TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 62, Issue II, June, 2019

AGING INFLUENCE UPON SOME MECHANICAL PROPERTIES OF SILICON RUBBER

Nicolae PANC, Mircea Cristian DUDESCU, Liana HANCU, Adrian POPESCU

Abstract: *Silicon rubber is a material used in many technical, medical, culinary, and other applications. Like any other material, silicon rubber loses its properties over time because a complex degradation phenomenon appears. The paper presents a five year case study that shows how silicon rubber's mechanical properties are influenced in time. The material model that best approximates the obtained experimental data has been identified as 3rd degree Yeoh model (also called the third-order reduced polynomial form).*
Key words: *degradation, mechanical properties, silicon rubber*

1. INTRODUCTION

Silicone rubber has many uses in industry and medicine. Some common applications are: flexible molds, sealing elements, vibration dampers, etc. The molds made of silicone rubber are used for manufacturing models from materials like wax or resin. In previous research paper Panc, [1] were studying the models manufacture in silicon rubber molds and the results on production accuracy, work parameters influence, manufacturing technologies, etc. were presented. Silicon rubber molds are designed to produce a relatively small number of models [1] and the models can be made even over a long period of time.

A review about the effects and chemical degradation process of silicones in outdoor environments can be found in Graiver et al. [2] and Li et al. in [3]. Tan et al. [4], studied the chemical and mechanical degradation of silicone rubber and also of other materials like polymer electrolyte membrane (PEM) and poly-phenol hydroxy EPDM, but not for a long period of time, and focused on chemical degradation.

There is little research on how silicon rubber behaves over a long period of time, when this material shows the aging phenomenon by material degrading. Aging degradation phenomenon is specific to polymers and rubber but behave differently for each of them. There are numerous studies about the way in which the properties of plastic materials are affected by aging degradation, but still we do not know enough about how these properties are affected in the case of silicone rubber.

This paper aims to study how silicon rubber mechanical properties are changed five years after its preparation. The research does not look only on clean silicon rubber, but also on fiberglass reinforced silicon rubber which has superior technological properties as it is shown in studies of Panc and Hancu [1]. In this article it is used the same methodology and research plan presented in [1] in order to compare the mechanical properties of clean silicon rubber and fiberglass reinforced silicon rubber after a five year period of time.

2. MATERIALS AND METHODS

In 2011, 14 batches of samples of silicone rubber with and without fiberglass reinforcement were made, using different ratio of glass fibers, and their compression strength and hardness properties have been determined. It was ascertained that compression strength and hardness of silicone rubber increases with increasing of fiber weight fraction [3]. The samples were stored at 25°C, in an atmosphere with 50-65% humidity. In 2016 compression and hardness tests were resumed on some of the specimens

2.1 Specimens manufacture

The specimens were made at an ISO 815-1:1995 standard dimension, in a cylinder form of 29.0 ± 0.5mm diameter and 13.0 ± 0.2 mm thicknesses. Three silicon rubber types were used with different technological properties that have been reinforced with fiberglass with a 10-11.25 µm thickness. Specimen's batches are presented in table 1, where SR is silicon rubber.

Table 1

Specimen lot	**SR type**	**SR hardness**	**Fiberglass reinforcement degree**				
			0 %	05 %	10 %	15 %	20 %
E291_1	E291	50 IRDH (36 Shore A1)	*	-	-	-	-
E291_2			-	*	-	-	-
E291_3			-	-	*	-	-
E291_4			-	-	-	*	-
E291_5			-	-	-	-	*
E125_1	E125	34 IRDH (24 Shore A1)	*	-	-	-	-
E125_2			-	*	-	-	-
E125_3			-	-	*	-	-
E125_4			-	-	-	*	-
ZC825_1	ZC 825	31 IRDH (21 Shore A1)	*	-	-	-	-
ZC825_2			-	*	-	-	-
ZC825_3			-	-	*	-	-
ZC825_4			-	-	-	*	-

No specimens were manufactured from E125 and ZC825 20% fiberglass reinforced silicon rubber because material viscosity prevented its flow for specimens casting.

2.2 Equipment and determinations

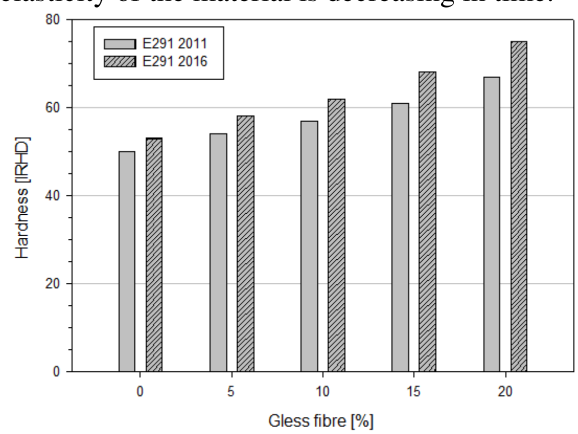
The specimens were used to determine compression strength and hardness. In order to determine the compression strength, it was used in 2011 a Zwick/Roel Materials testing machine Z150 with test Control PC and software testXpert II and Instron 3366 in 2016. Silicon rubber hardness was determined in International Rubber Hard Degree (IRDH) in accordance with ISO 7619-2:2010 standard.

3. ANALYSIS AND INTERPRETATION OF THE OBTAINED DATA

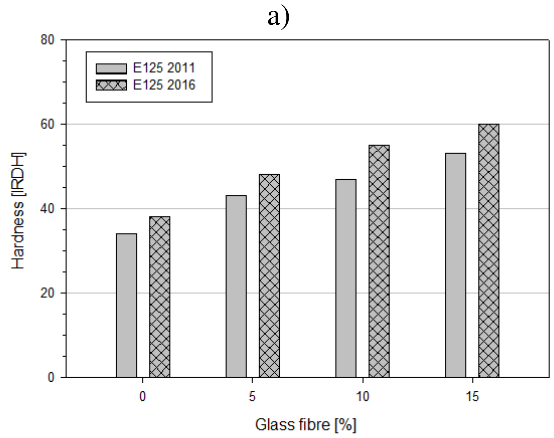
3.1 Analysis of samples hardness

Some of the mechanical properties of the silicone rubber changes when reinforcing the material with fiberglass. The degree of reinforcement influences the hardness of the material. Hardness variation is different for each silicon rubber type, reinforcement degree and is directly influenced by the initial hardness and each silicon rubber viscosity type.

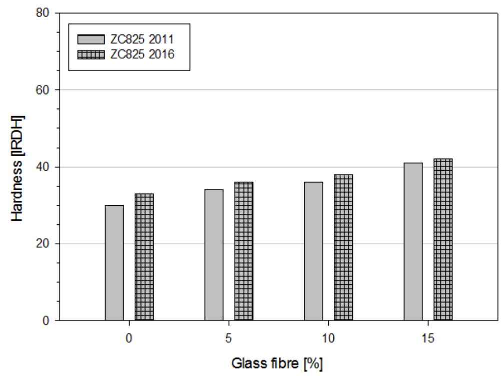
Hardness variations, influenced by the fiber weight fraction and by its aging are shown in figure 1. It can be observed that silicone rubber has the same behavior over time considering that hardness increases with the reinforcement degree. In the same time, due to its degradation over time, the values of hardness are higher. This observation allows us to consider that the elasticity of the material is decreasing in time.



a)



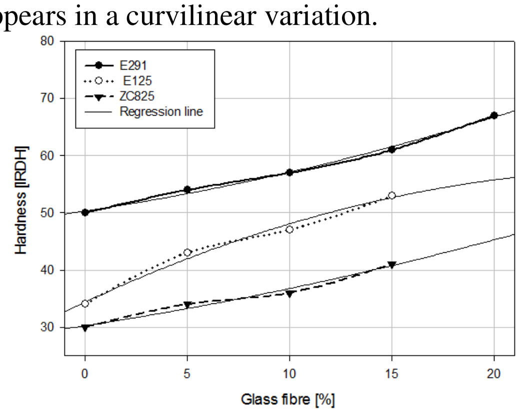
b)



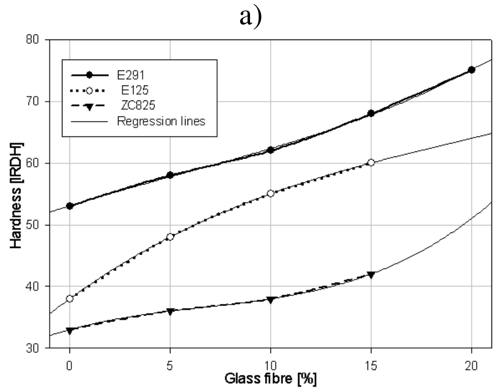
c)

Fig.1 Hardness variation according to the fiber weight fraction, a)E291, b)E125, c)ZC825

The fact that the hardness of the material increases in time seems to be clear but is this variation the same over time? The diagrams presented in figure 2 a, show that the fiber weight fraction influences the hardness in an approximately linear mode in initial state, which shows that the higher the reinforcement degree, the higher is the rubber hardness. In figure 2b, after rubber aging, an increasing in its hardness appears in a curvilinear variation.



a)



b)

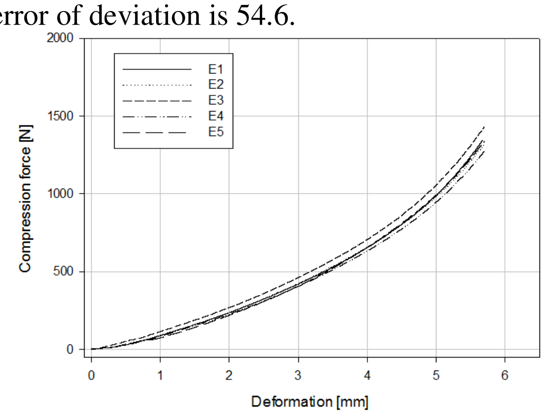
Fig.2 Silicon rubber hardness variation: a) 2011, b) 2016

3.2 Compression strength analysis

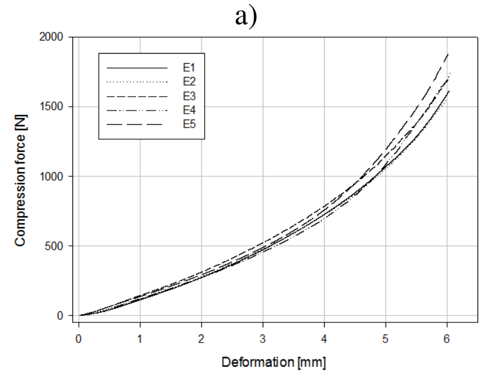
Compression strength determination was achieved by shortening the sample with 6 mm using a 10 mm/min compression speed. In 2011 and 2016 this test was conducted on a lot of five samples for each type of silicone rubber presented in table 1.

Figure 3 presents the influence of compression force upon deformation for E291 silicon rubber with no reinforcement. A five specimen lot has been used to statistically analyze the data in order to establish the samples homogeneity degree. Following the statistical analysis it was concluded that the lot is homogeneous. As it can be seen from figure 3, a) and b), the curves are similar in shape, the difference resulting from compression force variation necessary to specimens shorten.

After statistical processing of the obtained values for 6 mm shortened specimen the following data: for 2011 the average deformation is 1350 N, the standard deviation is 112, the standard error of deviation is 50.5, and for 2016 the average deformation is 1687.5 N, the standard deviation is 122.1, and the standard error of deviation is 54.6.



a)



b)

Fig.3 E291 silicon rubber forces-deformation curves: a) 2011, b) 2016

All of the other specimen's curves are similar, the only difference being the compression force variation necessary to shorten them. Because of this variation the curves are not presented for each lot of samples.

Increasing the fiberglass weight fraction leads to an increased compression force, which indicates the possibility of increasing the rubber compression strength with increasing the reinforcement degree. Compression force variation curve for different reinforcement degree for E291 silicon rubber are presented in figure 4. These values are characteristic for the lot of samples tested in 2016.

Statistical analysis of the data obtained after compression by reducing the height of the specimens up to 6 mm was achieved with SigmaStart 3.5 software. It can be noted that the values for standard deviation Sd are between 21.5 and 240.2, which means that the specimens lot has a homogeneous character.

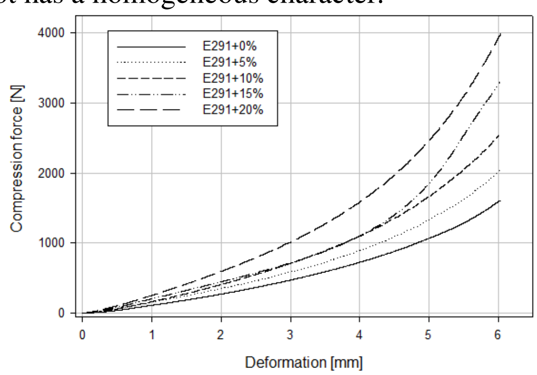
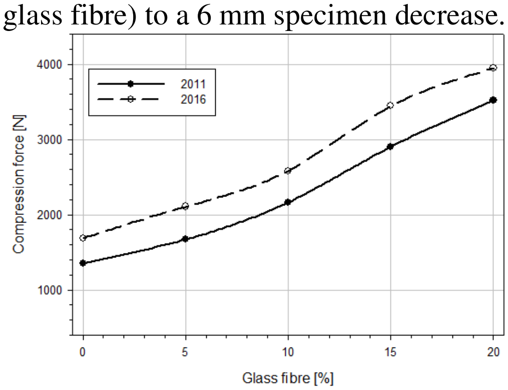
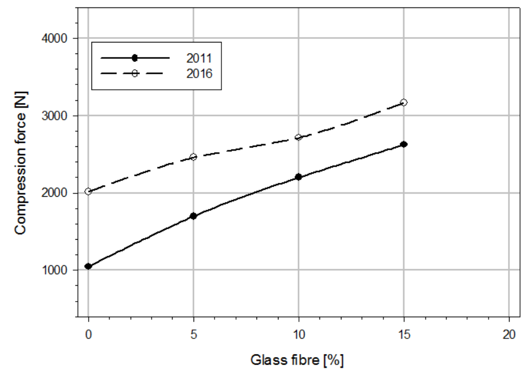


Fig.4 E291 silicon rubber forces-deformation curves depending on fiberglass percentage

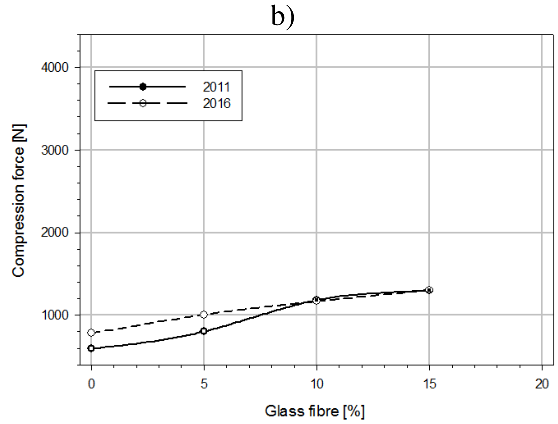
Figure 5 shows how the maximum compression force varies due to the fibre weight fraction (% of glass fibre) to a 6 mm specimen decrease.



a)



b)



c)

Fig.5 Deformation force variation due to the reinforcement degree: a) E291, b) E125, c) ZC825

The maximum compression force for the same lot of samples tested in 2011 and in 2016 are presented in the same graphics for three types of rubber. Note that the maximum force needed for sample compression increases with aging of the silicone rubber.

4. HYPERELASTIC CONSTITUTIVE MODEL

To describe the material behavior a constitutive law for silicone rubber is required. These material models operate on strain energy functions for large strains in accordance with the phenomenological theory of hyper-elastic materials [5]. Several models are available in the literature for these materials, based on the definition of an expression of the specific potential deformation energy. Among these, Mooney–Rivlin, Ogden and Yeoh models are the most used [7], [8]. In all the cases, at least uniaxial and biaxial stretching tests are required to fit the model and extract material parameters. The mechanical tests frequently performed on rubbers are of two types: compression and tension; while the compression state is always uniaxial, tension can be applied in a uniaxial, planar or equi-biaxial state. In this paper, the Yeoh material model (3rd order) in combination with the uniaxial compression test has been employed to determine the material model of the silicon rubber.

The Yeoh model [9] is a hyper-elastic material model that is based on a representation of the strain energy density in a 3-term expansion of the first strain invariant, I1. For incompressible uniaxial loading $I_1=\lambda^2+2\lambda^{-1}$, λ representing the applied stretch.

$$\sigma = 2\left(\lambda^2 - \frac{1}{\lambda}\right)\left[C_{10} + 2C_{20}(I_1-3) + 3C_{30}(I_1-3)^2\right]. \quad (1)$$

where C10, C20 and C30 are the material parameters.

The coefficients of strain energy density can be calibrated by a few simple stress state tests with a curve fitting procedure. The commercial finite element software ANSYS has implemented both the linear and nonlinear least square fit procedures to fit the experimental data. Based on experimental uniaxial compression data, the values of the material parameters have been calculated and are presented in Table 2. Figure 6 shows an example of experimental data fitting for the E125-0% silicon rubber.

Table 2

	C_{10} [MPa]	C_{20} [MPa]	C_{30} [MPa]
E125-00%	0.0869	0.5203	0.2352
E125-05%	0.1274	1.0182	-0.1282
E125-10%	0.1499	1.6240	-0.6128
E125-15%	0.1597	1.1932	0.1142

The quality of the predictions of the Yeoh material models was assessed by direct comparison with the experimental data for the silicon rubber. In figure 6 the comparison of the model with the uniaxial experimental data is presented.

The model presents good agreement with experimental data by using a relatively small number of material parameters.

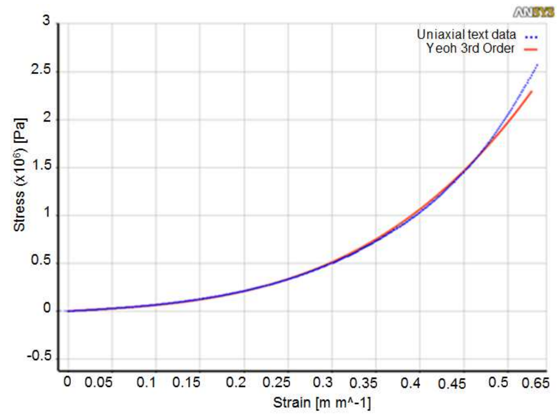


Fig. 6. Material model Yeoh 3rd order of the E125-0% silicon rubber compared with uniaxial test data

5. CONCLUSION

This paper presents how silicon rubber, by degradation due to time passing, changed its mechanical properties over a period of five years. This degradation is called the aging phenomenon.

As a result of the determinations on each batch of samples at manufacturing time and after aging, some conclusions can be drawn. For the studied silicon rubbers, aging lead to the increase of force necessary for compression. This is because the elasticity of the material is diminished in time and that leads to hardness increasing. Silicone rubber used for tests lost about 30% of the elastic properties during five years aging.

Therefore, aging process affects the parts made by using silicon rubber, simple or reinforced, so this aspect should not be neglected when using it after a period of time. It is recommended that in the case of flexible molds used for casting and injection, the time of usage should not be longer than 2-3 years after manufacturing as the rubber becomes more rigid and compromises models quality.

In the case of gasket seal, it should be taken into consideration the fact that by aging, the material becomes harder, and in the case of fiberglass reinforcement, the material becomes more fragile, some materials are even shattering on seal compression/stretch.

The 3rd order Yeoh material model studied in this research provide good predictions for the experimentally observed behaviour of the silicon rubber and therefore is more suitable for FE simulations.

6. REFERENCES

[1] N. Panc, L. Hancu, N. Balc; Research Regarding the Improvement of the Performance of Rubber Dies, Proceedings of the World Congress on Engineering, July 6-8, London, U.K., Vol I, WCE 2011: pp. 783-786, 2011.

[2] D. Graiver, K.W. Farminer, R. Narayan; A Review of the Fate and Effects of Silicones in the Environment, Journal of Polymers and the Environment, 11 (4): pp.129–136, 2003.

[3] G. Li, J. Tan, J. Gong; Degradation of the elastomeric gasket material in a simulated and four accelerated proton exchange membrane fuel cell environments, Journal of Power Sources, 205: pp. 244–251, 2012.

[4] J. Tan, Y.J. Chao, Y. Min, W.-K. Lee, J.W. Van Zee; Chemical and mechanical stability of a Silicone gasket material exposed to PEM fuel cell environment, International Journal of Hydrogen Energy, 36 (2): pp. 1846-1852, 2011.

[5] T.V. Korochkina, E.H. Jewell, T.C. Claypole, D.T. Gethin; Experimental and numerical investigation into nonlinear deformation of silicone rubber pads during ink transfer process, Polymer Testing, 27 (6): pp.778-791, 2008.

[6] C.P. Sasso, M. Pasquale, L. Giudici, S.H. Lim, S.M. Na; Characterization of hyperelastic rubber-like materials by biaxial and uniaxial stretching tests based on optical methods, Polymer Testing, 27 (8): pp. 995-1004, 2008.

[7] H. Khajehsaeid, J. Arghavani, R. Naghdabadi; A hyperelastic constitutive model for rubber-like materials, European Journal of Mechanics A/Solids, 38: pp.144-151, 2013.

[8] Michael Rackl; Curve fitting for Ogden, Yeoh and Polynomial models, ScilabTEC conference, DOI: 10.13140/RG.2.1.4441.3849, 2015.

[9] O. H. Yeoh; Some Forms of the Strain Energy Function for Rubber, Rubber Chemistry and Technology, 66 (5): pp. 754-771, 1993.

INFLUENTA DEGRADARII IN TIMP ASUPRA PROPRIETATILOR TEHNOLOGICE ALE CAUCIUCULUI SILICON

Rezumat: Cauciucul siliconic este un material utilizat in numeroase aplicatii tehnice, medicale, culinare, etc. Ca si orice material, cauciucul siliconic isi pierde proprietatile odata cu trecerea timpului deoarece apare un fenomen complex de degradare. Articolul prezinta un studiu de caz intins pe cinci ani care urmareste modul in care proprietatile mecanice ale cauciucului siliconic sunt influentate de trecerea timpului. Modelul de material care aproximează cel mai bine datele experimentale obținute a fost identificat drept modelul Yeoh de gradul 3 (numit și forma polinomială redusă).

Nicolae PANC, Ph.D. eng., Lecturer, Technical University of Cluj-Napoca, Department of Manufacturing Engineering, E-mail, nicolae.panc@tcm.utcluj.ro, No.103-105, Muncii Blvd.,400641, Cluj-Napoca

Mircea Cristian DUDESCU, Ph.D. eng., Professor, Technical University of Cluj-Napoca, Mechanical Engineering Department, E-mail, mircea.dudescu@rezi.utcluj.ro, No.103-105, Muncii Blvd.,400641, Cluj-Napoca

Liana HANCU, Ph.D. eng., Lecturer, Technical University of Cluj-Napoca, Department of Manufacturing Engineering, E-mail, liana.hancu@tcm.utcluj.ro, No.103-105, Muncii Blvd.,400641, Cluj-Napoca

Adrian POPESCU, Ph.D. eng., Lecturer, Technical University of Cluj-Napoca, Department of Manufacturing Engineering, E-mail, adrian.popescu@tcm.utcluj.ro, No.103-105, Muncii Blvd.,400641, Cluj-Napoca