ABOUT KINETIC THEORY OF THE ELASTICITY OF RUBBER

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ABSTRACT

In this paper we analyze theoretically and experimentally few sizes connected to the rubber elastic characteristic and we will determine elastic module and specified deformation energy. In the first part we obtain the characteristic relations for these two sizes (G,U) based on the kinetic theory of elasticity.In the second part we analyze the figures obtained experimentally by constraining a rubber piece to a monoaxial compression on a special stand to obtain the values for G and U. The values are graphically interpreted and they are also processed in a table. Finally, we make a comparison between the values obtained through the experiment and the ones obtained theoretically.

Keywords: elasticity, entropy, transversal elasticity module, own energy for deformation, rubber

1. INTRODUCTION

The rubber (rubber mixture) used for pieces fabrication contains, beside rubber itself (the elastomer) and other substances (ingredients). Vulcanised rubber mixture is a material whose character is mostly elastic, although it also keeps its plastic character. Consequently, rubber mixtures are considered as viscoelastic materials. Elasticity derives from the substance's molecular structure. Rubber's molecular structure is described by:

- Long macromolecular chains that rotate freely around the bands with neighbouring molecules.
- Bounded macromolecular chains forming space system.
- Molecules with large mobility.

2. THEORETICAL ASPECTS

Rubber elasticity is of kinetic nature, while crystalline material's elasticity is determined by the atom's interactions nature, so, rubber's particular elasticity is called high elasticity. The explanation of high elasticity has been provided by Mark an Kuhn through intermolecular thermal movement, having a particular entropy character [1, 2]. High elasticity is first treated by examining the phenomena at macromolecular scale [6]. This theory provides data for elastic and resistance rubber properties when the rubber is constrained to deformation that are smaller than 300%. For statistic treating of rubber elasticity, an ideal macromolecule is used. The ideal macromolecule is the simplest model possible, which does not correspond discretely to any certain molecular structure. This macromolecule contain n bonds of the same length l.
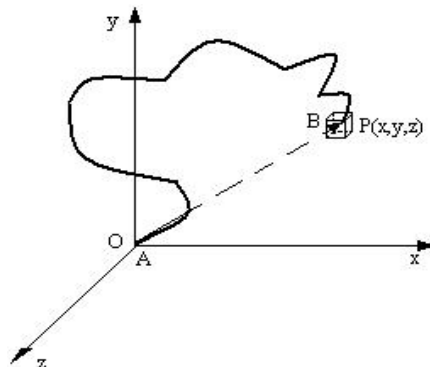

Figure 1. *Figure for determining the macromolecule's end*

Treating this macromolecule is not of interest to know the valence angle or any other restrictions over elements mobility from the macromolecule. It is considered that the macromolecule has the end A fixed in xOyz system origin and the end B mobile moving at random. Even if the macromolecule's end B's movement is at random all B's position do not have the same probability. For a particular position, P of coordinates x,y,z, there will be a probability associated in such manner that the end B will be located in a volume element in the shape of a cuboid, $d\tau = dxdydz$. The knowledge of this probability requests the evaluation of the relative number of configurations of the macromolecular chain that consists in different positions of point B.

The probability of any particular position is considered proportional with the number of configurations according to the relation:

$$p(x, y, z)dx.dy.dz = \frac{b^3}{\sqrt{\pi}} \exp\left\{-b^2\left(x^2 + y^2 + z^2\right)\right\}dx.dy.dz, \qquad (1)$$

Where:

$p(x,y,z)$ represents the probabillity density;

$$b^2 = \frac{3}{2nl^2}. \qquad (2)$$

The (1) relation gives the probability that the components of the vector r that gives the position of the macromolecular chain to be found in the intervals x to $x+dx$, y to $y+dy$, z to $z+dz$. The (1) relation has a great importance in the statistic theory of rubber's elasticity. The form of this relation is that of the Gaussien error and it is true only if the length of vector r is much smaller than the maximum length, nl of the macromolecular chain. The distribution function (probability density) of the macromolecule's free end has spherical symmetry and because of that it can be written like this:

$$p(x, y, z) = \left(\frac{b^3}{\sqrt{\pi}}\right)\exp.\left\{-b^2\left(x^2 + y^2 + z^2\right)\right\} = \left(\frac{b^3}{\sqrt{\pi}}\right)\exp.\left(-b^2 r^2\right). \qquad (3)$$

Considering the relation (3), the (1) relation can be written like:

$$p(x, y, z)dx.dy.dz = \frac{b^3}{\sqrt{\pi}}\exp(-b^2 r^2)d\tau. \qquad (4)$$

For the macromolecular chain, the entropy scan be determined, using the relation:

$$s = k[\ln p(x, y, z)d\tau], \qquad (5)$$

Where k is the Boltzmman constant. Replacing the (4) relation in the (5) relation:

$$s = k[\ln(const.) - b^2 r^2 + \ln d\tau]. \qquad (6)$$

But the volume element $d\tau$ is considered constant and that is why the (6) relation can be written:

$$s = c - kb^2 r^2, \qquad (7)$$

Where c is an arbitrary constant that includes the elementary volume $d\tau$. In any situation we are interested with the entropy variation between two states, c constant does not have an meaning in physics. From the (7) relation it can be observed that the entropy has maximum value when the two ends of the macromolecular chain are the same ($r=0$). Next an individual chain is considered subjected to a deformation. In the analysis of the rubber macromolecule's deformation, it is considered that the main deformation axis are the coordonate axis. Following a deformation defined by the $(\lambda_1, \lambda_2, \lambda_3)$, components, the macromolecule's end occupies a new position, in the elementary volume $dx.dy.dz$ and it is showed by the vector r, described by the (x,y,z) coordonates, which means that the initial vector is described by the $(x/\lambda_1, y/\lambda_2, z/\lambda_3)$ coordinates. The macromolecular chain's entropy in a non-deformed state is given by the relation:

$$s_0 = c - kb^2 r_0^2 = c - kb^2(x_0^2 + y_0^2 + z_0^2). \qquad (8)$$

The entropy of the same macromolecular chain extended is given by the following equation.

$$s = c - kb^2 r^2 = c - kb^2 (\lambda_1^2 x_0^2 + \lambda_2^2 y_0^2 + \lambda_3^2 z_0^2). \tag{9}$$

The entropy variation as a deformation result is found through the following equation:

$$\Delta s = s - s_0 = -kb^2 [(\lambda_1^2 - 1)x_0^2 + (\lambda_2^2 - 1)y_0^2 + (\lambda_3^2 - 1)z_0^2] \tag{10}$$

Total entropy for N macromolecular chains in the volume unit obtained because of the deformation is given by the relation:

$$\Delta S = \sum \Delta s = -kb^2 [(\lambda_1^2 - 1)\sum x_0^2 + (\lambda_2^2 - 1)\sum y_0^2 + (\lambda_3^2 - 1)\sum z_0^2],$$
$$\text{where: } \sum x_0^2 + \sum y_0^2 + \sum z_0^2 = \sum r_0^2. \tag{11}$$

Because the direction vector r_0 in non-deformed state is aleatory we consider:

$$\sum x_0^2 = \sum y_0^2 = \sum z_0^2 = \frac{1}{3}\sum r_0^2 ,$$

but using the position sum of the position vectors that characterize mobile ends of those N un-deformed macromolecules we can obtain quadratic average of position vector r_0 with relation:

$$\sum r_0^2 = N \overline{r_0^2} . \tag{12}$$

Introducing relation (12) in relation (11) the entropy variation of N macromolecules from volume unit we will obtain:

$$\Delta S = -\frac{1}{3} Nkb^2 \overline{r_0^2} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3). \tag{13}$$

If we know relation (2) and the fact that the quadratic average of position vector r_0 is comparable with maximum length, nl of the macromolecular chain, $\overline{r_0^2} = 3/2b^2$ then relation (13) will be:

$$\Delta S = -\frac{1}{2} Nk(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3). \tag{14}$$

To calculate the own deformation energy we use the variations of energy and deformation and:

$$\Delta S = -\frac{U}{T} \Rightarrow U = \frac{NkT}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3). \tag{15}$$

where U represents own deformation energy T represents temperature. In (15) relation the product $NkT = G$ (G represents the transversal elastic module).
Applying these to a monoaxial deformation and keeping in mind that rubber element is not compressible ($\lambda_1 \lambda_2 \lambda_3 = 1$), we obtain deformation energy on volume unit:

$$U = \frac{G}{2}(\lambda_1^2 + \frac{2}{\lambda_1} - 3). \tag{16}$$

To obtain tension σ we start from relation (16) and we use the fact that $dU = \sigma.d\lambda$ and we obtain $\sigma = \frac{dU}{d\lambda}$; and deriving relation of the own deformation energy we obtain:

$$\sigma = G(\lambda_1 - \frac{1}{\lambda_1^2}) \Rightarrow G = \frac{\sigma}{\lambda_1 - 1/\lambda_1^2}. \tag{17}$$

3. EXPERIMENTAL CHECKINGS

For determining the tension from the rubber mixture, epruvet have been used, like the one in Figure 2.

This rubber epruvet was constraint to deformation along the *Ox* axis, operation that was realized on a special dynamometer, the monoaxial deformation of the epruvet has been released with the constant velocity of 500 mm/min. The values for the active section, S_0 of the epruvet, for the force, *F,* for the deformation ratio, λ are found in the first and second tables. Processing the data in the first table and using the relation (17), we obtain the value $G=1.41.10^6$ N/m^2.
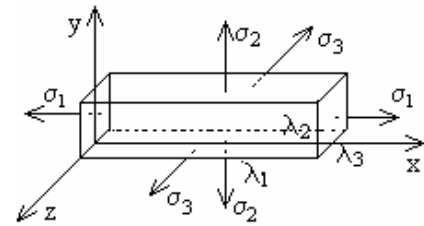

Figure 2. *Epruvet*

Table 1.

Nr. crt.	S_0 m^{-2}	λ	F N	$\sigma = F/S_0$ N/m^2	G N/m^2	$G_{med.}$ N/m^2
1	$12.56 \cdot 10^{-4}$	4.5	$75.36 \cdot 10^2$	$6.0 \cdot 10^6$	$1.34 \cdot 10^6$	$1,41 \cdot 10^6$
2	$12.56 \cdot 10^{-4}$	4.5	$81.4 \cdot 10^2$	$6.5 \cdot 10^6$	$1.46 \cdot 10^6$	$1,41 \cdot 10^6$
3	$12.56 \cdot 10^{-4}$	4.5	$80.52 \cdot 10^2$	$6.41 \cdot 10^6$	$1.44 \cdot 10^6$	$1,41 \cdot 10^6$

Considering the (16) relation and the values of *G*, the value obtained for the deformation energy per unit volume is $U = 12,50.10^6 \ J/m^3$.

Table 2

Nr. crt.	λ	G N/m^2	U J/m^3	$U_{med.}$ J/m^3
1	4.5	$1.34 \cdot 10^6$	$11.85 \cdot 10^6$	$12.50 \cdot 10^6$
2	4.5	$1.46 \cdot 10^6$	$12.90 \cdot 10^6$	$12.50 \cdot 10^6$
3	4.5	$1.44 \cdot 10^6$	$12.73 \cdot 10^6$	$12.50 \cdot 10^6$

4. CONCLUSIONS

The numeric values for *G* and *U* are obtained using statistic theory. The values obtained for the two measures are comparable with the values obtained using other methods found in different specialty papers [1]. This aspect shows that statistic theory explains relatively well the elastic character of rubber. Existent deviation between the numeric values obtained with statistic theory and other methods are because this theory explains the elastic characteristic of rubber and because that in experimental methods these measures are was determined on epruvets and rubber pieces. In the case of rubber pieces values of these measures does not depend only on the rubber mixture, and they also on the shape and size of rubber pieces. Bound to the theoretical aspects presented and experimentally determined you can conclude:

- the adhesion process it can base on the diffusion process;
- diffusion can be considered only if we admit that it exists a contact area where the London forces manifests.

5. REFERENCES

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