

DIFFUSION OF LIQUID MEDIA IN VULKANIZATSA. Alexandrov^{1 §}, G. Halil², M. Kolev³, M. Milenova⁴^{1,2,3,4}Department of Applied Mechanics

University of Chemical Technology and Metallurgy (UCTM)

8, Climent Ohridsky Blvd., Sofia 1756, BULGARIA

e-mail: alexa@uctm.edu

Abstract: In the present paper the kinetics of the diffusion of aggressive, liquid and industrial mediums in vulcanizers is concerned. We investigate the influence of diffusion on the mechanical characteristics as the deformation and strength. Our investigation is a continuation of a resent study by the same authors where a method matching the theoretical principles of fluid mechanics and the experimental data was established. Here we demonstrate that for different average concentrations, the diffusion coefficient may vary within close limits. Thus with a sufficient for the engineering practice accuracy our conclusion is that one may accept that the diffusion coefficient is a constant for polyisoprene vulcanizer and water, polyisoprene vulcanizer and machine oil, polyisoprene vulcanizer and sulfuric acid, butadiene-nitrile vulcanizer and water, butadiene-nitrile vulcanizer and machine oil, butadiene-nitrile vulcanizer and sulfuric acid.

AMS Subject Classification: 92E20, 76R50, 80A20, 80A30, 80A32, 76V05, 76M25, 74C10

Key Words: diffusion, coefficients of diffusion, sorption-weighing method, Fick's second law, vulkanizats

1. Introduction

The phenomena connected with density fluctuations undergoing diffusion and arising in some plastic and polymer materials can be described by a mathematical model containing a partial differential equation (PDE) called diffusion equation. It is also used to describe processes exhibiting diffusive-like behaviour. The diffusion equation

Received: February 7, 2011

[§]Correspondence author

is usually written as:

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} = \nabla \cdot [D(C, \mathbf{r}) \nabla C(\mathbf{r}, t)], \quad (1)$$

where the scalar function $C = C(\mathbf{r}, t)$ ($\frac{kg}{m^3}$) is the density of the diffusing material (liquid surrounding medium) at location $\mathbf{r} \equiv (x, y, z)$ and time t and $D(C, \mathbf{r})$ ($\frac{m^2}{s}$) is the collective diffusion coefficient for density C at location \mathbf{r} ; the nabla symbol $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)^t$ represents the vector differential operator acting on the space coordinates. If the diffusion coefficient depends on the density then the equation is nonlinear, otherwise it is linear. If there is constant D , then the diffusion equation reduces to the following linear equation:

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} = D \nabla^2 C(\mathbf{r}, t), \quad (2)$$

also called the heat equation (HE). More generally, when D is a symmetric positive definite matrix, the equation describes anisotropic diffusion, which is written (for three dimensional diffusion) as:

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} = \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial}{\partial x_i} \left[D_{ij}(C, \mathbf{r}) \frac{\partial C(\mathbf{r}, t)}{\partial x_j} \right], \quad (3)$$

The diffusion equation can be derived in a straightforward way from the continuity equation, which states that a change in density in any part of the system is due to inflow and outflow of material into and out of that part of the system. Effectively, no material is created or destroyed:

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (4)$$

where \vec{j} is the flux of the diffusing material. The diffusion equation can be obtained easily from this when combined with the phenomenological Fick's first law, which assumes that the flux of the diffusing material in any part of the system is proportional to the local density gradient:

$$\mathbf{j} = -D(C) \nabla C(\mathbf{r}, t). \quad (5)$$

If drift must be taken into account, the Smoluchowski equation provides an appropriate generalization, that reads

$$\frac{\partial G(r, t)}{\partial t} = D \nabla^2 G + \zeta^{-1} \nabla (G \nabla U), \quad (6)$$

where $G(\mathbf{r}, t)$ is a density, D a diffusion constant, ζ a friction coefficient, and $U(\mathbf{r}, t)$ a potential. We note that (6) is stochastic differential equation. It is formally identical to the Fokker-Planck equation, the only difference being the physical meaning of G : a spatial distribution for the Smoluchowski equation, a velocity distribution for the Fokker-Planck equation.

2. Preliminaries

Some evolutionary phenomena appearing in heat exchange, (see [1]-[3]) and mass exchange (see [4]-[7]) processes in regard to the synthesis, dimensioning and exploitation of polymer materials surrounded by liquid mediums and the influence of temperature and different variable loadings on the evolutionary processes were studied in previous research works by some of the authors of the present paper.

In the present paper the kinetics of the diffusion of aggressive, liquid and industrial mediums in vulcanizers are concerned in view of further investigation of the influence of diffusion on their deformation and strength characteristics. The following processes are possible under the influence of the liquid medium:

- (i) diffusion of the water molecules in the vulcanizer,
- (ii) swelling nearly to dissolving,
- (iii) chemical reaction.

The mentioned processes may run separately or simultaneously in different combinations. The present investigation concerns only mediums which do not react chemically with the vulcanizer and do not cause deep structural changes (swelling) i.e. such mediums in which despite its modified characteristics the vulcanization preserves its bearing capacity of a constructional material. It is known that usually the process of penetration (absorption) of liquid surrounding medium in a solid body is connected with the term sorption. This term includes adsorption and absorption. The penetration is realized through a diffusion i.e. the liquid migrates in the body's volume under the influence of the concentrative gradient. The distribution of the diffusing liquid's concentration in the different points of the body can be described by the Fick's second law (1), where C is the concentration of the diffused liquid in a particular point of the body's volume at a definite moment of time t , D is the coefficient of diffusion and is a basic parameter of the process. Some mathematical methods for solving the diffusion equation are established by Crank and Park in [8].

Let us consider the three dimensional diffusion equation in Cartesian coordinates (2) describing an isotropic medium with constant $D \in \mathbb{R}$, that is,

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right), \quad (7)$$

The solution of (7) depends on the shape of the given polymeric material (plastic body) and the initial and border conditions imposed on the problem under consideration. First we consider a liquid free rectangular parallelepiped measuring in \mathbb{R}^3 as follows:

$$-\frac{a}{2} < x < \frac{a}{2}, \quad -\frac{b}{2} < y < \frac{b}{2}, \quad -\frac{l}{2} < z < \frac{l}{2}.$$

Assume that the body and the liquid come in contact at the point $t = 0$, the concentration on the walls of the body remains constant and equal to the concentration of complete saturation C_∞ , i.e. $C = C_\infty$, the initial condition is

$$C(x, y, z, t) = 0, \quad (8)$$

and the border condition

$$\begin{aligned} C(\pm \frac{a}{2}, y, z, t) &= C_\infty, \\ C(x, \pm \frac{b}{2}, z, t) &= C_\infty, \\ C(x, y, \pm \frac{l}{2}, t) &= C_\infty. \end{aligned} \quad (9)$$

Under the above stated initial (8) and boundary (9) conditions the solution of (7) takes the form

$$\begin{aligned} C(x, y, z, t) &= c C_\infty = \\ &= C_\infty \left\{ 1 - \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} A_n A_m A_k \times \right. \\ &\quad \left. \times \cos \mu_n \frac{2x}{a} \cos \mu_m \frac{2y}{b} \cos \mu_k \frac{2z}{l} e^{-(\mu_n^2 K_1^2 + \mu_m^2 K_2^2 + \mu_k^2 K_3^2) F_0} \right\}, \end{aligned} \quad (10)$$

where

$$\begin{aligned} A_n &= (-1)^{n+1} \frac{2}{\mu_n}, & \mu_n &= (2n-1) \frac{\pi}{2}, \\ A_m &= (-1)^{m+1} \frac{2}{\mu_m}, & \mu_m &= (2m-1) \frac{\pi}{2}, \\ A_k &= (-1)^{k+1} \frac{2}{\mu_k}, & \mu_k &= (2k-1) \frac{\pi}{2}, \end{aligned}$$

$F_0 = \frac{Dt}{\lambda^2}$ - criterion of Fourier, λ - summary dimensions,

$$\begin{aligned} \frac{1}{\lambda^2} &= \frac{4}{a^2} + \frac{4}{b^2} + \frac{4}{l^2}, \\ K_1 &= \frac{2\lambda}{a}, & K_2 &= \frac{2\lambda}{b}, & K_3 &= \frac{2\lambda}{l}, \end{aligned}$$

$c = \frac{C}{C_\infty}$ [%] - dimensionless relative concentration.

It is known that the average concentration can be expressed by the formula

$$C_m = \frac{8}{a b l} \int_0^{\frac{a}{2}} \int_0^{\frac{b}{2}} \int_0^{\frac{l}{2}} C(x, y, z, t) dx dy dz . \quad (11)$$

Then having in mind the equalities (10) and (11) we obtain the quantity that call relative average concentration

$$\begin{aligned} c_m &= \frac{C_m}{C_\infty} = \\ &= 1 - \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} B_n B_m B_k \times \\ &\times \cos \mu_n e^{-(\mu_n^2 K_1^2 + \mu_m^2 K_2^2 + \mu_k^2 K_3^2) F_0}, \end{aligned} \quad (12)$$

where

$$B_n = \frac{2}{\mu_n^2}, \quad B_m = \frac{2}{\mu_m^2}, \quad B_k = \frac{2}{\mu_k^2}.$$

3. Main Result

Our goal is to obtain the diffusion's coefficient D as for this purpose apply the sorption-weighing method (see [9]) which is a convenient method of investigating the diffusion processes. It is based on measuring the change in the weight of the sample under the influence of the diffusing liquid. The diffusion process takes place in vessels with the relevant liquid medium at a temperature of $20^0 \pm 1^0 C$.

An Experimental Result

We give some description of our concret test. For our purposes we take out the samples periodically, and after drying up and putting them in the exicator for a half an hour estimate their mass m by an analytical balance. The experiments carry out by the moment of the complete saturation with the aim of receiving precised data characterising the diffusion process. It allow us to get a more exact mathematical description of the running processes in the exploring samples. The samples are membrane stamped and are in the form of strips measuring $a = 15$ [mm], $b = 3$ [mm], $l = 100$ [mm] adapted to the grasps of a stand for mechanical tests.

On Figure 1 Diffusion curves of liquid industrial mediums in polyisoprene vulcanizer: -1. Water, -2. Machine oil, -3. Naphtha, -4. Benzine, 5. 20 % solution of sulfuric acid.

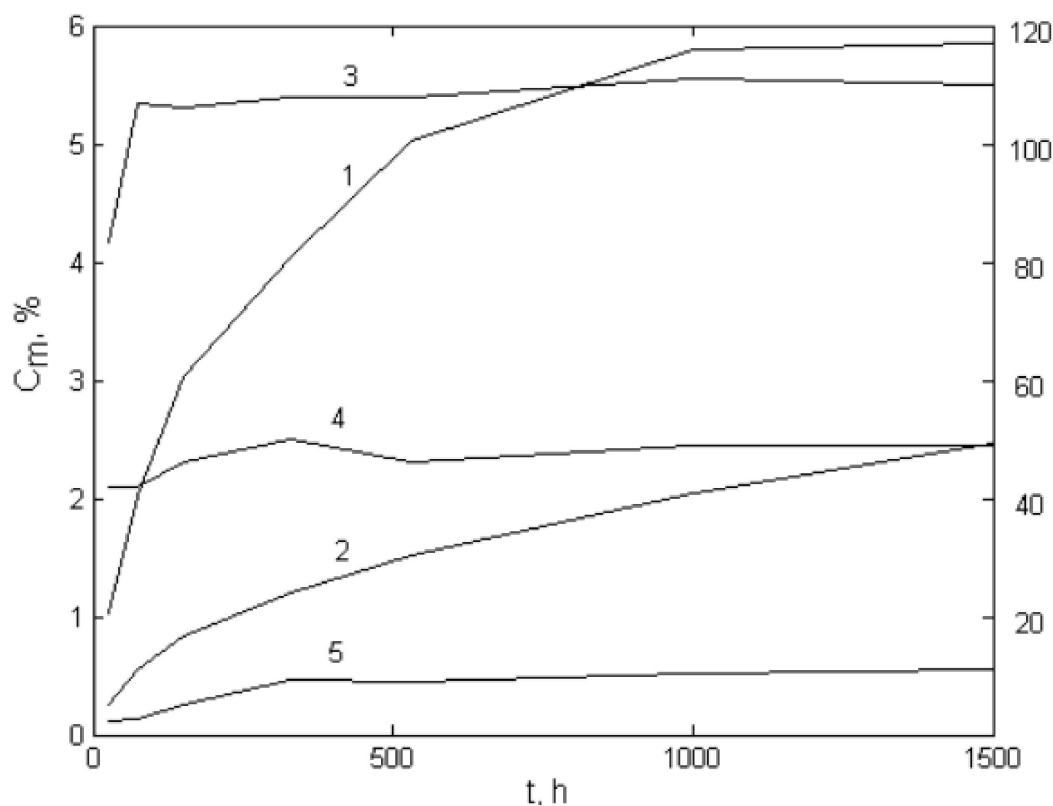


Figure 1

Diffusion curves of liquid industrial mediums in butadiene-nitrile vulcanizer: –6. Water, –7 Machine oil, –8. Naphtha, –9. Benzine, –10. 20 % solution of sulfuric acid.

On Figures 1 and 2 the data from the experiments are given in a form of a graphic correlation between the relative change of sample weight in percents $c_m = \frac{\Delta m}{m_0} \%$ and the time t , where $\Delta m = m - m_0$ is the absolute increase of the weight, m_0 is the initial weight of the dry sample. Each point of the graph corresponds to the math average result from the testing of three samples. Actually these curves are a statistical average result obtained by the program "MAT-CAD Professional 2001". These results correspond to the statistical average provided that certain scattering of experimental data exist.

On Figure 1 and Figure 2 the curves 1 and 6 depict the penetration of water correspondingly in polyisoprene and in butadiene-nitrile vulcanizer. As it is shown

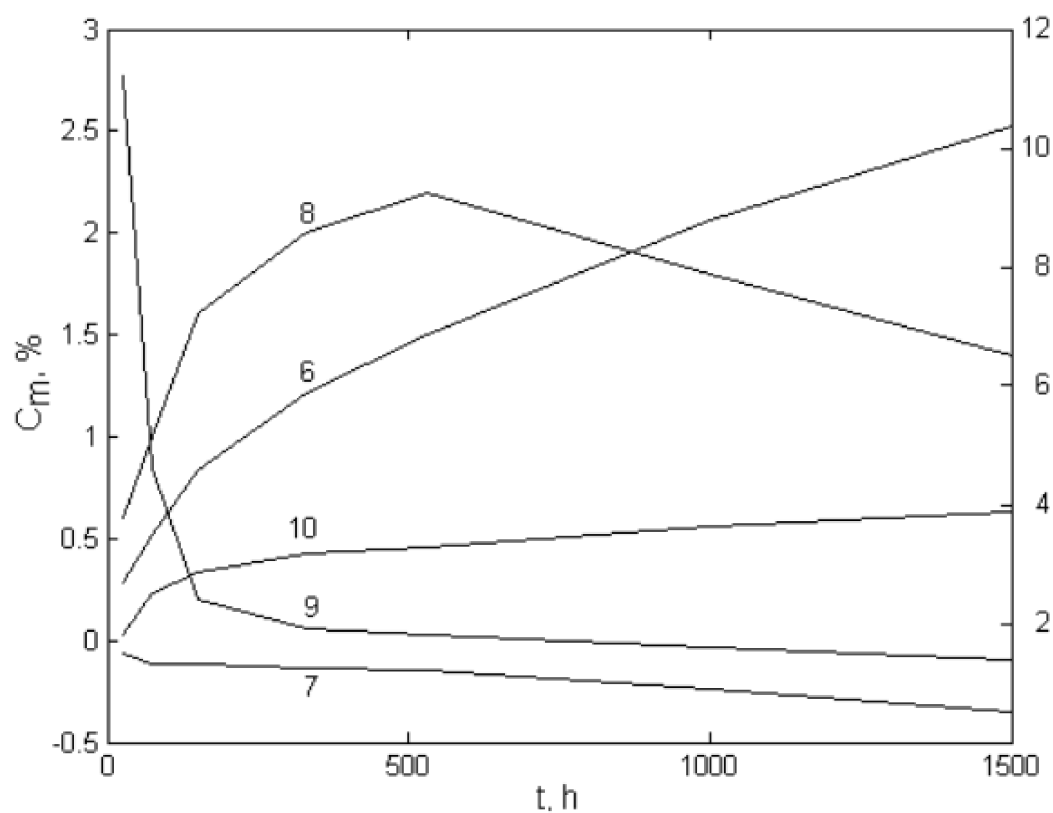


Figure 2

on the graphs the process is too quick. A complete saturation of the samples is achieved at a temperature of 20°C after approximately 1500 hours. Parallel with the mass measurements the samples are watched for changes in their dimensions. It was watched that the maximal increase in the sizes does not exceed 0.2 %. This provide grounds to draw the conclusion that the process of water penetration into the vulkanizer is not accompanied by a significant samples' swelling hence no changes in the initial material's structure.

Curves 2, 5, 7 and 10 depicts the penetration of the machine oil and the 20 % solution of sulfuric acid in the corresponding vulkanizers. The curves are smooth, aiming at an asymptote corresponding to the limit saturation of the samples. An insignificantly small swelling is observed as with the water therefore it may be assumed that the penetration of the molecules of oil and acid is realized mainly by the means of the activated diffusion.

A similar conclusion could not be drawn for the naphtha and the benzene, that is clearly seen from the graphs depicting the modification of their average concentra-

tion, i. e., the curves 3, 4 and 8, 9, respectively. After 1200 hours appears a decrease, but not an increase of the samples' weight. This provides grounds to suppose that parallel with the processes of diffusion it runs a process of material's dissolution and export of gradients.

To determine the qualitative connection between the liquid concentration in the sample and the change of its mechanical characteristics it is necessary to determine the coefficient of diffusion D .

In our case according to Figure 1, with tape shaped samples the diffusion is one-dimensional, bilateral and the penetration is realized through the direction of y , i. e. $\lambda = \frac{b}{2}$, and the equation (7) takes the form

$$\frac{\partial C(y, t)}{\partial t} = D \frac{\partial^2 C(y, t)}{\partial y^2} \quad (13)$$

under the zero initial condition

$$C(y, 0) = 0,$$

and boundary condition

$$C(\pm \frac{b}{2}, t) = C_\infty.$$

Then the above stated initial and boundary value problem has a solution

$$\begin{aligned} c_m &= \frac{C_m}{C_\infty} = \\ &= 1 - \sum_{n=1}^{\infty} \frac{8}{(2n-1)^2} e^{-\left(\frac{(2n-1)^2}{4}\right) \pi^2 F_0}, \end{aligned} \quad (14)$$

where $F_0 = \frac{D t}{(b/2)^2}$.

In the case of great values of F_0 the solution (14) can be restricted to a single term of the infinite series

$$\begin{aligned} c_m &= \frac{C_m}{C_\infty} = \\ &= 1 - \frac{8}{\pi^2} e^{-\left(\frac{1}{4}\right) \pi^2 F_0}. \end{aligned} \quad (15)$$

This equation serves to obtain the following formula for the diffusion coefficient

$$D = -\frac{b^2}{\pi^2 t} \left[\ln \frac{\pi^2}{8} + \ln \left(1 - \frac{C_m}{C_\infty} \right) \right]. \quad (16)$$

Having in mind the above stated facts and also the method shown in [10] we conclude that in the case of small values of $F_0 < 0.1$ the diffusion coefficient D could be obtained with a sufficient precision by

$$D = \frac{\pi b^2 C_m^2}{16 t C_\infty^2}. \quad (17)$$

Conclusion

After changing of variables (coordinates) in our problem and substituting the experimental data it turns out that we have a function $\ln\left(1 - \frac{C_m}{C_\infty}\right)$ depending on the absolute time of exposition t . It was ascertained that for two of the examined mediums - naphtha and benzene the correlations are not linear, which fact demonstrates that the reaction with these is a chemical therefore the Fick's law is not applicable.

For determining the diffusion coefficient D of the rest of the mediums in an initial stage of the diffusion was used the correlation (17), and in the remaining part expression (16).

Our calculations show that for different average concentrations, the diffusion coefficient may vary within close limits and with a sufficient for the engineering practice accuracy it may be accepted as a constant. Thus we get the following practical results of interest to the engineering methods:

- 1) $D = 0.0582$ for polyisoprene vulcanizer and water
- 2) $D_2 = 0.1159$ for polyisoprene vulcanizer and machine oil
- 3) $D_3 = 0.0929$ for polyisoprene vulcanizer and 20% sulfuric acid
- 4) $D_4 = 0.0545$ for butadiene-nitrile vulcanizer and water
- 5) $D_5 = 0.0361$ for butadiene-nitrile vulcanizer and machine oil
- 6) $D_6 = 0.0941$ for butadiene-nitrile vulcanizer and 20% sulfuric acid

Acknowledgments

The present study was supported by the grant No /NIS/ 2011 of the University of Chemical Technology and Metallurgy (UCTM) - Sofia, Bulgaria.

References

- [1] A. Alexandrov, Tz. Tzolov, Thermal conductivity tensor of fiber reinforced pipe viscous element, *Journal of the University of Chemical Technology and Metallurgy*, **XXXVII**, No. 1 (2002), 73-76.
- [2] A. Alexandrov, D. Donchev, Tz. Tzolov, Thermal effects in rubber-metal products, *Journal of Mechanics of Machines*, BulKToMM (2003).
- [3] A. Alexandrov, D. Dontchev, Tz. Tzolov, Heat formation under cyclic viscoelastic deformation of rubber-metal technical products, In: *International Conference on Mechanics and Technology of Composite Materials*.

- [4] Ts. Ivancheva, A. Alexandrov, Method and programme for quantity analyses of diffusion mass exchange process of liquid media in polimer tubes, *BCD*, **413** (1983).
- [5] A. Alexandrov, Ts. Ivancheva, Two-dimensional stressed state of pure torsion on kinetics absorption of liquid media in tubes of polymeric materials. Note 2, *Report TNTM*, UCTM, Book 1, Sofia (1982).
- [6] K. Hadjov, A. Alexandrov, *Damage Model to Predict the Life-Time in 3D*, Limhp, Universite Paris Nord, Franse (2003).
- [7] A. Alexandrov, K. Hadjov, D. Dontchev, Tz. Tzolov, G. Halil, Study of vulcanizers in terms of mechanical load and aggressive media, *Contract No. 10530*, NIS-UCTM (2004).
- [8] J. Crank, G. Park, *Diffusion in Polymere*, Acad. Press, London (1968).
- [9] B. Dollezhal, *Corrosion of Plastic Materials and Rubber*, Chemistry, Moscow (1964).
- [10] A. Lyakov, *Conductivity Theory*, Vaishia Shkola, Moskow (1977).
- [11] *Wikipedia, the Free Encyclopedia*, Diffusion equation, http://en.wikipedia.org/wiki/Diffusion_equation