Scientific Journal of Physical Science Innovations
Volume 6, Number 3, 2021
ISSN:3492 - 4562
Published by University Press

EFFECT OF THERMAL AGEING ON MECHANICAL PROPERTIES OF STYRENE-BUTADIENE (SBR) RUBBERS

Clement Ogbonda and Amaechi Jeoffrey
Department of Physics, Ignatius Ajuru University of Education
Rumuolumeni, Port Harcourt, Rivers State, Nigeria

ABSTRACT:

The mechanical properties, the temperature dependence of dynamic behaviour of SBR and post thermal ageing properties of Soda-lime-silicate (SLS) glass were investigated. The glass specimens were heated at a temperature of 100 °C in a ventilated air oven with natural convection for 1, 3, 7, 14 and 21 days, respectively. The specimens were then tested in the tensile strength, elongation at break and their dynamic mechanical properties were determined by means of DMA at different frequencies and amplitudes. The dependence of the hardness on the ageing was also investigated.

INTRODUCTION

In order to determine rate-dependent properties of examined glass we previously performed experimental measurements of the time dependent response and of damping properties of glass materials consisting of creep and stress relaxation tests which were convenient for studying material response at long times. The behaviour at different strain levels was examined in detail through quasistatic cyclic tests and in simple and multistep relaxation tests. The viscosity-induced rate-dependent effects were described and parameters of the material model were determined. The model was implemented into FE code (Marvalova 2008). Next we focused on the dynamic mechanical analysis of silicate-reinforced glass. The dependence of the storage and dissipation moduli on the static pre-strain, on the deformation amplitude and on the frequency was investigated (Petrikova & Marvalova 2010).

The dynamic mechanical analysis (DMA) is well suited for the identification of the short-time range of glass response. DMA consists of dynamic tests, in which the force resulting from a sinusoidal strain controlled loading is measured. Payne (1965) first pointed out that the moduli of carbon black filled rubber decrease with increasing deformation amplitudes. By means of further tests he reached the conclusion that this behaviour has to be attributed to a thixotropic change. Lion (1998) observed that both the storage and the dissipation modulus depend on the frequency of the deformation process. This variation is weakly pronounced and it is of power series type approximately. In terms of the theory of linear viscoelasticity this behavior corresponds to a continuous relaxation time distribution. With increasing temperatures (Lion 1998) observed both a decrease in moduli and a lessening of the frequency dependence. The dependence of the dynamic moduli on the filler content and the static pre-strain is investigated in detail by Namboodiri and Tripathy (1994). When a viscoelastic material is subjected to a sinusoidally varying strain after some initial transients the stationary stress-response will be reached in which the resulting stress is also sinusoidal, having the same angular frequency but advanced in phase by an angle δ. Then the strain lags the stress by the phase angle δ. The axial displacement $u(t)$ consists of a static pre-strain μ_0 under tension which is superimposed by small sinusoidal oscillations:

$$u(t) = u_0 + \Delta u \sin(2\pi f t). \qquad 1$$

Stresses and strains are calculated with respect to the reference geometry (Lion & Kardelky 2004) of the pre-deformed specimen

$$\varepsilon_o = \frac{u_o}{L_O + u_o}, \qquad \Delta\varepsilon = \frac{\Delta u}{L_O + u_o} \qquad 2$$

where *L*0 is the undeformed length of the specimen. The force response *F*(*t*) of the specimen is a harmonic function and can be written as:

$$F(t) = F_o + \Delta F \sin(2\pi f t + \delta) \qquad 3$$

F_O is the static force depending only on the predeformation μ_0. The force amplitude ΔF and the phase angle δ depend, in general, on the predeformation, the frequency and the strain amplitude (Lion & Kardelky 2004, Hofer & Lion 2009).

If the incompressibility of the rubber is assumed $A_0 L_0 = A(L_0 + \mu_0)$, where A_0 is the cross-sectional area of the undeformed specimen, we can relate the force to the cross-sectional area *A* of the pre-deformed specimen:

$$\sigma(t) = \frac{F(t)}{A} = \sigma_0 + \Delta\sigma[cos\delta \sin(2\pi f t) + sin\delta \cos(2\pi f t)] \qquad 4$$

The dynamic stress-response $\sigma(t)$ normalized by the deformation amplitude $\Delta\varepsilon$ can be written:

$$\sigma(t) = \sigma_0 + \Delta\varepsilon[E^i(\varepsilon_0, f, \Delta\varepsilon) \sin(2\pi f t) + E^i(\varepsilon_0, f, \Delta\varepsilon) \cos(2\pi f t)] \qquad 5$$

Where

$$E^i(\varepsilon_0, f, \Delta\varepsilon) = \frac{\Delta\sigma}{\Delta\varepsilon} \cos(\delta) \qquad 6$$

and

$$E^i(\varepsilon_0, f, \Delta\varepsilon) = \frac{\Delta\sigma}{\Delta\varepsilon} \sin(\delta) \qquad 7$$

are the storage and dissipation moduli respectively and δ is the phase angle. In general, carbon black reinforced rubber has fairly weak frequency dependence in conjunction with a pronounced amplitude dependence (Hofer & Lion 2009). If the strain amplitude $\Delta\varepsilon$ increases, the storage modulus *E*' lessens and the dissipation modulus *E*" shows a more or less pronounced sigmoidal behaviour - Payne effect. If the material is linear viscoelastic, then these two moduli depend neither on the deformation amplitude nor on the static pre-strain. The damping factor or loss tangent (tan δ) which is the ratio *E*"/ *E*' is the measure of mechanical energy dissipated as heat during the dynamic cycle. If the dynamic strain amplitude is constant in time, we can observe time

independent moduli (Lion 1998). These phenomena are frequently interpreted as a dynamic state of equilibrium between breakage and recovery of physical bonds linking adjacent filler clusters. The most common model of this state is Kraus model (Kraus1984, Ulmer 1996) which describes the amplitude dependence of dynamic moduli. The influence of static pre-deformation $\varepsilon 0$ is included in different models (Kim et al 2004, Cho & Youn 2006) and the uniaxial form of the frequency, amplitude and prestrain dependent dynamical moduli is proposed by Lion (2004).
The purpose of present paper is to summarize the results of experimental research of the behaviour of rubber under dynamic loading conditions in harmonic strain-controlled tests under tension and to show the dependence of the storage and dissipation modulion the frequency, on the deformation amplitude, on the static pre-strain and different temperatures

EXPERIMENTAL MEASUREMENT

The carbon-black-filled rubbers investigated were obtained from commercial sources. They are based on common formulations containing 30–40% carbon black for the manufacturing of O-rings, seals and other products. The materials examined were styrene-butadiene (SBR) rubbers which have been characterized previously (Marvalova et al 2010).DMA tests under sinusoidal tension mode were carried out on an electro-dynamic testing machine Instron ElectroPuls E3000 equipped with an environmental chamber and with Wave Matrix software. The specimens were thin rectangular strips of length 160 mm, width 25 mm and thickness 2.75 mm. The basic sampling frequency was 100 Hz and was increased up to 500 Hz when needed according to the testing frequency used. The dynamic properties of SBR were investigated at different temperature levels. The tensile loading was strain-controlled. Every test was performed on a virgin specimen. At the chosen static pre deformation $\varepsilon 0$, the frequency and the strain amplitude $\Delta\varepsilon$ were changed in order to determine their influence to the storage (SM) and loss moduli (LM) and to hysteretic losses. Before each test the virgin specimens were preconditioned in order to exclude the Mullins effect. The preloading process started on the static pre-strain $\varepsilon 0$ and consisted of 10 cycles with the maximum strain amplitude to be reached in the subsequent experiment. After that specimens relaxed 15 min at static pre-strain ε_0. After this preconditioning, the mean stress $\sigma 0$ changed only little in the subsequent cyclic loading. Raw test data were recorded by a PC and evaluated in the Matlab Signal Processing Toolbox. The discrete Fourier transform was used to determine the frequency content of force and displacement signals and to calculate the phase delay δ between them. Furthermore, we determined the complex dynamic modulus as the ratio between the amplitudes of stress and strain and dynamic moduli were calculated according to the Eqn. (5-7).

Testing at ambient temperature

In order to determine the dependence of the dynamic moduli we carried out the tests at the temperature 22°C with five frequencies and amplitudes $\Delta\varepsilon$ and with three static pre-strains $\varepsilon 0$ as shown in Tab. 1.

Table 1. Parameters of testing at 22°C

$\Delta\varepsilon$	f(Hz)	ε_0
0.014	**1.0**	**0.17**
0.028	**2.5**	**0.17**

0.042	**5.0**	**0.21**
0.056	**7.5**	**0.21**
0.070	**10.0**	**0.25**

After the preconditioning at the given pre-strainε_0 the test started at the smallest amplitude and the frequency sweep in the chosen range was performed then the amplitude was raised to the next value. The number of cycles executed at each frequency step was between 200 and 300 and was adapted to achieve a steady state.

RESULTS AND DISCUSSION

The results on the experimental test carried out on the thermal ageing on mechanical properties of Soda line glass is as presented. Figures 1-3 shows where the storage and dissipation moduli and the loss angle (LA) are plotted as a function of frequency and amplitude for the static pre-deformation ε_0 as a parameter. The following important can is observed

1. The storage and dissipation moduli increase and the loss angle decreases with increasing static pre strain ε_0
2. The storage modulus and the loss modulus increase slightly with increasing frequency i.e. increasing frequencies lead to an increase in stiffness and an increase in energy loss. The graph of the loss angle has a convex shape and shows a slight maximum in the range of applied frequencies and amplitudes.
3. Both moduli show a pronounced decrease with an increasing strain amplitudes – so called Payne effect.

The Payne effect is explained by a concept (Lion1998, Lion & Kardelky 2004, Drozdov & Dorfmann 2000) that during cyclic deformations the weak physical bonds between molecules of glass and clusters of filler are breaking and recovering continually. The rate of breakage is assumed to be an increasing function of the strain amplitude and the rate of recovery is a decreasing function. The storage modulus is assumed to be proportional to the total number of intact bonds and the dissipation modulus to the rate of breakage per unit of time. The detailed dependence of the storage and dissipation moduli on amplitude for different frequencies .. The both moduli decrease monotonically with increasing strain amplitudes. In our range of amplitudes the loss modulus does not show any sigmoidal behaviour which was reported by Lion & Kardelky (2004).

Temperature Dependency of Dynamic Properties

In order to determine the influence of temperature on dynamic properties of examined SLS glass another series of tests was carried on with the temperature sweep for different frequencies and amplitudes and with a sole static pre-strain ε_0= 0.29. The tests were accomplished in the Instron 4019 Environmental Chamber suitable for a temperature range from -70° to +250°C.
The first series of tests was lead with the temperature sweep from -10°C to 100°C with a step 10°C. The frequency of the strain controlled loading was fixed at 5 Hz.

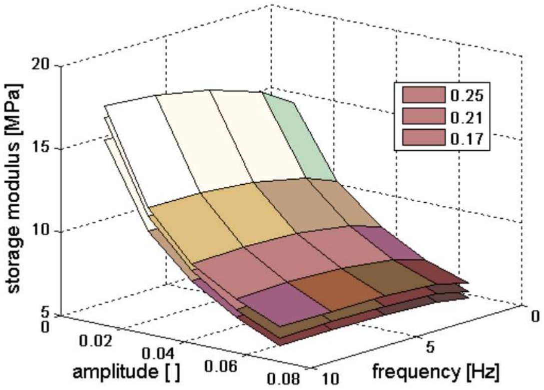


Figure 1. SM amplitude and frequency dependence

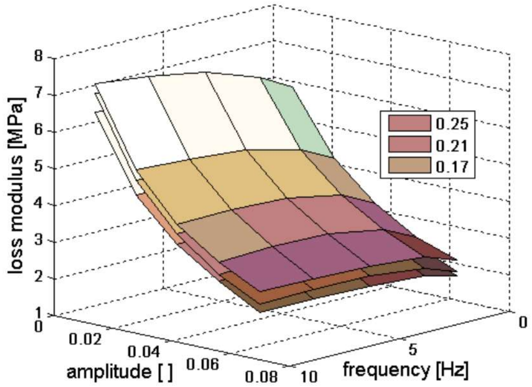


Figure 2. LM amplitude and frequency dependence.

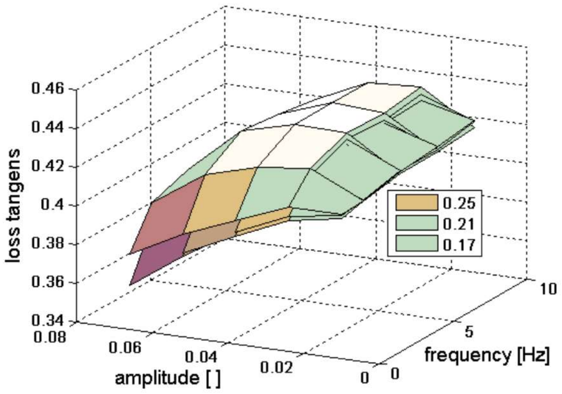
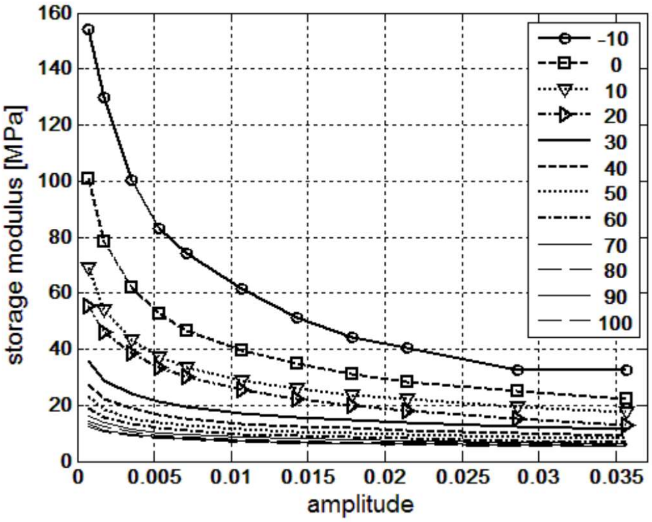


Figure 3. LA amplitude and frequency dependence

After each temperature step the specimens relaxed 15 min at the static pre-strain. Then the cyclic loading started and the amplitude sweep was performed in a range from 0.001 to 0.036. The number of cycles was 200 at each amplitude. We can see a similar dependency of the storage and loss moduli on the temperature and strain amplitude. Both moduli are rising sharply with decreasing temperature but their dependence on the strain amplitude (Payne effect) is much more pronounced in the low temperature zone as can also be seen on the detailed graphs in Figures 6 and 7 where the amplitude dependency is displayed with the temperature as a parameter. All dynamic properties deteriorate considerably at higher temperatures. Described tests were conducted also at frequencies 2.5 Hz and 7.5 Hz. The values of investigated quantities did not show substantial differences in this frequency range.



. Figure 6. SM amplitude and temperature dependence.

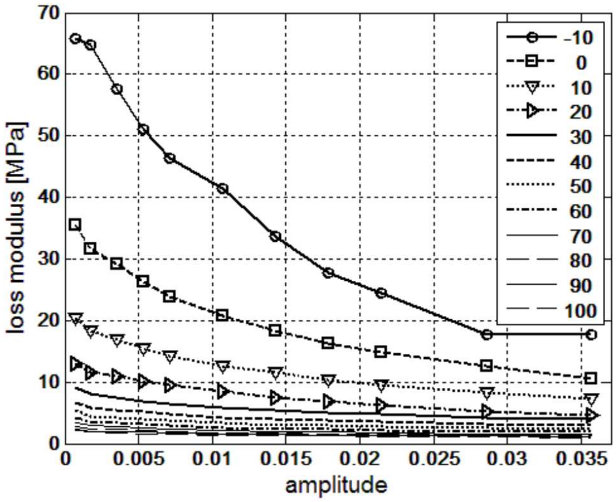


Figure 7. LM amplitude and frequency dependence.

Thermal ageing of rubber samples

Glass samples (25x160 mm) were thermally aged in an air-circulated oven at 100°C. Samples were removed from the oven after given periods of time up to 21 days. Tests were performed at room temperature. Intervals of ageing were 24 hours, 72 hours = 3 days, 7, 14 and 21 days. Mechanical properties as hardness, storage and loss moduli, loss tangent and stress relaxation in dependency of ageing were investigated. The relaxation behaviour of new samples and ageing samples is examined in tension relaxation test with displacement 15 mm. The stress relaxation was recorded for 1200 s. The Figure 8 shows the loss of stresses for different ageing time of rubber samples. All curves reveal the existence of a very fast stress relaxation during the first 10 seconds followed by a very slow rate of relaxation that continues in an asymptotic sense. The stress-strain diagram from tensile tests of ageing rubber is shown in Figure 9. The breaking of the samples occurs at similar values of stress but the elongations are different. Glass with longer ageing period show significantly lower values of strain. The hardness of samples increases with time of thermal ageing as shown in Figure 10. The hardness of specimens increases with increasing of number days of ageing. Dynamic properties were measured by means of the DMA on artificial ageing samples. The storage modulus, loss modulus and loss tangent were investigated at samples with different time of ageing at the same regime see Tab. 1.

Variation of storage moduli, loss moduli and loss tangent are displayed as a function of amplitudes and frequencies in the Figures 11-13. The storage modulus and the loss modulus increase slightly with increasing frequency i.e. increasing frequencies lead to an increase in stiffness and an increase in energy loss. The graph of the loss angle has a convex shape and shows a slight maximum in the range of applied frequencies and amplitudes. The detailed dependence of the storage and dissipation moduli on amplitude for different frequencies is shown in Figures 14, 15. The both moduli decrease monotonically with increasing strain amplitudes. Comparison of storage moduli of specimens with different ageing time is on Figure 14, loss moduli dependency on ageing time is on Figure 15. We observe a considerable fall of storage moduli of all samples with increasing values of amplitude. The values of the storage moduli and loss moduli of samples are increased with time of ageing.The loss tangent (Fig. 16) rapidly falls at the first days of ageing. The difference of tangent loss values after 7 days of ageing is small. The storage modulus and the loss modulus increase slightly with increasing frequency i.e. increasing frequencies lead to an increase in stiffness and an increase in energy loss. The graph of the loss angle has a convex shape and shows a slight maximum in the range of applied frequencies and amplitudes. All dynamic properties deteriorate considerably at higher temperatures. Glass loses its elasticity and damping properties.

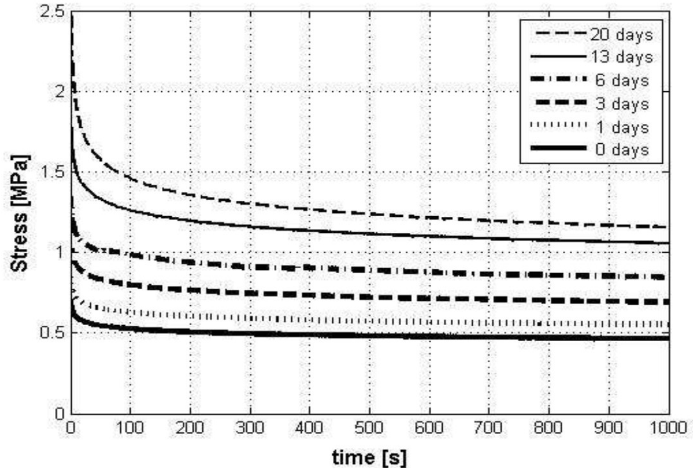


Figure 8. Stress relaxations.

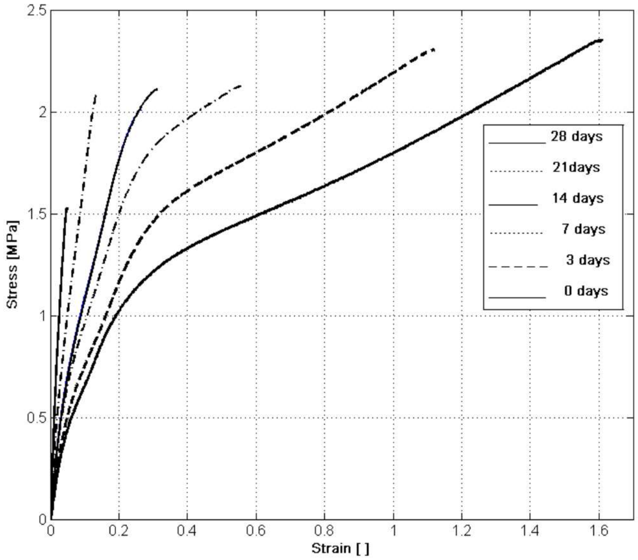


Figure 9. Stress-strain diagram.

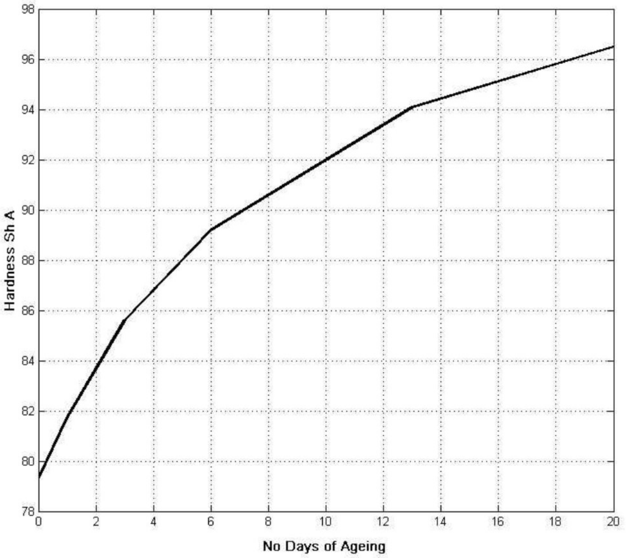


Figure 10 Hardness.

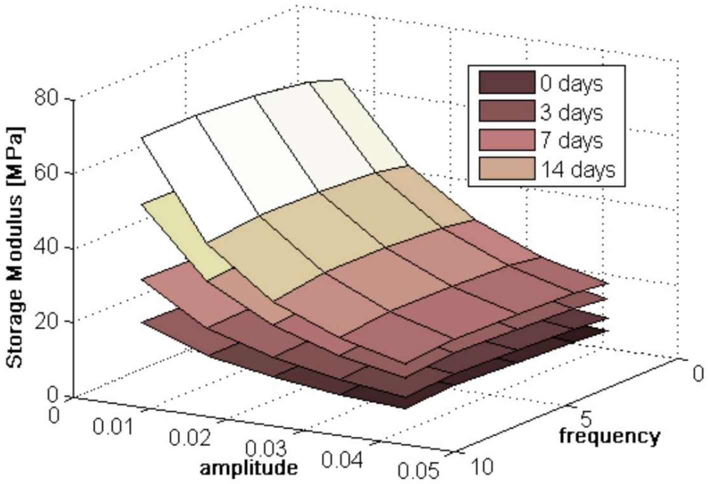


Figure 11. SM amplitude and frequency dependence.

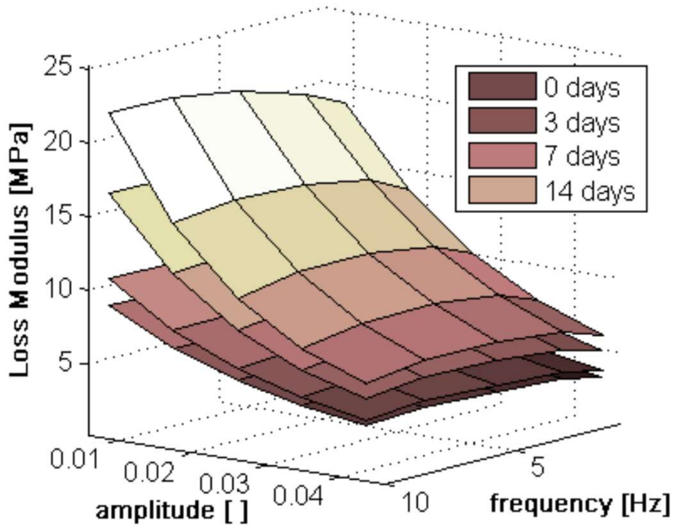


Figure 12. LM amplitude and frequency dependence.

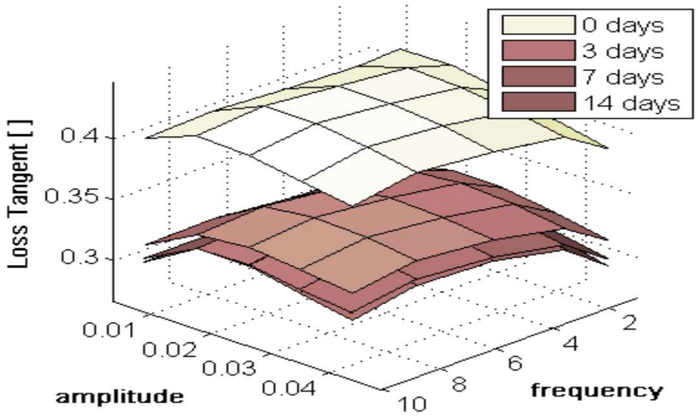


Figure 13. LA amplitude and frequency dependence.

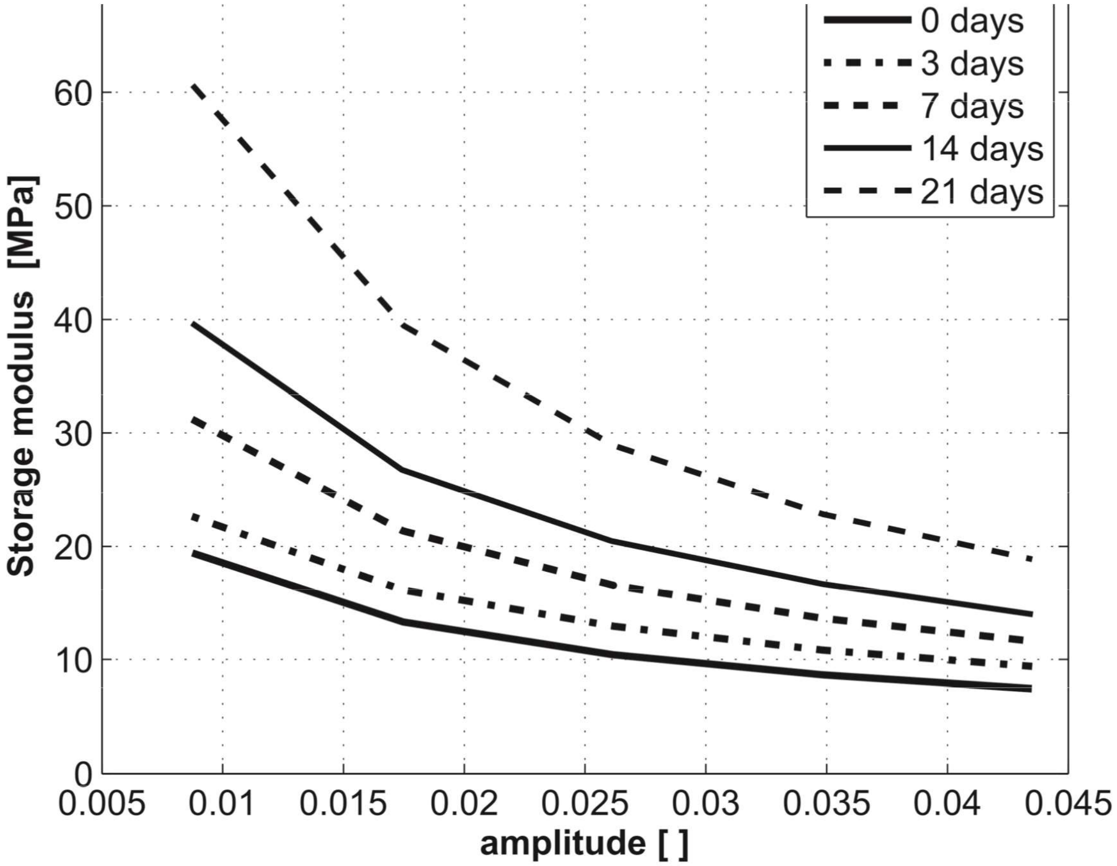


Figure 14. SM amplitude dependency.

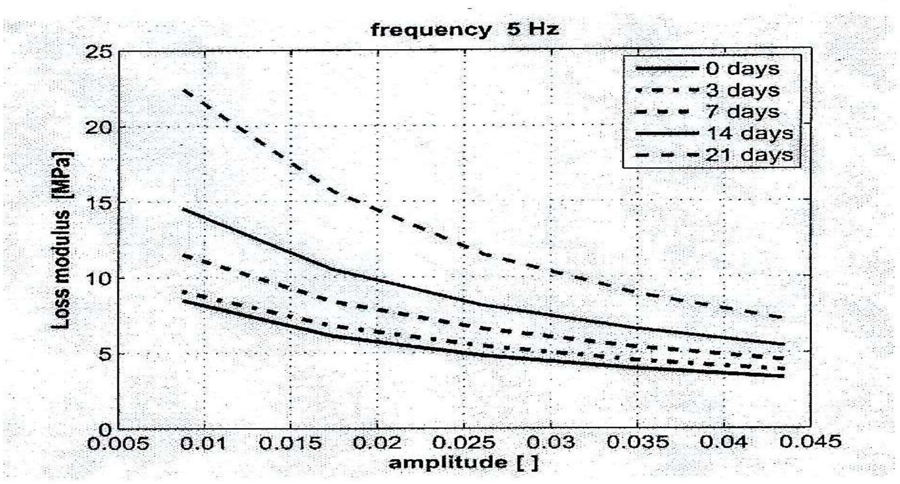


Figure 15. LM amplitude dependency.

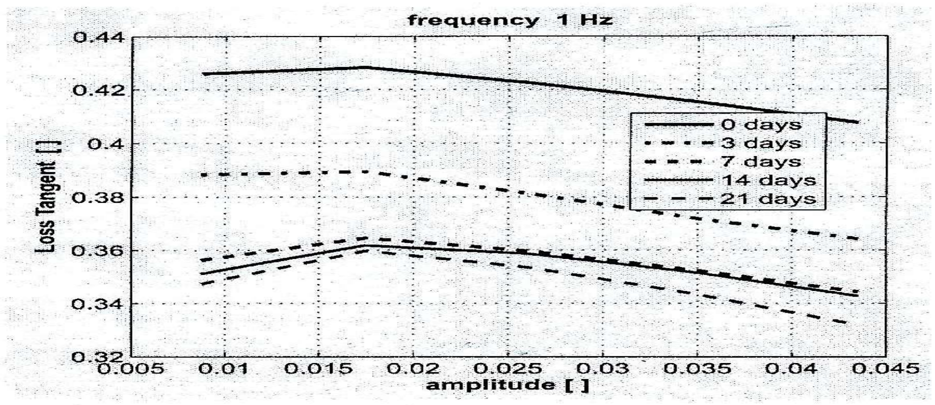


Figure 16. LA amplitude dependency.

The study present the results of testing of SLS glass under different conditions. In order to investigate the internal damping of glass a complex experimental research of dynamic properties was lead by DMA at different frequencies, strain amplitudes and temperatures. The dependency of storage and loss moduli and of loss angle on these quantities was identified and displayed synoptically. It is observed that the mechanical properties of glass are affected by the temperature to a great extent. Results show that the response of glass changes at temperatures even slightly different than the ambient temperature which leads to a drastic change in the mechanical properties. Effect of artificial ageing on mechanical properties of glass is also considerable.

REFERENCES

1. Cho, J. H. & Youn, S. K. (2006). A Viscoelastic Constitutive Model of Rubber under Small Oscillatory Load Superimposed on Large Static Deformation Considering the Payne Effect. *Arch. Appl. Mech* 75: 275-288.

2. Drozdov, A. & Dorfmann, A. (2000). The Payne effect for particle-reinf. elastomers. arXiv:cond-mat/0011223v1.

3 Hofer, P. & Lion, A. (2009). Modelling of Frequency-and Amplitude-dependent Material Properties of Filler-reinforced Rubber. *J. Mech. Phys. Solids* 57: 500–520.

4. Kim, B. K., Youn, S. K. & Lee, W. S. (2004). A Constitutive Model and FEA of Rubber under Small Oscillatory Load Superimposed on Large Static Deformation. *Arch. Appl.Mech.* 73: 781-798.

5. Kraus, G. (1984). Mechanical Losses in Carbon Black Filled Rubbers. *Journa of. Appl. Polym. Sci*. 39: 75–92.

6. Lion, A. (1998). Thixotropic Behaviour of Rubber under Dynamic Loading Histories: Experiments and Theory". *Journal.Mech. Phys. Solids* 46(5): 895-930.

7. Lion, A. (2004). Phenomenological Modelling of the Material Behaviour of Carbon Black-filled Rubber. *Kautschuk Gummi Kunststoffe* 57(4): 184-190.

8. Lion, A. & Kardelky, C. (2004). The Payne Effect in Finite Viscoelasticity: Constitutive Modelling Based on Fractional Derivatives and Intrinsic Time Scales. *Int. J. Plasticity* 20: 1313-1345.

9. Lion, A., Retka, J. & Rendek, M. (2009). On the Calculation of Pre-strain-dependent Dynamic Modulus Tensors in Finite Nonlinear Viscoelasticity. *Mechanics Research Communications* 36(6): 653-658.

10. Marvalova, B. 2008. Viscoelastic properties of filled rubber - Experimental observations and material modelling, In A.

11. Boukamel, L. Laiarinandrasana, S. Meo & E. Verron (2009), *Proceedings of the 5th European Conference on Constitutive Models for Rubber*, London: Taylor & Francis.

12. Marvalova, B., Petrikova, I., Cirkl, D. (2010.) Tribological and Viscoelastic Behaviour of Carbon Black Filled Rubber. In *ASME 10th Biennial Conference on Engineering Systems Design and Analysis. ESDA* 2010. 12-14 July 2010, Istanbul.

13. Namboodiri, C. & Tripathy, D. (1994). Static and Dynamic Strain-Dependent Viscoelastic Behaviour of Black-Filled EPDM Vulkanisates. *Journal of Applied Polymer Science* 5: 877-889.

14. Payne, A. R. (1965). Dynamic Properties of Natural Rubber Containing Heat Treated Carbon Black. *Journal of AppliedPolymer Science* 9: 3245-54.

15. Petrikova, I. & Marvalova, B. (2010). Experimental determination of the mechanical properties of naturally aged rubber.

16. In G. Heinrich, M. Kaliske, A. Lion and S. Reese (eds),(2009) *Proceedings of the 6th European Conference on Constitutive Models for Rubber,.*Taylor & Francis: London.

17. Udoka , K (2023) thermal agsing

18.. Ulmer, J. D. (1996). Strain Dependence of Dynamic Mechanical Properties of Carbon Black-filled Rubber Compounds. *Rubber chem. technol.* 69(1): 15-47.