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НОВЫЕ ТЕРМОЭЛАСТОПЛАСТЫ НА ОСНОВЕ ПВДФ/КАУЧУК СКФ-32: ВЛИЯНИЕ СОСТАВА НА ТЕХНОЛОГИЧЕСКИЕ И ЭКСПЛУАТАЦИОННЫЕ СВОЙСТВА

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В работе исследованы смесевые термоэластопласты на основе фторкаучука СКФ-32 и поливинилиденфторида (содержание поливинилиденфторида от 30 до 70% относительно каучука), полученные с использованием роторного микросмесителя типа Brabender, которые могут выступать альтернативой традиционным масло-бензостойким резинам на основе бутадиен-нитрильных каучуков и могут быть использованы для производства рукавов, шлангов и трубок для перекачки агрессивных жидкостей и газов, изоляции проводов и кабелей, емкостей для хранения горючего, клапанов и др. Для полученных материалов могут быть использованы традиционные методы переработки пластмасс. В полученных композициях с ростом содержания поливинилиденфторида отмечается увеличение доли кристаллической фазы, что подтверждено данными ИК-Фурье-спектроскопии и дифференциальной сканирующей калориметрии. Показано, что с ростом содержания ПВДФ значения твердости и прочности композиций увеличиваются, при этом полученные значения напряжения при разрыве для композиций, содержащих 50% и более ПВДФ выше, чем для традиционной масло-бензостойкой резины ИРП 1078. Подтверждено, что полученные композиции обладают высокой стойкостью к действию бензина АИ-92, серной кислоты концентрацией 80%, натрия гидроокиси концентрацией 50% и масла И-40, а также сохраняют свои физико-механические свойства даже после трех циклов повторной переработки. Для композиции, в которой соотношение термопласт : эластомер составляло 1:1, была проведена вулканизация с использованием перекисной вулканизующей системы в различных дозировках. Протекание динамической вулканизации подтверждено снижением степени набухания полученных композиций в растворителях с ростом содержания вулканизующего агента. Динамическая вулканизация с использованием перекиси в качестве вулканизующего агента не привела к существенному возрастанию физико-механических показателей, но при этом обеспечила рост агрессивостойкости для полученного материала.

Ключевые слова: термоэластопласт, фторкаучук СКФ-32, поливинилиденфторид, динамическая вулканизация, агрессивостойкость

NOVEL THERMOPLASTIC ELASTOMERS BASED ON PVDF/SKF-32: EFFECT OF COMPOSITION ON TECHNOLOGICAL AND PERFORMANCE CHARACTERISTICS

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Thermoplastic elastomers (TPE) based on SKF-32 fluorine rubber and polyvinylidene fluoride, PVDF (polyvinylidene fluoride content ranges from 30 to 70% relative to rubber) were investigated. The mixes have been produced by using a Brabender-type rotary micromixer. Such thermoplastic elastomers can be an alternative to traditional oil & fuel resistant butadiene-nitrile-based rubbers and can be used in manufacture of sleeves, hoses and tubes for pumping aggressive liquids and gases, wires/cables insulation, fuel storage tanks, valves, etc. Traditional methods of plastics processing can be used to manufacture this materials. It was established that the crystallinity degree increases with the rise of PVDF content. That fact is confirmed by the IR-Fourier spectroscopy data and differential scanning calorimetry. It was shown that the hardness and strength of TPEs increases with the rise of PVDF content. The tensile stress for TPEs containing 50% or more of PVDF are higher than those for conventional oil & fuel resistant rubber IRP 1078. The obtained TPEs possess high resistance against AI-92 grade gasoline, 80% sulfuric acid, 50% sodium hydroxide, and I-40 oil. They also retain their physical and mechanical properties even after three cycles of reprocessing. The TPE with the 1:1 thermoplastic : elastomer ratio, has been vulcanized using a peroxide vulcanizing system at varying concentrations. The dynamic vulcanization is confirmed by a decrease in the swelling degree of the obtained materials in solvents with an increase in the content of the vulcanizing agent. Peroxide dynamic vulcanization has not lead to a significant increase in physical and mechanical parameters, however, it resulted in an increase in chemical resistance of against aggressive solvents.

Key words: thermoplastic elastomer, SKF-32 fluoroelastomer, polyvinylidene fluoride, dynamic vulcanization, chemical resistance

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INTRODUCTION

Industry for hazardous operating conditions uses a special type of rubber – fluorine rubber. The most widely available on the market are copolymers of hexafluoropropylene and vinylidene fluoride, manufactured by The Chemours Company under the trademark of Viton™, and Halopolymer, JSC under the trademark of SKF-26. The copolymers of vinylidene fluoride and trifluorochloroethylene are also marketed under the trademarks of Kel F (3M Company) and SKF-32 (Halopolymer, JSC).

Due to the presence of fluorine atoms, the strength of the fluorine-carbon bond and the absence of unsaturated bonds in the main chain, the copolymer-based rubbers demonstrate excellent chemical resistance, high mechanical strength, a wide range of operating temperatures, and, in addition, are incombustible [1-6]. Fluorine rubbers are used to manufacture sealing rings, cuffs, sealants, coatings, vibration dampers, plugs, diaphragms, heat-resistant sealing rings, sleeves, hoses and tubes for pumping hot aggressive liquids and gases, wire/cable insulation, fuel tanks, valves and other products contacting oils, oxidants and other aggressive media at temperatures of 200 °C and above.

At operating temperature interval is –40 - +150 °C butadiene-nitrile rubber, for example IRP 1078, can be used to insulate wires and cables, seals, valves and other oil-contacting parts [7, 8].

Manufacturing of rubbers, including the fluorine- and nitrile-butadiene ones, implies the mandatory vulcanization stage, meaning significant per unit manufacture time, the use of complex equipment and hefty investments. Moreover, due to the presence of cross-linked structures formed in the process of vulcanization, rubber is either completely unrecyclable, or such recycling is cost-ineffective and does not produce a value-added product [9], while the waste accumulation can be a significant ecological problem.

As an alternative to conventional rubbers, thermoplastic elastomers (TPE) are increasingly used. These materials combine two important qualities: elasticity at operation, which implies their application in the same areas as conventional elastomers, and the possibility of recycling as a thermoplastic polymer [10]. The TPE manufacture does not imply a separate vulcanization stage, which reduces capital and current production costs.

The TPEs include two groups of materials: block copolymers, the properties of which are set at their synthesis and the combinations of hard polymer/elastomer. The combinations of hard polymer/elastomer are gaining in importance, since in this case the production raw base oriented, while the required properties can be easily adjusted by changing the components ratio. The combination can be simple either non-cross-linked rubber component (mixed TPE) mixes, or mixes in which the rubber phase is cross-linked through the so-called dynamic vulcanization (thermoplastic vulcanizate, TPV). Thermoplastic vulcanizates, of cross-linked rubber as a dispersed component and a thermoplastic as a continuous phase [11-13], are actively used as a replacement for non-recyclable rubbers, which contributes to resource saving and environmental protection [14].

Authors have analyzed publications on TPEs containing fluorine rubber as a rubber component, and found that such studies are not numerous. The majority of the studies cover, only rubbers, which are a copolymer of hexafluoropropylene and vinylidene fluoride, as the elastomeric phase. Various type of plastics have been mentioned as a thermoplastic component in such combinations: polyamide-6 [15, 16], polyvinylidene fluoride [17-19], thermoplastic polyurethane [20, 21], and a copolymer of ethylene and trifluorochloroethylene [22].

The publications mention both simple mixtures and cross-linked rubber component mixes. Vulcanizing systems mentioned are amine [16, 17], phenolic [17, 18, 22], peroxide [17, 18, 19, 22] ones.

Only a few studies are devoted to the study of TPEs, containing a copolymer of trifluoroethylene and vinylidene fluoride [20, 21] as a rubber component.

The aim of this study is a creating SKF-32 rubber and polyvinylidene fluoride (PVDF) based TPE and TPV, which can be recycled, have high chemical resistance, and can retain their operating properties at temperatures up to +150 °C. Such materials can be an alternative to conventional oil & fuel resistant butadiene-nitrile rubbers, while demonstrating much better manufacturability.

METHODOLOGY

Fluoroplast-2M grade A (PVDF) polyvinylidene fluoride and SKF-32 rubber, a copolymer of trifluorochloroethylene and vinylidene fluoridefluorine were used.

Peroxide – di-(2-tert-butyl peroxyisopropyl)-benzene (Retic 40 CC) was used as the vulcanizing agent.

Compositions with a PVDF content of 30 to 70% relative to SKF-32 rubber were prepared using a 0.1 L Brabender-type rotary micromixer (Russia) at a temperature of 175 °C at 40 rpm. In total the mixing lasted for 15 min.

The rheological characteristics determine the possibility of processing. The melt flow index (MFI) was astimated according GOST 11645-2021 (ASTM D 1238) at a temperature of 230 °C and a load of 21.6 kg at the IIRT-5M unit (Russia).

Identification of functional groups in the structure of polymer materials was carried out by the IR Fourier spectrometer Infralum FT-801 (Russia).

To assess the temperature and enthalpy of melting, the crystallinity degree, a Shimadzu DSC-60 (Japan) differential scanning calorimeter was used, as it was equipped with a purge air supply (150 ml/min). Samples of 15±1 mg were placed in sealed aluminum crucibles. Thermal characteristics of polymeric materials might vary depending on their thermal history (molding, curing, heating conditions); therefore, measurements were taken twice. The samples were heated at a rate of 10 °C/min from 40 to 200 °C. The results obtained during the second measurement were used to estimate the melting point (Tm), the enthalpy of melting (Hm) and the crystallinity degree. The crystallinity degree (χ_C) was calculated by the following equation (1):

$$\chi_C = \frac{H_m}{H_m^*} \cdot 100\%, \qquad (1)$$

where Hm is the melting enthalpy calculated from the melting peak of the DSC curve, J/g; H∗m is the melting enthalpy of totally crystallized PVDF (104.7 J/g), J/g [23, 24].

The tensile strenght and elongation at break of the materials were astimated according ASTM D638 at the Shimadzu AGX (Japan) machine at room temperature on samples Type 4 at 500 mm/min of grip travel speed.

The hardness of the materials was astimated according ASTM D2240 by using two types of durometers (A, D) at room temperature.

To investigate chemical resistance acetone of the "pure for analysis" grade per GOST 2603-79, sodium hydroxide of the "pure for analysis" grade per GOST 4328-77, sulfuric acid of the "chemically pure" grade per GOST 4204-77, glacial acetic acid of the "chemically pure" grade per GOST 61-75 rev. 1.3 manufactured by CHIMREAKTIV, JSC (Nizhny Novgorod, Russia), EKTO-92 (AI-92-K5) motor gasoline per GOST 32513-2013 (Togliattinefteprodukt Service, LLC petrol depot), and I-40 industrial oil per GOST 20799-88 (LLK-INTERNATION, LLC lubricants manufacturing company) were used.

Chemical resistance was assessed by the weight change in samples the size of 10×10×2 mm after effect of solvents (acetone, AI-92 gasoline, 80% sulfuric acid, 50% sodium hydroxide, glacial acetic acid, I-40 oil) for 24 h at room temperature.

RESULTS AND DISCUSSION

The solubility parameters for PVDF and SKF-32 rubber were estimated by the grouping method [25], and were as 13.7 J/m^3 and 14.5 J/m^3, respectively. Comparing the solubility parameters of PVDF and *SKF-32*, authors expect their high compatibility in the mixture.

The rheological and temperature characteristics of obtained TPEs are presented in Table 1. IR spectra of the obtained comcompositions are shown in Fig. 1.

Table 1

Rheological and temperature characteristics of the compositions under study

Таблица 1. **Реологические и температурные характеристики исследуемых композиций**

Index	Value				
SKF-32/ PVDF ratio	70/30	60/40	50/50	40/60	30/70
MFI, g/10 min	1.4	3.2	5.3	9.1	15
Tm, °C	158.16	158.46	158.92	158.3	159.43
Hm, J/g	-8.47	-10.95	-11.13	-19.07	-24.17
χ_C, %	8.1	10.5	10.6	18.2	23.1

As it is shown in Table 1, the rise of PVDF content, caused the increase in the MFI. So the traditntional plastics processing methods such as injection molding and extrusion can be used (usually polymer materials with lower MFI values are better suited for extrusion rather than for injection molding) [26].

Analysis of the TPE' IR-spectra demonstrated that in all cases the increase in the PVDF content in the compositionn caused an increase in the peak intensity at 840 cm^{-1} wavelength, which indicated the presence of the crystalline phase [27-29]. The obtained data correlated with the DSC results: the crystallinity degree of materials also increased with the rise of the PVDF content.

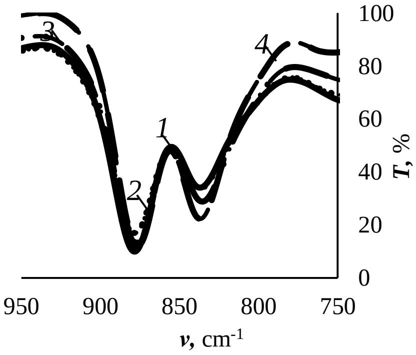

Fig. 1. Fragments of IR spectra for TPE with different SKF-32/PVDF ratio: 1 – 60/40; 2 – 50/50; 3 – 40/60; 4 – 30/70

Рис. 1. Фрагменты ИК спектров композиций с различным соотношением СКФ-32/ПВДФ: 1 – 60/40; 2 – 50/50; 3 – 40/60; 4 – 30/70

Physical and mechanical properties of the obtained compounds are presented in Table 2.

As it can be seeb the tensile strength f_z increases with the rise of PVDF content. The tensile strength f_z of prepared TPEs lower than those described in publications for PVDF/FKM composition [17]. Probably the reason is the initially lower strength properties of the SKF-32 rubber [1]. At the same time, the tensile strength f_z for compositions containing 50% or more PVDF are higher than those for IRP 1078 rubber (11.8 MPa according to [7]). The hardness of the TPEs increases with the rise of PVDF content, and varies in the range from 34 Shore D to 97 Shore A, which makes it possible to choose in manufacturing either a more elastic material or a more rigid one.

Table 2

Physical and mechanical properties of studied mixed TPEs

***Таблица 1.* Физико-механические показатели исследуемых смесевых ТЭП**

Index	Value				
SKF-32/ PVDF ratio	70/30	60/40	50/50	40/60	30/70
fz, MPa	5.8	8.2	11.3	14.2	17.1
ε, %	167	145	128	126	95
Hardness Shore A	71	89	92	95	97
Hardness Shore D	34	40	50	54	60

To confirm the possibility of recycling, the TPEs were ground, homogenized in a Brabender-type micromixer for 7 min at a temperature of 180 °C at 40 rpm. This process was repeated three times. Physical and mechanical parameters for TPEs after each re-processing cycle are shown in Fig. 2.

It was found out that after three cycles of re-processing there was no deterioration of elastic-strength characteristics. The stress values at 100% elongation f100 after three cycles of re-processing practically did not change dramatically, which confirm the absence of any processes of either curing or destruction.

The increase of tensile strength and stress values at 100% elongation in some cases can be explained by an improvement of ingredients dispergation in each subsequent re-processing cycle (in all cases the values are in the range ±10%).

Under operational conditions, the materials are exposed not only to various mechanical influences, but also to some external factors, including aggressive environment. So the chemical resistance **(**swelling degree, *Q***)** of obtained TPEs were investigated.

After the exposition in AI-92 gasoline, 80% sulfuric acid, 50% sodium hydroxide, and I-40 oil for 24 h there wasn't observed any changing in mass. The change in the mass of all studied specimens did not exceed 1% even after three months exposure.

Since the effect of the selected solvents was insignificant and did not make it possible to assess the chemical resistance of the materials, the experiment with the solvents to which vulcanizates based on SKF-32 rubber are inherently unstable (acetone and glacial acetic acid) were organized. Exposure to acetone and glacial acetic acid caused a significant change in mass (Fig. 3).

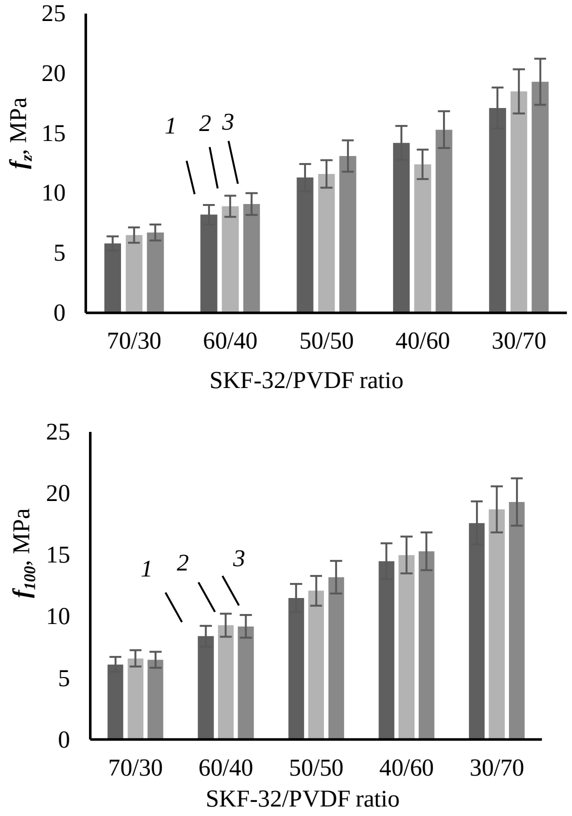

Fig. 2. Properties change after three cycles of re-processing of TPEs: 1 – the first; 2 – the second; 3 – the third cycles of re-processing a) tensile strength, b) stress values at 100% elongation
Рис. 2. Изменение свойств после трех циклов переработки композиций СКФ-32/ПВДФ: 1 – первый; 2 – второй; 3 – третий циклы переработки

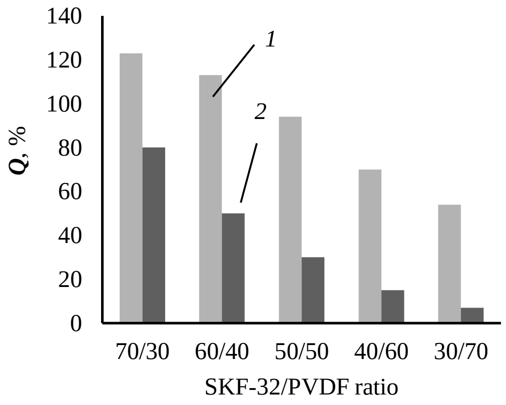

Fig. 3. Swelling degree of TPEs in acetone (1) and glacial acetic acid (2)
Рис. 3. Степень набухания композиций в ацетоне (1) и ледяной уксусной кислоте (2)

As Fig. 3 demonstrates, the resistance of the TPEs to acetone and glacial acetic acid decreases with an increase of SKF-32 content because of low resistance of the rubber itself.

It is reported [30, 31] that dynamic vulcanization leads to improvement in the physical and mechanical properties as well as the chemical resistance of thermoplastic elastomers.

In this regard, it was decided to vulcanize the composition with the thermoplastic : elastomer ratio of 1:1 using a peroxide vulcanizing system (Retic 40 CC). This vulcanizing system was chose because it is safe for storage and handling and easily introduce into the rubber stock [2]. This ratio is selected on the basis of two considerations. Firstly, to obtain a highly elastic TPV, the elastomer/thermoplastic ratio is usually supposed to be greater than or equal to 1 [31]. Secondly, for TPE with such ratio tensile streangh comparable to those of IRP-1078 vulcanizate [7], while the elongation at break exceeds 100%, which makes it possible to class the material as an elastic one.

The TPV was carried out in two stages. At the first stage, a mix of rubber and a vulcanizing agent was rolled at 0.5 and 1 ppm of rubber. The mix of rubber and a vulcanizing agent have been prepared in LB800 160/160 rollers, at 45-55 °C. At the second stage the mixing of thermoplastic and rubber containing the vulcanizing agent was carried out in a Brabender-type micromixer at 180 °C and 40 rpm; the duration of mixing after the introduction of all the components was three min. To get 2 mm-thick plates, the composition were then placed under a press at a temperature of 180 °C for two minutes. The confirmation of complete of the dynamic vulcanization was the decreacing of swelling degree in solvents with the rise of vulcanization agent content, as described in detail below.

Physical and mechanical parameters and resistance to acetone and glacial acetic acid were determined for the obtained TPVs. The results are presented in Table 3 (for convenience, the table presents numerical values for TPE with a similar SKF-32/PVDF ratio).

As it is evident from the data in the presented table, the dynamic vulcanization affected the strength properties and chemical resistance. The resistance of the 1 ppm vulcanizing group containing TPV against acetone increased by more than 25% , against glacial acetic acid – by 40%. The cTPVs strength characteristics changed slightly, seemingly due to the low rubber crosslinking efficiency by peroxide in the absence of free radical acceptors, e.g. triallyl isocyanurate (TAIC) [2].

Table 3

Characteristics of dynamically vulcanized TPVs with different contents of vulcanizing agent

Таблица 3. **Характеристика динамически вулканизованных ТЭП с разным содержанием вулканизующего агента**

Index	Vulcanizing group content, ppm		
	0	0.5	1
fz, MPa	11.3	11.7	13.6
ε, %	128	103	134
Swelling degree in acetone, %	94	87	68
Swelling degree in glacial acetic acid, %	30	19	18

CONCLUSION

The given research has established that, based on SKF-32 rubber and PVDF, thermoplastic elastomers resistant to acids and bases, oils and gasoline can be obtained. Such materials can be recycled by the traditntional plastics processing methods such as injection molding, extrusion, etc. The possibility of recycling of the produced materials has been confirmed. The operational and manufacturing properties can be adjusted within a wide range by varying the ratio of the components used.

An example of a compound containing thermoplastic (PVDF) and elastomer (SKF-32) in 1:1 ratio has demonstrated the possibility of dynamic peroxide vulcanization. Peroxide dynamic vulcanization has not lead to a significant increase in physical and mechanical parameters, however, at the same time, it promotes an increase in chemical resistance of the produced material.

Further research is aimed at the peroxide dynamic vulcanization facilitated by free radical acceptors, copper-added vulcanization, and determination of the operational temperature intervals of the obtained materials.

Possible application areas of the developed materials may be seals, aggressive-media pipes-lines, and storage tanks and containers lining.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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