HIGHLY FILLED RUBBER PLASTICS FOR SOFT ROAD SURFACES: EFFECT OF A MATRIX COMPOSITION ON THE MECHANICAL PROPERTIES

V. A. Shishkinskaya,*[a] G. P. Goncharuk,[b] and O. A. Serenko[a]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, str. 1, Moscow, 119334 Russia*
[b] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, Moscow, 117393 Russia*

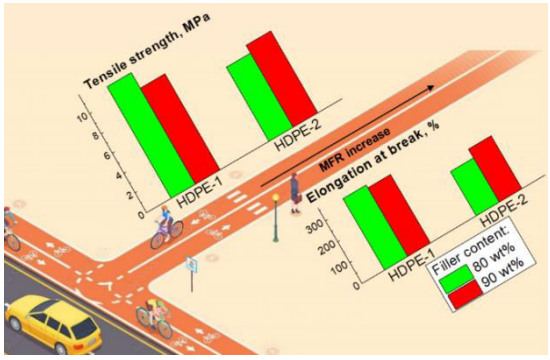
Cite this: *INEOS OPEN*, **2024**, *7 (4–5)*, 154–158
DOI: 10.32931/io2455a

Received 16 October 2024,
Accepted 7 December 2024

http://ineosopen.org

Abstract

Today, rubber crumb is used as the main component in the compositions for construction of soft road surfaces. This report presents the results of investigations on the mechanical properties of rubber–plastic composites containing 80 and 90 wt % of rubber crumb, based on different polyethylene matrices. It was established that, at high contents of rubber particles, there is no need to control the following characteristics of the matrix polymer to obtain the rubber–plastic composites deformable to at least 150%: the melt flow index, the content of HDPE or LDPE in the mixed matrix. The prospects for using the composites obtained were outlined.



Key words: rubber plastics, rubber crumb, polyethylene, mechanical properties.

Introduction

Obsolete rubber products make up a considerable part of solid household and industrial waste. The need for their recycling is dictated not only by the environmental concerns but also by the technical and economic factors, since they represent resources for obtaining new materials.

The main industrially implemented method of recycling rubber waste is grinding. Research into the possibility of reusing rubber crumb or powder, determining the directions of their rational, long-term use have been actively conducted since the 1980s [1, 2]. Nowadays, rubber crumb is widely used in asphalt bitumen coatings [3–5], waterproofing, roofing materials, *etc.* [6]. However, the volumes of consumption of crushed rubber waste are inferior to the volumes of their accumulation [7]. As a result, the investigations aimed at developing materials and products that contribute to the expansion of further application scope of rubber crumb remain highly urgent. This is evidenced by the numerous publications devoted to the problem (see, for example, only some of them: [8–14]).

The materials, the main component of which is rubber crumb, reactivate the valuable properties of elastomers, while saving primary raw materials [12]. The most successful solutions in the production of popular highly filled composites containing up to 90 wt % of rubber particles include coatings for injury-safe fields of sports facilities, running and cycling tracks, and playgrounds [11, 14–16]. For their production, epoxy [17], polyester [18] or polyurethane resins [19, 20] are used as a binder. The production stages of such coatings, including mixing rubber crumb with resin, application, leveling and subsequent curing of a binder in the composition, are similar to the technological stages of construction of road surfaces with asphalt concrete pavement. However, unlike the latter, the process of constructing soft coatings is based mainly on the use of manual labor [21]. This circumstance reduces the productivity of the process. It could seem that the use of devices and mechanisms designed to perform the main technological operations during mixing and laying of asphalt concrete mixtures would solve the problem. It can be assumed that the restraining factor is the corrosion instability of asphalt pavers to the effects of resin components used for these compositions.

Rubber plastics are composites based on polyolefins and crushed waste rubber products [6, 22]. The temperature range for mixing these components when using polyethylene as a matrix polymer does not exceed the temperature range for mixing asphalt bitumen compositions, namely, 120–160 °C [6, 22, 23]. In addition, both polyolefins and rubber crumb are not aggressive substances capable of causing corrosion of machine parts used in the construction of road surfaces. These circumstances allow us to assume that highly filled rubber plastics are potentially suitable for the production of soft road surfaces. This work is devoted to studying the effect of the composition of the matrix polymer and the filler type on the mechanical properties of highly filled rubber plastics containing 80 and 90 wt % of rubber crumb.

Results and discussion

During road construction, the convenience and quality of laying a highly filled mixture with its subsequent compaction depend on the viscosity of the composition, which, in turn, is determined by the binder viscosity and, in the case of rubber plastics, by the viscosity of the matrix polymer. The technological characteristic of the viscosity of thermoplastics is

the melt flow index (MFI). This parameter also allows for estimating an average molecular weight of the polymer [24], which affects such characteristics as critical crack opening, the probability of formation of dangerous defects in the filled polymer, and, in general, the crack resistance of the matrix and the composite based on it [25–28]. For example, the critical crack opening of LDPE-2 (MFI = 2 g/10 min) is 1400 μm and is greater than the corresponding value of LDPE-3 (MFI = 8 g/10 min), which is 1050 μm [29]. The effect of the polymer MFI on its crack resistance is more clearly manifested in the case of HDPE: the critical crack opening of HDPE-1 (MFI = 0.9 g/10 min) is 680 μm and that of HDPE-2 (MFI = 20 g/10 min) is 40 μm [29].

To study the effect of the viscosity of polyethylene matrices on the properties of rubber plastics, LDPEs with the following MFI values were used: 0.3 g/10 min (LDPE-1), 2 g/10 min (LDPE-2), and 7 g/10 min (LDPE-3). Figure 1 (a, c) shows the histograms of the change in tensile strength and strain at break of the rubber plastics containing 80 and 90 wt % of EPDM rubber crumb, depending on the MFI of the matrix. As the MFI of the LDPE increase from 0.3 g/10 min to 7 g/10 min, the tensile strength of these composites decreases by only 3 MPa in the case of the EPDM content of 80 or 90 wt %. The strain at break of the highly filled rubber plastics based on LDPE only slightly depends on the MFI of the matrix polymer.

In the case of the HDPE-based rubber plastics, on passing from the polymer with a low MFI value to the polymer with a high MFI value, both mechanical characteristics of the material reduce (tensile strength and strain at break). The difference in the values of tensile strength between the composites based on HDPE-1 and HDPE-2, containing 90 wt % of rubber particles, is no more than 1.4 MPa, while the strain at break of the same rubber plastics decreases by 74%.

The dependence of the mechanical properties of the highly filled rubber plastics on the MFI of the matrix polymer is caused by a decrease in its crack resistance with an increase in the MFI values, or more correctly, with a decrease in its molecular weight [24–26]. However, independent of the type of polyethylene in use, its MFI, the rubber plastics with 90 wt % of rubber crumb are capable of deforming by more than 200%. Thus, the relative elongation of these composites is in the range of 220–330%, and the tensile strength is 5–10 MPa. This fact indicates the applicability of these composites as external road surfaces [12–16]. In addition, these results allow for concluding that there is no need to impose requirements on the MFI value of the matrix polymer used to obtain them.

From the viewpoint of the rational use of polymer waste, it is reasonable to use not only crushed rubber waste, but also polyolefin waste for obtaining rubber plastics. Polyethylene waste after all stages of its processing and subsequent granulation most often represents a mixture of low- and high-density polyethylenes. The content of each of them in HDPE waste or LDPE waste is a poorly controlled process due to the difficult separation of these polymers. To determine the effect of the polyethylene matrix composition on the mechanical properties of rubber plastics, we studied a number of model mixtures, changing the LDPE/HDPE ratio, namely, 100/0, 30/70, 50/50, 70/30 and 0/100. To avoid heterogeneity in the distribution of one polymer in another, the method of joint

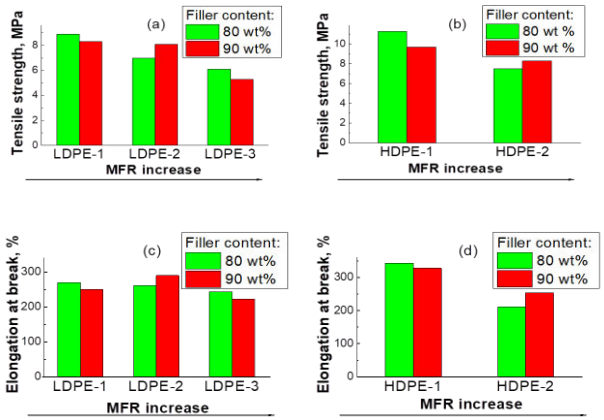


Figure 1. Tensile strength (***a***, ***b***) and strain (***c***, ***d***) at break of rubber plastics based on LDPE (***a***, ***c***) or HDPE (***b***, ***d***) and EPDM particles at different MFI values of the matrix polymers.

elastic deformational grinding was used. Table 3 lists the mechanical properties of the samples of the LDPE/HDPE mixtures of different compositions. At a predominant content of one of the polymers (LDPE or HDPE) in the mixture, the samples deform plastically with the formation of a neck and decompose at a strain of 150% (LDPE/HDPE = 30/70) or 470% (LDPE/HDPE = 70/30). Another deformation behavior is demonstrated by the samples from the mixture with equal LDPE/HDPE contents (50/50). They are destroyed brittlely and their strain at break does not exceed 20% (Table 3).

Figure 2 shows histograms of changes in tensile strength and strain at break of the rubber plastics based on LDPE/HDPE blends with a rubber crumb content of 80 and 90 wt %. The presence of 30 wt % of HDPE in LDPE and, conversely, 30 wt % of HDPE in LDPE does not have a negative effect on the mechanical properties of the highly filled rubber plastics compared to the composites based on 100% LDPE or HDPE, respectively. Moreover, as the proportion of HDPE in the matrix increases, the deformation and strength properties of the rubber plastics increase monotonically. In other words, there is no significant difference in the strength values, and most importantly in the strain at break between the rubber plastics based on the brittle matrix of the LDPE/HDPE composition = 50/50 and based on the plastic matrices with a lower or higher content of LDPE in HDPE (30/70 or 70/30). Moreover, the rubber plastic sample based on LDPE/HDPE = 50/50 is close in properties to that based on HDPE.

The observed effect of leveling the brittle deformation behavior of the matrix when introducing 80 or 90 wt % of rubber particles into it is due to the specific mechanism of deformation of highly filled rubber plastics [30]. At these contents of the elastic filler, they are deformed uniformly at the macro level and non-uniformly at the micro level, while up to some degrees of sample elongation, joint stretching of the matrix with the filler occurs [31]. Let us clarify that non-uniform stretching at the micro level is plastic deformation of the matrix in thin layers between rubber particles. At the elastic filler content of 80 wt % or more, the stretching of thin layers of the matrix will proceed plastically, but without the formation of a neck [32].

As can be seen from Fig. 2, an increase in the content of

rubber particles from 80 to 90 wt % is expected to lead to a slight decrease in the deformation and strength properties of the rubber plastics.

The results obtained allow us to conclude that the content of HDPE in LDPE waste up to 30 wt % or LDPE in HDPE waste up to 50 wt % inclusive does not lead to deterioration of the mechanical properties of the highly filled rubber plastics. Consequently, in the case of obtaining these materials both from crushed rubber waste and from polyethylene waste, there is no need to control the composition of mixed polyethylene waste and, consequently, in the preliminary technological stages of separating LDPE and HDPE. The exclusion of this stage from the general technological process of treatment of polyethylene waste not only simplifies their processing, but also reduces the cost of secondary polyethylene intended for obtaining highly filled composites.

In addition to the deformation and strength properties discussed above, the elastic modulus and residual strain are also important characteristics for safe road surfaces. As can be seen from Table 1, the values of residual strain for the materials containing 90 wt % of EPDM are not high, *i.e.*, rubber plastics behave as rubber-like materials. However, at the lower filler content (80 wt %), the effect of the plastic matrix polymer on these characteristics increases and leads to an increase in residual strain: for LDPE more than two times and for HDPE almost six times.

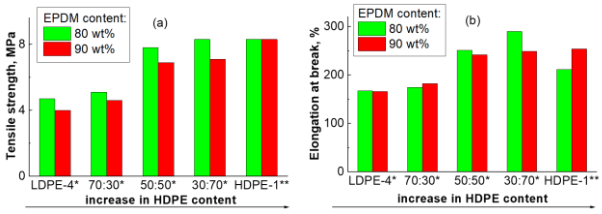


Figure 2. Histograms of changes in tensile strength (***a***) and strain (***b***) of the rubber plastics depending on the HDPE content in the matrix (*—powder, **—granules).

Table 1. Mechanical properties of some rubber plastics containing 80 and 90 wt % of EPDM

Matrix polymer	Tensile strength, MPa		Strain at break, %	
	80	**90**	**80**	**90**
LDPE-2	17	10	56	24
HDPE-2	60	18	66	12
30LDPE/70HDPE	29	23	68	12
50LDPE/50HDPE	28	12	56	15

The results presented above relate to the rubber plastics obtained using crushed rubber technical waste based on EPDM. It was shown earlier that these particles are characterized by good adhesion to polyolefin matrices, which predetermines joint deformation with the matrix polymer. The destruction of rubber plastics is initiated by the rupture of elastic particles [31].

Hence, to obtain highly filled rubber plastic materials with a maximum strain of more than 200% (for example, when using LDPE, Fig. 2b), it is preferable to use rubber crumb based on EPDM. However, the main "source of accumulation" of rubber waste are worn-out automobile tires, the main component of which is isoprene and nitrile rubber. Unlike EPDM particles, rubber crumb obtained by grinding worn-out automobile tires has poor adhesion to polyethylene [30, 31]. In this case, rubber particles peel off from the matrix polymer during stretching of the rubber plastic samples, forming pores that quickly develop into dangerous defects.

For comparison, Table 2 presents the mechanical properties of the rubber plastics based on LDPE-3 containing 80 wt % of EPDM rubber particles and automobile tires (FGRP). In the first case, the strain at break is higher.

One of the ways to improve adhesion between the matrix and the filler is to introduce a compatibilizer. In the case of rubber plastics, this function can be performed by PEVA [32]. It was previously shown that 5 wt % relative to the matrix polymer is the optimal concentration of this additive [33]. To obtain modified rubber plastics, LDPE-3 was used, the content of FGRP was 80 wt %. Table 2 shows the mechanical properties of the resulting materials. When PEVA was used, the deformation properties of the material increased almost two times, but did not reach the level of deformation of the composite with EPDM particles.

The question arises about the suitability of FGRP for obtaining soft injury-safe coatings if the ultimate strain of the material is used as a criterion. Currently, there are no documents regulating the characteristics of injury-safe soft coatings based on rubber crumb. Thus, in accordance with the TU (Specifications) developed at the OOO NPP Ekoresurs (Penza, Russia), the strength of such coatings should be at least 1.9–2.1 MPa with a strain at break of 130–160% [34]. According to these parameters, highly filled rubber plastics based on modified polyethylene and FGRP are suitable for obtaining such coatings.

Table 2. Mechanical properties of different rubber plastics containing 80 wt % of crushed rubber particles

Matrix polymer	Filler	Tensile strength, MPa	Strain at break, %
LDPE-3	EPDM	6.1 ± 0.5	244 ± 20
	FGRP	2.5 ± 0.3	60 ± 10
LDPE-3 5 wt % of PEVA	FGRP	3.4 ± 0.4	130 ± 20
Composition based on SKDP-N (TU (Specifications) 38.103342-82) [34]		1.9–2.2	130–160

Experimental section

Materials

The work was concerned with HDPE of grades F 3802B (HDPE-1) produced by OOO Stavrolen and 277-73 (HDPE-2) produced by OAO Kazanorgsintez, as well as LDPE of grades 10204-003 (LDPE-1), 15803-020 (LDPE-2), 16803-070 (LDPE-3), and 10803-020 (LDPE-4) produced by OAO Kazanorgsintez. In addition, the mixtures with different LDPE/HDPE ratios were used as the polymer matrices. The properties of the used HDPE, LDPE, and their mixtures are presented in Table 3. Ethylene–vinyl acetate copolymer (PEVA) of grade 11306-075 produced by OAO Kazanorgsintez was used as a modifier.

Two types of rubber crumb were used as the fillers:

– rubber crumb obtained by elastic deformational grinding of automobile seals based on ethylene propylene diene rubber (EPDM);

Table 3. Properties of the matrix polymers

Parameter	HDPE[a]		LDPE[b]				LDPE-4/HDPE-2 mixtures[b]		
	HDPE-1	HDPE-2	LDPE-1	LDPE-2	LDPE-3	LDPE-4	30/70	50/50	70/30
MFI at 190 °C, g/10 min	0.9	21.0	0.3	2.0	7.0	2.0	10.3	6.5	4.0
Upper yield point, MPa	21	29	11	10	8	9	19	20	13
Neck propagation stress, MPa	16	16	11	10	8	9	15	8	11
Tensile strength, MPa	27	16	13	17	13	12	15	8	14
Strain at break, %	720	280	555	600	450	550	151	20	473

[a] MFI at loading of 5 kg; [b] MFI at loading of 2.16 kg

– finely ground rubber powder (FGRP), obtained by grinding worn-out automobile tires, produced by the Chekhov Regenerative Plant (TU (Specifications) 38.108035).

Sample production technique

Granules of the polyethylene or LDPE/HDPE powder mixture and rubber crumb were loaded into a chamber of a single-screw laboratory extruder (L/D = 12) with two heating zones (Table 4). After mixing, the resulting composition was processed into plates by hot pressing at 150–160 °C and a pressure of 10 MPa for 10 min, followed by cooling under pressure to 20 °C for ~15 min. Then, double-sided blades were cut from the plates.

The powder LDPE/HDPE mixtures were obtained by elastic deformational grinding, preliminarily mixing the polymer granules at a given ratio [35].

Table 4. Temperatures in the heating zones of the extruder during mixing the polymers with the filler and pressing of the mixtures

Polymer	Temperatures in the extruder zones, °C		Pressing temperature, °C
	T_1	T_2	
LDPE	140	150	150
HDPE	160	170	160
LDPE/HDPE mixtures	160	170	160

It should be noted that it is impossible to obtain a monolithic sample from the rubber crumb based on EPDM (100%) under the same hot-pressing conditions.

Methods

The melt flow index was determined according to GOST (State Standard) 11645-2021 using an IIRT unit with a capillary 8 mm long and 2.09 mm in diameter. The temperature and load during measurements are given in Table 3.

The mechanical properties of the resulting samples were determined in the uniaxial tension mode on a 203P-005 dynamometer with a stretching rate of 20 mm/min. The samples in use were double-sided blades with a working area of 5×35 mm and a thickness of 2 mm.

Conclusions

Based on the results obtained, the following conclusions can be outlined. Independent of the polyethylene type in use, the composition of the polyethylene matrix, rubber plastics containing 90 wt % of rubber crumb based on EPDM are capable of deforming by more than 150%: the relative elongation of these composites is in the range of 160–330% and the tensile strength is 4–10 MPa. The mechanical characteristics of the highly filled materials allow us to consider these compositions as potentially suitable for external road surfaces.

The use of crushed rubber based on EPDM in the formulation of road surfaces allows for neglecting (or reducing) such requirements for the matrix polyethylene as the type of polyethylene, the MFI of the matrix polymer, and the content of LDPE or HDPE in the mixture. In the case of crushed rubber from worn-out automobile tires, it is necessary to provide for the introduction of an additional component into the formulation, namely, a compatibilizer that increases the level of adhesion between the surface of the rubber particles and the matrix.

Based on the values of elastic modulus and residual strain, the highly filled rubber plastics can be classified as rubber-like materials and, as a consequence, in the application to road surfaces, as soft, injury-safe surfaces. The advantage of rubber plastics over polymer coatings based on thermoset plastics is the possibility of mixing and subsequent laying using standard road construction equipment.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00277-24-00).

Corresponding author

* E-mail: dia-diaa@bk.ru (V. A. Shishkinskaya).

References

1. V. M. Makarov, V. F. Drozdovsky, The use of shock-absorbing tires and waste rubber products, Khimiya, Leningrad, **1986** (in Russian).
2. S. A. Wolfson, V. G. Nikolsky, *Plast. Massy*, **1997**, *5*, 39–44.
3. N. S. Mashaan, A. H. Ali, M. R. Karim, M. Abdelaziz, *Sci. World J.*, **2014**, *2014*, 214612. DOI: 10.1155/2014/214612
4. H. R. Radeef, N. A. Hassan, Y. Katman, M. Z. H. Mahmud, A. R. Z. Abidin, C. R. Ismail, *Case Stud. Constr. Mater.*, **2022**, *16*, e00913. DOI: 10.1016/j.cscm.2022.e00913
5. S. Aldagari, J. Karam, M. Kazemi, K. Kaloush, E. H. Fini, *J. Cleaner Prod.*, **2024**, *437*, 140540. DOI: 10.1016/j.jclepro.2023.140540
6. Patent RF 2129133 C1, **1999**.
7. B. Adhikari, D. De, S. Maiti, *Prog. Polym. Sci.*, **2000**, *25*, 909–948. DOI: 10.1016/S0079-6700(00)00020-4
8. A. J. Topacio, N. C. Gozo, S. R. V. Marquez, R. V. M. Poblete, H. S. Ramos, *IJCSER*, **2015**, *3*, 95–132.
9. N. I. Potrasov, *Tverd. Bytovye Otkhody*, **2016**, *5*, 41–43.
10. A. Mohajerani, L. Burnett, J. V. Smith, S. Markovski, G. Rodwell, M. T. Rahman, H. Kurmus, M. Mirzababaei, A.

Arulrajah, S. Horpibulsuk, F. Maghool, *Resour., Conserv., Recycl.*, **2020**, *155*, 104679. DOI: 10.1016/j.resconrec.2020.104679

11. A. Hejna, J. Korol, M. Przybysz-Romatowska, L. Zedler, B. Chmielnicki, K. Formela, *Waste Manage.*, **2020**, *108*, 106–118. DOI: 10.1016/j.wasman.2020.04.032
12. V. Lapkovskis, V. Mironovs, A. Kasperovich, V. Myadelets, D. Goljandin, *Recycling*, **2020**, *5*, 32. DOI: 10.3390/recycling5040032
13. N. Ayrilmis, U. Buyuksari, E. Avci, *Waste Manage.*, **2009**, *29*, 2553–2557. DOI: 10.1016/j.wasman.2009.05.017
14. R. M. Dolinskaya, N. R. Prokopchuk, *Proc. BSTU*, **2022**, *2*, 37–47.
15. A. D. Gusev, L. N. Petryanina, M. A. Derina, *Ecol. Ind. Russ.*, **2021**, *25*, 12–17. DOI: 10.18412/1816-0395-2021-2-12-17
16. T. Moreno, A. Balasch, R. Bartrolí, E. Eljarrat, *Sci. Total Environ.*, **2023**, *868*, 161648. DOI: 10.1016/j.scitotenv.2023.161648
17. R. Bagheri, B. T. Marouf, R. A. Pearson, *Polym. Rev.*, **2009**, *49*, 201–225. DOI: 10.1080/15583720903048227
18. B. Abu-Jdayil, A. H. Mourad, A. Hussain, *Constr. Build. Mater.*, **2016**, *105*, 472–479. DOI: 10.1016/j.conbuildmat.2015.12.180
19. A. Danch, W. W. Sułkowski, M. Moczyn´ski, A. Radon´, F. Stelzer, S. Jurga, *J. Appl. Polym. Sci.*, **2004**, *94*, 1186–1193. DOI: 10.1002/app.21027
20. L. S. Durosov, M. E. Solovyov, V. I. Salnikova, A. G. Kireev, A. A. Kirikov, *ChemChemTech*, **2012**, *55*, 68–70.
21. https://unionpolymers.ru.
22. V. P. Skvortsov, L. O. Bunina, V. N. Kuleznev, V. I. Sergeev, E. V. Grosheva, G. Z. Veksler, *Plast. Massy*, **1988**, *6*, 48–49.
23. V. P. Podolsky, P. I. Pospelov, A. V. Glagolev, A. V. Smirnov, Construction of highways. Road surfaces, Akademiya, Moscow, **2015** (in Russian).
24. V. B. Bogutsky, L. B. Shron, *J. Sci. Educ. North-West Russ.*, **2021**, *7*, 22-29.
25. G. M. Bartenev, Strength and mechanism of destruction of polymers, Khimiya, Moscow, **1984** (in Russian).
26. H. H. Kausch, Polymer fracture, Springer, Berlin, **1978**.
27. S. Bazhenov, *J. Mater. Sci.*, **1997**, *32*, 797–802. DOI: 10.1023/A:1018572726615
28. J. Kaiser, C. Bonten, M. Kreutzbruck, *Proc. Struct. Integr.*, **2024**, *54*, 26–33. DOI: 10.1016/j.prostr.2024.01.052
29. O. A. Serenko, S. L. Bazhenov, I. N. Nasrullaev, A. A. Berlin, *Polym. Sci.*, *Ser. A*, **2005**, *47*, 49–56.
30. O. A. Serenko, G. P. Goncharuk, E. S. Obolonkova, S. L. Bazhenov, *Polym. Sci.*, *Ser. A*, **2006**, *48*, 302–313. DOI: 10.1134/S0965545X06030114
31. O. A. Serenko, A. A. Karaeva, G. P. Goncharuk, T. V. Zaderenko, S. L. Bazhenov, *Tech. Phys.*, **2009**, *54*, 854–859. DOI: 10.1134/S1063784209060139
32. D. L. Titov, S. A. Pershin, M. I. Knunyants, A. N. Kryuchkov, *Vysokomol. Soedin*., *Ser. A*, **1994**, *36*, 1353–1357.
33. O. A. Serenko, V. S. Avinkin, M. Yu. Vdovin, A. N. Kryuchkov, *Vysokomol. Soedin.*, *Ser. A*, **2001**, *43*, 246–251.
34. Patent RF 2263693 C1, **2005**.
35. A. N. Kryuchkov, I. Y. Dorfman, N. A. Yerina, M. I. Knunyants, E. V. Prut, N. S. Yenikolopyan, *Polym. Sci*., **1985**, *27*, 2230–2235. DOI: 10.1016/0032-3950(85)90510-6