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МОДИФИКАЦИЯ НИЗКОМОЛЕКУЛЯРНОГО СОПОЛИМЕРА ИЗ ПОБОЧНЫХ ПРОДУКТОВ ПРОИЗВОДСТВА БУТАДИЕНОВОГО КАУЧУКА ВТОРИЧНЫМ ПЕНОПОЛИСТИРОЛОМ

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Из литературных данных известно, что в промышленном и гражданском строительстве широко используется пенополистирол в качестве теплоизоляционного материала, который является востребованным на рынке. В целях решения ряда экологических задач, в данной работе предприняты попытки химического совмещения двух видов полимерных отходов (побочные продукты нефтехимии в присутствии пенополистирола) для получения пропитывающих составов на молекулярном уровне за счет проведения их совместной деструкции и применения для защитной обработки древесных материалов. Полученные древеснополимерные композиты из натуральной древесины (березы) и древесноволокнистых плит (ДВП) были исследованы на устойчивость к действию воды и влаги. Показатели испытаний древесины на водопоглощение и разбухание в радиальном и тангенциальном направлениях указывают на то, что исследуемые образцы обладают повышенными гидрофобными свойствами. Модифицированные ДВП приобретают кроме повышенных гидрофобных свойств и более высокие прочностные показатели. Это связано со сшивкой молекул олигомера в структурах древесины с образованием древеснополимерного каркаса и образованием водородных и эфирных связей между компонетами древесины и окисленным модифицированным олигомером. Образование таких связей позволяет снизить такой недостаток пропитывающих составов, как вымываемость из изделий в процессе их эксплуатации. Уменьшение непредельности олигомерного модификатора снижает его гидрофильные свойства. Комплексное использование отходов и побочных продуктов позволяет целенаправленно утилизировать их и применять для защитной обработки материалов, в состав которых входят древесные компоненты, что способствует повышению срока службы изделий.

Ключевые слова: олигомеры, бутадиеновые каучуки, лакокрасочные материалы, пенополистирол, стирол, макромолекулы, деструкция, водопоглащение, деполимеризация

MODIFICATION OF LOW-MOLECULAR COPOLYMER FROM BY-PRODUCTS OF BUTADIENE RUBBER BY SECONDARY EXPANDED POLYSTYRENE

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From the literature data it is known that in industrial and civil construction it is widely used expanded polystyrene as a heat-insulating material, which is in demand on the market. In order to solve a number of ecological problems, in this work attempts have been made to chemically combine two types of polymer waste (by-products of petrochemistry in the presence of expanded polystyrene) to obtain impregnating compounds at the molecular level by carrying out their joint destruction and applying wood products for protective treatment. Obtained wood-polymer composites from natural wood (birch) and wood fiber boards (DVP) were investigated for resistance to water and moisture. Indicators of tests of wood for water absorption and swelling in the radial and tangential directions indicate that the samples under investigation have increased hydrophobic properties. Modified fiberboards acquire, in addition to increased hydrophobic properties and higher strength parameters. This is due to the cross-linking of oligomer molecules in wood structures with the formation of a wood-polymer framework and the formation of hydrogen and ether bonds between the wood components and the oxidized modified oligomer. The formation of such bonds makes it possible to reduce such a shortage of impregnating compositions as washability from products during their operation. Reducing the uncertainty of the oligomeric modifier reduces its hydrophilic properties. Integrated use of waste and by-products allows to purposefully dispose of them and use them for protective processing of materials, which include wood components, which contributes to the increase of the service life of products.

Key words: oligomers, butadiene rubbers, paint and varnish materials, expanded polystyrene, styrene, macromolecules, destruction, water absorption, depolymerization

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INTRODUCTION

At present, much attention is paid to the processing and use of waste and by-products from various industries. An integrated approach to the solution of this issue allows more complete and rational use of existing wastes [1, 2]. For example, production of low-molecular polymeric products (oligomers) based on by-products of the production of butadiene rubber (PPPB), which for several years was used in the production of paint and varnish materials (LMB), was mastered on an industrial scale [3, 4]. The main links in the structure of the PPPB-based oligomer were styrene, 4-vinylcyclohexene (VCH), cyclododecatriene-1,5,9 (CDT), *n*-dodecatetraene-2,4,6,10 (NDT), and others [5-7].

The best complex of properties were oligomers based on PPPB, obtained with a styrene content in the initial monomer mixture of 70-80%. Reducing the content of expensive and deficit styrene up to 30-50% leads to a deterioration in the quality of the resulting paint and varnish materials. The question arises where the oligomers based on PPPB obtained with a low styrene content in the initial monomer mixture (charge) could be used. One of the promising such areas is the protective treatment of wood and products based on it, used in industrial and civil construction [8-12].

At the same time, in industrial and civil construction, expanded polystyrene is widely used as a heat-insulating material (for warming walls, floors, roofs, foundations) [13, 14]. A huge advantage of using expanded polystyrene is the protection of pipes from freezing, etc. According to the Moscow research Institute of hygiene. F.F. Erisman polystyrene due to the small density is indispensable for the renovation of old buildings, where the change in the load bearing surface of structures at times critical. Erisman in air samples in rooms with wall panels with a middle layer of polystyrene insulation styrene was not detected (according to the conclusion of the Moscow Scientific Research Institute of Hygiene named after FF Erisman N. 03 / PM8) [15]. Published results of work on the use of oligomers based on petrochemicals have shown that the best results are obtained when oligomers based on by-products of petrochemicals with a high styrene content are used for the protective treatment of wood materials [16]. This is due to the fact that an increase in the content of styrene in an oligomer based on petrochemical waste can increase its hydrophobic properties by reducing the number of double bonds that increase the hydrophilicity of the oligomer.

However, styrene is an expensive and scarce product that is widely used in the production of primary polymeric materials. Partial replacement of styrene by secondary expanded polystyrene (SEPS) will yield a new low molecular weight copolymer that can be used for the protective treatment of wood materials. At the same time, one can expect that, in terms of its indicators, the PPPB oligomer with a low styrene content will approach the high-styrene one. Chemical combination of two types of polymer waste is possible at the molecular level due to their joint destruction [17-19].

EXPERIMENTAL PROCEDURE

A PPPB oligomer with a styrene content of 50% in the reactor was mixed with SEPS in amounts of 10, 20, 30 and 40% per 100% of the oligomer. The resulting mixtures were subjected to a high-temperature treatment at 200 ± 5 °C for 3-5 h in the presence of air oxygen and naphthenate siccative NF-1 (GOST 1003-73), introduced in an amount of 2-3% for polymers. The use of additives of desiccant for the joint destruction of polymer waste is based on the fact that it does not need to be removed from the system after the process. This is due to the fact that the remaining desiccant will perform the function of a structuring agent after treatment with a destroyed composite of wood and products based on it. With this treatment, two competing processes will occur: the destruction of expanded polystyrene and the oligomer and the structuring of the resulting decomposition products. As a result of a number of successive and parallel processes, new macromolecules were formed that contained an increased content of styrene in their structure. In addition, the course of destructive processes in the presence of air oxygen will promote the appearance of oxygen-containing functional groups in the structure of the resulting oligomer, increasing its affinity for the components of wood substance – cellulose, hemicelluloses and lignin. The indices of this product are presented in table 1. The molecular weight of the synthesized products, determined by the viscosimetric method, varied from 5000 to 10000.

Table 1

Acid number and bromine number of oligomers based on products of butadiene rubber (PPPB) modified with secondary expanded polystyrene

Таблица 1. **Кислотное число и бромное число олигомеров на основе продуктов бутадиенового каучука (PPPB), модифицированных вторичным вспененным полистиролом**

Products	Duration of treatment, h	Acid number, mg KOH /g	Bromine number, mg Br_2 / 100 g
Oligomer based on PPPB with the addition of secondary expanded polystyrene 10%	1	2.34	108
	3	2.92	99
	5	3.44	93
	7	3.57	91
Oligomer based on PPPB with the addition of secondary expanded polystyrene 20%	1	2.07	101
	3	2.25	95
	5	2.38	90
	7	2.40	87
Oligomer based on PPPB with the addition of secondary expanded polystyrene 30%	1	1.92	94
	3	1.96	90
	5	2.06	86
	7	2.11	84
Oligomer based on PPPB with the addition of secondary expanded polystyrene 40%	1	1.90	87
	3	1.84	80
	5	1.73	76
	7	1.70	73

The formation of such bonds will allow to reduce such a shortage of impregnating compositions, as washing out of products during their operation. Indicators of testing wood for water absorption and swelling are presented in Table 2.

Analysis of the experimental data shows that the best indicators are samples of birch wood, where as an impregnating composition a PPPB-based oligomer with additives of 40% SEPS was used.

Improved water resistance of modified wood samples is due to the fact that the product obtained contains fewer double bonds that increase its hydrophilic properties.

RESULTS AND ITS DISCUSSION

The purpose of this study is to determine the effect of the oligomers obtained on the parameters of samples of natural wood (birch) and wood fiber boards.

One of the promising directions for using the product obtained is the protective treatment of wood [20]. For the modification of wood, a polymer material based on the oligomer of PPPB with a toluene concentration of ~ 50% and 10, 20, 30, and 40% secondary polystyrene foam was used. For this purpose, samples of birch wood were immersed in the above polymer solution and held for one hour at a temperature of 80-90 °C. Impregnated samples of wood were removed from the solution and, after drying, were placed in a drying cabinet and held for 1 to 2 h at a temperature of 100-110 °C to remove the solvent. After that, the temperature was raised to 160-165 °C and at this temperature it was kept for 3 more h. For a given period of time, oligomer molecules were cross-linked in wood structures to form a wood-polymer framework, and also the formation of ester bonds between the components of the wood substance (cellulose, hemicellulose and lignin) with an oxidized modified oligomer.

Processes involving the oxygen of the air, intensively flow in the surface layers. The limited availability of oxygen to the interior of the composition reduces the proportion of oxidative processes, the increasing role is played by the reactions of high-temperature polymerization. This reaction is activated by various radicals present in the system (R •, RO •, ROO •).

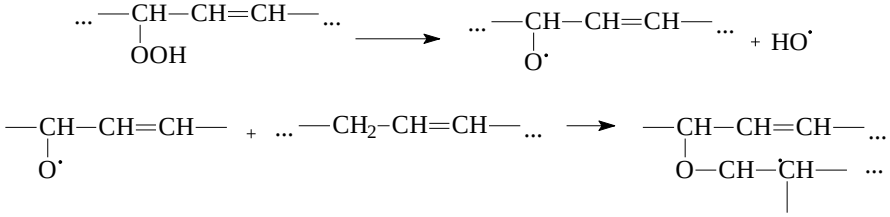

Table 2

The effect expanded polystyrene content on water absorption and swelling of birch wood samples

Таблица 2. **Влияние содержания расширенного полистирола на поглощение воды и набухание образцов березовой древесины**

Indicators	The dosage of SEPS in PPPB, %				
	0	10	20	30	40
Water absorption, %	25.7 68.0	25.0 66.8	24.7 65.1	23.0 62.3	21.2 59.0
Swelling in the radial swelling, %	3.3 6.5	3.3 6.2	3.0 5.8	2.7 5.4	2.5 5.1
Swelling in the tangential direction, %	4.4 8.4	4.0 8.0	3.9 7.9	3.7 7.6	3.6 7.5

Table 3

Experimental values of indicators of fiberboard samples treated with a modified PPPB-based oligomer

***Таблица 3.* Экспериментальные значения показателей образцов ДВП, обработанных модифицированным олигомером на основе PPPB**

	Dosage of secondary expanded polystyrene in oligomer from PPPB, %				
	0	10	20	30	40
Flexural strength, MPa	45.1	47.5	50.7	54.9	55.1
Water absorption, %	14.3	13.3	12.1	11.4	11.1
Swelling in thickness, %	11.7	10.9	10.0	10.3	9.3

Further, the possibility of increasing the indicator fiberboard with the use of the oligomer of PPPB, the modified SEPS, was investigated. The processing of fiberboard was carried out in the manner described above for natural wood. The results of the tests are shown in Table 3.

Analysis of the experimental data shows that fiberboard impregnated with oligomer composition based on PPPB modified SEPS have increased strength characteristics and resistance to water and moisture. With the increase in the content of SEPS in the oligomer from the PPPB, the strength of the fiberboard increased, and the water absorption and swelling decreased.

CONCLUSIONS

The impregnating compositions obtained on the basis of by-products of petrochemistry make it possible to impart increased hydrophobic properties, form stability to wood products, and, in addition, strength properties for fiberboard.

ЛИТЕРАТУРА

1. **Соколов Л.И.** Переработка и использование нефтесодержащих отходов. М.: Инфра-Инженерия. 2017. 128 с.
2. **Булатов М.А.** Комплексная переработка многокомпонентных жидких систем. М.: Мир. 2012. 304 с.
3. **Никулин С.С., Сергеев Ю.А., Шеин В.С.** Использование олигомеров бутадиена в лакокрасочной промышленности. *Лакокрас. матер. и их примен.* 1986. № 4. С. 15-16.
4. **Никулин С.С., Сергеев Ю.А., Тертышник Г.В., Струкова И.Ю., Шаповалова Н.Н.** Свойства пленкообразователей на основе отходов производства синтетического каучука. *Лакокрас. матер. и их примен.* 1988. № 4. С. 26-28.
5. **Никулина Н.С., Никулин С.С.** Сополимеризация непредельных соединений, содержащихся в кубовом остатке очистки возвратного растворителя производства полибутадиена в присутствии хлорида алюминия. *Промышл. пр-во и использ. эластомеров*. 2013. № 4. С. 41-43.
6. **Никулин С.С., Седых В.А., Никулина Н.С.** Пластификация полибутадиена олигомером, полученным на основе побочных продуктов производства растворного каучука. *Хим. технология.* 2012. Т. 13. № 4. С. 210-215.
7. **Никулина Н.С., Стадник Л.Н., Пугачева И.Н., Никулин С.С.** Утилизация отходов производства полибутадиена, содержащих 4-винилциклогексен. *Химия в интересах устойч. развития.* 2015. Т. 23. № 1.С. 49-53.
8. **Никулин С.С., Филимонова О.Н., Никулина Н.С., Болдырев В.С.** Применение низкомолекулярных сополимеров на основе побочных продуктов производства полибутадиена с низким содержанием стирола как модификаторов древесноволокнистых плит. *Хим. пром-ть сегодня*. 2005. № 4. С. 15-17.
9. **Никулина Н.С., Филимонова О.Н., Никулин С.С.** Защитная обработка древесины низкомолекулярными сополимерами из отходов производства полибутадиена с пониженным содержанием стирола. *Пр-во и использ. эластомеров*. 2005. № 3. С. 16-19.
10. **Черных О.Н., Никулин С.С.** Модификация древесины окисленным стиролсодержащим олигомером из побочных продуктов производства полибутадиена. *Изв. вузов. Химия и хим. технология*. 2007. Т. 50. Вып. 2. С. 65-69.

REFERENCES

1. **Sokolov L.I.** Processing and use of oily waste. M.: Infra-Engineering. 2017. 128 p. (in Russian).
2. **Bulatov M.A.** Complex processing of multicomponent liquid systems. M.: Mir. 2012. 304 p. (in Russian).
3. **Nikulin S.S., Sergeev Yu.A., Shein V.S.** Use of oligomers of butadiene in the paint and varnish industry. *Lakokras. Mater. i Ikh Primenenie.* 1986. N 4. P. 15-16 (in Russian).
4. **Nikulin S.S., Sergeev Yu.A., Tertyshnik G.V., Strukova I.Yu., Shapovalova N.N.** Properties of film-forming agents based on synthetic rubber waste. *Lakokras. Mater. i Ikh Primenenie.* 1988. N 4. P. 26-28 (in Russian).
5. **Nikulina N.S., Nikulin S.S.** Copolymerization of unsaturated compounds contained in the bottoms of the purification of the return solvent of polybutadiene production in the presence of aluminum chloride. *Promyshl. Pr-vo i Ispolz. Elastomerov*. 2013. N 4. P. 41-43 (in Russian).
6. **Nikulin S.S., Sedykh V.A., Nikulina N.S.** Plastification of polybutadiene by an oligomer obtained on the basis of by-products of the production of solution rubber. *Khim. Tekhnologiya*. 2012. V. 13. N 4. P. 210-215 (in Russian).
7. **Nikulina N.S., Stadnik L.N., Pugacheva I.N., Nikulin S.S.** Disposal of waste products of polybutadiene containing 4-vinylcyclohexene. *Khimiya v Interesakh Ustoych. Razvitiya*. 2015. V. 23. N 1. P. 49-53 (in Russian).
8. **Nikulin S.S., Filimonova O.N., Nikulina N.S., Boldyrev V.S.** The use of low molecular weight copolymers on the basis of by-products of polybutadiene production with low styrene content as wood fiber board modifiers. *Khim. Prom-t' Segodnya*. 2005. N 4. P. 15-17 (in Russian).
9. **Nikulina N.S., Filimonova O.N., Nikulin S.S.** Protective treatment of wood with low molecular weight copolymers from waste products of polybutadiene with a reduced content of styrene. *Pr-vo i Ispolzovanie Elastomerov*. 2005. N 3. P. 16-19 (in Russian).
10. **Chernykh O.N., Nikulin S.S.** Modification of wood by oxidized styrene-containing oligomer from by-products of polybutadiene production. Proceedings of high schools. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2007. V. 50. N 2. P. 65-69 (in Russian).

11. **Угрюмов С.А., Осетров А.В., Свиридов А.В.** Оценка свойств модифицированных фенол-формальдегидных олигомеров и древесных плит на их основе. *Клеи. Герметики. Технологии*. 2014. № 10. С. 24-26.
12. **Клесов А.А.** Древесно-полимерные композиты. СПб.: Научные основы и технологии. 2010. 736 с.
13. **Соколов В.В.** Отечественное производство и применение теплоизоляции на объектах транспортного строительства. *Транспорт. строительство.* 2008. № 2. С. 17-20.
14. **Пак А.А.** Пенополистирол – аргументы «за» и «против» его применения в строительстве. *Север промышленный*. 2011. № 3. С. 28-30.
15. **Никулина Н.С., Филимонова О.Н., Дмитренков А.И. Никулин С.С.** Влияние содержание стирола в низкомолекулярных сополимерах из побочных продуктов полибутадиена на свойства обработанной древесины березы. *Науч. вестн. ВГЛТА*. 2009. С. 105-110.
16. Горение, деструкция и стабилизация полимеров. Под ред. Г.Е. Заикова. СПб.: Научные основы и технологии. 2008. 422 с.
17. **Заиков Г.Е., Разумовский С.Д., Кочнев А.М., Стоянов О.В., Шкодич В.Ф., Наумов С.В.** Деструкция как метод модификации полимерных изделий. Вестн. Казан. технол. ун-та. 2012. Т. 15. № 6. С. 55-66.
18. **Базунова М.В., Прочухан Ю.А.** Способы утилизации отходов полимеров. Вестн. Башкир. ун-та. 2008. Т. 13. № 4. С. 875-885.
19. **Зархина Т.С., Аксенова Н.А., Соловьева А.Б.** Влияние безметальных порфиринов на термоокислительную деструкцию биосовместимых полимеров. *Журн. физ. химии*. 2017. Т. 91. № 6. С. 945-951.
20. **Шамаев В.А., Никулина Н.С., Медвелев И.Н.** Модифицирование древесины. М.: ФЛИНТА. 2013. 448 с.

11. **Ugryumov S.A., Osetrov A.V., Sviridov A.V.** Evaluation of the properties of modified phenol-formaldehyde oligomers and wood based boards. *Klei. Germetiki. Tekhnologii*. 2014. N 10. P. 24-26 (in Russian).
12. **Klesov A.A.** Wood-polymer composites. SPb.: Scientific Foundations and Technologies. 2010. 736 p. (in Russian).
13. **Sokolov V.V.** Domestic production and use of thermal insulation at transport construction sites. *Transport. Stroitelstvo*. 2008. N 2. P. 17-20 (in Russian).
14. **Pak A.A.** Styrofoam - the arguments "for" and "against" its use in construction. *Sever Promyshlennyy*. 2011. N 3. P. 28-30 (in Russian).
15. **Nikulina N.S., Filimonova O.N., Dmitrenkov A.I., Nikulin S.S.** Effect of styrene content in low molecular weight copolymers from polybutadiene by-products on the properties of treated birch wood. *Nauchn. Vestn. VGLTA*. 2009. P. 105-110 (in Russian).
16. Combustion, destruction and stabilization of polymers. Ed. by G.E. Zaikov. SPb.: Scientific bases and technologies. 2008. 422 p.
17. **Zaikov G.E., Razumovsky S.D., Kochnev A.M., Stoyanov O.V., Shkodich V.F., Naumov S.V.** Destruction as a method of modification of polymeric products. *Vestn. Kazan. Tekhnol. Un-ta*. 2012. V. 15. N 6. P. 55-66 (in Russian).
18. **Bazunova M.V., Prochukhan Yu.A.** Methods of utilization of polymers waste. Vestn. Baskir. Un-ta. 2008. V. 13. N 4. P. 875-885 (in Russian).
19. **Zarkhina T.S., Aksenova N.A., Solovyova A.B.** Influence of non-metallic porphyrins on the thermooxidative degradation of biocompatible polymers. *Zhurn. Fiz. Khim*. 2017. V. 91. N 6. P. 945-951 (in Russian).
20. **Shamaev V.A., Nikulina N.S., Medvedev I.N.** Modification of wood. M.: Flint. 2013. 448 p. (in Russian).

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