UDC 699.82

Voronezh State Technological Academy
Postgraduate Student of Department of Polymer Processing Technology
A. I. Chernikov
D. Sc. in Engineering, Prof., Head of Department of Polymer Processing Technology
Yu. F. Shutilin
Ph. D. in Engineering, Assoc. Prof. of Polymer Processing Technology
T. I. Igumenova
Engineer of Department of Polymer Processing Technology
M. P. Zavyalov
Russia, Voronezh, tel.: +7(4732)78-13-05; +7(4732) 49-27-28;
e-mail: Chernikovy@mail.ru; regant7@rambler.ru

A. I. Chernikov, Yu. F. Shutilin, T. I. Igumenova, M. P. Zavyalov

DEVELOPMENT OF FORMULATIONS OF BUILDING HERMETIC COMPOUNDS

Problem statement. Possibility of development of hermetic seal material intended for a waterproofing of concrete joints in large-panel building construction based of ethylene propylene rubber (СКЭПТ-40) and bentonite as hydrophilic filler is considered.

Results and conclusions. The comparative analysis of the material obtained and foreign analogues is performed, and its fundamental characteristics are defined. Properties of hermetic compounds are studied with the use of combinations of rubbers and vulcanizing group.

Keywords: sealant, bentonite, swelling degree, chemical additives, activation, rubbers-additives, combinations of rubbers, vulcanization.

Introduction

Since water-swelling gaskets [1] are more and more widely used in construction, the development of the compound composition for obtaining them requires undivided attention. Compositions of sealing materials used in construction are constantly refined and improved due to some peculiarities of their operating conditions. Much attention is presently given to

the development of various patterns for designing compounds with the use of natural materials and minerals available. The major task while designing new types of gaskets is to increase their endurance and reliability.

1. Comparative analysis of different types of gaskets

We know about sealing materials on the basis of butyl rubber whose swelling index in water according to the applied requirements is 200 % and more Although the practical tests performed by the example of samples produced in Poland and Germany showed that in the conditions close to operating ones there is a drastic change (up to complete destruction) in properties and size of gaskets of this type (Fig. 1).

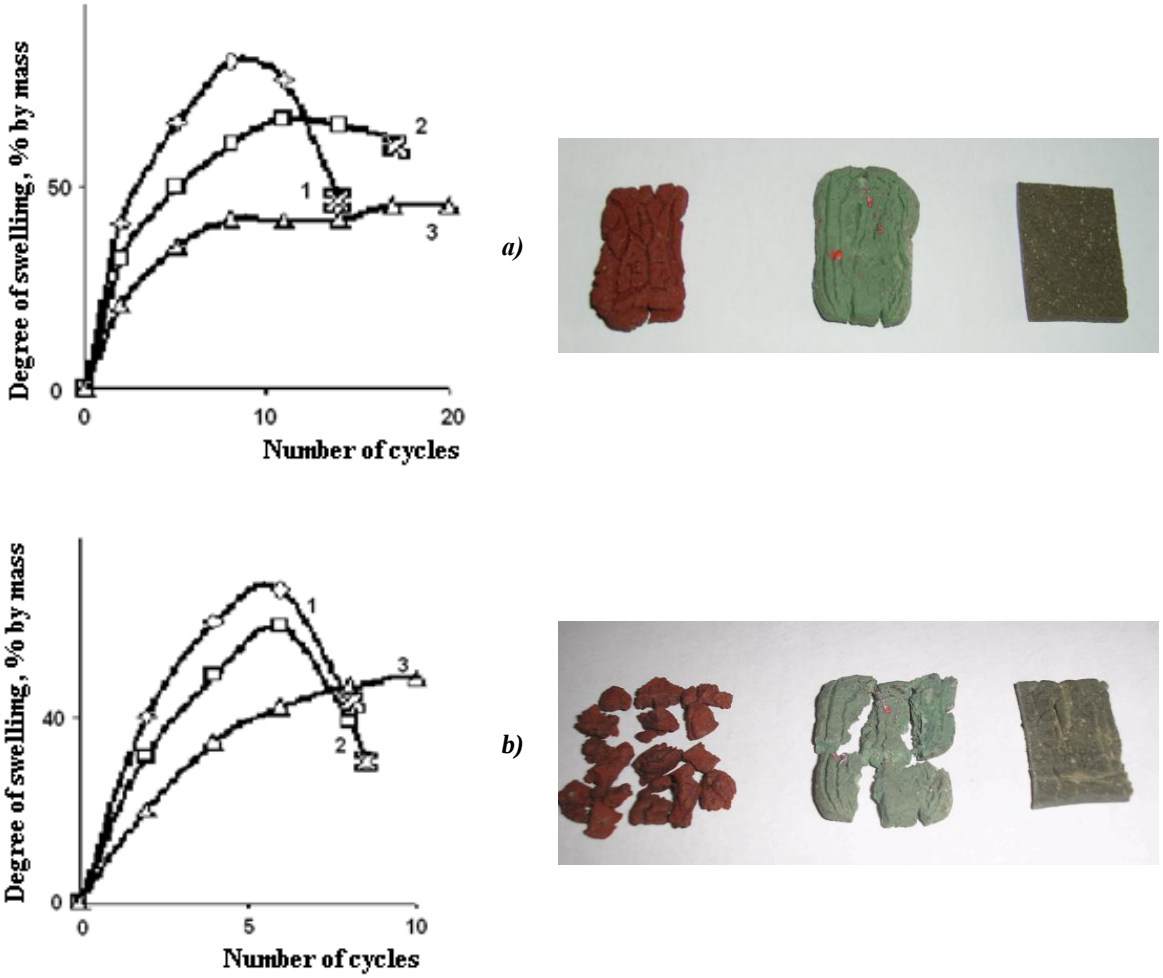

Fig. 1. Swelling kinetics and visual appearance of the samples produced in Poland (1), Germany (2) and the experimental material on the basis of the rubber СКЭПТ-40 (3) after the completion of the cyclic experiments; swelling and drying (a) and swelling and drying with intervening freezing (b)

Operating conditions of the compounds were simulated in the following way:

a) in the cycles of swelling and drying plates were held in water for 24 hours, dried for the same amount of time and then the swelling index α was determined, % of mass;
b) under the cyclic influence of swelling and drying with intervening freezing the patterns were placed in water for 24 hours, were held at the temperature of -12 ^{o}C for 12 hours, dried for 12 hours as well. Their swelling index was then calculated.

The research showed that the samples produced in Poland and Germany decrease in size due to the leaching of the components. The experiment was carried out before the samples transformed into solid, leathery products (see Fig. 1a) or before their destruction (see Fig. 1b). Both case are marked 'X'. A slight change in the form was observed in the suggested compound 3 as α tended to asymptotic values (see Fig. 1).

In order to design an experimental compound, ethylene-propylene rubber СКЭПТ-40 was used. It was filled with natural bentonite of the Nikolsk deposit (Voronezh region) by blending the ingredients on a rolling mill with a further release of profiles on the extruder. Bentonite as aluminium silicate [2, 3] with the general formula $Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$ forms 'three-dimensional' chain structures [4], which cause the swelling of compounds of this type in water.

2. The study of the properties of sealing compounds with natural bentonite

In foreign compounds butyl rubber was used as a foundation. We performed comparative analysis of samples with the use of butyl rubber (БК-1575) and of triple ethylene-propylene rubber СКЭПТ-40.

With the same filling, the compounds containing butyl rubber have a higher water swelling index (Fig. 2).

However, during the cycle of swelling and drying a leaching of components and a volume decrease up to cracking of the material takes place in the samples based on butyl rubber (Fig. 3). It should be noted that mixtures on the base of butyl rubber showed better technological properties, most notably extrudability.

The research on improving extrusion properties of ethylene-propylene rubbers of different types (СКЭП and СКЭПТ) was performed by their multiple extrusion through a capillary of

viscosimeter of the ИИРТ type at the temperature of 100—200°C in compliance with the method suggested earlier [5]. The rubbers were processed in a wide range of temperatures and shear rates. Reprocessing conditions of СКЭП (Т) providing the improvement of extrusion properties were picked for this process.

Nevertheless practical tests of this method did not help to achieve the required level of technological properties, especially at high levels of filling. Although a slight increase in the swelling index of the compounds was noted.

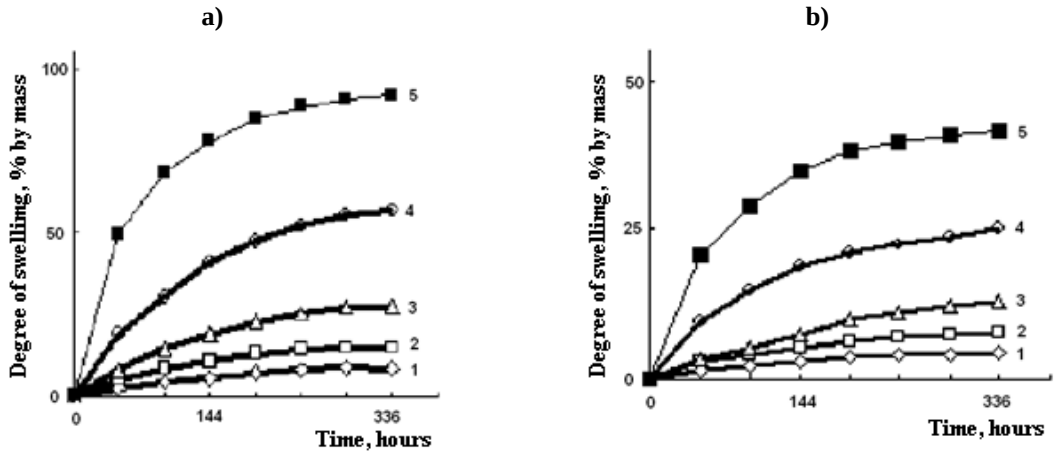

Fig. 2. Water swelling kinetics of the samples based on butyl rubber (a)
and СКЭПТ (b) containing 0 (1), 10 (2), 30 (3), 100 (4) and 200 (5) mass proportion of natural bentonite

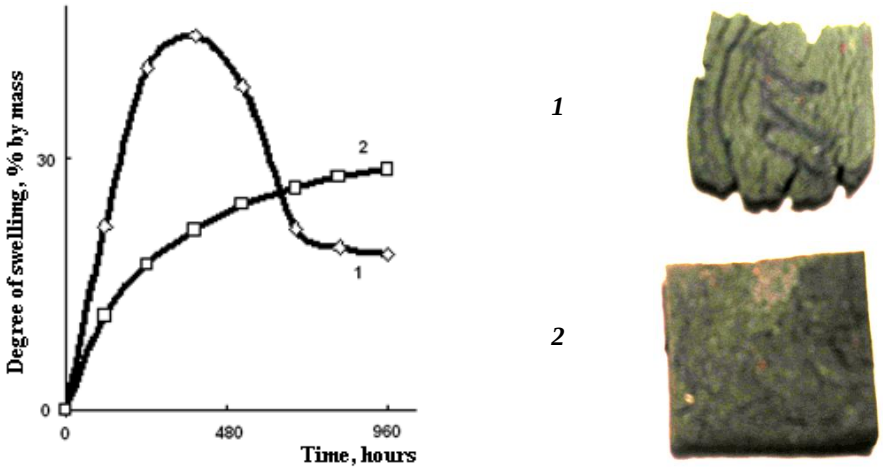

Fig. 3. Kinetics of swelling-index change in the cycles of swelling and drying and visual appearance
of the samples on the base of butyl rubber (1)
and СКЭПТ (2) containing 100 mass fractions of bentonite each

3. Bentonite activation by modifying additives

The compounds based on СКЭПТ-40 are more resistant to external effects but they are at a disadvantage in relation to butyl rubber analogs in terms of the swelling index. To eliminate this flaw and improve technological properties of polymer mixtures, natural bentonite was activated, as recommended by the authors [4], by natrium-containing chemicals, namely by NaCl, Na_2CO_3, $NaHCO_3$, Na_3PO_4 , natrium salts of fatty acids (Na-SFA) with the dosage from 0.5 to 7 % of mass. Bentonite modification was performed by grinding in the dry form.

Bentonite activated by various additives provides a significant increase in the maximum swelling index of the compounds and, among other things, improvement of their technological, physical-mechanical characteristics (Table 1).

Table 1

Major characteristics of sealing compounds containing СКЭПТ and 100 mass fractions of activated bentonite

Bentonite activator and its dosage, mass fraction	Properties					
	Maximum swelling index, %	Strength, MPa	Relative elongation, %	Plasticity, Conventional unit	Elastic regeneration	Muni Viscocity at 100 °C, conventional unit
Without the activator	25.40	0.43	80	0.20	5.0	83
NaCl, 4 %	51.30	0.47	100	0.30	3.3	89
Na_2CO_3, 3 %	77.20	0.49	120	0.35	2.9	87
Without the activator	25.40	0.43	80	0.20	5.0	83
NaCl, 4 %	51.30	0.47	100	0.30	3.3	89
Na_2CO_3, 3 %	77.20	0.49	120	0.35	2.9	87
$NaHCO_3$, 3 %	69.80	0.48	100	0.30	3.3	88
Na_3PO_4, 4 %	58.50	0.46	90	0.22	4.5	89
Na–СЖК, 3 %	58.66	0.475	110	0.28	3.6	88
Na_2CO_3 + Na–SFA, 3 %	46.10	0.465	110	0.30	3.3	89

The samples with the best complex of properties were obtained with the use of soda ash with the dosage of 3 % of mass as a bentonite activator, therefore this method was chosen for the further study.

4. The analysis of properties of sealing materials on the base of the compound СКЭПТ-40 with diene rubbers

Development of the formulation of the compounds was performed using rubber mixtures [6] with diene polymers such as СКИ-3, СКД and СКС-30АРКП as additives to СКЭПТ. The analysis of the obtained data showed that СКД and БСК are favourable for an increase in the swelling index of the samples, and yet it does not provide the compounds with sufficient technological properties (Fig. 4). The addition of СКИ-3 enhances the procession of rubber mixtures (optimal dosage is 5 % of mass).

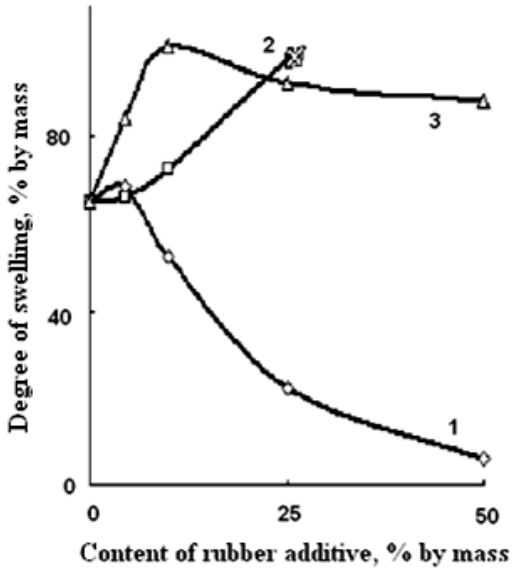

Fig. 4. Maximum swelling index of mixtures filled with bentonite activated by 3 % of mass Na_2CO_3 with the combination with СКИ-3 (1), СКД (2) and СКС-30АРКП (3)

Combinations of several polymers providing improvement of rubber properties [3, 6] are well known. We examined the compounds on the basis of ‘triple’ rubber combinations such as СКЭПТ + СКИ-3 + СКД, СКЭПТ + СКИ-3 + СКС-30АРКП and СКЭПТ + СКД + СКС-30АРКП. The analysis of technological and physical mechanical properties of the materials showed that the combination of СКЭПТ-40 with with the rubbers СКИ-3 and СКС-30АРКП provides an increase in cohesive strength and plasticity of the compounds during the

simultaneous increase in the water-swelling index (Table 2). The use of triple rubber combination СКЭПТ-40: СКИ-3: СКС-30АРКП in the proportion 80:10:10 is the most rational, since it helps samples to achieve a higher swelling index. In addition, the mixture shows satisfactory technological properties during processing.

Table 2

Major characteristics of sealing materials on the basis of 'triple' rubber combination and activated bentonite

Rubbers	Proportion of the rubbers	Properties					
		Maximum swelling index, %	Strength, MPa	Relative elongation, %	Plasticity, conventional unit	Elastic regeneration	Muni viscosity at 100 °C, conventional unit
СКЭПТ-40: СКИ-3: СКД	90:5:5	51.46	0.48	120	0.36	2.8	83
	80:10:10	59.70	0.485	115	0.37	2.7	83
	50:25:25	66.20	0.48	110	0.37	2.7	84
СКЭПТ40: СКС-30АРКП: СКД	90:5:5	80.50	0.48	120	0.35	2.9	83
	80:10:10	82.95	0.475	120	0.35	2.9	82
	50:25:25	98.41	0.47	115	0.34	2.9	82
СКЭПТ-40: СКИ-3: СКС-30АРКП	90:5:5	59.25	0.48	110	0.37	2.7	83
	80:10:10	70.50	0.485	100	0.39	2.6	80
	50:25:25	50.90	0.49	80	0.43	2.3	77

Hence, the use of diene rubber additives to СКЭПТ-40 in the formulation of water-swelling gaskets allows to improve the processing and greatly cut down the material prices and, among other things, creates prerequisites for obtaining vulcanizing polymer compositions.

5. The study of the properties of sealing materials containing a vulcanizing group

It is known [3] that vulcanization largely increases physical mechanical properties of rubbers, and yet it makes production technology of goods more complicated. It was suggested to

eliminate this flaw by using as a vulcanizing group a specially selected combination of sulphur with tiuram, captax and diphenylguanidine providing self-vulcanization at the temperatures of 40—60 C and even 20 ^{o}C .

Such a formulation allows to vulcanize a gasket ‘in its place’, as in such conditions it can heat up to the temperature of 40 ^{o}C and more. Modelling of sealing compound operating conditions was performed at 60 and 80^{o}C. It showed that during heating there is some decrease in the swelling index of the samples during simultaneous growth of the gel amount (Fig. 5).

In addition, a significant growth of physical and mechanical properties of the obtained rubbers. The volume increase by 80—100 % observed for vulcanized compositions is fairly enough for their practical application as gaskets for building constructions.

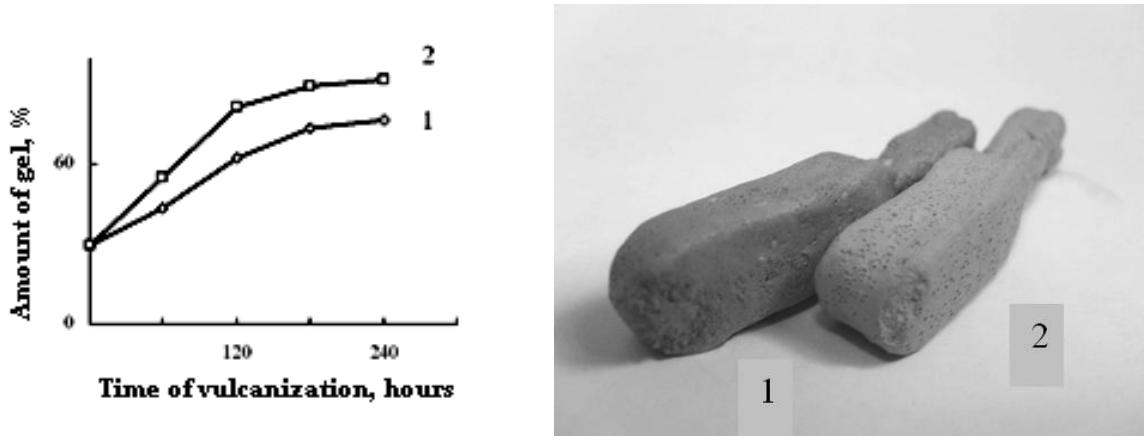

Fig. 5. Gel content and visual appearance of the samples on the basis of the mixture СКЭПТ+СКИ-3+СКС-30АРКП (80:10:10) containing 100 mass fractions of bentonite activated by Na_2CO_3, 1 mass fraction of sulphur and 0.5 mass fraction each; DFG, tiuram, captax vulacanized at 60 ^{o}C (1) and 80 ^{o}C (2)

Conclusions

1. A possibility of designing a sealing compound with improved properties on the basis of ethylene-propylene rubber and activated bentonite are found. It is proved that the suggested compound on the basis of СКЭПТ-40 surpasses foreign materials in performance under cyclic effects such as swelling and drying and swelling and drying with intervening freezing.

2. It is found that natural bentonite activation by modifying additives contributes to the improvement of the complex of gasket compounds technical properties. Besides, a better activating capacity is provided by soda ash with the dosage of 3 % of mass.

3. The use of diene rubber additives with СКЭПТ-40 enhances the improvement of technological properties of goods and makes self-vulcanization of the sealing compounds under study possible. The selected vulcanizing group provides a gasket self-vulcanization at temperatures close to operating ones.

References

1. **Пат. 2004108912 РФ**, МПК[7] С 09 К 3/10. Герметизирующая композиция / Г. А. Савченкова, Т. А. Артамонова. = **Patent 2004108912 Russian Federation**, МПК[7] С 09 К 3/10. Hermetic compounds / G. A. Savchenko, T. A. Artamonov.
2. **Горюшкин, В. В.** Бентонитовые глины юго-востока Центрально-Черноземного района / В. В. Горюшкин, А. Д. Савко; науч. ред. Г. В. Холмовой. — Воронеж: Воронеж. гос. ун-т, 2006.— 176 с. — (Труды НИИ геологии ВГУ; Вып. 37). = **Goryushkin, V. V.,** Savko A. D. Bentonite clays of the southeast of Central Black Earth area. Voronezh, 2006. 176 pp.
3. **Шутилин, Ю. Ф.** Справочное пособие по свойствам и применению эластомеров / Ю. Ф. Шутилин. — Воронеж: Воронеж. гос. технолог. акад., 2003. — 871 с. = **Shutilin, Yu. F.** Handbook on properties and applications of elastomers. Voronezh, 2003. 871 pp.
4. **Догадкин, Б.** Структура и свойства наполненных резиновых смесей / Б. Догадкин, К. Печковская, Л. Черникина // Коллоидный журнал. — 1946. — Т. VIII, № 1—2. — С. 31—44. = **Dogadkin B.,** Pechkovskaja K., Chernikina L. Structure and properties of the filled rubber mixes. Colloid journal. 1946. Vol. VIII, № 1—2. 31—44 pp.
5. **Шутилин, Ю. Ф.** Аномалии в измерениях вязкости каучуков / Ю. Ф. Шутилин, М. С. Босых, Н. Н. Тройнина, Н. Л. Клейменова // Каучук и резина. — 2003. — № 5. — С. 43—48. = **Shutilin, Yu. F.,** Bosyh, M. S., Trojnina, N. N., Kleymenova, N. L. Anomalies in measurements of rubber viscosity. Caoutchouc and rubber. 2003. № 5. P. 43—48.
6. **Кулезнев, В. Н.** Смеси полимеров / В. Н. Кулезнев. — М.: Химия, 1980. — 304 с. = **Kuleznev, V. N.** Mixes of polymers. Moscow, 1980. 304 pp.