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DAMAGE OF RUBBERS IN AGGRESSIVE MEDIA

■ **Abstract:**

This work aims to determine the durability of highly deformable viscous solids under tensile loads. It is based on the damage accumulation in relation with two specific areas. The first one is initially intact and the second one contains in the beginning initial imperfections due to the structure or to the penetration of an environmental fluid. The durability assessment is based on damage accumulation. The durability of two kinds of rubbers is established by introducing the criterion of critical concentration of damage - determined by tests at two speeds. Power and exponential law are used to describe the rate of damage. Wöhlers curves thus obtained are compared with experimental data.

■ **DETERMINATION OF THE INITIAL IMPERFECTIONS**

On the basis of our previous works [1, 2] a two-phase damage model is assumed, regarding different phase structures. The first phase (zone) is without initial imperfections, while the second one contains defects that have different nature - one can always find them in real structures. The first zone can be considered as a zone with reduced damage development in the beginning, while in the second one the damage occurs at higher rate in the beginning destroying the initial imperfections. The two phases are bonded to each other and perform in parallel - figure 1. The volume content of the first phase is f while that of the second one - (1-f). The material of the first phase undergoes continuously increasing effective stresses $-\sigma_{eff,1}$. In the uniaxial stress state we may express them on the basis of the Kachanov's model [3], i.e.

$$\sigma_{eff,1} = \frac{\sigma}{1-D} f,\qquad (1)$$

where D is the damage parameter and σ is the nominal stress. Here the damage rate grows continuously until material damage saturation takes place.

The material of the second phase is initially subjected to large effective stresses $\sigma_{eff,2}$ due to the presence of initial imperfections.

The effective stresses continuously decrease, owing to the stress redistribution and destruction of the initial imperfections. We may write for $\sigma_{eff,2}$ that

$$\sigma_{eff,2} = \frac{\sigma}{D}(1-f)\qquad (2)$$
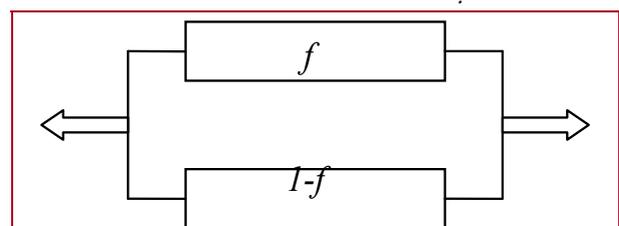

Figure 1. Scheme of the two phase damage model

Here, the damage rate continuously decreases until defect saturation of the material takes place. Summarizing the two effective stresses – equations (1) and (2), for the resulting effective stresses we get the following expression

$$\sigma_{eff} = \frac{\sigma}{1-D}f + \frac{\sigma}{D}(1-f) = \varphi(D)\sigma \ . \qquad (3)$$

Moreover, it stands clear that the function

$$\varphi(D) = \frac{f}{1-D} + \frac{1-f}{D} \qquad (4)$$

represents a concentration function. The volume fraction of the "ideal" part f is a structure parameter.
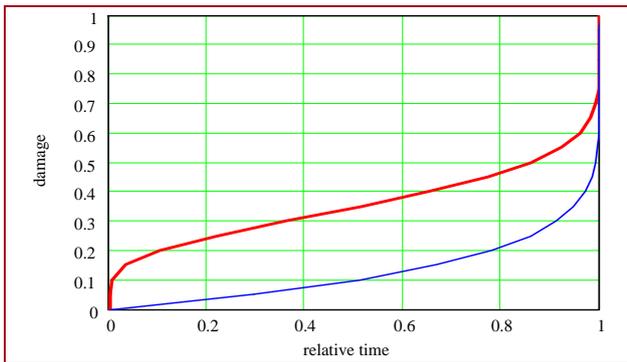

Figure 2. Damage accumulation using our model (upper line) and those of Kachanov (lower line)

The model here discussed, can have different interpretation. In the case of environmental diffusive fluid the first zone can be considered as a zone with low concentration (first critical concentration) and reduced damage development in the beginning according to the Kachanov's model, while in the second one the concentration is higher and damage occurs at higher rate in the beginning – equation (2). The damage curves here proposed possess an inflection point whose position depends from the structure parameter f - figure 2. On this figure the time is normalized (dividing the real time by the failure one). The material critical state is attaint when the damage parameter D reaches some critical value $D^* < 1$. This critical stage can be obtained experimenttally according to the elastic module degradation or in the case of rubbers using a two strain rate tests-see & 3.

■ LAW OF DAMAGE RATE

We complete the model by introducing a non-linear damage law that may be a power function of the effective stresses or an exponential one (Arrhenius) [4, 5]

$$\frac{dD}{dt} = H(\sigma_{eff})^m = H\varphi(D)^m\sigma^m , \qquad (5)$$

$$dD/dt = \frac{1}{A_o}\exp - \frac{E - \gamma\sigma_{eff}}{kT} =$$

$$dD/dt = \frac{1}{A_o}\exp - \frac{E - \gamma\varphi(D)\sigma}{kT} . \qquad (6)$$

Here t – is the time; H, m respectively A_o, E, γ - experimentally deduced parameters; k – the Boltzmann constant and T – the absolute temperature. The second low (6) possesses certain advantage considering perfect structures (strongly oriented polymers). In this case A_o, E, γ are respectively the period of atom vibration, the activation energy of the chemical bounds destruction and the atomic volume. Considering real solids these parameters should be adjusted. After integration of equation (5), respectively (6) one obtain the damage – time curves - figure 2.

$$t = \frac{\int_0^D \varphi^{-m}dD}{H\sigma^m} , \qquad (7)$$

$$t = A_o\int_0^D \exp\frac{E - \gamma\varphi(D)\sigma}{kT}dD. \qquad (8)$$

The analysis of these relations shows that the curves of damage accumulation are S - shaped (see figure 2). A number of experimental data prove that the damage curves are S-curves - [6, 7, 8]. Plumtree, Shen and Talrejas propose in [6, 7] a second-degree model for describing those curves. They introduce the term "critical damage state" and describe separately the two damage processes – without and with a crack. The studies introduce also a number of experimental parameters, and significant efforts are required to prepare the experimental set up.

■ CRITICAL DAMAGE CONCENTRATION AND WÖHLER'S CURVE

It is well known [4, 6], that the Katchanov's damage parameter D varying from 0 (intact solid) to 1 (fully damaged solid) do not reach the value of 1 due to the crack interactions. We employ here a simple method to determine the critical damage concentration (CDC) – an important parameter related with the durability [2, 4, 6].

In [9] was proposed and in [10] was developed an approach to find the time damage dependence experimentally, which consists in

the following elements. One accepts a critical damage criterion (failure). Considering brittle materials, that can be the fracture. For ductile or viscous ones that can be the maximal stress on the stress-strain diagram. Considering rubbers the failure criterion can be choose as the beginning of the color change of the material. At the place of the classical damage equation $\dot{D} = \dot{D}(\sigma, D)$ - see eq. (5), we introduce the strain rate, which can be easily imposed and controlled during the experimentation.

$$\dot{D} = \dot{D}(\dot{\varepsilon}, D) . \qquad (9)$$

We present here briefly the experimental scheme to obtain the damage curve. Probes are predeformed with high strain rate $\dot{\varepsilon}_e$ (damage) during some time t_1, then the strain rate decrease considerably - $\dot{\varepsilon}_o$ (without damage comparing with the case with the strain rate $\dot{\varepsilon}_e$) until failure (defined previously) occurs. The second test with the highest strain rate $\dot{\varepsilon}_e$ continue longer - $t_2 > t_1$ and then the lowest strain rate is imposed until failure. This manipulation imposing different increasing times $t_i > t_{i-1}$ continue until failure with the maximal strain rate $\dot{\varepsilon}_e$. The limit strains (until failure occurs according to the adopted criterion) are shorter than the foregoing ones obtained by shorter pre-exposition times with $\dot{\varepsilon}_e$. One suppose that the difference between the limit strain with strain rate $\dot{\varepsilon}_o$ without pre-exposition with $\dot{\varepsilon}_e$ and the respective limit strains with increasing pre-exposition times represent an integral value characterizing the damage accumulation. Dividing this difference on the limit strain without pre-exposition one obtain the damage accumulation parameter of Kachanov - D. Imposing different damage degrees (from t_1 to t_n) one can obtain n points from the damage curve. The relative limit strain with the maximal possible pre-exposition time corresponds to the limit (critical) damage accumulation. This approach can be used to obtain the Wöhler's curves - eqs (7, 8). If in equations (7 and 8) one pose $D \to D^*$ one obtain the relation critical stress – failure time. The respective curve $(\sigma_f - t_f)$ concerning the first law of damage rate is derived from equations (7) for $D \to D^*$ and $t \to t_f$

$$t_f = \frac{\int_0^{D^*} \varphi^{-m}(D)\, dD}{H^m (\sigma_f)^m} . \qquad (10)$$

Concerning the other law of damage rate, from eq. (8) we have respectively

$$t_f = A_o \int_0^{D^*} \exp \frac{E - \gamma \varphi(D) \sigma_f}{kT} \, dD . \qquad (11)$$

The curves using eq.(10) for our rubbers are illustrated on figure 4 and the next ones.

■ WÖHLER'S CURVES CONCERNING THE INVESTIGATED RUBBERS

On the figure 3 we have put the experimental points and the Wöhler's curves according to eq. (10) and (11) for the BN rubber and the first critical concentration of oxygen.
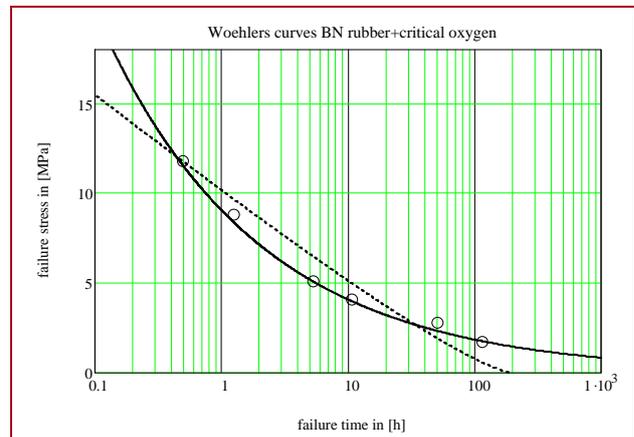

Figure 3. Wöhler's curves for BN rubber – first critical concentration of oxygen. Solid line – eq.(10), dashed line – eq.(11).

Obviously we can't apply eq. (11) for our rubbers, because in logarithmic scale that is a right line. The experimental data here are: in eq.(10) $m = 2.879$, $H = 2.606 \times 10^{-6}$, in eq.(11)

$$D^* = 0.321, \ A_o = 1.917 \times 10^{-8} [1/\text{sec}],$$

$$k = 1.3806 \times 10^{-23} [\text{J/K}], \ U = 0.99 \times 10^{-19} [\text{J}],$$

$$\gamma = 0.7 \times 10^{-27} [\text{m}^3], \ T = 297 [K], \ f = 0.531 .$$

On the figure 4 one can see the Wöhler's curve for BN and the first critical water concentration. The parameters are $m = 3.548$, $H = 2.885 \times 10^{-6}$. On the figure 5 we have illustrated the Wöhler's curve for BN and the first critical concentration of engine oil. The parameters are $m = 3.548$, $H = 2.885 \times 10^{-6}$.
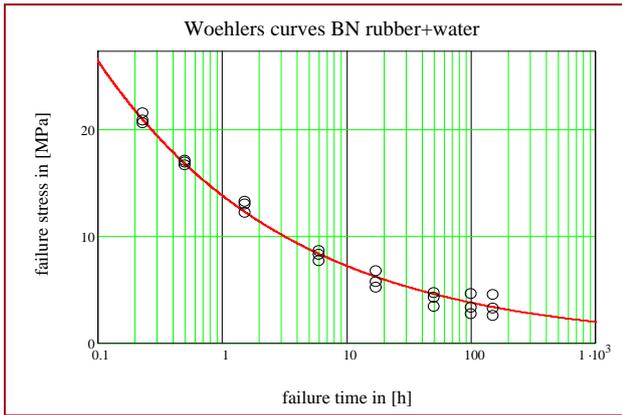
Figure 4. Wöhler's curve for BN – first critical water concentration. Solid line - eq.(10), points – experimental data (3 tests for every stress level).

Note. All the points are illustrated only in figure 4. To the other ones we have put only the averaged values.
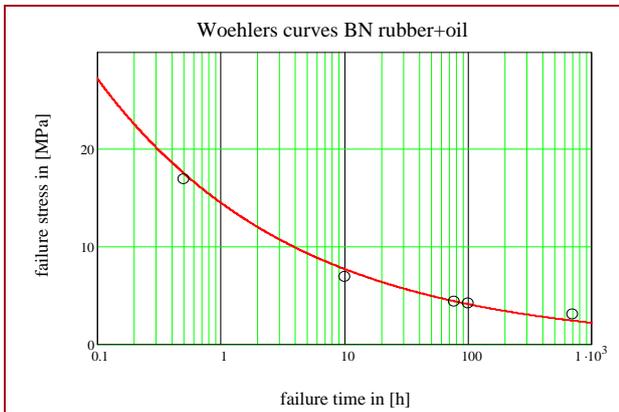

Figure 5. Wöhler's curve for BN – first critical concentration of engine oil

On the figure 6 we have illustrated the Wöhler's curve for BN and the first critical concentration for 20% sulphuric acid. The parameters are $m = 3.548$, $H = 2.885 \times 10^{-6}$. On the figure 7 we have illustrated the Wöhler's curve for PI and the first critical concentration for oxygen. Here we have $m = 3.548$, $H = 2.885 \times 10^{-6}$. On the figure 8 we have illustrated the Wöhler's curve for PI and the first critical concentration for water, here $m = 3.548$, $H = 2.885 \times 10^{-6}$. On the figure 9 we have illustrated the Wöhler's curve for PI and the first critical concentration for engine oil. Here $m = 3.548$, $H = 2.885 \times 10^{-6}$. On the last figure 10 on can see the Wöhler's curve for BN and the first critical concentration of 20% solution of sulphuric acid. The parameters are $m = 3.548$, $H = 2.885 \times 10^{-6}$.
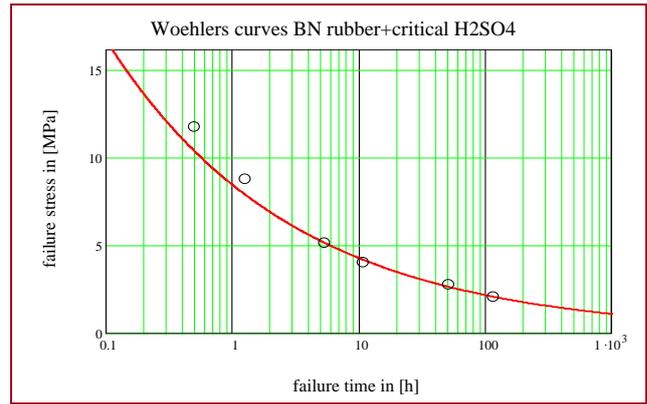

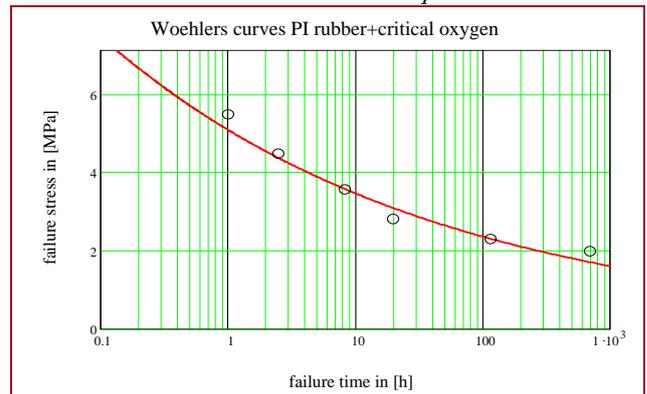*Figure 6. Wöhler's curve for BN – first critical concentration of 20% of sulphuric acid*

Figure 7. Wöhler's curve for PI – first critical concentration of oxygen
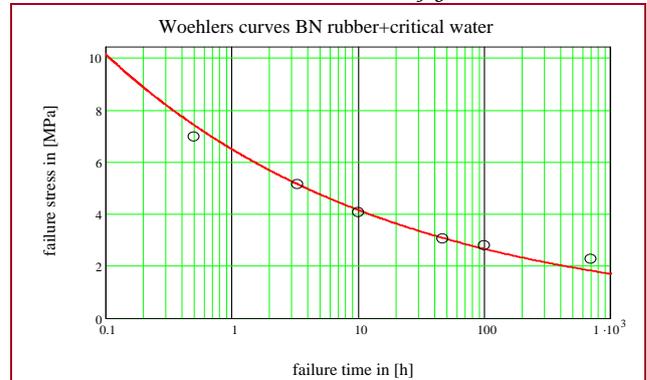

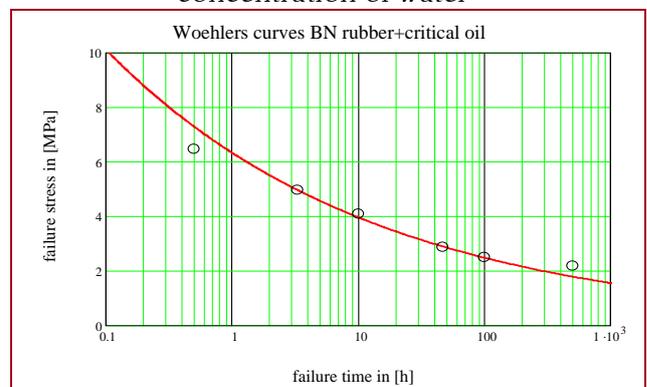*Figure 8. Wöhler's curve for PI – first concentration of water*

Figure 9. Wöhler's curve for PI – first critical concentration of engine oil
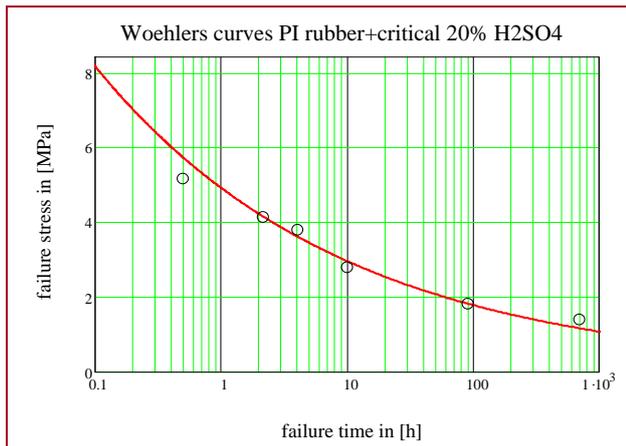
Figure 10. Wöhler's curve for PI - first critical concentration of 20% solution of sulphuric acid

■ CONCLUSION

One can make the following conclusions. Many investigations show that the critical damage D^* is limited between 0.2 (brittle state) and 0.8 (ductile state). Here we have obtained helpful relations to determine the critical damage. The proposed model describes successfully the mechanical comportment of different couple rubber-environment for static charges. The S curve of the damage accumulation is also adequately described using one equation, against the existing two-stage approaches. The introduction of initial imperfections is very important concerning materials containing technological defects or (and that is important concerning this investigation) in the case of materials surrounded by aggressive media (penetrating fluids). The relative penetration surface represents an initial imperfection zone because of the accelerated damage in this zone.

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