

Dynamic-Mechanical Investigation of Cured Filled Polymeric System of Hydroxyl Terminated Poly(Butadiene)/Isophorone Diisocyanate

Saša Brzić¹⁾
Jovan Radulović¹⁾

The aim of this work was a dynamic-mechanical testing of the cured filled polymeric system of hydroxyl-terminated poly(butadiene)-HTPB/isophorone diisocyanate-IPDI. The temperature and frequency dependence of the dynamic mechanical properties – storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta = G''/G'$) - are presented.

The shift factors, a_T , and the coefficients C_1 and C_2 in the WLF equation are determined. A good agreement was observed between the experimental and calculated values of the shift factors, a_T , so one can conclude that, for the tested HTPB/IPDI sample, the WLF equation with the calculated values of the constants C_1 and C_2 is valid in the whole temperature range of the test.

Key words: polymeric materials, polymeric systems, hydroxyl-terminated poly(butadiene) dynamic testing, mechanical testing.

Introduction

IN order to meet the increasing demand of various working environments and, at the same time, to reduce the cost, polymers have been treated with the addition of suitable fillers and/or fibers to enhance their overall performance in terms of mechanical, thermal, electrical, photonic and others actions as well as their structural stability.

The shortest but a clear enough definition of a polymer could be that a polymer is a large molecule made up of chains or rings of linked monomer units.

Polymeric materials

The development of polymeric materials caused a new aspect of investigation i.e. rheology of materials. The term rheology, in a broad sense, means a science of all aspects of deformation under the influence of stress, i.e. a response of a material to an action of any force.

The most important difference between polymeric materials and other materials (for example metals at room temperature) is a fact that the characteristics of polymeric materials are time dependent. To design a polymeric component, it is necessary to have complete information, at relevant service temperatures, on the time dependent behavior (viscoelastic behavior) of the material over the whole range of the stress to be experienced by the component.

Any force or load acting on a body results in stress and strain in the body. Stress represents the intensity of the force at any point in the body measured as a force acting per plane area unit. The deformation or alteration in the shape or the dimensions of the body, resulting from the

stress, is called strain. There are three main types of stress (tensile, compressive and shear) and three corresponding types of strain (tensile strain expressed as elongation per length unit, compressive strain expressed as contractions per length unit and shear strain representing a displacement of a certain plane relative to the other one caused by shear stress alone) [1-5].

The main object of rheology is the investigation of two idealized deformations.

In perfectly elastic (Hookean) materials, the stress (σ) is directly proportional to the strain (ε). For uniaxial stress and strain, the relation may be written as:

$$\sigma = E \times \varepsilon \quad (1)$$

where is: E - modulus of material elasticity.

In perfectly viscous (Newtonian) liquid, the shear stress (τ) is directly proportional to the rate of strain ($\dot{\gamma}$) and the relation may be written as:

$$\tau = \eta \times \dot{\gamma} \quad (2)$$

where: η - viscosity of liquid.

Polymeric materials exhibit stress-strain behaviour which falls between these two ideal cases, hence, they are termed viscoelastic. In viscoelastic materials, stress is a function of both strain and time and this may be described by the equation of the following form:

$$\sigma = f(\varepsilon, t) \quad (3)$$

where: t - time.

The most characteristic feature of viscoelastic materials is that they exhibit time-dependent deformation or strain, when subjected to constant stress (creep phenomena) and

¹⁾ Military Technical Institute (VTI), Ratka Resanovića 1, 11132 Belgrade, SERBIA

time-dependent stress subjected to constant strain (stress relaxation phenomena).

When a mass of polymer is exposed to the action of a load, a produced deformation can be considered as a sum of the following three deformations:

1. A deformation due to bond bending and stretching in macromolecules, which is instantaneous, recoverable and independent of temperature (ordinary elastic deformation, ε_{0e}) shown in Fig.1a.
2. A deformation due to chain uncoiling, which is recoverable but not instantaneous and whose rate depends on temperature (high elastic deformation, ε_{he}) shown in Fig.1b.
3. A deformation due to slippage of polymer molecules passing one another (viscous deformation, ε_v) shown in Fig.1c. It is considered that the rate of such viscous irrecoverable deformation do not change with time, if applied stress is constant.

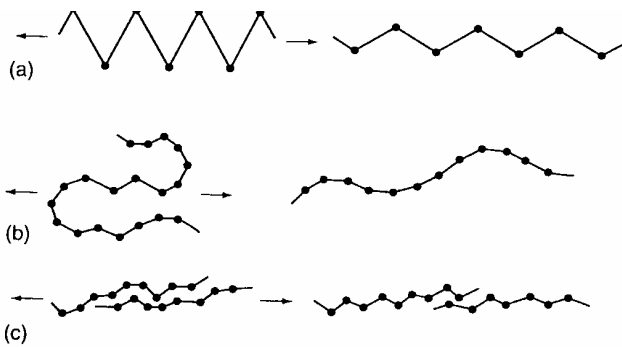


Figure 1. Structural deformation changes in a plastic material

In each case, the stress is imposed at the time t_0 and held at a constant value until the time t_1 , when it is removed (Fig.2a).

Fig.2. shows schematically the mentioned types of a single deformational response as a result of fixed stress imposed to:

1. first, body showing ordinary elastic deformation, only (Fig.2b),
2. second, body showing high elastic deformation, only (Fig. 2c and
3. third, body showing viscous deformation, only (Fig.2d).

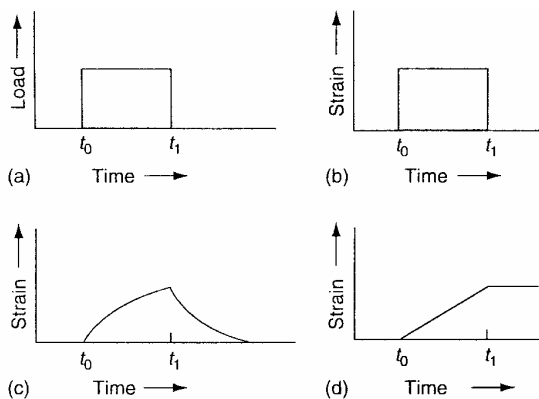


Figure 2. Schematic presentation of single deformation changes in a polymeric material

Real polymers exhibit stress-strain curves which are a combination of three basic responses, and a total or combined deformation (ε) is given by the expression:

$$\varepsilon = \varepsilon_{0e} + \varepsilon_{he} + \varepsilon_v \quad (4)$$

A typical deformation-time curve for a real polymer material is shown in Fig.3, where recoverable and irrecoverable components of total deformation can be observed [5].

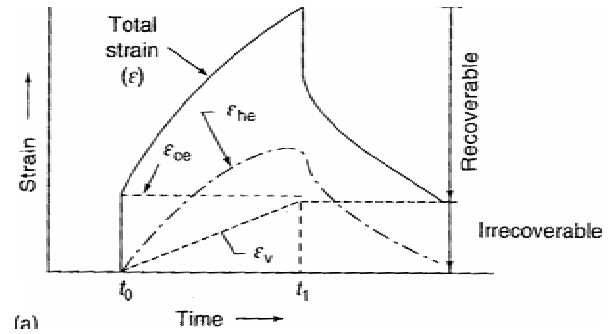


Figure 3. Schematic presentation of real deformation changes in a polymeric material

For a polymeric segment to move from its position to its adjacent site, there must be some holes in the mass of the material into which a segment can move and simultaneously leave a vacant into which another segment can move. It is important to point out that a molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume.

It is usual to express the temperature coefficient of the free volume as a difference between the thermal coefficient above and under the glass transition temperature (T_g):

$$f = f_g + (\alpha_a - \alpha_b)(T - T_g) = f_g + \Delta\alpha(T - T_g) \quad (5)$$

where:

f - fractional free volume at the temperature T ,
 f_g - fractional free volume at the temperature T_g ,
 α_a and α_b - coefficient of thermal expansion above and under T_g , respectively.

Viscosity is related to the fractional free volume by the expressions of the form:

$$1/\eta_T = Ke^{-Af/f} \quad \text{and} \quad 1/\eta_{Tg} = Ke^{-Af_g} \quad (6)$$

where :

K - constant,

A - constant.

Substituting and rearranging the mentioned expressions, an equation of general validity is obtained:

$$\log(\eta_T / \eta_{Tg}) = -17,44(T - T_g) / 51,6 + (T - T_g) \quad (7)$$

where:

η_T - viscosity at the temperature T ,

η_{Tg} - viscosity at the temperature T_g .

This is a well-known WLF equation, the name of which has the initials of the researchers who proposed it (William, Landel, Ferry). This equation implies that if viscosity at some temperature T is known, viscosity at the glass transition temperature T_g can be estimated and from this estimation viscosity at another temperature T_1 can be estimated, i.e. this WLF equation gives the effect of temperature on viscosity. There are, also, other applications of the WLF equation. In brief, if a value of a material property changes with temperature and this change arises from the change in the viscosity of the system, then it may be possible to apply the WLF equation to the property change [5].

One example of this is in the relation of stress relaxation. If a polymer is deformed to some fixed strain at a constant temperature, the force required to maintain this strain will decrease with time due to the viscous slippage of macromolecules. One measure of this rate of decrease or stress relaxation is the relaxation time λ , which can be defined as the time taken for the stress to decrease to $1/e$ of its initial value on the application of strain. In this case, the WLF equation has the same expression as in (7):

$$\log(\lambda_T / \lambda_{T_g}) = -17,44(T - T_g) / 51,6 + (T - T_g) \quad (8)$$

where:

λ_T - relaxation time at the temperature T ,

λ_{T_g} - relaxation time at the temperature T_g .

In engineering practice, it is often necessary to design using some material over a long period of time. A common parameter to use in design is the modulus of elasticity. It is known for polymers that the modulus of elasticity decreases with increasing time under load.

Accumulation of long-term data for design with plastic materials can be a very inconvenient and expensive procedure. A method is thus needed to extrapolate data from shorter time studies at higher temperatures to longer time over several decades of the time scale at desired temperatures so that a lower limit of the modulus can be determined for use in design. On the other hand, it is sometimes difficult to obtain data over a very short time scale. One must then extrapolate the data obtained under practicable experimental conditions for these very short time scales.

The aforesaid extrapolations are possible using a time-temperature superposition principle which is based on the fact that time and temperature have essentially equivalent effects on the modulus values of amorphous and low and high cured polymers, and, in general, of polymer systems where structure does not change during the period of testing.

Because of the equivalent effect of the time and temperature, data at different temperature can be superposed on data taken at a specified reference temperature merely by shifting individual curves along a $\log(t)$ axis about the reference temperature.

A time-temperature superposition procedure has an effect of producing a single continuous curve of modulus values extending over many decades of $\log(t)$ at the reference temperature. A curve constructed in this manner is known as a master curve. The procedure asserts that the effect of changing the test temperature on viscoelastic properties is the same as that of multiplying or dividing the time scale by a constant quantity at each temperature. The quantity marked as a_T is called the shift factor and must be obtained directly from the experimental curve by measuring the amount of shift along the $\log(t)$ scale necessary to match the curve. The parameter a_T is chosen as a unity at the reference temperature and is a function of the temperature alone, decreasing with the temperature increase.

It is common practice to use a glass transition temperature (T_g) as a reference temperature for master curve construction. The shift factor a_T for most polymers, at any temperature, is given quite well by the equation:

$$\begin{aligned} \log a_T &= \log [t(T) / t(T_g)] = \\ &= -17,44(T - T_g) / 51,6 + (T - T_g) \end{aligned} \quad (9)$$

This is another form of the well-known WLF equation.

Dynamic mechanical properties

A complete description of the viscoelastic properties of materials requires information over very long time (from 15 to 17 decades). To supplement creep and stress relaxation measurements which are limited by experimental limitations, there are experiments in which oscillating stress or strain is applied to a material specimen.

Oscillatory experiments (also referred to as dynamic mechanical experiments) thus represent a powerful technique to measure a molecular structure and morphology. A significant feature of this procedure is the available range of the time scale spectrum from 10^{-5} cycles/second to 10^{+8} cycles/second.

In a dynamic experiment, the stress will be directly proportional to the strain if the magnitude of the strain is small enough. If the stress is of a sinusoidal type, the resulting strain, also, varies sinusoidally. The same holds true if the strain is the input and the stress is the output. In general, strain will be out of the phase with stress and this phenomenon can be presented by a rotating vector scheme [5]. A scheme of the rotating stress vector and the decomposition of the strain vector onto two components in a dynamic experiment is shown in Fig.4.

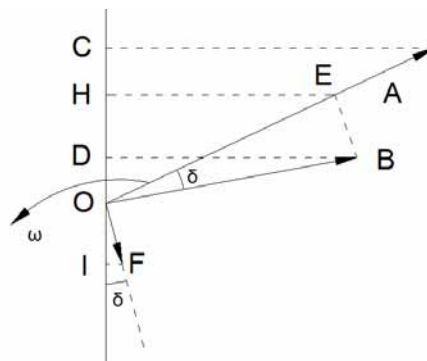


Figure 4. Scheme of the rotating stress vector and the decomposition of the strain vector onto two components in a dynamic experiment

The magnitude of the stress at any time can be presented by the projection OC of the vector OA on the vertical axis. The vector OA rotates with the frequency ω equal to the sinusoidally varying stress. The length of the vector OA is the stress amplitude (maximum stress) involved in the experiment. The strain (ϵ) is presented by the projection OD of the vector OB on the vertical axis. The strain vector OB rotates in the same direction as the stress vector OA with the frequency ω but it lags the stress vector OA by the angle δ . The loss tangent is defined as $\tan \delta$.

The strain vector OB can be resolved into two components:

- vector OE along the direction of the stress vector OA, and
- vector OF perpendicular to the stress vector OA.

The projection OH of the vector OE onto the vertical axis is the magnitude of the strain which is in the phase with the stress at any time. The projection OI of the vector OF is the magnitude of the strain which is $\pi/2$ rad (one quarter cycle) out of phase with the stress.

Similarly to the presented principle, the stress can be resolved into two components:

- one which is along the direction of the strain vector OB ($\sigma' = \sigma_0 \cos \delta$), and
- another one which is out of phase with the strain vector OB ($\sigma'' = \sigma_0 \sin \delta$) by $\pi/2$ rad.

The ratio of the stress component which is in phase with the strain (σ') and the strain amplitude (ϵ_0) is called the

storage modulus (E' in a tensile test, G' in a shear test):

$$E' = \sigma' / \varepsilon_0 = (\sigma_0 / \varepsilon_0) \cos \delta \quad (10)$$

The storage modulus is associated with periodic storage and a complete release of energy in a sinusoidal deformation process.

The ratio of the stress component which is out of phase with the strain (σ'') and the strain amplitude (ε_0) is called the modulus of loss energy or loss modulus (E'' in a tensile test, G'' in a shear test):

$$E'' = \sigma'' / \varepsilon_0 = (\sigma_0 / \varepsilon_0) \sin \delta \quad (11)$$

The loss modulus, on the other hand, reflects the irrecoverable use of the applied mechanical energy to cause a viscous flow in the material (most often loss as thermal energy).

A phase delay angle or a loss tangent ($\tan \delta$) is defined as a ratio of the loss modulus and the storage modulus:

$$\tan \delta = E'' / E' \quad (12)$$

From the above equation, it is obvious that ($\tan \delta$) is equal to the ratio of loss energy due to the flow and maximum potential energy stored in the test material. For an ideal elastic material ($\tan \delta$) is zero (for metals), while for polymers, especially in the transition region from the glassy state to the viscoelastic state, the delay angle can be up to 30° [5].

In accordance with the measuring principle, there are instruments with forced and free oscillations, used for dynamic mechanical testing.

The dynamic mechanical analysis (DMA) is one of the most sensitive methods for the analysis of the mechanical behaviour of materials. The principle of this method is based on monitoring the viscoelastic response of materials to cyclic (sinusoidal) strain.

The main goal of this paper was to analyze the properties of a cured filled polymeric system of hydroxyl terminated poly(butadiene)/isophorone diisocyanate obtained by dynamic mechanical measurements under small forced deformation.

The polyurethane network obtained by curing hydroxyl terminated poly(butadiene) with a suitable diisocyanate provides an adequate matrix for dispersing inorganic filler and metallic components.

Amani Ramadan Ali Moussa and coworkers [6] compare the dynamic viscoelastic properties of resin with three different softener/hardener monomer ratios and silicon resilient liners. In a dynamic viscoelastic analysis at a frequency of 1 Hz at 37°C the shear storage (G'), the loss (G'') moduli and the loss tangent ($\tan \delta$) were obtained, and it was concluded that the resin showed different viscoelastic properties, while the silicone material demonstrated elastic properties.

Seung-Hyun Chae et al. [7] investigated a molding compound for microelectronics packaging and stress relaxation experiments were performed on a tested material in the time domain. Using the time-temperature equivalence assumption, the master curve at a reference temperature was obtained and shifted to every measured temperature for the comparison with the experimental data.

Gregorova A. et al. [8] studied the viscoelastic properties of unfilled poly(oxy propionate) acid and filled with 20 mass. % of three mineral fillers (Mica, Zeolite, and Vansil), differing in the particle shape and the surface area. The viscoelastic results demonstrate that Zeolite was better distributed in the mentioned matrix than two other used fillers.

Experimental part

Production of a test system

The polymeric system investigated in this paper consists of a liquid phase and a solid phase.

The liquid phase (15 mass. % of the system) consists of prepolymer butadiene with hydroxyl end groups, shortly HTPB (11.08 mass. % of the system) and a curing agent isophorone with two isocyanate groups, shortly IPDI (0.92 mass. % of the system). The curing reaction took place between the hydroxyl groups of the prepolymer HTPB and the isocyanate groups of the curing agent IPDI and is presented in Fig.5:

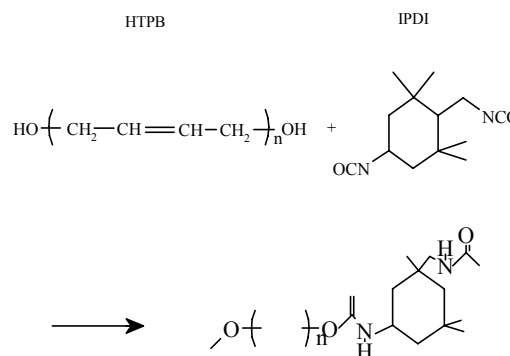


Figure 5. Scheme of hydroxyl and isocyanate groups reaction

The used prepolymer, produced by Sartomer, has the molar mass 2700 g/mol and the trade mark R45HT..

The used curing agent of the trade mark IPDI is produced by Sigma Aldrich, Germany.

The NCO/OH ratio i.e. the ratio between the isocyanate moieties on the curing agent to the hydroxyl moieties on the prepolymer was 0.87.

Besides the mentioned ingredients, a liquid phase consists of:

- dioctyl adipate, trade mark DOA, produced by Fluka AG, Switzerland, (2,77 mass. % of the system),
- phenyl- β -naphthylamine, trade mark F β NA, produced by Fluka AG, Switzerland, (0,17 mass. % of the system),
- triethylenetetramine, trade mark TET, produced by Riedel and Haen, (0,06 mass. % of the system).

The solid phase (85 mass. % of the system) consists of an anorganic filler and a metal component.

The anorganic filler (72 mass. % of the system), is ammonium perchlorate with two particle sizes (200 μm and 10 μm in a ratio of 80/20).

The metallic component (13 mass. % of the system) is aluminium with two particle sizes (30 μm and 15 μm in a ratio of 50/50).

Mixing of the system ingredients was conducted at a temperature of 60°C in a planetary mixer of a volume of 4.54 dm^3 produced by Perkins Elmer Company.

The curing of the system was performed for 120 h at 70°C .

Testing of the dynamic mechanical properties of the system

Testing of the dynamic mechanical properties of the cured filled polymeric hydroxyl terminated polybutadiene/isophorone diisocyanate system (in the further text: HTPB/IPDI system) were carried out using a mechanical spectrometer model „RMS-605“, produced by „Rheometrics“, in the torsion mode, under the following

testing conditions:

- fixed frequency mode,
- frequency of the oscillatory load (W): 1 Hz,
- thermal soak time, 30 s,
- amplitude of deformation: 0.1%,
- heating rate: 5°C/min,
- temperature range for:
- temperature dependences: -90°C to +60°C,
- frequency dependences: -60°C to +60°C.

The samples for the dynamic mechanical analysis were of a rectangular bar shape (63 mm x 12 mm x from 3 mm to 4 mm).

Temperature dependences of the dynamic mechanical properties of the HTPB/IDPI system were investigated. Considering that the tested system has a polymeric cured structure, degradation of the mentioned structures is possible at higher temperatures. The temperature region, in which it is possible to use the HTPB/IDPI system, including a border of this region, is of essential importance. The frequency dependence of the dynamic mechanical properties of the tested system was determined. The frequency varied in a relatively narrow range of three decades (from 0.1 rads^{-1} to 100 rads^{-1}), through 16 equidistant temperature values on the logarithmic scale. The first measured temperature was the glass transition temperature of the tested system, and a temperature step was 10°C.

Temperature dependence of the dynamic mechanical properties of the tested system

The temperature dependence of the storage modulus, (E' or G'), the loss modulus, (E'' or G''), and the loss tangent, ($\tan\delta$), represents the most common form of the presentation of rheological parameters, obtained by DMA.

The dependence of the dynamic mechanical properties (G' , G'' and $\tan\delta$) of the tested system, versus the temperature at 1 Hz constant frequency, is presented in Fig.6 [9].

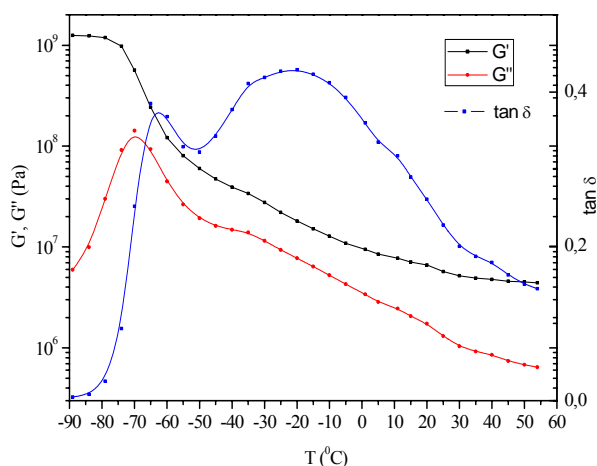


Figure 6. Dynamic mechanical properties of the tested HTPB/IPDI system versus the temperature

From the DMA thermogram of the tested HTPB/IPDI system (Fig.6) it can be seen that the storage modulus (G') in the glassy state below -80°C is almost constant and has a maximum value of 1.246 MPa ($G'_{-90^\circ\text{C}} = 1.246 \text{ MPa}$). As temperature increases, the storage modulus significantly decreases. The most pronounced decrease of the storage modulus value was recorded in the glass transition region (-80°C < T_g < -60°C). In this region, the storage modulus decreases for about 200 times (from 1.246 MPa at -90°C, to 5.7 MPa at 25°C). This change is connected with the

softening of the tested sample. That is also an approximate value of the loss modulus in the rubbery plateau region.

It is known that the transition from the glassy region to the viscoelastic region does not occur at a strictly defined point, and it takes place in a temperature range.

However, by the common agreement, the T_g is taken as a temperature of the maximum peak in the loss modulus curve, which, in this case, is $T_g = -70^\circ\text{C}$. The maximum value of the loss modulus is 142.3 MPa.

It should be noted that the position of T_g depends on the experimental techniques and conditions of the experiment (eg. heating rate of the sample). The data shown are obtained using a heating rate of 5°C/min.

The temperature dependence of the loss tangent curve is a reflection of the macromolecules chain flexibility [9]. At the glassy state $\tan\delta$ has a very low value ($\tan\delta_{-90^\circ\text{C}} = 0.0048$), which is a consequence of the low flexibility of the macromolecule units in the glassy state. As the temperature increases, the mobility of kinetic units increases, so does the value of $\tan\delta$. By further heating of the HTPB/IDPI system, when the sample temperature reached -50°C, there was a sudden increase of the value $\tan\delta$. Above T_g the loss tangent curve of the tested system exhibits a broad peak covering a wide temperature range (-50°C to +10°C).

On the experimentally obtained curves which pointed out the dynamical mechanical properties of the HTPB/IDPI system versus temperature, three characteristic regions can be distinguished:

- The region below the glass transition temperature ($T < -70^\circ\text{C}$), i.e. the glassy state region. In this region, the storage modulus has the highest value, while $\tan\delta$ has the lowest value, as a result of the almost negligible mobility of kinetic units in the tested system. The storage modulus is significantly higher than the loss modulus value in this area, so during periodic deformation, the HTPB/IDPI system saves much more energy than it loses.
- The region between the glass transition temperature and the transition temperature to the rubbery state, i.e. the region of the viscoelastic state (-80°C < T_g < -60°C). This region is characterized by the beginning of the movement of kinetic units of macromolecules. Due to the increased mobility of kinetic units in the viscoelastic region, the value of the storage modulus decreases, the value of $\tan\delta$ increases, while the loss modulus reaches the maximum value.
- The region above the transition temperature to the rubbery state ($T > -60^\circ\text{C}$), i.e. the region of the rubbery state. In practical terms, this is exactly the region of the greatest interest because it coincides with the temperature range of possible usage of the mentioned polymeric system. Also, from the technological point of view, this area includes the temperature at which the HTPB/IDPI system is produced.

Master curve formation of the dynamic mechanical properties of the HTPB/IPDI system

Based on the values of the storage modulus, G' , experimentally determined at different temperatures, a single isothermal curve is constructed. This so-called master curve covers a much wider frequency interval compared to that in which the measurement was done. Using the dependence given by the equation:

$$G'_0 = \frac{G' T_0 \rho_0}{T \rho} = f(\omega a_T) \quad (13)$$

where:

G'_0 - storage modulus at the reference temperature T_0 ,

G' - storage modulus at the test temperature T ,

T_0 - reference temperature,

T - test temperature,

ρ - density at the test temperature T ,

ρ_0 - density at the test temperature T_0 .

the individual curves in Fig.7 are moved along the axis $\log G'$ and $\log \omega$ until it folded into a single aggregate curve for the selected reference temperature T_0 .

The distance that each curve must cover in order to realise a satisfactory overlap of the results is called the shift factor, denoted a_T , where the index « T » indicates its temperature dependence. The value of $\log a_T$ is zero for the reference temperature, T_0 , positive for temperatures above and negative for temperatures below T_0 . The density change from T to T_0 is negligible.

The result of the above-mentioned «reduction» procedure for the tested HTPB/IPDI system is shown in Fig.7, which contains the curves obtained by experimental measurements at 14 different temperatures, and the resulting aggregate «master» curve for the reference temperature $T_0 = 0^\circ\text{C}$, but with the new coordinates obtained after the introduction of the shift factors, a_T [10].

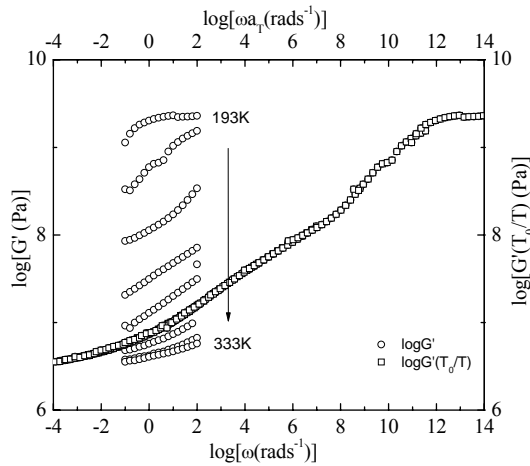


Figure 7. Storage modulus single curves and the master curve of the tested HTPB/IPDI system

As it can be seen in Fig.7, the data collected from the experiment within three decades of frequency, by the described procedure, are extended to almost 18 logarithmic decades.

Besides the constructed master curve for the storage modulus at the reference temperature $T_0 = 0^\circ\text{C}$, numerous values of the shift factors a_T are obtained for all temperatures at which the frequency dependence of the storage modulus, G' , was experimentally determined. These experimentally obtained values of the shift factors at different temperatures for the tested HTPB/IPDI system are denoted as $\log a_T(\text{exp.})$ and presented in Table 1.

The deviations of the experimental shift factor values from the calculated shift factor values at appropriate temperatures are presented in Table 1, as well. The deviations (in the further text: Δ) are calculated using the equation of the form:

$$\Delta = [\log a_T(\text{exp}) - \log a_T(\text{calc}) / \log a_T(\text{exp})] \times 100$$

where:

Δ - deviation of the experimental shift factor value from the calculated shift factor value (%),

$\log a_T(\text{exp.})$ - experimental shift factor value,

$\log a_T(\text{calc.})$ - calculated shift factor value.

Table 1. Experimental and calculated shift factor values a_T of the HTPB/IPDI system for different tested temperatures

$T(^{\circ}\text{C})$	$T-T_0(^{\circ}\text{C})$	$\log a_T(\text{exp.})$	$\log a_T(\text{calc.})$	Δ (%)
-60.062	-60.002	6.816	6.373	6.5
-40.062	-40.002	3.568	3.598	8.4
-21.375	-21.315	1.544	1.677	8.6
-0.062	-0.002	0	0	0
19.937	19.997	-1.209	-1.232	1.9
40	40.06	-2.448	-2.233	9.2
59.937	59.997	-2.913	-3.055	4.8

From Table 1 it can be seen that deviations are small and of acceptable values, so it can be stated that there is a good agreement between the experimental and calculated values of the shift factors, a_T .

Determination of the constants in the WLF equation

Modern approaches to the temperature dependence of rheological parameters are associated with the free volume concept and expressed by the mentioned William-Landel-Ferry (so-called WLF) equation, which defines the law of the shift factor, a_T , temperature change [9]:

$$\log a_T = \log \frac{G'}{G'_0} = \frac{-C_1(T-T_0)}{C_2+T-T_0} \quad (14)$$

where are:

C_1 -constant,

C_2 -constant.

The equation can be used in the temperature interval from T_g to $(T_g + 100)^\circ\text{C}$. The use of this equation supposes the existence of a set of temperatures and shift factors values obtained by the reduction procedure and the master curve forming. The set of the mentioned parameters is shown in Table 1. For the reference temperature T_0 , a temperature $T_0 = 0^\circ\text{C}$ was chosen.

For the tested HTPB/IPDI system, the linearisation of the experimental values of the shift factor a_T , was performed in accordance with the WLF equation (14), using its transformed form, where $(T-T_0)/\log a_T$ are expressed in a function of $(T-T_0)$ [11]. The procedure applied on the tested sample is shown in Fig.8.

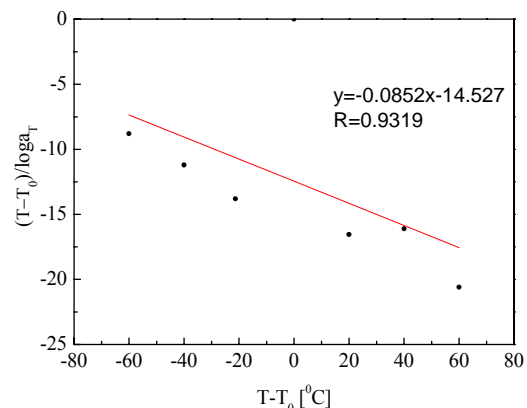


Figure 8. Linearization of the experimental shift factors values in accordance with the WLF equation

The constants C_1 and C_2 are found from the slope « s » and the intercept « i » of a straight line through a plot of $(T-T_0)/\log a_T$ vs. $(T-T_0)$, using the next equations:

$$C_1 = \frac{-i}{s} \quad \text{and} \quad C_2 = \frac{i}{s} \quad (15)$$

The values of the constants $C_1=11.74$ and $C_2=170.50$ were obtained for the tested HTPB/IPDI system.

By substituting these values into the basic form of the WLF equation, noting that the reference temperature is $T_0 = 0^\circ\text{C}$, the values of the shift factors a_T are calculated for each test temperature. The calculated numerical values of a_T are shown in Fig.9, as $\log a_{T(\text{calc.})}$ and in Table 1, with a mark (calc.).

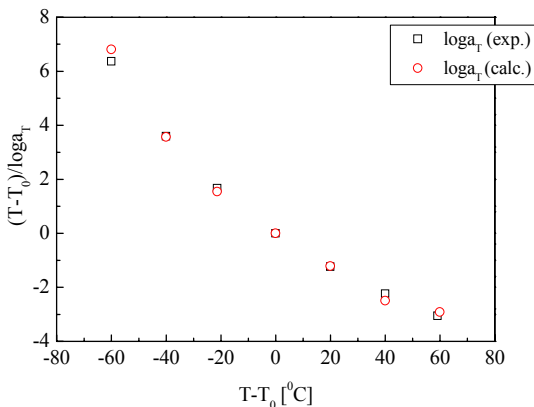


Figure 9. Temperature dependence for the experimental and calculated values of the shift factors of the HTPB/IPDI system

Fig.9 shows that the curve that presents the dependence of the experimental shift factor values versus temperature is almost identical with the curve that presents the dependence of the calculated shift factor values versus temperature, so it is obvious that there is a good agreement between the experimental and calculated values of the shift factors, a_T .

Conclusions

1. The dynamic mechanical characteristics of a cured polymeric system of hydroxyl terminated poly(butadiene)/isophorone diisocyanate, which contains an anorganic filler (ammonium perchlorate) and a metallic filler (aluminium), were investigated.
2. The temperature and frequency dependences of the dynamic mechanical characteristics of the HTPB/IPDI system were determined.
3. The temperature dependence of the dynamic mechanical properties pointed out that the glassy, transition and rubbery plateau region of the viscoelastic behaviour of the tested system were obtained by DMA measurements.
4. The changes of the experimentally obtained dynamic mechanical characteristics (storage modulus, loss modulus and loss tangent) are explained by the structure changes of the HTPB/IPDI system.
5. Based on the test data obtained in three log frequency decades and in the temperature region from -60°C to

$+60^\circ\text{C}$ and the «reduction» principle, a master curve, covering 18 log decades, was constructed while the experimental values of the shift factors, i.e. $\log a_T$ (exp.), were defined.

6. Choosing T_g as a reference temperature, the constants of the WLF equation were determined and by a subsequent «linearisation» of the available data, the so-called numerical shift factors i.e. $\log a_T$ (calc.) were calculated.
7. A good agreement between the experimental and calculated values of the log shift factors pointed out that the equation with the calculated constants C_1 and C_2 is valid in the whole tested temperature range for the HTPB/IPDI system.
8. The lower limit of a possibly useful area of the HTPB/IPDI system is just above the transition temperature to the rubbery state ($T > -60^\circ\text{C}$).

Literature

- [1] RADULOVIĆ,J.: *Characterization of Filamentwound Polymeric Composite Materials*, Scientific Technical Review, ISSN 1820-0206, 2008, Vol.LVIII, No.1, pp.66-75.
- [2] RADULOVIĆ,J.: *Thin Wall and Thick Wall Filament Wound Polymeric Composite Tubes: Mechanical Characteristics Caused by Internal Hydraulic Pressure*, Scientific Technical Review, ISSN 1820-0206, 2013, Vol.63, No.1, pp.63-69.
- [3] Chemistry Glossary /Definition of Polymer/, About.com Guide.
- [4] DEEPA,URS M.V., RANGANATHAIAH,C., RAMANI,R., BABU,L., SARFARAZ,A.: *Diffusion of seawater in unsaturated polyester resin and its glass fiber reinforced composites in the presence of titanium dioxide as UV absorber*, Journal of Applied Polymer Science, Wiley Periodicals, 2006, Vol..102, pp.2784-2794.
- [5] MANAS,C., SALIL,K.R.: *Plastics Technology Handbook*, 4th Edition, CRC Press, Taylor and Francis Group, Boca Raton, 2007.
- [6] AMANI RAMADAN ALI MOUSSA, DALIA YEHIA IBRAHIM ZAKI and AHMED WAEL ABOU ZEID: *Viscoelastic properties of Thermo-Elastic resin reline with different ratios*, Journal of Applied Sciences Research, 8(3): 1477-1483, 2012.
- [7] SEUNG-HYUN CHAE, JIE-HUA ZHAO, DARVIN R. EDWARDS and PAUL S. HO: *Characterization of the viscoelasticity of molding compounds in the time domain*, Journal of Electronic Materials, 2010, Vol.39, No.4.
- [8] GREGOROVA,A., MACHOVSKY,M. WIMMER,R.: *Viscoelastic properties of mineral-filled Poly(lactic acid) composites*, *International Journal of Polymer Science Volume*, Hindawi Publishing Corporation, 2012.
- [9] BRZIĆ,S., POPOVIĆ,B., TOMIĆ,M.: *Viscoelastic properties of composite rocket propellants based on hydroxyl-terminated poly(butadiene) and isophorone diisocyanate polyurethane*, 5th International Scientific Conference on Defensive Technologies, Belgrade, Serbia, OTEH 2012, Proceedings, 2012, pp.345-349.
- [10] EMRI,I.: *Rheology of solid polymers*, The British Society of Rheology, (www.bsr.org.uk), 2003.
- [11] STACER,R.G., HUSBAND,D.M., STACER,H.L.: *Viscoelastic response and adhesion properties of highly filled elastomers*, Rubber Chemistry and Technology, May-June 1987, Vol.60, No.2

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Dinamička-mehanička ispitivanja očvrsllog punjenog polimernog sistema hidroksiterminirani polibutadien/izoforon diizocijanat

Cilj ovog rada je bilo dinamičko-mehaničko ispitivanje očvrsllog punjenog polimernog sistema hidroksiterminirani polibutadien-HTPB/izoforon diizocijanat-IDPI. Prikazane su temperaturna i frekvenciona zavisnost dinamičko-mehaničkih osobina-modul skladištene energije (G'), modul izgubljene energije (G'') i tangens ugla gubitaka ($\tan\delta=G''/G'$). Faktor pomeraja, a_T , i koeficijenti C_1 i C_2 u WLF jednačini su određeni. Utvrđeno je dobro slaganje između eksperimentalno i računski određenih vrednosti faktora pomeraja, tako da se može zaključiti da za ispitivani HTPB/IDPI uzorak WLF jednačina sa izračunatim vrednostima za koeficijente C_1 i C_2 važi u celom ispitivanom temperaturnom opsegu.

Ključne reči: polimerni materijali, polimerni sistemi, hidroksiterminirani polibutadien, dinamičko ispitivanje, mehaničko ispitivanje.

Динамическо-механические испытания отверждённой полимерной системы заполненной гидроксиполибутадиен / изофорондиизоцианатом

Целью данного исследования было динамико – механическое испытание отверждённых полимерных систем заполненных гидроксиполибутадиен-HTPB/изофорон диизоцианатом-IDPI. Показаны температурная и частотная зависимость динамическо-механических свойств - модуля накопления энергии (G'), модуля потерь энергии (G'') и тангенс угла потерь ($\tan\delta=G''/G'$). Коэффициент сменности, A_T , и коэффициенты C_1 и C_2 в уравнении WLF были определены. Доказано хорошее согласие между экспериментальными и расчётными значениями определенных факторов сдвигов, поэтому можно сделать вывод, что исследованные HTPB / IDPI образца WLF уравнения с вычисленными значениями для коэффициентов C_1 и C_2 действительны во всём исследованном температурном интервале.

Ключевые слова: полимерные материалы, полимерные системы, гидроксиполибутадиен, динамические испытания, механические испытания.

Examen dynamique et mécanique du système polymère durci hydroxyle terminé polybutadiène / isophorone diisocyanate

Le but de ce travail est l'examen dynamique et mécanique du système polymère durci et chargé hydroxyle terminé polybutadiène – HTPB /isophorone diisocyanate – IDPI . On a présenté la dépendance des propriétés dynamiques et mécaniques de la température et de la fréquence – module de l'énergie déposée (G'), module de l'énergie perdue (G'') et la tangente de l'angle de perte ($\tan\delta=G''/G'$). Le facteur de déplacement ainsi que les coefficients C_1 et C_2 dans l'équation WLF ont été déterminés. On a constaté bon accord entre les facteurs déterminés par la voie expérimentale et les facteurs déterminés numériquement chez le déplacement . En conclusion on peut dire que l'échantillon examiné HTPB / IDPI de l'équation WLF avec les valeurs calculées pour les coefficients C_1 et C_2 est valable dans la totalité du domaine de température.

Mots clés: matériaux polymères, systèmes polymères, polybutadiène hydroxyle terminé, examen dynamique, examen mécanique.