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## FT-IR internal reflection study of migration and surface segregation of carboxylic acids in butadiene-styrene rubber

**Summary** — The subject of our study was kinetics of migration and surface segregation of linear aliphatic carboxylic acids (11—18 C atoms) in butadiene-styrene rubber (SBR). The iteration procedure has been proposed for determination of thickness of acid's surface layer formed as a result of segregation as well as for determination of acid diffusion coefficient. With the aim of determining these kinetic curves of migration FT-IR IRS spectra analyses have been used. Differences in final thickness of surface layer of particular acids (after 24 h) have been explained on the basis of differences in their solubility in SBR at temperature of spectroscopic measurement equal to 23 °C.

**Key words:** butadiene-styrene rubber, linear aliphatic carboxylic acids, solubility, diffusion kinetics, surface layers, FT-IR spectroscopy.

Migration of low molecular weight additives towards the rubber surface has been studied extensively for many years. Most of papers consider ageing protection by blooms of waxes [1—3] and antioxidants [4—9]. Migration of components of crosslinking system was also studied, especially in blends of rubbers, their uneven distribution between polymer phases has been taken into consideration [10—12]. Migration of low molecular weight additives can also influence the range of application of rubber products [13, 14].

Most of low molecular weight additives migrating towards the rubber surface are solid substances, incorporated into rubber matrix in an amounts exceeding their limits of solubility. Migration used to be quantified by measurement of bloom thickness after definite time [2, 3] or by determination of changes of the additive concentration in the bulk of vulcanizate [6—9]. Such methods do not allow to study a kinetics of blooming and, as a consequence, the mechanism of solid substances' migration in rubber matrix has not been recognised well enough [15, 16].

In this paper migration and surface segregation of linear aliphatic carboxylic acids (used as activator) in butadiene-styrene rubber (SBR) vulcanizates was studied. Blooming kinetics was determined with the use of FT-IR internal reflection spectroscopy. Calculation procedure, based on calculation of Fickian diffusion fronts

with the use of final element method, is presented and the results obtained discussed.

### EXPERIMENTAL

#### Materials

The following materials were used in this work:  
— butadiene-styrene rubber (SBR, Ker 1500, Z. Chem. Oświęcim, Poland),  
— carboxylic acids RCOOH (where R is C<sub>10</sub>H<sub>21</sub>—C<sub>17</sub>H<sub>35</sub>) of purities at least 95 wt. % (denotations — C<sub>n</sub>, where *n* is the number of carbon atoms),  
— dicumyl peroxide (DCP) 98 wt. % of purity (Merck-Schuhardt, Germany).

#### Sample preparation

Carboxylic acids were admixed to SBR in amount of 4 phr. Prior to processing the rubber was extracted with boiling acetone (48 hrs in a Soxhlet apparatus) to remove antioxidants and other low molecular weight residues, that can affect the migration of the acids studied [9]. Mixes (SC<sub>n</sub>) were prepared using the laboratory two-rolls mill (David Bridge Co., UK). Each rubber mix was cured with 1 phr of DCP. Samples were vulcanized in a form of cube (with side 1 cm) in a steel mold at 160 °C for 20 min, as determined rheometrically (ISO 3417). Table 1 contains thermodynamical characteristics of the acids studied. Prior to admixing to the rubber, thermal stability of the acids was examined. The temperature of 5

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wt. % loss (determined using TGA at heating rate of 10 °C/min) exceeded 160 °C — from 163 °C for undecanoic acid up to 205 °C for stearic acid. It means that there is practically neither degradation nor evaporation of the acids from the rubber during vulcanization.

**Table 1.** Thermodynamical characteristics of the carboxylic acids studied<sup>a)</sup>

Acid, C <sub>n</sub>	T <sub>m</sub> , °C	ΔH, J/g	Δδ, J <sup>0.5</sup> /cm <sup>1.5</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> COOH, C <sub>11</sub>	28.6 <sup>a)</sup>	139.7 <sup>a)</sup>	0.20
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH, C <sub>12</sub>	44.0 <sup>b)</sup>	181.5 <sup>b)</sup>	0.35
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> COOH, C <sub>13</sub>	42.0 <sup>a)</sup>	157.6 <sup>a)</sup>	0.48
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH, C <sub>14</sub>	54.3 <sup>b)</sup>	197.8 <sup>b)</sup>	0.58
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> COOH, C <sub>15</sub>	52.7 <sup>a)</sup>	171.6 <sup>a)</sup>	0.67
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH, C <sub>16</sub>	62.7 <sup>b)</sup>	209.8 <sup>b)</sup>	0.77
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> COOH, C <sub>17</sub>	61.3 <sup>a)</sup>	190.2 <sup>a)</sup>	0.85
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH, C <sub>18</sub>	69.5 <sup>b)</sup>	215.5 <sup>b)</sup>	0.91

<sup>a)</sup> T<sub>m</sub> — melting temperature, ΔH — enthalpy of melting, Δδ — difference between solubility parameter of SBR and the acid, calculated according to the method by Van Krevelen [17].

<sup>a)</sup> reference [18], <sup>b)</sup> reference [19].

## FT-IR spectroscopy

Experiments were carried out at ambient temperature (T = 23 ± 1 °C) using FT-IR instrument BIO-RAD FTS 175C (Germany) equipped with IRS microscopic accessory (Split-Pea, Harrick Scientific, USA). The rubber specimen prior to experiment was accommodated in FT-IR spectrometer chamber for 2 hrs. Procedure of spectra collecting started on fresh cross-sectioned surface of the sample. Spectra were collected during 15 hrs every 1 min with resolution of 4 cm<sup>-1</sup>.

## KINETICS OF BLOOMING DESCRIPTION

Kinetics of the surface migration of carboxylic acids in rubber was determined from FT-IR spectra. For evaluation of changes in bloom thickness and description of a rate of diffusion the following procedure was applied.

Penetration depth (d<sub>p</sub>) of infrared beam can be calculated according to Harrick's formula [20]:

$$d_p = \frac{\lambda}{2 \cdot \Pi \cdot n_1 \cdot \left[ \sin^2(\theta) - \left( \frac{n_1}{n_2} \right)^2 \right]^{\frac{1}{2}}} \quad (1)$$

where: λ — wavelength; n<sub>1</sub>, n<sub>2</sub> — refraction indices of the material studied and silicone crystal, respectively (n<sub>2</sub> = 3.9); θ = 60° — incident angle of the infrared beam.

Refraction indices of carboxylic acids studied were measured using Abbe refractometer, at ambient temperature. Because of various crystalline forms structures and their content in the compounds the obtained values

of coefficients of refraction varied in the range 1.46—1.52. Values of refraction indices of SBR and all the acids studied were then taken as n<sub>1</sub> = 1.5 [21] for all further calculations. Penetration depth of infrared radiation, calculated according to eq. (1) (for 1700 cm<sup>-1</sup>) d<sub>p</sub> = 0.8 μm represents an average value. Considering that wave intensity decreases exponentially along distance (x) into material, absorption of radiation at time t [A(t)] associated with concentration of carboxylic acid (C) can be described by the following equation [22]:

$$A(t) = \int_0^{\infty} C(t, x) \cdot a \cdot e^{-\frac{2 \cdot x}{d_p}} \cdot dx \quad (2)$$

where: C(t, x) — molar concentration of carboxylic acid at the depth x from the surface of a sample at time t, a — coefficient of absorption.

In our calculations we had to make some simplifications to find bloom thickness from FT-IR spectra, i.e. that absorption coefficient (a) is concentration independent. For bloom present on the rubber surface eq. (2) can then be redrawn into the following form:

$$A(t) = \int_0^{x_B} C_B \cdot a \cdot e^{-\frac{2 \cdot x}{d_p}} \cdot dx + \int_{x_B}^{\infty} C(t) \cdot a \cdot e^{-\frac{2 \cdot x}{d_p}} \cdot dx \quad (3)$$

where: C(t) — molar concentration of acid in the surface layer of rubber as a function of time, C<sub>B</sub> — molar concentration of acid in the bloom (time independent), x<sub>B</sub> — bloom thickness.

Integration of eq. (3) gives:

$$A(t) = \frac{C_B \cdot a \cdot d_p}{2} \left( 1 - e^{-\frac{2 \cdot x_B}{d_p}} \right) + \frac{C(t) \cdot a \cdot d_p}{2} \cdot e^{-\frac{2 \cdot x_B}{d_p}} \quad (4)$$

From the eq. (4), the bloom thickness can be derived:

$$x_B = x_B(t) = -\frac{d_p}{2} \ln \left( \frac{C_B - \frac{2 \cdot A(t)}{a \cdot d_p}}{C_B - C(t)} \right) \quad (5)$$

To calculate x<sub>B</sub>(t) from FT-IR kinetics we needed to know the value of coefficient of absorption (a) and a function describing concentration of the acid in the surface layer of rubber [C(t)]. Coefficient of absorption was calculated using the following formula:

$$a = \frac{A_B}{C_B \cdot d_p} \quad (6)$$

where: A<sub>B</sub> — absorption at 1700 cm<sup>-1</sup> from reflection spectra representing pure acid.

C(t) still reminds unknown because it is impossible to determine it directly.

A rate of diffusion of low molecular weight compounds in rubber matrix can be described by the second Fick's law [23]:

$$\frac{dC(t, x)}{dt} = D \cdot \frac{d^2 C(t, x)}{d^2 x} \quad (7)$$

where:  $D$  — diffusion coefficient.

Eq. (7) was solved applying the method of final element analysis with  $x$  step of  $1 \mu\text{m}$ ,  $t$  step of 1 s, and starting value of  $D = 200 \cdot 10^{-8} \text{ cm}^2/\text{s}$  for 1 mm thick sample and time of experiment in which the bloom thickness does not exceed  $2d_p$ . Preselection of time range was applied to avoid an influence of deviations in absorption on the result. The dependence of bloom thickness ( $x_B$ ) vs. absorption (Fig. 1) illustrates that an accept-

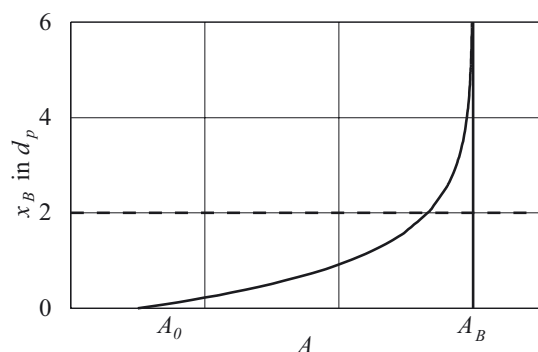


Fig. 1. Dependence of bloom thickness ( $x_B$ ) on absorption ( $A$ ) of infrared radiation in internal reflection FT-IR experiment

able sensitivity of the method is below the value of bloom thickness of  $x_B = 2d_p$ . It was assumed however, that chemical potential of an acid in the bloom is equal to its chemical potential in rubber when below the solubility limit. On the above basis, for  $C(t, 0)$  the solubility limit was put for calculation of diffusion process. Solubility limits of the acids studied were determined from FT-IR spectra of fresh cross-sections of rubber samples after 3 months of their conditioning at  $23 \text{ }^\circ\text{C}$ . To obtain numerical representation of  $C(t, x)$  function, the  $C(t, 1 \mu\text{m})$  was then taken as  $C(t)$  in eq. (5) and the experimental bloom thickness ( $x_{Bexp}$ ) was obtained using FT-IR data. Calculated bloom thickness ( $x_{Bcalc}$ ) was determined from  $C(t, x)$  numerical data and compared with the results of FT-IR measurements. To precise  $D$  value and  $C(t)$  function, the dependence of experimental bloom thickness vs. calculated one was approximated with linear fit:

$$x_{Bexp} = \alpha \cdot x_{Bcalc} \quad (8)$$

New value of  $D$  was then precised as  $D_n$ :

$$D_n = \alpha \cdot D \quad (9)$$

The iteration procedure was performed until coefficient  $\alpha$  reached the value of  $1 \pm 0.001$ , in order to obtain  $D$  value and time characteristics of  $x_{Bexp}$  and  $x_{Bcalc}$ .

To estimate an accuracy of the calculated diffusion coefficients the standard deviation  $SD_\alpha$  of  $D$  was calculated according to the following formula:

$$SD_\alpha = S\alpha \cdot D \quad (10)$$

where:  $S\alpha$  — standard deviation of  $\alpha$  in eq. (8).

To proof whether solubility of acids in SBR was determined with sufficient accuracy the values of diffusion coefficients and their standard deviations ( $SD_{C_S}$ ) were calculated assuming as the solubility limit ( $C_S$ ) the value of  $C_S \pm SC_S$  ( $SC_S$  — standard deviation of  $C_S$ ).

## RESULTS AND DISCUSSION

An appearance of  $1700 \text{ cm}^{-1}$  band of carboxylic acids' bloom has been observed for FT-IR spectra. It is shown in Fig. 2 for octadecanoic acid as an example. A peak

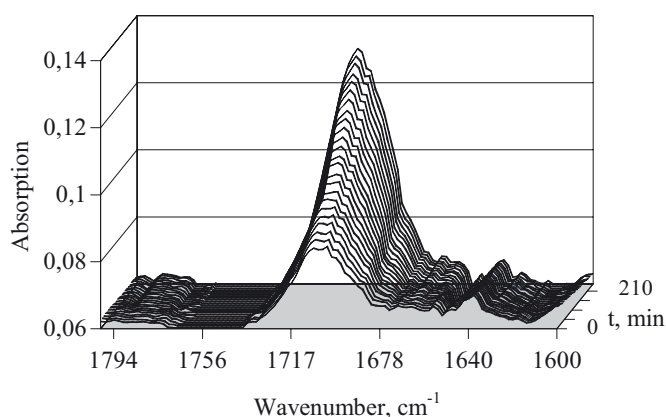


Fig. 2. An increase of  $1700 \text{ cm}^{-1}$  band for octadecanoic acid bloom obtained with FT-IR IRS method; spectra are presented every 10 min

area of the absorption band at  $1700 \text{ cm}^{-1}$  was calculated. Band at  $1700 \text{ cm}^{-1}$  has been chosen because it comes from  $\text{C}=\text{O}$  bond stretching and this band is not present in spectra of SBR (Fig. 3). Blooming kinetics obtained from FT-IR measurements are shown in Fig. 4.

FT-IR kinetic data of the surface segregation of acids are given in Fig. 5 and Table 2. Accuracy of diffusion coefficient determination ( $SD_\alpha$ ) using the method applied is quite high if considered only from the point of view of FT-IR kinetic measurements. However the results of  $D$  values calculation could be strongly affected by accuracy of the solubility limit ( $SC_S$ ) determination. It was expected that solubility limit should be inversely proportional to difference between solubility parameters of polymer and studied substance ( $\Delta\delta$ , see Table 1). Despite the observed apparent decrease in solubility with increase in  $\Delta\delta$ , the reason of very high difference between solubility of tridecanoic and tetradecanoic acid is not clear. However, sharp increase in the solubility limit of low molecular weight compounds near their melting temperature is well known [1]. In our case temperature of experiment ( $T_{exp} = 23 \text{ }^\circ\text{C}$ ) was kept constant, so an excess of the melting temperature values of the acids studied ( $T_m$ ) over  $T_{exp}$  varied from acid to acid. Regularity of changes related to hydrocarbon chain growth has been additionally perturbed by known alternation effect.

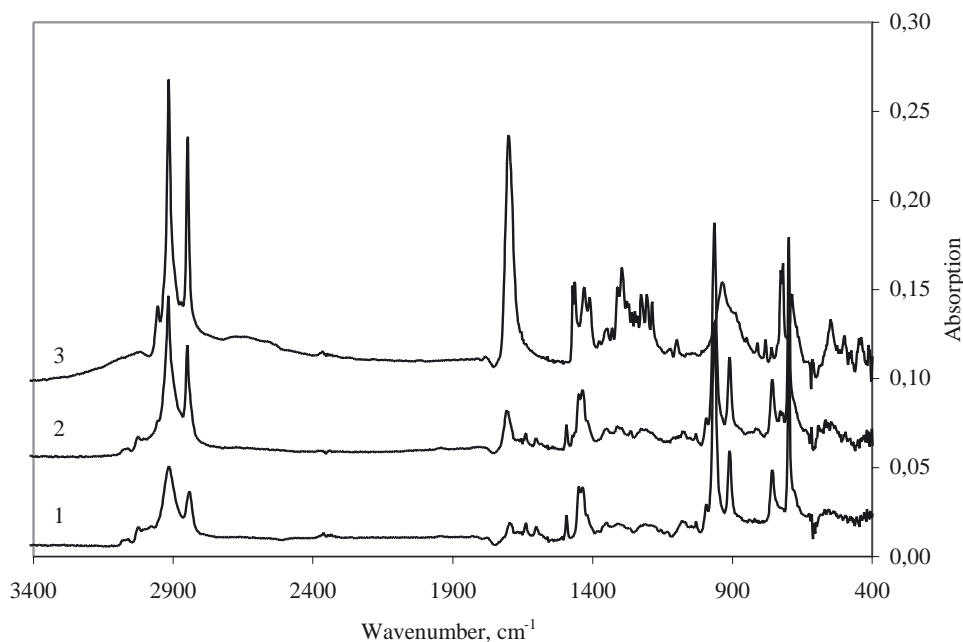


Fig. 3. FT-IR spectra of SBR reference sample (1), fresh cross-section of SBR containing octadecanoic acid (2) and octadecanoic acid (3)

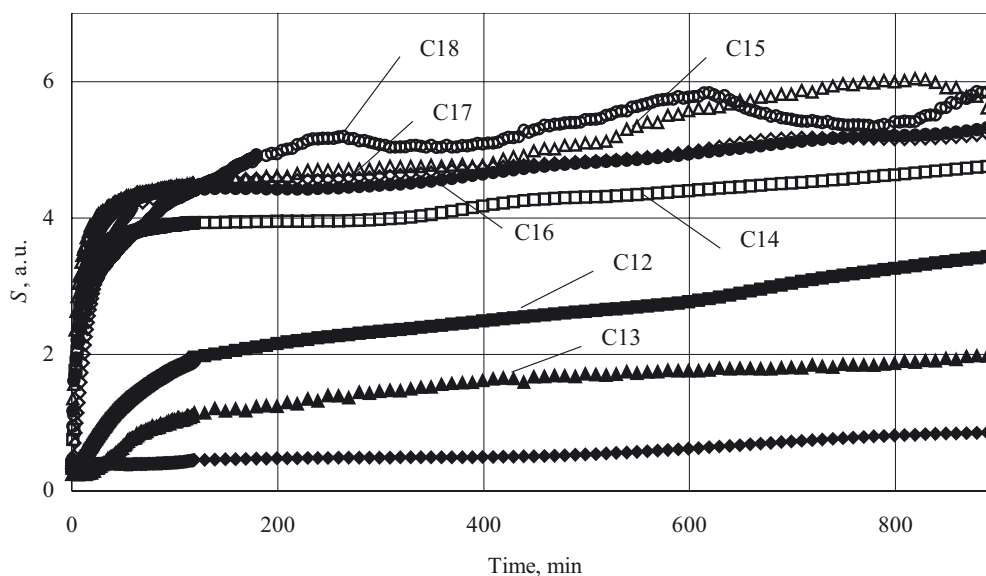


Fig. 4. Kinetics of blooming observed by changes of peak area ( $S$ ) of the absorption band at  $1700\text{ cm}^{-1}$

**Table 2.** Parameters of diffusion of the carboxylic acids towards SBR surface obtained from FT-IR studies<sup>\*)</sup>

Mix symbol	$C_s$ , phr	$C_s$ mmol/dm <sup>3</sup>	$SC_s$ mmol/dm <sup>3</sup>	$C_0$ mmol/dm <sup>3</sup>	$D \cdot 10^8$ cm <sup>2</sup> /s	$SD_{C_s} \cdot 10^8$ cm <sup>2</sup> /s	$SD_\alpha \cdot 10^8$ cm <sup>2</sup> /s	$R_\alpha$	$x_B$ 24 h, $\mu\text{m}$
SC11	3.89	199	4	205	13.55	7.93	0.34	0.775	0.13
SC12	2.73	130	8	190	8.02	2.39	0.08	0.990	1.04
SC13	2.47	110	7	178	1.98	0.41	0.01	0.985	0.67
SC14	0.72	30	9	167	40.28	5.22	0.12	0.996	6.57
SC15	0.76	30	8	157	41.15	5.11	0.21	0.987	6.56
SC16	0.59	22	7	149	29.22	3.16	0.09	0.995	5.81
SC17	0.60	21	9	141	13.38	1.98	0.13	0.981	3.92
SC18	0.51	17	8	134	4.34	0.58	0.02	0.989	2.28

<sup>\*)</sup>  $C_s$  — solubility limit of carboxylic acid in SBR,  $SC_s$  — standard deviation of the solubility limit,  $C_0$  — initial concentration of an acid in SBR sample,  $D$  — diffusion coefficient,  $SD_{C_s}$  — standard deviation of diffusion coefficient by the accuracy of  $C_s$  determination,  $SD_\alpha$  — standard deviation of diffusion coefficient assuming FT-IR data correlation with the second Fick's law,  $R_\alpha$  — coefficient of correlation between FT-IR data and the second Fick's law,  $x_B$  24 h — bloom thickness after 24 hrs.

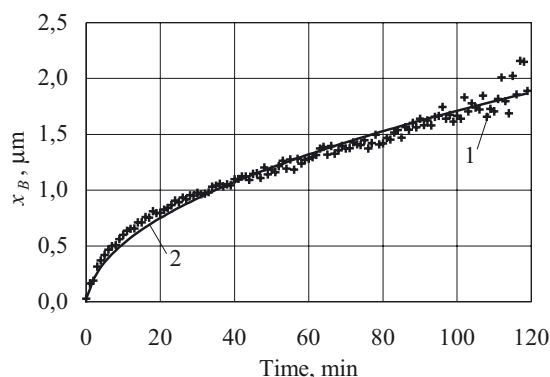


Fig. 5. Comparison between experimental and calculated kinetics of blooming: 1 — experimental values ( $x_{Bexp}$ ), 2 — calculated values ( $x_{Bcalc}$ )

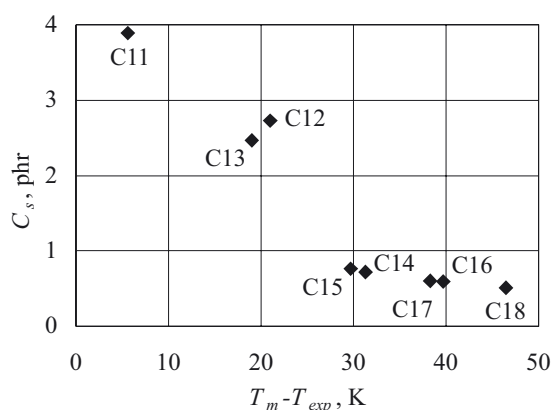


Fig. 6. Solubility limit ( $C_s$ ) vs. excess of  $T_m$  over  $T_{exp}$  ( $23^\circ\text{C}$ ) for the acids studied

In Fig. 6 the dependence between the solubility limit and the above mentioned difference in temperature values is presented. It seems to be clear, that determination of the solubility limit for substances of  $T_m$  near  $T_{exp}$  can be strongly affected by temperature instability of  $T_{exp}$  during long-lasting experiment.

Diffusion coefficient depends on mobility of the carboxylic acid molecules penetrating the rubber matrix. There are many factors influencing the mobility, namely: size, shape and free rotation in skeleton of the molecules, intermolecular interactions between them and with the matrix, as well as ability to crystallization and finally a degree of matrix's crosslinking [2, 15]. A decrease in diffusion coefficient with an increase in chain length was found for the first three acids [from undecanoic (C11) to tridecanoic (C13) one], but after that a sharp increase in the diffusion coefficient was observed (Table 2). This phenomenon can be explained by some change of the diffusion mechanism with the chain length. For the first three acids the excess of acid over the solubility limit is so low that allows only gradient of concentration to work as the driving force for diffusion. For the acids of longer molecules [from tetradecanoic (C14) to octadecanoic (C18) one] the extend of the concentration over the solubility limit was very high and could produce

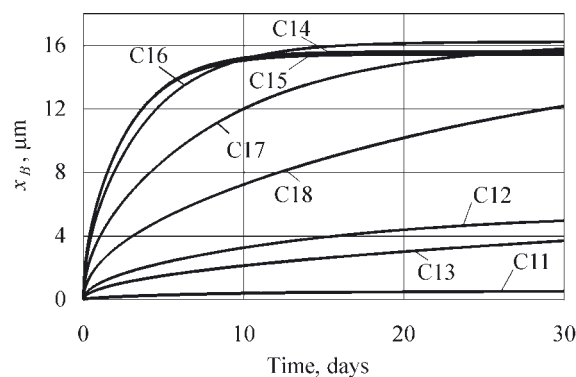


Fig. 7. Thickness of blooms of the carboxylic acids ( $x_B$ ), extrapolated to 30 days

a stress in the elastomer network [23], particularly because the excess of acid can not crystallize in SBR matrix [24]. The stress in network can be an additional driving force for migration, being responsible for the fact, that diffusion coefficient was found to be strongly dependent on concentration. The complete comparison of blooming kinetics of the acids studied is given in Fig. 7.

The stress of network can be taken into consideration by adding its representation to diffusion equation as described by Edwards [23]. This method however requires series of mixes of various concentrations of migrating substance, what is tedious procedure. Instead, Zhang proposed very simple equation, describing dependence between diffusion coefficient and concentration of a penetrant [25]:

$$D_S = D_x \left( \frac{C_S}{C_x} \right)^3 \quad (11)$$

where:  $D_S$ ,  $D_x$  — diffusion coefficients at concentration equal to solubility limit ( $C_S$ ) and at higher concentration ( $C_x$ ) respectively.

We have applied the Zhang's method to calculate  $D_S$  values. Dependence of  $D_S$  on a number of carbon atoms in acid molecule is presented in Fig. 8. An apparent de-

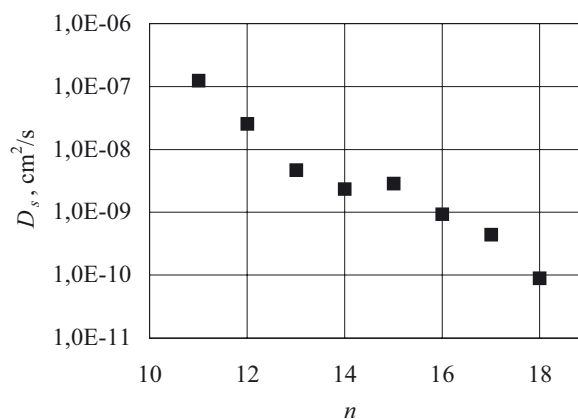


Fig. 8. Dependence of diffusion coefficient at concentration equal to solubility limit ( $D_S$ ) on number of carbon atoms in the molecule ( $n$ )



crease in diffusion coefficient with an increase in molecular size of the acids studied can be observed.

#### CONCLUSIONS

FT-IR internal reflection spectroscopy can be applied for quantitative analysis of surface migration of low molecular weight additives in elastomers. Experimental procedure is based on final element analysis applied for diffusion process in a form of iteration of FT-IR absorption data. The described procedure allows to calculate the values of diffusion coefficient and a rate of blooming. Accuracy of the method proposed is reasonably good but the results are strongly affected by accuracy of the solubility limit determination.

Although diffusion mechanisms are far from being understood completely, the presented procedure can be very useful to predict and compare behavior of various processing additives in elastomers.

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