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EMPLOYMENT OF THE DYNAMIC METHOD OF STUDIES FOR EVALUATION OF THE RUBBER VISCOELASTIC PROPERTIES

by

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PROPERTIES

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Study of rubber by the dynamic mechanical methods provides with a great deal of information concerning the rubber structure as well as the influence of composition and of production conditions on this structure. The viscoelastic parameters of rubber, which are designated as a function of temperature, enabling to provide with the miscibility evaluations of the rubber's individual components. Due to easiness of the selection of the deformation frequency and amplitude, one very often carries out the studies of the dynamic mechanical properties of rubber, bringing into existence the sinusoidal deformation of the studied sample [1-4].

Let presume that the viscoelastic element is subjected to harmonically changing deformations:

\[ E(t) = E_0 e^{i\omega t} = E_0 (\cos \omega t + i \sin \omega t) \]  

\( E(t) \) - deformation;
\( E_0 \) - deformation amplitude;
\( \omega \) - circular frequency of the forced vibration;
\( t \) - time.

Applying the Boltzman superposition [5] the dependence between tension and deformation can be presented as:

[translator's note: module = modulus]
\[
\sigma(t) = \int_{-\infty}^{t} \frac{\partial E(u)}{\partial u} \psi(t-u) du \quad (2)
\]

where:
- \(\sigma(t)\) — tension;
- \(\psi(t-u)\) — relaxation function;

Substituting \(\tau = t-u\) we will obtain:

\[
\sigma(t) = -\int_{0}^{\infty} \frac{\partial E(t-\tau)}{\partial \tau} \psi(\tau) d\tau \quad (3)
\]

Taking into consideration dependence (1) dependence (3) will turn into

\[
\sigma(t) = E(t) \int_{0}^{\infty} i\omega e^{i\omega \tau} \psi(\tau) d\tau \quad (4)
\]

or

\[
\frac{\sigma(t)}{E(t)} = \int_{0}^{\infty} i\omega e^{i\omega \tau} \psi(\tau) d\tau
\]

The proportionality constant between the tension and deformation is called module.

\[
\frac{\sigma(t)}{E(t)} = E^w
\]

Using the complex number properties, equation (4) can be written in the form of:

\[
E^w = \int_{0}^{\infty} \omega (\sin\omega \tau) \psi(\tau) d\tau = \int_{0}^{\infty} \omega (\cos\omega \tau) \psi(\tau) d\tau \quad (5)
\]
Therefore, the E module consists of the actual and imaginative part. If to designate

\[
E'(\omega) = \omega \int_{0}^{\infty} \sin(\omega \tau) \Psi(\tau) d\tau \\
E''(\omega) = \omega \int_{0}^{\infty} \cos(\omega \tau) \Psi(\tau) d\tau
\]

we will obtain:

\[E^* = E' + iE''\]

Consequently, the \(E^*\) module is a complex number and therefore it is called very often a complex module or a complex dynamic module. Every complex number can be presented in the trigonometric form.

\[E^* = E' + iE'' = |E^*| (\cos \delta + i \sin \delta)\]

where

\[|E^*| = \sqrt{(E')^2 + (E'')^2} \quad \text{absolute value of the complex module}\]

\[\delta = \arctg \frac{E''}{E'} \quad \text{phase shift angle}\]

i.e.,

The \(\delta\) parameter, the phase shift angle between stress and deformation or between \(E'\) and \(E^*\), characterizes the damping capacity of the rubber under testing. The bigger the value of the phase shift angle, the more energy is consumed by the rubber in every cycle of deformation.

Methods of Testing

Forced Vibrations

Testing with employment of forced vibrations without resonance enable to define the mechanical dynamic properties of rubber on a
single sample within the range of several frequency or amplitude series under the same temperature. When a deformation frequency is permanent, the test can be carried out by changing the temperature. The devices which are used for testing the dynamic properties of rubber differ from each other mostly in their construction and measuring principles. They are very often equipped with electronic circuits which make the result reading, control over equipment performance and testing result computations easier.

As an example of a frequently used device which operates on the principle of the forced vibration is RHEOVIBRON DDV-II (See Figure 1), which was produced by "Toyo Measuring Instruments Co Ltd" [6, 7] and whose main purpose is to measure the module within the range of $10^6$–$10^{12}$ dyne/cm$^2$ under cyclic stretching of the sample in the form of a belt.

![Figure 1. The scheme of the device for the dynamic tests (Rheovibren Model DDV-II-C). 1 - oscillator (.01-1 Hz); 2 - oscillator (3.5-110 Hz); 3 - phase regulation; 4 - power regulator; 5 - amplifier; 6 - vibrator; 7 - deformation indicator; 8 - tension indicator; 9 - converter; 10 - power amplifier; 11 - recorder; 12 - meter; 13 - sample.]

The deformation frequency can change from .01 up to 110 Hz. Studies are also being carried out within the wide range of temperatures (from -140°C up to +200°C). The tension and deformation amplitudes as well as the $\tan \delta$, which are measured by proper indicators, serve for the computation of the $E^*$ dynamic module as well as its components designated as $E'$ and $E''$.

Another device for dynamic tests, which operates on the principle of forced vibrations, has been worked out in RAPRA. It is being
produce by the "Wallace" firm [1]. The above-mentioned device, whatever version is chosen, is adjusted for tests under the variable deformation amplitude which varies from .001 to .5 and the variable frequency varying from .0001 to 30 Hz within the temperature range from -70 up to +200°C.

The D8 device (see Figure 2) of the "Wallace" firm [8] is designated for tests with a single frequency which is equal to .25 Hz, but it can operate within wide range of amplitudes as well as temperatures from +25°C to 150°C. The test principle is laid in a forcible deformation (cutting off) of a sample consisting of two cylinders which are glued between motionless plates and a movable plate which causes deformation. The plates shift (the complete deformation) as well as force are measured by means of indicators and an indicating meter. The data obtained are recorded on the oscilloscope. Besides the above-mentioned this device is equipped with a circuit which secures the direct measurement of the $\delta$ or the phase shift angle.

Figure 2. The scheme of the D8 device produced by the "Wallace" firm [8]. 1 - sample; 2 - force indicator; 3 - deformation indicator; 4 - intermediate springs; 5 - photo-cell; 6 - movable plate; 7 - disk with two slots.

Key: (1) to oscilloscope.
The determined tension, deformation and phase shift angle are the foundation for computing the complex module designated as $G$ (the transverse elasticity) as well as its $G'$ and $G''$ components.

Free Vibrations

The rubber dynamic properties can be also studied by means of the twisting pendulums under the free vibration conditions [9-12].

Most devices which are designated for this kind of studies have relatively simple design. However, they cannot secure the determination of the vibration frequency, since it depends on the sample reaction. Through changing the measurement temperature we can simultaneously obtain the frequency change under the same inertia moment.

In practice there are two principal methods (A, B) which are used for testing. The difference is in fixing the inert mass. In the A method the mass increasing the pendulum inertia moment is fixed directly at the lower sample holder. In case of the rubber testing it can cause the sample deformation, which in its turn influences the measurement result and therefore, requires proper corrections during the results' computations.

In the B method the inert mass is fixed over the sample. This mass's weight counterbalances the lever system which supports the inert mass by means of a steel cord. This cord, introduced to a movable system, also influences the measurement results. This influence is represented in the form of the $f_0$ correction which corresponds to the system vibration frequency without a sample.

In both of these methods the measurement result is an attenuating harmonic curve which is being recorded by means of the optical, sparking or electrical system. On the basis of the course of vibrations the $A$ logarithmic decrement and $G^*$ dynamic module can be computed [12].
Factors Influencing the Rubber Visco-Elastic Properties

The Influence of the Sample Form and Test Time

During the test, especially when it is being accompanied by significant frequencies and amplitudes, the energy dispersion takes place. The reason for that is damping which is caused by the rubber. In its turn it causes a local increase in temperature influencing the test results. As the result of the above-mentioned during the test a change of module and of damping takes place [13] (See Figure 3).

![Figure 3](image)

Figure 3. Changes in the hysteresis cycle as a function of the test time [13]. A - at the time from 0 to 30 sec from starting the device; B - after 30 sec; C - after 2 minutes; D - after 5 minutes.

Key: (1) Tension, lb; (2) Total deformation, om.

The solution of this problem can be achieved by employment of the fast single deformation technique (shot) which is made possible when modern electronics are involved (e.g. the digit memory) [14]. When testing with a small frequency and amplitude, the heating effect is of no significance. The testing results are also influenced by the type of tension and sample shape.

The dynamic module of the longitudinal elasticity designated as $E^*$ and this of the transverse one designated as $G^*$ are reciprocally computed, basing themselves on Poisson's ratio which is designated as $\mu$.

$$E^* = 2G^* (1) \text{ or } G^* = \frac{E^*}{2(1+\mu)} \quad (9)$$
The influence of the sample dimensions and shape is a complicated phenomenon in case of the samples with irregular shapes. For the majority of studies which were being carried out under the forced vibration condition, the shape factor is being computed as relation of the loaded surface to the unloaded one [1, 15]. When tests are being carried out by means of the twisting pendulum, the sample shape is considered in the computational sample.

The Influence of the Deformation Frequency, Temperature and Amplitude

The dynamic module and extinction coefficient and consequently, the parameters describing the rubber viscoelastic character, undergo significant changes when the test temperature and frequency change. This corresponds to the changes occurring in the rubber.

Interesting information can be provided by rubber testing at a low temperature.

On Figure 4 [6] one can notice the maximum on the $E''$ component which is typical for transformation in the glassy state. The test of the temperature of the transition into glassy state ($T_g$) has great recognizable significance [1, 16].

![Figure 4. The $E'$ elastic and $E''$ plastic components of the complex module of the copolymer butadiene-styrene (CBS) vulcanizates filled with silica as a function of temperature [6].](image)

Key: (1) Module dyne/cm$^2$.

Familiarization with the information concerning the rubber structure and possibility of its employment.
Such copolymers as butadiene-styrene (about 25 percent of styrene) with a different structure (from the statistical structure to the block one) produce the typical shift $T_g$ (Figure 5) [17, 18]. Besides this, two points of change within another temperature range show up in the block copolymer. The appearance of two pronounced maximums on the $\tan \delta$ curve (or $E''$), which is presented as a function of temperature, is evidence of the non-uniformity of the system under study.

The copolymers with intermediate structure have transitional properties between the statistical properties and the ideal block ones.

The dynamic modulus and damping ($\Lambda$) also depend on the vibration frequency in a different way, which is a function of vulcanizate composition. As an example one can mention the change in the elastic component $E'$ of the dynamic modulus of natural rubber vulcanizates which are filled with different types of carbon black [19] (Figure 6). The vulcanizates which are filled with carbon black with a bigger specific surface show less dependence on frequency. The damping of the rubber, which is made of different kinds of pure rubber, changes also along with the frequency change. Figure 7 presents the changes, as a function of frequency, in $\tan \delta$ of vulcanizates of natural rubber (NR), cis-1, 4 (BR-1) butadiene rubber, butadiene rubber containing 68% of the trans-1, 4 BR-2) isomer, and butadiene-styrene rubber (SBR) with different content of styrene.

There is a pronounced increase in $\tan \delta$ with an increase in the styrene content of copolymer butadiene-styrene (CBS). In the case of butadiene rubber the predominance of the trans- structure results in increased damping. The testing results which were obtained through the frequency decrease are similar to those which were obtained through the frequency decrease are similar to those which were obtained through the temperature increase. During the temperature decrease one can obtain the same effect which can be obtained with
Figure 5. Tangent of the phase shift angle (tg δ) as a function of the temperature of the block- and statistical copolymers (butadiene-styrene) [17, 18]. A – homogeneously statistical; B – statistical; C – block; D – ideal block.

Figure 6. The elastic component of the E' modulus of the natural rubber vulcanizates KN filled with different carbon blacks as a function of frequency [19].

Figure 7. The tg δ changes of different rubber vulcanizates as a function of frequency. NR – natural rubber; BR – butadiene rubber; SBR – butadiene-styrene rubber.

Figure 8. Changes of the G' module of the butyl rubber vulcanizates with different degree of filling with the HAF black as a function of the deformation amplitude [1].
the frequency undergoing increase. In practice this is taken care of through the use of "reduced variables" [3-5].

A great deal of very interesting information concerning the rubber structure is provided by the studies which are being carried out with different deformation amplitude (Figure 8) [1]. Exceeding a certain amplitude value causes the rupture of the filler internal structure which is expressed by a sudden modulus decrease.

It is typical that the greater the degree of filling is for the rubber, the bigger the modulus decrease is. It is understandable that in the unfilled rubber there is no phenomenon like this. As it follows from the above-mentioned the modulus decrease is the value characterizing the filler effect and can be used for the evaluation of filler.

The Influence of the Filler Type and Quantity

The filler quantity and type significantly change the rubber characteristics, especially its mechanical dynamic characteristics, [1, 6, 7, 20-28]. Along with variations of the filler type, dependences of the dynamic modulus vary as functions of temperature and frequency. The influence of the filler quantity on the value of the dynamic modulus of the butyl vulcanizates with a different degree of filling with the HAF black is shown on Figure 8 [1]. This figure shows very distinctly how the complex modulus grows along with the increase of the filler quantity.

The parameter determining the influence of carbon black on the complex modulus with a small deformation amplitude is the specific surface (Figure 9). Dependence of the \( G^* \) modulus on the black specific surface is linear; the black type - either furnace or lamp does not influence this dependence. Smaller modulus values are typical for the channel black. They also lie along the single curve.
The values given on Figure 9 should be regarded as tentative due to existence of many other parameters influencing the modulus value.

A similar profile characterizes the dependence of the modulus on the specific surface of the vulcanizates which are filled with the precipitated silica [6]. Figure 10 presents the dependence of the $E'$ modulus on the statistical stretching of the copolymer butadiene-styrene vulcanizates filled with different kinds of silica.

The modulus grows significantly along with the specific surface whose indicator is the nitrogen absorption. However, even nowadays when there are many scientific works devoted to this problem, there is no complete solution for it. Employment of the well known equations of Gurth and Gold or Smoolwood does not always give results which coincide with our practical experience. However, attempts to introduce corrections into these equations [19-21] bring satisfactory results in certain systems. This involves the introduction of corrections with respect to the shape of the filler particles or to bound rubber.

The Influence of the Net Density

The test of influence of the net density on the modulus and damping is important not only from the practical point of view. As a rule the dependences obtained are difficult to generalize, since changes in the modulus and damping depend not only on the net density but also on many other factors. In the case of the natural rubber and butadiene styrene rubber vulcanizate, the $[\text{KN and KBS}] \, \text{tg} \, \delta$ decreases along with the net density (Figure 11) [18]. Besides significant differences between the damping factors of the unfilled vulcanizates, after filling 50 parts of the HAF black the damping of these vulcanizates levels off and shows dependence only on the net density.
specific surface

Figure 9. The G' module changes depending on the filler specific surface (nitrogen absorption) [1].

Figure 10. The elastic component of the E' module of the copolymer butadiene-styrene (KBS) filled with silica having different specific surfaces, as well as copolymer butadiene-styrene which remains unfilled, as a function of stretching [6].

Figure 11. The tgδ changes of the copolymer butadiene-styrene and natural rubber vulcanizates which are unfilled, as well as those filled with the HAP black (50%), as a function of the network density [28].
The Influence of the Softener type and Quantity

Softeners are added to the rubber mixtures in order to improve their processing properties, though it causes changes of the rubber dynamic properties. The above-mentioned changes depend on the rubber type, the filler quantity and type as well as on the softener quantity and type. The influence of a filler type on the $G'$ dynamic modulus of the vulcanizates from the natural rubber and copolymer butadiene styrene which are filled with the HAF black is shown on Figure 12 [29, 30]. The elastic component of the $G'$ dynamic modulus of a mixture containing aromatic oil decreases abruptly when the temperature increases. A smaller $G'$ decline caused by the temperature is produced by a mixture which contains paraffin oil. On the other hand, the value decline of the $G''$ mixtures without a softener is insignificant.

Figure 12. The $G'$ modulus of the natural rubber and copolymer butadiene-styrene vulcanizates including different types of softeners, as a function of temperature: 1 - aromatized oil; 2 - no softener; 3 - paraffin oil.

Figure 13 [8] presents the changes of the damping of vulcanizates with different fillers (silica, the active black with the developed and undeveloped structure) depending on the bulging degree in the butyl phthalane. The vulcanizates filled with the black whose structure is undeveloped have a noticeable maximum damping in the butyl phthalane when bulging reaches about 5% of the volume. The vulcanizeate with silica shows the maximum after bulging by about 15% of the volume in the butyl phthalane and changes of this vulcanizate's damping are significantly smaller. It is typical that when it comes to a big bulging (even to the state of equilibrium), damping of all vulcanizates are approaching the
Figure 13. The \( \delta \) dependence of vulcanizates of the natural rubber which includes different types of fillers, as a function of the bulging degree in the butyl phthalane [8]. 1 - silica; 2 - HAF-HS black; 3 - HAF black; 4 - HAF-LS black.

same value. At present there is no satisfactory model which could describe a mutual effect between softener and elastomer. The softener effect on the viscoelastic parameters can be sometimes interpreted as an effect of apparent decrease of the mass of the particle elastomer, especially when analyzing \( T_g \).

The Influence of the Rubber Mixture Preparation

Besides the composition, the rubber dynamic properties are influenced also to a significant extent by the method of mixture preparation as well as by the condition of vulcanization [31-33]. Payne [33] examined the influence of the mixing time on the dynamic properties of the copolymer butadiene styrene vulcanizates with the ISAF black (Figure 14). During extension of the mixing time the elastic component of the \( G' \) modulus noticeably decreases (when amplitudes are small). The smallest decline of the \( G' \) is typical for the mixture which was prepared in two stages. The \( G' \) modulus values during all times of mixing at a very large deformation amplitude have a tendency to reach the same value. When the filler dispersion is small and mixing time is short, the bonding between the filler and rubber becomes stronger. A very big value of the \( G' \) module gives evidence to this. The modulus differences fade away under big vibration amplitudes.

Besides that, by means of the dynamic testing one can determine the effect of the type of technological equipment which is employed for the rubber mixture preparation, the forming method, and the vulcanization time and temperature.
In recent years, because of increasing demands for the rubber production, a need to carry out tests of the dynamic mechanical properties of rubber on a wide scale has come into being. The above-mentioned tests are being carried out on complicated equipment and the interpretation of results sometimes is far from being easy. The qualitative analysis of the studied phenomena as it is seen in this article is relatively simple. Serious difficulties appear only when the qualitative analysis of the studied phenomena as it is seen in this article is relatively simple. Serious difficulties appear only when the quantitative analysis of the collected experimental data is being carried out. This is due to the non-linear pattern of the tension – deformation dependence as well as to the complicated structure of rubber.

The previous tests of the analytical representation of these dependences [15, 17-20, 24-27, 34-38] deal only with strictly determined systems and generally limit themselves to the determination of a single factor's effect on the dynamic properties of rubber when the remaining factors are left constant.
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