Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies. 2023;18(6):534–548

SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

ISSN 2686-7575 (Online)
https://doi.org/10.32362/2410-6593-2023-18-3-534-548
UDC 541.64:536.4

RESEARCH ARTICLE

Swelling of rubbers of different chemical natures in supercritical carbon dioxide

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Abstract

Objectives. *To investigate the swelling of the main types of rubbers used in the rubber industry in carbon dioxide in a supercritical state (SC-CO_2), in order to assess the possibility of obtaining elastomeric materials with porous structures using fluid technology, based on them.*
Methods. *The process of swelling of rubbers in SC-CO_2 and subsequent foaming was carried out according to a specially developed technique using the original installation. This is a high-pressure apparatus with transparent windows, allowing for the use of an optical technique to directly measure the geometric dimensions of samples during swelling and foaming using a digital video camera. The study of the porous structure of foamed rubbers was carried out using scanning electron microscopy.*
Results. *The study established experimental curves of the swelling kinetics in SC-CO_2 of isoprene, butadiene, styrene butadiene, ethylene propylene, chloroprene, ethylene acrylate, siloxane, and organofluorine rubbers. The influence of temperature and pressure on the rate and equilibrium degree of swelling was studied. The diffusion coefficients of SC-CO_2 in rubbers of various chemical natures were also determined.*

Conclusions. *It was shown that the equilibrium swelling degree of rubbers in SC-CO$_2$ depends on the chemical nature of rubbers. It does not correlate with the value of their solubility parameters, changes directly proportional to the diffusion coefficient and increases with increasing temperature and pressure. It was found that irrespective of the degree of swelling in SC-CO$_2$, all the rubbers studied are intensively foamed at a sharp pressure drop. The size of the pores formed is tens of microns: significantly smaller than the size of pores formed when chemical pore formers are used.*

Keywords: *supercritical fluid technology, rubber, porosity, carbon dioxide, swelling*

For citation: Mikhailova S.T., Reznichenko S.V., Krasnikov E.A., Tsygankov P.Yu., Menshutina N.V., Simonov-Emel'yanov I.D. Swelling of rubbers of different chemical natures in supercritical carbon dioxide. *Tonk. Khim. Tekhnol.* = *Fine Chem. Technol*. 2023;18(6):534–548. https://doi.org/10.32362/2410-6593-2023-18-6-534-548

НАУЧНАЯ СТАТЬЯ

Исследование набухания каучуков различной химической природы в сверхкритическом диоксиде углерода

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Аннотация

Цели. *Исследование набухания основных типов каучуков, применяющихся в резиновой промышленности, в диоксиде углерода, находящемся в сверхкритическом состоянии (СК-CO$_2$), для оценки возможности получения на их основе эластомерных материалов с пористыми структурами с использованием флюидной технологии.*
Методы. *Процесс набухания каучуков в СК-CO$_2$ и последующее их вспенивание проводили по специально разработанной методике на оригинальной установке, представляющей собой аппарат высокого давления с прозрачными окнами, позволяющими использовать оптическую методику непосредственного измерения геометрических размеров образцов в процессе набухания и вспенивания с помощью цифровой видеокамеры. Исследование пористой структуры вспененных каучуков проводили с помощью сканирующей электронной микроскопии.*

Результаты. *Получены экспериментальные кривые кинетики набухания в СК-CO_2 изопренового, бутадиенового, бутадиен-стирольного, этиленпропиленового, хлоропренового, этилен-акрилатного, силоксанового и фторорганического каучуков. Исследовано влияние температуры и давления на скорость и равновесную степень набухания. Определены коэффициенты диффузии СК-CO_2 в каучуках различной химической природы.*

Выводы. *Показано, что степень равновесного набухания каучуков в СК-CO_2 зависит от химической природы каучуков, не коррелирует с величиной их параметров растворимости, изменяется прямо пропорционально коэффициенту диффузии и увеличивается с ростом температуры и давления. Установлено, что независимо от степени набухания в СК-CO_2 все исследованные каучуки интенсивно вспениваются при резком сбросе давления. Размер образующихся пор составляет десятки микрон, что существенно меньше размера пор, образующихся при использовании химических порообразователей.*

Ключевые слова: *сверхкритическая флюидная технология, каучук, пористость, диоксид углерода, набухание*

Для цитирования: Михайлова С.Т., Резниченко С.В., Красников Е.А., Цыганков П.Ю., Меньшутина Н.В., Симонов-Емельянов И.Д. Исследование набухания каучуков различной химической природы в сверхкритическом диоксиде углерода. *Тонкие химические технологии*. 2023;18(6):534–548. https://doi.org/10.32362/2410-6593-2023-18-6-534-548

INTRODUCTION

Porous (foamed) elastomeric materials are widely used in many fields of engineering due to their unique heat-insulating, sound-insulating and deformation properties. The presence of a porous structure in elastomeric materials allows their density to be significantly reduced and the material intensity of products to be reduced.

At the present time, chemical pore formers are mainly used, in order to obtain porous elastomeric materials. The gaseous decomposition products lead to foaming of rubber mixtures, and the subsequent vulcanization stage defines the formed porous structure. Russian industry uses oxydibenzene sulfonylhydrazide and azodicarbonamide as foaming agents: with a decomposition temperature of 160 and 190°C, respectively. The disadvantages of porous materials production technologies using chemical pore formers are the presence of toxic chemical products in the porous structures of elastomeric materials. They are hazardous to humans and the environment, and possess quite large and poorly regulated pore sizes. It has a strong influence on the mechanical properties of elastomeric materials. In addition, the high decomposition temperatures of foaming agents, at which the vulcanization process may start prematurely, and their high chemical activity do not allow the use of these pore-forming agents for obtaining porous rubbers from rubber compounds of a number of formulations.

One of the promising areas for obtaining porous polymeric materials is the use of fluid technology. This has been successfully developed in recent years for the production, modification, and processing of polymers [1].

The method of porous polymeric materials production using fluids consists in the swelling of polymeric material in a substance in a supercritical (SC) state at elevated pressure. The subsequent sharp pressure release can lead to the transition of this substance into a gaseous state and pore formation in the polymeric material [2].

Substances in the SC state have intermediate properties between those of liquids and gases. Thus, unlike gases, they can dissolve many organic and inorganic substances; unlike ordinary liquids, SC liquids can shrink when pressure increases and change their dissolving ability with changes in pressure and temperature [3–6].

Carbon dioxide in the SC state (SC-CO_2) appears to be the most suitable for elastomeric porous materials [7, 8]. The solubility parameter of SC-CO_2 can vary from 2.7 to 15.0 MJ/m^3 with temperature and pressure changes [9], i.e., it is a solvent for polymers of different chemical natures. Carbon dioxide can change to the SC state at a relatively low temperature and low pressure (minimum temperature ~31°C, minimum pressure ~7.38 MPa). In addition, carbon dioxide is a non-toxic, non-flammable and relatively inexpensive substance which exists under normal conditions in gaseous form, facilitating its removal after the completion of the foaming process.

In the literature, only a small number of publications contain systematic studies of pore formation processes in elastomers (mainly in elastomers based on polyorganosiloxanes) using SC-CO_2 [10–15].

The aim of this work is to investigate the swelling processes in the SC-CO_2 medium of the main types of rubbers used in the rubber industry, in order to evaluate the possibility of obtaining elastomeric materials with porous structures on their basis.

EXPERIMENTAL

Types, trademarks, and some characteristics of the studied rubbers are given in Table 1.

The research samples were prepared according to the scheme shown in Fig. 1. The rubbers were homogenized for several minutes using mixing rollers with the 1:1.25 friction ratio. Then they were removed in the form of ~3-mm thick plates.

Table 1. General characteristics of the investigated rubbers

No.	Rubber type, brand, manufacturer, and country of origin	ρ, g/cm³	δ, MJ/m³	Monomer formula	T_G, °C	Mooney viscosity ML (1+4) 100°C
1	Natural, NR STR, *Natural Art & Technology Co.*, Thailand	0.92	16.8	$(C_5H_8)_n$	−72	80–95
2	Polyisoprene, SKI-3, *SIBUR*, Russia	0.91	16.9	$(C_5H_8)_n$	−70	75–85
3	Butadiene nitrile, BNKS-40 AN, *SIBUR*, Russia	0.96	18.8	$[–(CH_2–CH{=}CH–H_2)_n–(–CH(CN)–]_m$	−20	100–120
4	Styrene-butadiene, DSSK-1810F, *Voronezhsintezkauchuk*, Russia	0.97	17.4	$[–(CH_2–CH{=}CH–CH_2)_m–CH(C_6H_5)––CH_2)]_n$	−90	77–82
5	Ethylene-propylene, SKEPT-50, *Ufaorgsintez*, Russia	0.85	15.5	$[–CH_2CH_2–]_n–[–CH(CH_3)CH_2–]_m$	−58	55–60
6	Siloxane, SKTV-1, *S.V. Lebedev Institute of Synthetic Rubber*, Russia	1.23	7.0–9.0	$(R–O)_n–(R'–SiO–)_m$	−120	–
7	Fluorocarbon rubber, SKF-26, *HaloPolymer*, Russia	1.83	19.0[1]	$[–CF_2–CH_2–CF_2–CF–(CF_3)]_n$	−15	80–105

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Table 1. Continued

No.	Rubber type, brand, manufacturer, and country of origin	ρ, g/cm^3	δ, MJ/m^3	Monomer formula	T_G, °C	Mooney viscosity ML (1+4) 100 °C
8	Chloroprene rubber, Baypren® 611, *Arlanxeo Holding B.V.*, The Netherlands	1.23	19.2	$(–H_2C–CCl=CH–CH_2–)_n$	−40	35–48
9	Ethylene acrylate rubber, Vamac® Ultra LT, *DuPont de Nemours*, USA	0.98	–	$[–CH_2CH_2–]_n–[–CH_2–CH(COOCH_3)_m–$ $–[–CH_2CHR]_k$	−30	11

Note: ρ is the rubber density, g/cm^3; δ is the rubber solubility parameter, MJ/m^3 [16–18]; T_G is the glass transition temperature, °C.

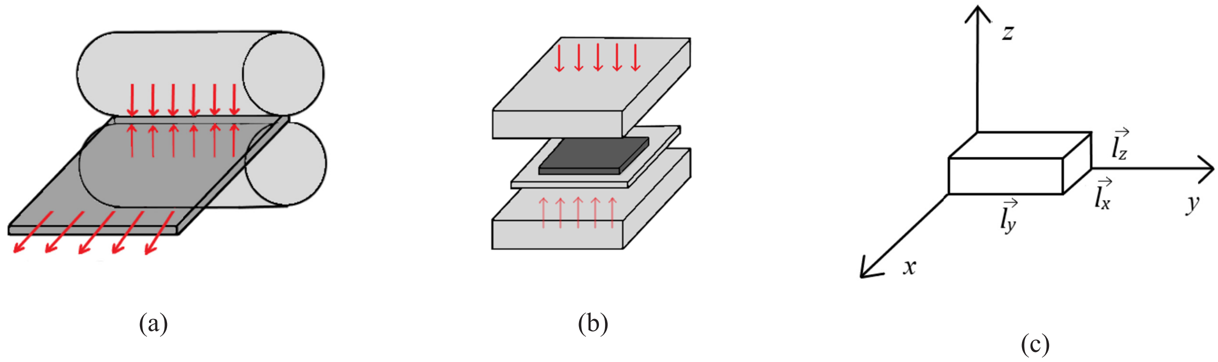


Fig. 1. Scheme of sample preparation for swelling in SC-CO$_2$:
(a) rolling; (b) pressing; (c) three-dimensional coordinates of the sample after pressing.

Calibrated 2-mm thick plates taken from them were molded in a hydraulic press at a temperature of 100°C. Samples were cut from the plates thus obtained in the form of a parallelepiped with dimensions of ~5 mm in length, and ~3 mm in width. The direction of compression on the *z*-axis and the direction of spreading on the *x*- and *y*-axes were defined in the samples.

The study of the processes of rubber swelling in SC-CO$_2$ and their subsequent foaming was carried out by means of a specially developed optical technique of direct measurement of the linear dimensions of samples in three coordinates. This uses an original setup as shown in Fig. 2.

The high-pressure apparatus was made in the form of a steel cylinder with a volume of 0.25 L, equipped with observation windows made of borosilicate glass.

In order to record the changes in the sample sizes occurring during the experiments, a digital video camera was placed in front of one of the windows. An electric lamp was installed opposite the other window to illuminate the samples. At the beginning of each experiment, the high-pressure apparatus was dried with compressed air and purged with high-purity (99.99%) carbon dioxide. The test samples were placed in the high-pressure apparatus, heated to a given temperature on a special stand. After that, carbon dioxide was fed into the apparatus which at a given pressure and temperature passed into the SC state. Using a video camera, changes in the linear dimensions of the samples in length l_x, width l_y, and height l_z during their swelling in SC-CO$_2$ were recorded. The accuracy of measuring the geometric dimensions of the samples was ~5%.

By measuring the linear dimensions of the samples during the swelling process, the volume values of the swelling samples were calculated and kinetic curves of swelling were plotted.

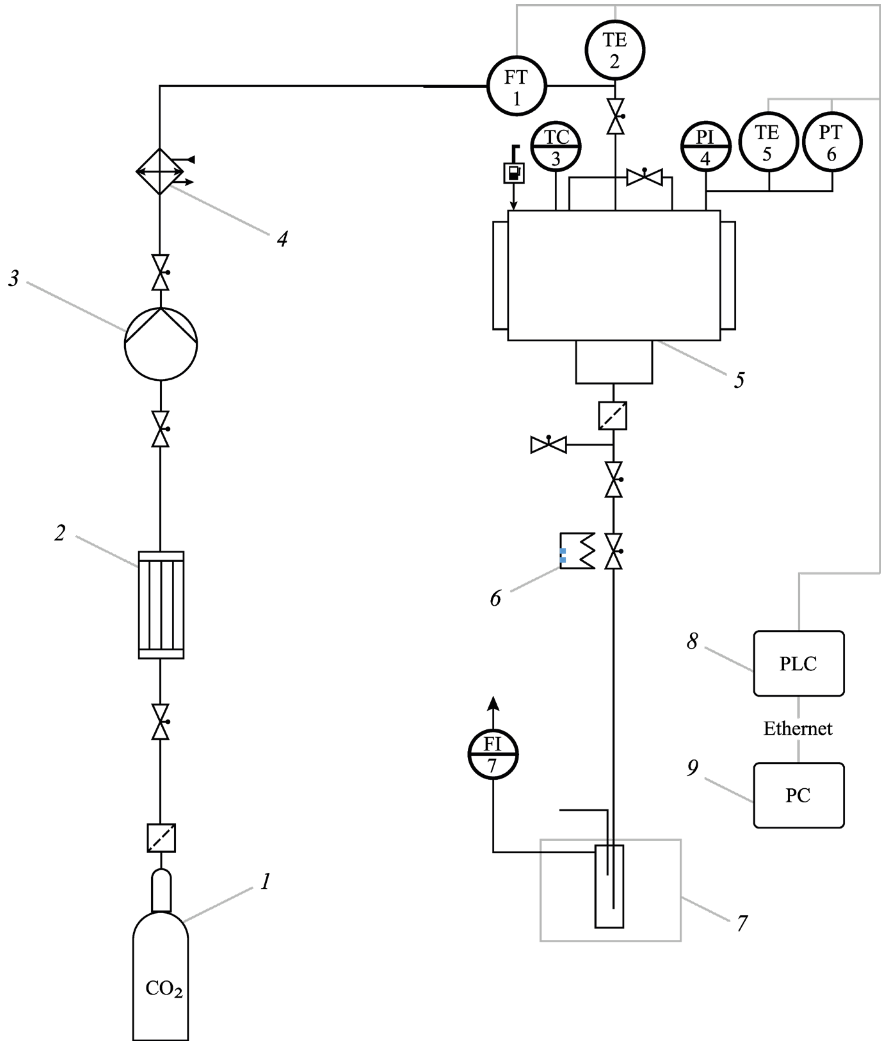
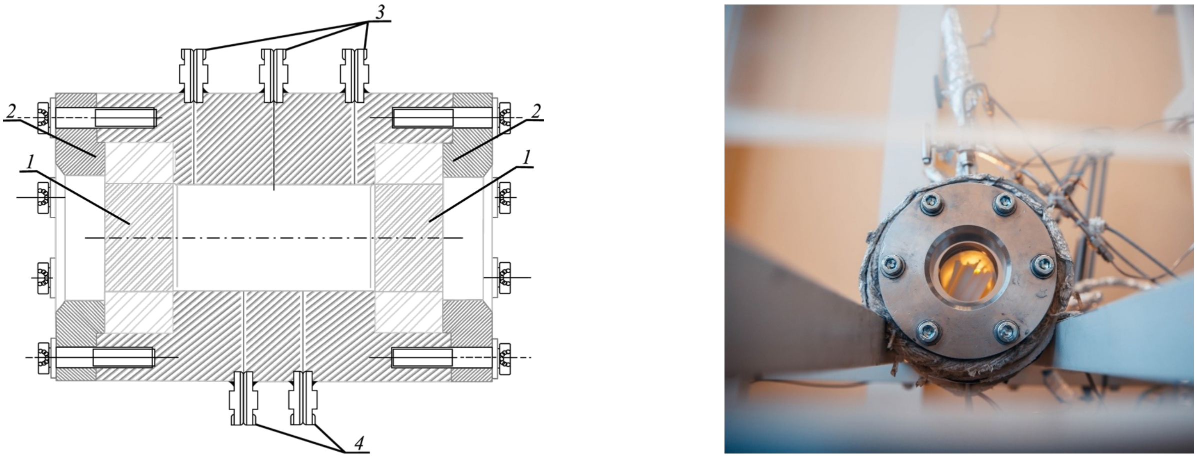


Fig. 2. Principle scheme of the installation for swelling processes in SC-CO_2:
(*1*) carbon dioxide cylinder (60 bar); (*2*) condenser; (*3*) pump; (*4*) heat exchanger; (*5*) 250 mL high-pressure apparatus; (*6*) heating element; (*7*) solvent collector with cooling jacket; (*8*) programmable logic controller (PLC); (*9*) personal computer (PC). PI4 — pressure gauge; TC3 — temperature controller; FT5 — Coriolis flowmeter; TE2 and TE5 — thermoelectric converters; PT6 — pressure transducer; FI7 — rotameter.



(a)

(b)

Fig. 3. (a) Sketch of the high pressure apparatus: (*1*) inspection windows; (*2*) pressure flange; (*3*) inlet connections; (*4*) outlet connections. (b) External view of the apparatus from the side of the inspection window.

The swelling degree S of samples in SC-CO$_2$ was calculated using Eq. (1):

$$S = \frac{V_1 - V_0}{V_0} \times 100\%, \quad (1)$$

where V_1 is the volume of the swollen sample, V_0 is the volume of the initial rubber sample.

The change in the size Δl of the samples in the process of swelling was determined using Eq. (2):

$$\Delta l = \frac{l_1 - l_0}{l_0} \times 100\%, \quad (2)$$

where l_1 is the size of the swollen sample, mm; l_0 is the size of the initial rubber sample, mm.

After completion of the process of swelling the samples up to the equilibrium state, foaming was carried out. The pressure in the apparatus was sharply released, and the sizes of foamed samples were recorded. The study of the porous structure of foamed rubbers was carried out using scanning electron microscopy on an EVO 10 electron microscope (*Zeiss*, Germany).

RESULTS AND DISCUSSION

The measurements of the dimensions of rubber samples in the process of their swelling showed that swelling of samples along the x, y, and z axes occurs unevenly (Fig. 4). There is a significant increase in the dimensions of samples along the z axis corresponding to the direction of compression of samples during pressing. There is also a small change in the dimensions of samples along the x and y axes corresponding to the direction of deformation of samples during spreading. The reason for this phenomenon may be the processes of orientation of rubber macromolecules in the process of its spreading along the x and y axes during rolling and pressing of samples [19]. Indeed, as the experiments (Fig. 5a) have shown, if the pressed samples are not removed immediately from the press after molding, but left in the press at elevated temperature (100°C), which accelerates the transition of oriented rubber macromolecules to the equilibrium non-oriented state, the difference in the swelling degrees of the samples along the three axes gradually decreases and disappears. Similar regularities are observed when toluene is used as a solvent instead of SC-CO$_2$. The degree of swelling of rubber in this solvent is higher and the orientation effects disappear faster (Fig. 5b).

As shown by preliminary experiments, the presence of oriented macromolecules in rubber samples lowers the value of equilibrium volume swelling of rubbers. Therefore, in order to investigate the swelling kinetics, we used samples aged in the press after molding for at least 3 h at temperatures of 90–180°C to remove the orientation effects.

Figures 6 and 7 show typical kinetic curves of swelling of different rubbers in SC-CO$_2$. Their character indicates limited swelling of all types of rubbers, when after reaching a certain limit swelling stops. The swollen samples retain their shape and a clear interface with the supercritical medium.

As is known, the maximum equilibrium degree of swelling of polymers is determined by its nature as well as the nature of the solvent or affinity between them. In practical terms, the degree is judged by the proximity of their solubility parameters.

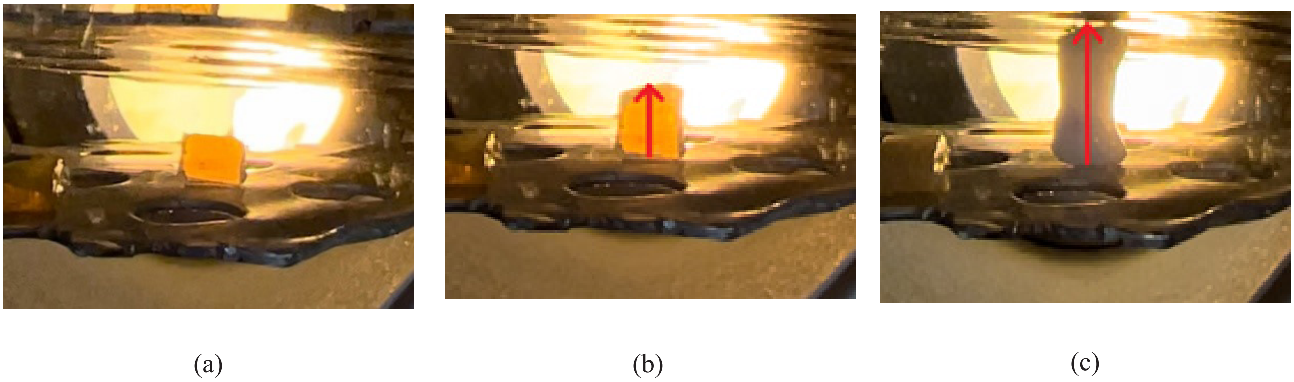
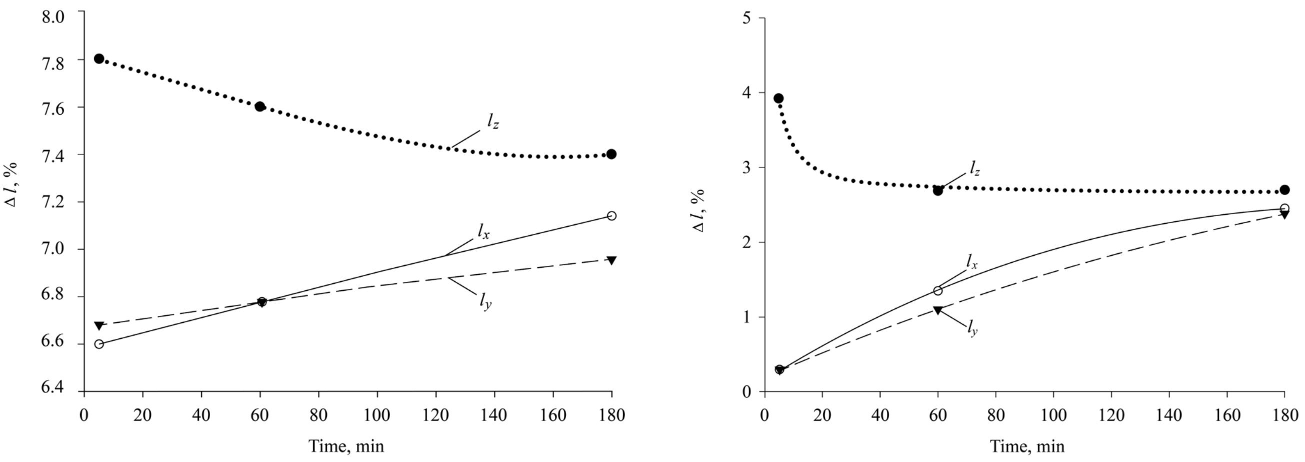

(a) (b) (c)

Fig. 4. Swelling of SCTV-1 rubber in SC-CO$_2$ at 50°C and 15 MPa:
(a) original sample, (b) 1 min swelling, (c) 10 min swelling.



(a) (b)

Fig. 5. Variation of linear dimensions of SCF-26 fluorocarbon rubber samples in the state of equilibrium swelling in SC-CO_2 (a) and in toluene (b) as a function of the time of holding the samples at 100°C before swelling.

Indeed, as can be seen from Fig. 6, the maximum degree of swelling (about 100%) is characteristic of siloxane rubber which has the closest value of the solubility parameter to the solubility parameter of SC-CO_2 (Table 1). Butadiene-styrene, butadiene-nitrile, ethylene-propylene rubbers, which along with siloxane rubber belong to the first group of rubbers, also swell by tens of percentages. The time to reach maximum swelling for these rubbers is 40–60 min.

A significantly lower degree of swelling (less than 10%) is observed for the second group of rubbers, including synthetic and natural polyisoprene, chloroprene and fluorocarbon rubber (Fig. 7). In comparison to other rubbers, they have solubility parameters which differ more from the solubility parameters of SC-CO_2. These rubbers are also characterized by faster (within 10–20 min) achievement of the degree of equilibrium swelling. However, monotonic dependence of the ultimate degree of swelling on the solubility parameters of rubbers is not observed.

Butadiene-nitrile and butadiene-styrene rubbers with solubility parameters almost equal to the solubility parameters of polyisoprenes and fluorocarbon rubber have a significantly higher degree of swelling and take more time to reach equilibrium swelling (40–60 min), when compared

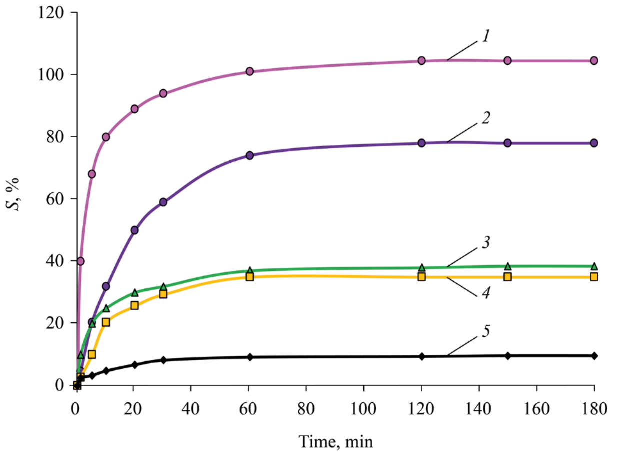


Fig. 6. Kinetic curves of rubber swelling in SC-CO_2 at 50°C and 15 MPa pressure: siloxane (*1*), butadiene-nitrile (*2*), butadiene-styrene (*3*), ethylene-propylene (*4*), and ethylene-acrylate (*5*) rubbers.

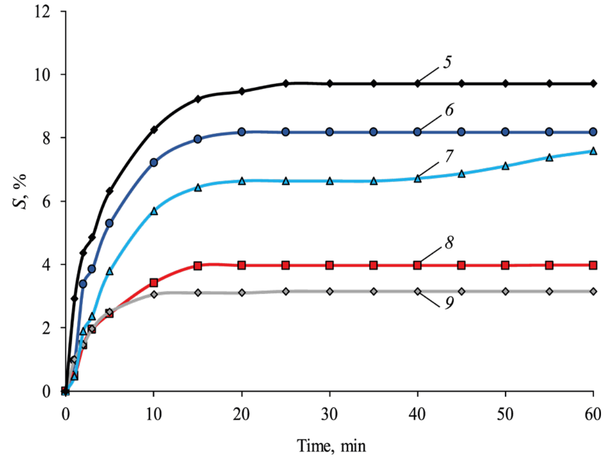


Fig. 7. Kinetic curves of rubber swelling in SC-CO_2 at 50°C and 15 MPa pressure: ethylene acrylate (*5*), fluorocarbon (*6*), chloroprene (*7*), polyisoprene (*8*), and natural (*9*) rubbers.

to the second group of rubbers. Polychloroprene differs more in its solubility parameter from SC-CO_2 and swells more when compared to polyisoprenes. A possible reason for this is the specific interactions of SC-CO_2 with rubbers of different chemical nature.

Figure 8 shows the influence of pressure on the swelling kinetics of SCF-26 rubber in SC-CO_2. It can be seen that with increasing pressure from 5.0 to 20.0 MPa, the value of equilibrium swelling of samples in the medium of SC-CO_2 increases.

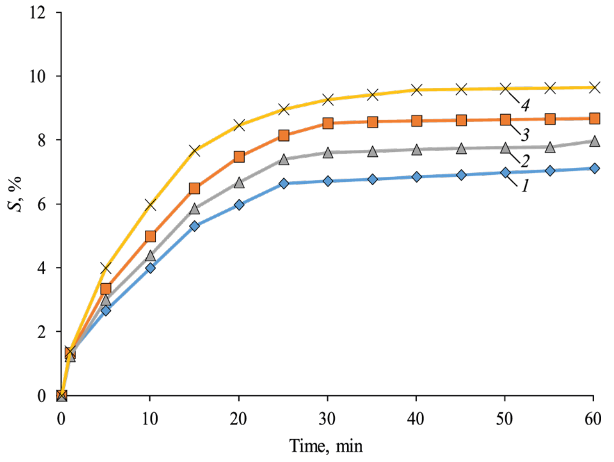


Fig. 8. Time dependence of swelling degree of SCF-26 rubber in SC-CO_2 at 50°C and pressures of 5 (*1*), 10 (*2*), 15 (*3*), and 20 MPa (*4*).

Similar dependencies of the equilibrium swelling value on pressure can be observed for all types of rubbers (Fig. 9).

As seen in Fig. 10, an increase in the equilibrium swelling also leads to an increase in the swelling temperature.

Thus, by varying the pressure and temperature, it is possible to change the equilibrium degree of swelling of rubbers in SC-CO_2.

The swelling of polysiloxanes in SC-CO_2 is known [8] to occur by diffusion mechanism, and the siloxane rubber/SC-CO_2 system obeys Fick's second law (3):

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}, \tag{3}$$

where c is the concentration of CO_2 in the polymer, D is the diffusion factor, cm^2/s.

In order to understand the main regularities of swelling of the studied rubbers in the SC-CO_2 medium and to calculate the diffusion coefficients of SC-CO_2 in rubbers, it was first of all necessary to establish whether the rubber/SC-CO_2 systems under study obey this law, despite the above-mentioned possible specific interactions between them.

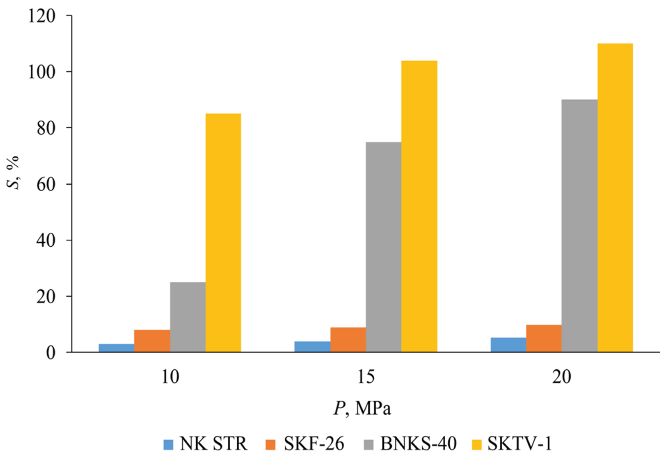


Fig. 9. Effect of pressure *P* on the equilibrium swelling of different rubbers at 50°C.

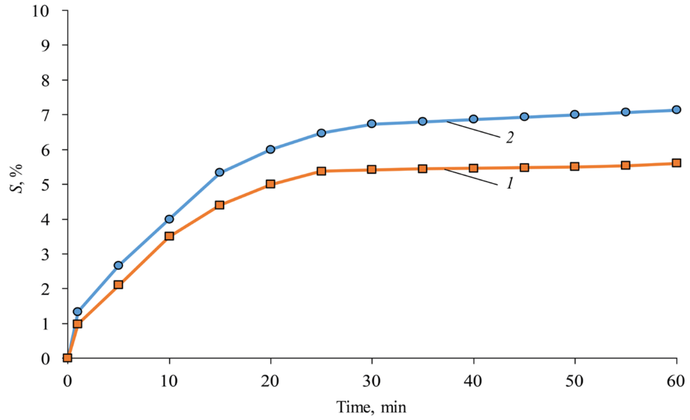


Fig. 10. Time dependence of the swelling degree of SCF-26 in SC-CO_2 at temperatures of 40 (*1*) and 50°C (*2*).

The equation describing Fick's second law is known to have a number of solutions depending on the boundary conditions [20]. If the sample sorbing SC-CO_2 has the shape of a plate with thickness l, then under the boundary conditions $0 < x < l$ and $0 < c < c_{eq}$ (equilibrium concentration), the solution of the equation has the form (4):

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \tag{4}$$

where M_t is the amount of adsorbed substance over time t, M_∞ is the equilibrium amount of the adsorbed substance.

Assuming [8], the degree of swelling is equal to:

$$\frac{M_t}{M_\infty} = \frac{V_t - V_0}{V_\infty - V_0}\ , \qquad (5)$$

where V_0 is the initial sample volume; V_t is the volume of swollen sample over time *t*; V_∞ is the equilibrium volume of the swollen sample.

Equation (5) can be written in the following form (6):

$$\frac{V_t - V_0}{V_\infty - V_0} = f\left(t^{\frac{1}{2}}\right). \qquad (6)$$

For systems obeying Fick's law, the dependence $\frac{V_t - V_0}{V_\infty - V_0}$ from $t^{1/2}$ should have the form of a straight line, the tangent of the angle of which allows calculating the value of *D* [21].

The root mean square dependence $\frac{V_t - V_0}{V_\infty - V_0}$ of swelling time in SC-CO_2 medium for different rubbers is shown in Fig. 11.

The data in Fig. 11 indicates that Fick's second law is observed for all types of rubbers and SC-CO_2.

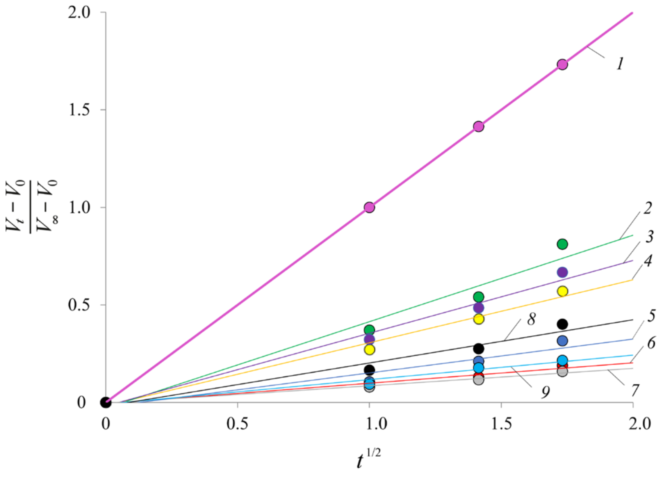


Fig. 11. Dependence $\frac{V_t - V_0}{V_\infty - V_0}$ on the square root of the swelling time of samples of different rubbers: siloxane (*1*), butadiene-styrene (*2*), butadiene-nitrile (*3*), ethylene-propylene (*4*), fluorocarbon (*5*), natural (*6*), isoprene (*7*), chloroprene (*8*), ethylene-acrylate (*9*).

Table 2 shows the values of diffusion coefficients of SC-CO_2 in different rubbers calculated from the tangent of the angle of slope of the straight lines presented in Fig. 11.

Figure 12 shows that the diffusion coefficients depend linearly on the values of the equilibrium degree of swelling of rubbers.

Thus, the swelling ability of rubbers grows in direct proportion to the diffusion coefficient of SC-CO_2 in them. The experimental data for all types of rubbers fits into one straight line. Therefore, it is not the solubility parameter of rubber but the diffusion coefficient of SC-CO_2 into it which may serve as a more accurate characteristic of the affinity degree of SC-CO_2 and rubber.

The rubber samples which reached equilibrium swelling were subjected to foaming. It was found that all rubbers swollen to equilibrium state foamed intensively, regardless of their degree of equilibrium swelling, varying from a few to 100%.

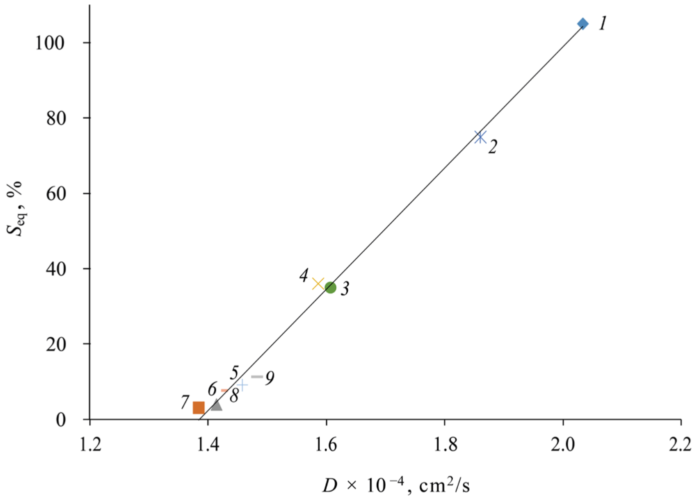


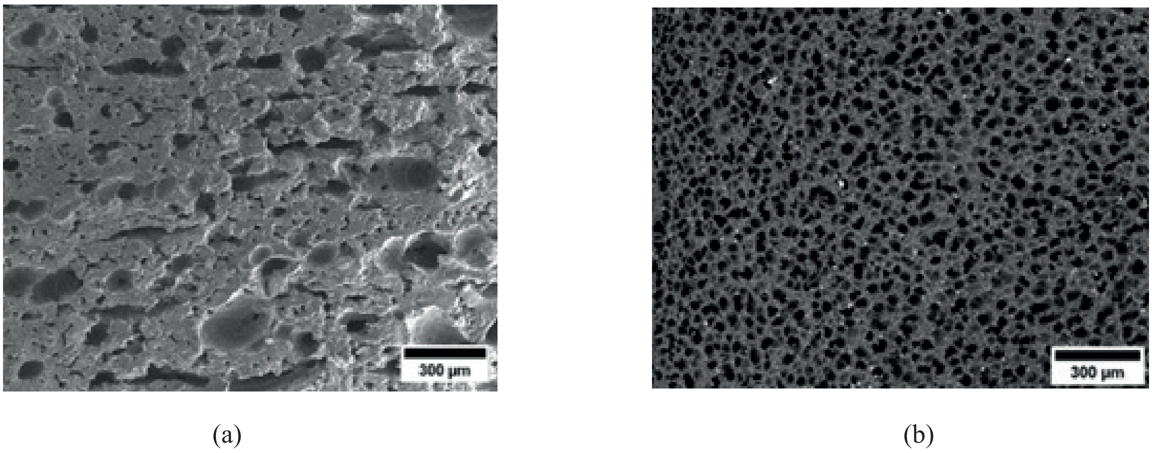
Fig. 12. Dependence of the equilibrium degree of swelling of rubbers S_{eq} on the diffusion coefficient *D* of SC-CO_2 in them. (*1*) Siloxane, (*2*) butadiene-styrene, (*3*) butadiene-nitrile, (*4*) ethylene-propylene, (*5*) fluorocarbon, (*6*) natural, (*7*) polyisoprene, (*8*) chloroprene, (*9*) ethylene acrylate rubbers.

The typical porous structure of foamed rubber samples obtained using SC-CO_2 is shown in Fig. 13 using a sample from SCF-26 rubber as an example. For comparison, the porous structure of this rubber obtained using a chemical pore former (azodicarbonamide) used as a pore former in the rubber industry is also shown here.

The high uniformity of the porous structure of the obtained materials and significantly smaller pore sizes of tens of microns, when compared

Table 2. SC-CO_2 diffusion coefficient in rubbers of different chemical nature

Rubber brand	Diffusion coefficient $D \times 10^{-4}$, cm^2/s
NR STR	1.40
SKI-3	1.38
BNKS-40 AN	1.83
DSSK1810F	1.61
SKEPT-50	1.58
SKTV-1	2.12
SKF-26	1.45
Baypren® 611	1.41
Vamac® Ultra LT	1.48



(a) (b)

Fig. 13. Electron micrographs of the structure of SCF-26 foamed rubber samples obtained using chemical foaming agent (a) and SC-CO_2 (b).

to the pore sizes of hundreds of microns for samples obtained with chemical pore formers, indicate the undoubted advantages of fluid technology in obtaining finely porous elastomeric materials.

The influence of technological parameters of foaming of various rubbers in SC-CO_2 and formulations of rubber mixtures on the structure of the resulting porous elastomeric materials will be investigated in a subsequent report, being prepared for publication by the authors of this article.

CONCLUSIONS

1. An optical technique has been developed for studying the process of rubber swelling in supercritical carbon dioxide using the original setup, consisting in the direct measurement of geometric dimensions of swelling samples using a digital video camera. The experimental study of swelling in SC-CO_2 of the main types of rubbers used in the manufacture of rubber products was carried out using the developed methodology.

2. The diffusion coefficients of SC-CO_2 in rubbers of different chemical nature were calculated for the first time using mathematical modeling and swelling data.

3. It has been shown that the dependence of the equilibrium swelling degree of rubbers in SC-CO_2 on their solubility parameters is non-monotonic. This is probably related to the specific interaction of SC-CO_2 with some types of rubbers. The equilibrium swelling degree of rubbers in SC-CO_2 increases in direct proportion to its diffusion coefficient and increases with rising pressure and temperature.

4. It has been established that intensive foaming occurs when rubber swells in SC-CO_2 by only a few percent at a sharp pressure drop. The size of the pores formed in rubbers is tens of microns, significantly smaller than the pore size formed when using chemical pore formers and is an undeniable advantage of the fluid technology of porous elastomeric materials production in comparison with the traditional one. With the help of this technology, all the main types of rubbers studied here and used in the rubber industry can be used for production of porous rubbers.

Authors' contributions

S.T. Mikhailova – carrying out the experiment, analyzing, collecting, and processing the material, writing the article;

S.V. Reznichenko – formulating research aims and objectives, analyzing, processing results, writing the text of the article;

E.A. Krasnikov – carrying out the experiment;

P.Yu. Tsygankov – scientific and technical support, editing the text of the article;

N.V. Menshutina – scientific advising, editing the text of the article;

I.D. Simonov-Emel'yanov – scientific advising, editing the text of the article.

The authors declare no conflicts of interest.

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The article was submitted: April 19, 2023; approved after reviewing: August 29, 2023; accepted for publication: November 17, 2023.

Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Dr. David Mossop