstrate very good coincidence.

Keywords: rubber, mechanical properties, rheology, large deformations

INTRODUCTION

Rubbers are increasingly used in modern industry [1-4]. Resinous materials and rubbers are elastoviscous solids. They are very deformable and possess non-linear behaviour. Their creep is also non-linear according to the applied stresses. The last non-linearity can be observed excluding the time from the creep curves (the so-called isochrones). Thus, rubbers require identification and description of two different kinds of nonlinearities. Here we examine two compositions: the first one is the Butadiennitril rubber (BN) and the other one - the Polyisoprene rubber (PI) [5]. In the first rubber composition is used rubber with 40% acrylonitril in the macromolecule [5]. In the second composition is used polyisoprene rubber - an analogue of the natural rubber. The microstructure conciste of 1,4 cispolyisoprene with content of these units almost 98% [5]. Both elastomeric compositions include fillers (cinders) with a developed surface respectively 75 and 50 m²/ g.

THEORETICAL

Nonlinear elasto-viscosity at small deformations

The hereditary linear equations can be generalized to account the nonlinear mechanical behaviour using the Rabotnov-Rzanitzin approach [6, 7]. This approach requires similarity in the stress - strain curves for different moments

$$\varepsilon(t)=\frac{\sigma}{E}\Big[1 \;+f(\sigma)\int_0^t K(t-\tau)d\tau\Big], \tag{1}$$

where $\varepsilon(t)$ is the strain, σ - the applied stress, $f(\sigma)$ - the nonlinearity function, $K(t\text{-}\tau)$ - the creep kernel, t - the current time and $0\le\tau\le t$. Concerning the creep kernel we can say the following. It is the resolving kernel of the relaxation one. As kernels in the integral equations of Volterra like eq. (1) it is recommended to take singular kernels which better describe the enhanced creep and relaxation rate at the beginning. In this work we assume the singular relaxation kernel of Koltunov [7]

$$R(t)=A\frac{e^{-\beta t}}{t^{\alpha}} \quad , \tag{2a}$$

whose resolving kernel (the creep kernel) looks like [7].

$$K(t)=\frac{e^{-\beta t}}{t}\sum_{n=1}^{\infty}A\Gamma(\alpha)^n t^{\alpha n}/\Gamma(\alpha n) \;, \tag{2b}$$

The function of the nonlinearity $f(\sigma)$ is determined from the isochrone curves. This presentation of the nonlinearity involves a coincidence of the initial points at the strain scale and requires a similarity of the isochrones. If at low stresses (up to the limit axial stress of the linearity σ_o) the behaviour is linear, equation (1) can be generalized as follows:

$$\varepsilon(t)=\frac{\sigma}{E}\Big[1 \;+(\sigma/\sigma_o)^n\int_0^t K(t-\tau)d\tau\Big] \tag{3}$$

In equation (3) n is the potency which can be determined from the isochrones. Eq. (3) remains valid if $\sigma\ge\sigma_o$. In the opposite case the behaviour is linear and $\sigma/\sigma_o=1$. Such a presentation of the viscous nonlinearity is used in many practical problems [8].

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Nonlinear elasticity at large deformations

Rubbers are very deformable and their elastic behaviour cannot be described by the Hooke's law. Here as elastic behaviour it is mean the instantaneous elasticity of equation (3) given by the ratio before the brackets. This expression should be changed to be able to account the large elastic deformations of the rubbers.

Here it is used the theory of the large deformations described in [9]. The material is considered as isotropic and incompressible. To describe the mechanical behaviour of rubbers and other resinous materials as successful models are accepted the neo-Hookean and the Mooney-Rivlin ones [9]. According to the above models the following thermodynamic potentials are introduced

$$W = \frac{G}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \ , \tag{4a}$$

$$W = \frac{1}{2}(\varsigma - \chi)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{\chi}{4}(\lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 - 3) \tag{4b}$$

where G is the second module of Young, ζ and χ are experimentally determined parameters based on the instantaneous force-extension curves and λ_i are the large relative extensions in the main directions

$$\lambda_i = 1 + \varepsilon_i \, . \tag{5a}$$

Here $i = 1, 2, 3$ and ε_i are the main Cauchy's strains (the classic ones in the case of small displacements).

In the case of incompressible materials $\lambda_1\lambda_2\lambda_3 = 1$ and by traction it follows

$$\lambda_1 = \lambda, \quad \lambda_2 = \lambda_3 = \lambda^{-1/2}. \tag{5b}$$

Therefore, to the potentials (4a) and (4b) follows

$$W = \frac{G}{2}(\lambda^2 + 2\lambda^{-1/2} - 3) \, , \tag{6a}$$

$$W = \frac{1}{2}(\varsigma - \chi)(\lambda^2 + 2/\lambda - 3) + \frac{\chi}{4}(1/\lambda^2 + 2\lambda - 3) \tag{6b}$$

In the theory of large deformations [9] the axial tensile force is given by the expression

$$Q(\lambda) = S_o \frac{dW}{d\lambda} \, , \tag{7}$$

where S_o is the initial section of the sample associated with the current section $S(\lambda)$ as

$$S(\lambda) = \frac{S_o}{\lambda} \, . \tag{8}$$

So, based on equations (6a), (6b) and (7) to the axial tensile force of highly deformable materials are obtained the following expressions (depending on the relative extension) concerning both models respectively

$$Q(\lambda) = S_o G \frac{\lambda^3 - 1}{\lambda^2} \, , \tag{9a}$$

$$Q(\lambda) = S_o G \frac{\lambda^3 - 1}{\lambda^2}(\varsigma - \chi(\frac{1}{2\lambda} - 1)) \tag{9b}$$

Relations (9) must be expressed through the deformations of Cauchy and replaced in (3) in order to take into account the large deformations. This can be done as follows. Based on eq.(9) is deduced the relationships instantaneous stress-strain concerning both models which give the non-linearity in the elastic part of the hereditary equation (3). In the case of incompressible materials between the instantaneous Young modules one has the following relation

$$G = \frac{E}{2(1+\nu)} = \frac{E}{3} \tag{10}$$

This is because the Poisson ratio is $\nu = 0.5$. Moreover, from equations (7), (8) there is the relationship

$$\sigma(\lambda) = \frac{Q(\lambda)}{S(\lambda)} = \frac{Q(\lambda)}{S_o}\lambda \, . \tag{11}$$

Then from equations (9), (10) and (11) it is obtained the following relations stress-elongation

$$\sigma(\lambda) = \frac{E}{3}\frac{\lambda^3 - 1}{\lambda} \tag{12a}$$

$$\sigma(\lambda) = \frac{E}{3}\frac{\lambda^3 - 1}{\lambda}(\varsigma - \chi(\frac{1}{2\lambda} - 1)) \tag{12b}$$

Equations (12) may also be represented as a relation stress-strain according to eq. (5a). These expressions have the form

$$\sigma(\varepsilon) = \frac{E}{3}\frac{(1+\varepsilon)^3 - 1}{1+\varepsilon} \tag{13a}$$

$$\sigma(\varepsilon) = \frac{E}{3}\frac{(1+\varepsilon)^3 - 1}{1+\varepsilon}(\varsigma - \chi(\frac{1}{2(1+\varepsilon)} - 1)) \tag{13b}$$

Equations (13) should be resolved about the strains in order to obtain the non-linear stress-strain relation for highly deformable materials. These equations are of third and fourth degree respectively and can be represented in the following form using equations (12)

$$\lambda^3 - \frac{3\sigma}{E}\lambda - 1 = 0 \, , \tag{14a}$$

$$(\varsigma+\chi)\lambda^4-0.5\chi\lambda^3-\frac{3\sigma}{E}\lambda^2-(\varsigma+\chi)\lambda+0.5\chi=0 \quad (14b)$$

The solution of equation (14a) using the Cardano's formula [10] taking into account (5a) looks like

$$\varepsilon=\varepsilon(\sigma)=\sqrt[3]{0.5+\sqrt{0.25-(\sigma/E)^3}}+\sqrt[3]{0.5-\sqrt{0.25-(\sigma/E)^3}}-1 \quad (15a)$$

The solution of equation (14b) using the Ferrari's formula [10] taking into account (5a) looks like

$$\varepsilon=\varepsilon(\sigma)=\frac{-0.5\chi}{4(\varsigma-\chi)}+\frac{W(\sigma)+\sqrt{-(3\alpha(\sigma)+2y(\sigma)+2\beta(\sigma)/W(\sigma))}}{2}-1, \quad (15b)$$

where:

$$\alpha(\sigma)=\frac{-3(0.5\chi)^2}{8(\varsigma+\chi)^2}-\frac{3\sigma/E}{\varsigma+\chi},$$

$$\beta(\sigma)=\frac{-(0.5\chi)^3}{8(\varsigma+\chi)^3}+\frac{3\sigma\chi/E}{4(\varsigma+\chi)^2}-1$$

$$\gamma(\sigma)=\frac{-3(0.5\chi)^4}{256(\varsigma+\chi)^4}-\frac{3\sigma(0.5\chi)^2/E}{16(\varsigma+\chi)^3}+\frac{3\chi}{8(\varsigma+\chi)}$$

$$Q(\sigma)=-\frac{1}{108}\alpha^3(\sigma)+\frac{1}{3}\alpha(\sigma)\gamma(\sigma)-\frac{1}{8}\beta^2(\sigma),$$

$$P(\sigma)=-\frac{1}{12}\alpha(\sigma)-\gamma(\sigma)$$

$$R(\sigma)=-\frac{1}{2}Q(\sigma)-\sqrt{\frac{Q^2(\sigma)}{4}+\frac{P^3(\sigma)}{27}},$$

$$y(\sigma)=\frac{5}{6}\alpha(\sigma)+\sqrt[3]{R(\sigma)}-\frac{P(\sigma)}{3\sqrt[3]{R(\sigma)}},$$

$$W(\sigma)+\sqrt{\alpha(\sigma)+2y(\sigma)}.$$

Nonlinear elastoviscosity at large deformations

The relationship of the Cauchy's deformations with the stresses in the form (15) is used as instantaneous nonlinearity in the hereditary equation (2). Equation (2) based on (15) looks like

$$\varepsilon(t)=\varepsilon_o(\sigma)\left[1 \;+(\sigma/\sigma_o)^n\int_0^t K(t-\tau)d\tau\right] \quad (16)$$

The creep law (16) contains parameters that need to be experimentally identified. The necessary experimentations are as follows:

- Instantaneous (with constant strain rate or otherwise) identified from (15). Note that eq. (15a) is a very successful equation containing only one parameter to describe the complex nonlinear elasticity and this is the elastic module *E*.
- Tests based on the curves of stress relaxation (or creep) in the linear region at small imposed strains. These parameters are identifiable from (3) at low stresses $\sigma \leq \sigma_0$.
- Tests based on the isochrone curves of creep (or relaxation). These parameters are identifiable from equation (3) at high stresses $\sigma > \sigma_0$.

EXPERIMENTAL

Fig.1 and Fig.2 show the instantaneous nonlinearity of the butadienenitril (BN) and polyizoprene (PI) rubbers.

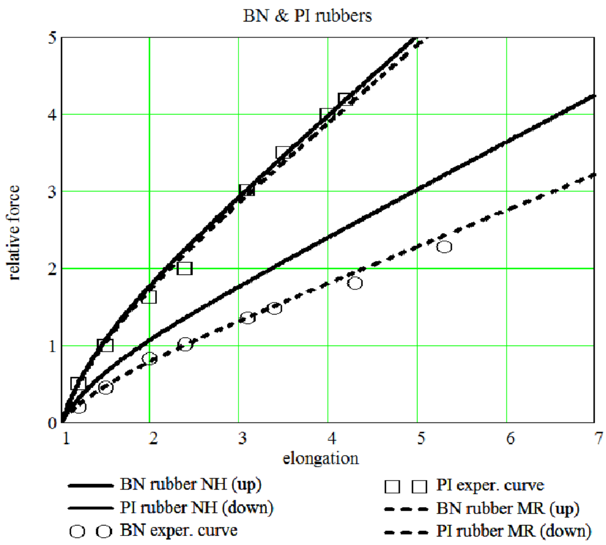

Fig.1. Relative tensile force - relative elongation according to the Neo-Hookean and according to the Mooney-Rivlin law for both rubbers

Both rubbers are produced on open mixer with dimensions 400x150 [mm] at T=50^{0}C. Time of vulcanization is determined on oscillating rheometer type "Moncanto". Vulcanization of tested specimens is done at hydraulic press with automatic control of pressure and temperature.

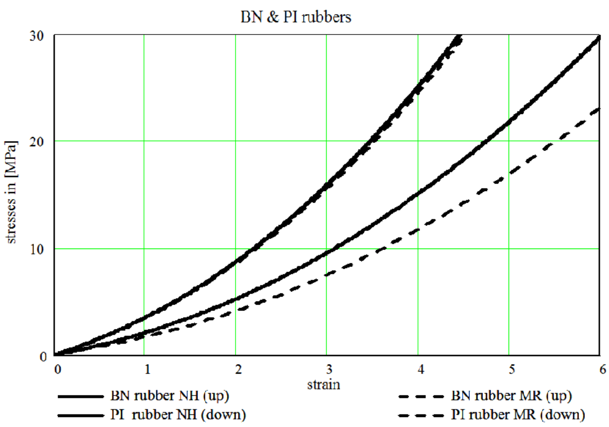

Fig.2. Tensile stress - strain according to the Neo-Hookean - equation (14a) and to the Mooney-Rivlin law - equation (14 b) for both rubbers. Solid lines - the Neo-Hookean, dashed lines - the M. Rivlin model, above - PI rubber, below - BN rubber

Fig.3 and Fig.4 illustrate the identification of the above parameters concerning both rubbers. Figure 3 shows the stress relaxation of the BN by constant strain. Fig.4 shows the corresponding creep curve for BN at stresses on the limit of the nonlinearity (see Table 1a and Table 1b). The same is done in Fig.5 and Fig.6 for the PI rubber.

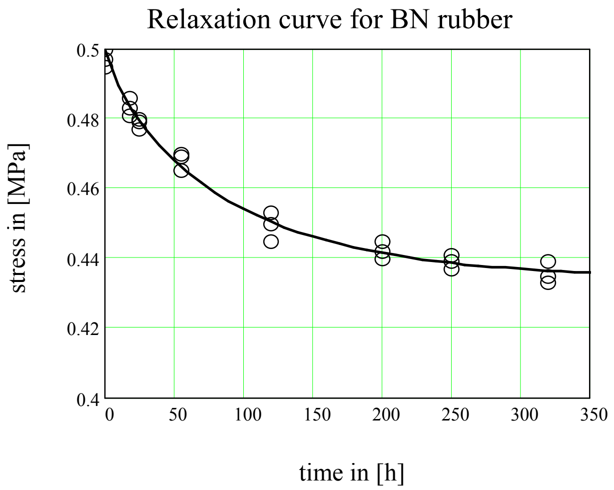

Fig.3. Stress relaxation of BN rubber

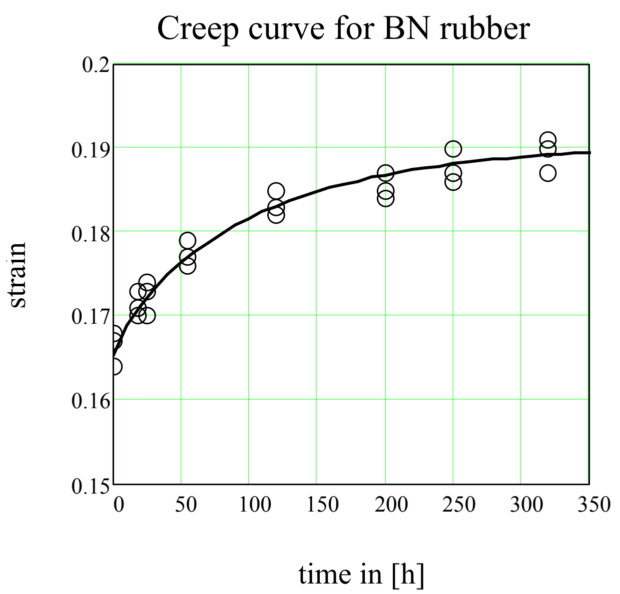

Fig.4. Creep curve of BN rubber

Note: In Fig,3 and Fig.4 are shown all the experimental points. In the next figures - just the averaged values.

Creep curves are not necessary to predict the behaviour and can be used only for verification. In practice, the parameters in the Koltunov's kernel can be identified from the relaxation curves, which can be obtained much easily than the creep curves.

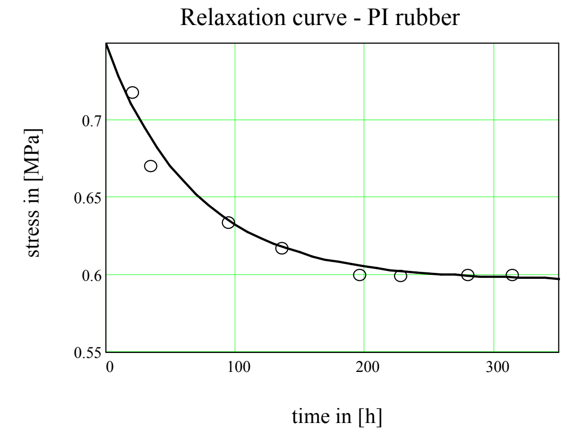

Fig.5. Stress relaxation of PI rubber

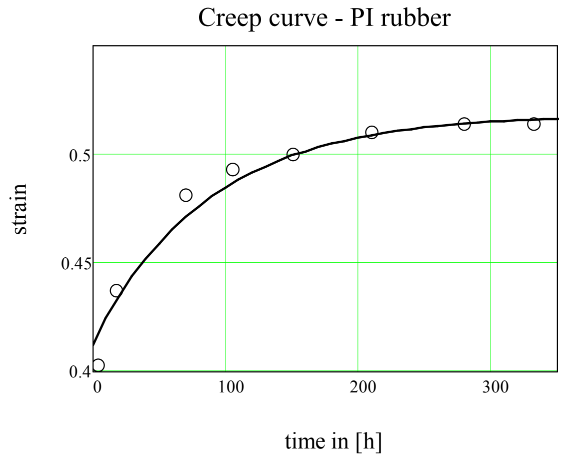

Fig.6. Creep curve of PI rubber

In the next two Fig.7 and Fig.8 are shown the nonlinear isochrone curves stress-strains at stresses greater than the limit of non-linearity.

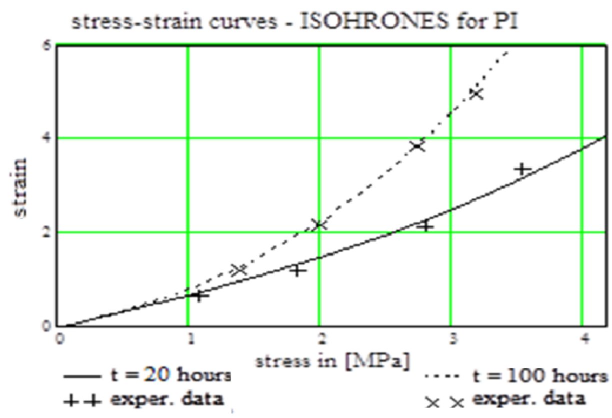

Fig.7. Rubber nonlinearity of PI rubber (isochrones at 20 and 100 hours)

Fig.9 and Fig.10 show the creep of the PI and BN rubbers at two stress levels according to equation (16).

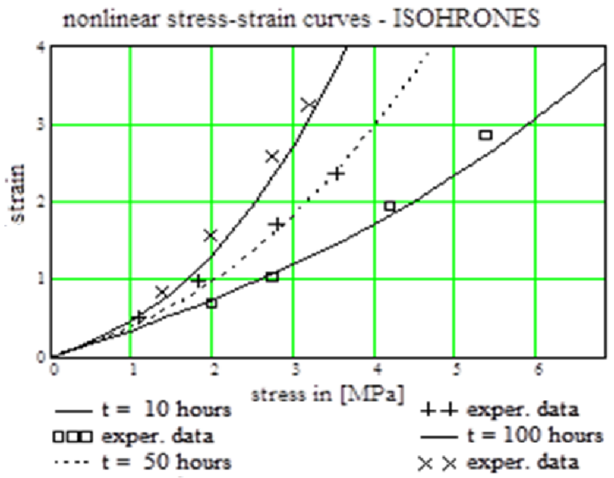

Fig.8. Rubber nonlinearity of BN rubber (isochrones at 10, 50 and 100 hours)

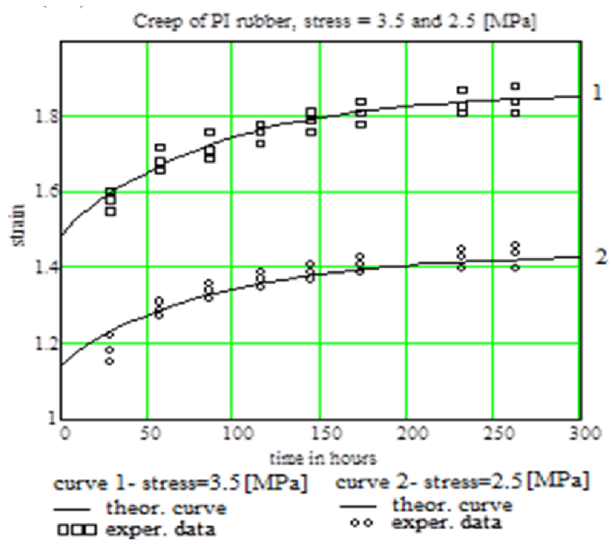

Fig.9. Creep at large deformation of PI

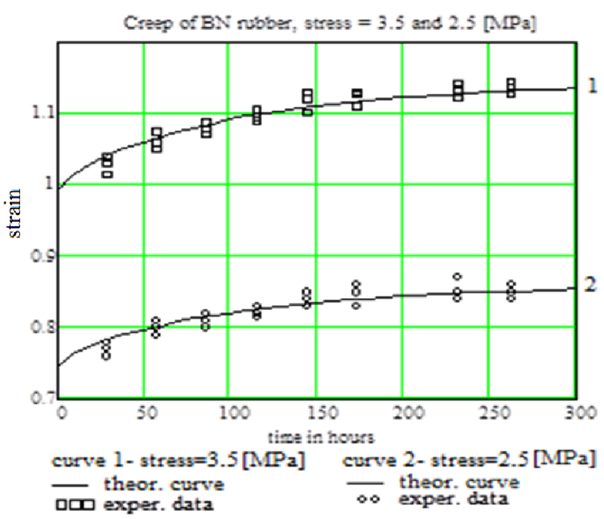

Fig.10. Creep at large deformation of BN

From both figures we can see that under bigger stress for studied time interval creep has unidentified character.

Finally, in Table 1(a and b) are systematized all the parameters obtained from the experimental curves above.

Table 1. (a and b) Elastoviscous characteristics of the investigated rubbers

Table 1a. Instantaneous (elastic) characteristics

Character	Elastoviscous instantaneous (elastic)				
Parameters	E	σ_o	N	χ	ς
Dimension	[MPa]	[MPa]	-	-	-
PI rubber	1.820	0.75	1.71	0.124	0.642
BN rubber	3.025	0.50	1.55	0.018	0.960

Table 1b. Hereditary (viscous) characteristics

Character	elastoviscous hereditary (viscous)		
Parameters	A	α	β
Dimension	-	-	-
PI rubber	0.0032	00.97	0.0140
BN rubber	0.0029	00.77	0.0089

RESULTS AND DISCUSSION

For the BN rubber both models give good results. Therefore for BN rubbers it is used the neo-Hookean model. It has the advantage that it does not require the entire force-displacement curve to determine the parameters (the elastic module is sufficient). The PI rubber however, requires the use of the 3-parameter model of Mooney-Rivlin.

Stress-strain curves according to equations (12a, b) or also to (15a, b) appear as shown in Fig.2. The experimental results in figure 1 show that the neo-Hookean law well describes the instantaneous behaviour of the BN rubber but to the PI rubber should be applied the more flexible model of Mooney-Rivlin.

The assumption of incompressibility for the rubbers is perfectly acceptable. For our materials the Poisson's ratio values are 0.485 to the BN rubber and 0.49 to the PI rubber.

The hereditary theory with kernel of Koltunov well describes the temporary effects due to the viscosity.

CONCLUSION

Using the integral equations of Volterra to describe the nonlinear elastoviscous behaviour are obtained equations predicting the time dependent behaviour taking into account the stress-strain nonlinearity. On the basis of the Neo-Hookean and Mooney-Rivlin models concerning the instantaneous nonlinearity at large deformations are derived the respective strain-stress constitutive relations in analytical form. Both Neo-Hookean and Mooney-Rivlin models well describe the instantaneous mechanical behaviour at large deformations for the BN rubber. Concerning the PI rubber, only the Mooney-Rivlin model is able to well predict the stress-strain instantaneous constitutive relation. These strain-stress constitutive relations are incorporated in the hereditary theory of Volterra to obtain the complex time dependent mechanical behaviour of rubbers at large deformations. The theoretical predictions show very good coincidence with the experimental data for PI and BN rubbers.

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