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NEW COMPOSITE PVC-MATERIAL FOR FINISHING PURPOSES, PLASTICIZED BY BUTOXYALKYLPHENOXYALKYL PHTHALATES

НОВЫЕ КОМПОЗИЦИОННЫЕ ПВХ-МАТЕРИАЛЫ ОТДЕЛОЧНОГО НАЗНАЧЕНИЯ, ПЛАСТИФИЦИРОВАННЫЕ БУТОКСИАЛКИЛФЕНОКСИАЛКИЛФТАЛАТАМИ

G.F. Aminova, A.I. Gabitov, A.R. Maskova, G.G. Yagafarova,
L.Z. Rolnik, M.S. Klyavlin
FSBEI of HPE "Ufa State Petroleum Technological University",
Ufa, the Russian Federation

Аминова Г.Ф., Габитов А.И., Маскова А.Р., Ягафарова Г.Г.,
Рольник Л.З., Клявлин М.С.
ФГБОУ ВПО «Уфимский государственный нефтяной технический университет»,
Уфа, Российская Федерация

e-mail: asunasf@mail.ru

Abstract. At the present time polyvinyl chloride (PVC) due to wide application capabilities is one of most required polymeric material. High demand on PVC associated with possibility of polyvinyl chloride's modification and obtaining a large variety of materials with improved properties, and also with economically sound balance cost – productivity, available raw materials, saving of natural resources. The unique character of PVC is that depending on production method, formulation and treatment process this polymer gives a wide range of materials and products with different properties. PVC is characterized by many useful technical properties: chemical stability in different media, good electrical properties etc. However, at ordinary temperature polyvinyl chloride is brittle and inelastic, that limit the fields of using PVC. Production of goods on the base of PVC is impossible without using of plasticizers – low-molecular compounds, which allow directionally regulate physical and mechanical properties of polymer. Production of plasticizers became the one of important branch of petrochemical industry. During the obtaining of plasticates in the initial PVC plasticizer is added (esters of phtalic, phosphoric, sebacic, adipinic acids, chlorated paraffines etc.) Introduction of plasticizers in PVC composition allow to obtain materials with desired elasticity, which remains unchanged in the wide range of temperature, increased impact number under bending, high breaking elongation. Plasticizers greatly improve the possibility of PVC's processing by changing its physico-mechanical characteristics. Using of plasticizers simplifies processing of polymer, increases the low temperature resistance, fire resistance and improves other service characteristics. .In this work the results of investigation of methods for producing and physico-chemical properties of

butoxyalkylphenoxyalkylphthalates are shown. The results of examination of plasticizing properties of butoxyalkylphenoxyalkylphthalates in the formulation of PVC-films are presented. It is noticed that, films obtained by introducing of developed plasticizers in the PVC-formulation, comply with requirements of current standards and even better than standard plasticizers. Obtain results demonstrate that using of butoxyalkylphenoxyalkylphthalates in the quality of PVC plasticizers is prospectively.

Аннотация. Поливинилхлорид (ПВХ), благодаря его широким прикладным возможностям, в настоящее время, является одним из самых востребованных полимерных материалов. Высокий спрос на ПВХ обусловлен возможностью его модификации и получения широкого ассортимента материалов и изделий с улучшенными свойствами, а также экономически выгодным соотношением цена - производительность, доступности сырья, сбережением природных ресурсов. Уникальность ПВХ состоит в том, что в зависимости от способа получения, рецептуры и технологии переработки этот полимер дает большой ассортимент материалов и изделий, характеризующихся различными свойствами. ПВХ характеризуется многими полезными техническими свойствами: химическая стойкость в различных средах, хорошие электрические свойства и т.д. Однако при обычной температуре поливинилхлорид хрупок и неэластичен, что ограничивает область его применения. Выпуск изделий на основе ПВХ был бы невозможен без применения пластификаторов - низкомолекулярных веществ, позволяющих направленно регулировать физико-механические свойства полимера. Производство пластификаторов стало одной из самых важных отраслей нефтехимической промышленности. При получении пластиката в исходный ПВХ добавляют пластификатор (эфиры фталевой, фосфорной, себациновой или адипиновой кислот, хлорированные парафины и т.д.). Введение пластификаторов в состав ПВХ-композиций позволяет получать материалы с заданной эластичностью, сохраняющейся в широком интервале температур, с повышенной ударной вязкостью при изгибе, большим относительным удлинением при разрыве. Пластификаторы значительно улучшают возможности обработки ПВХ путем изменения его физико-механических свойств. Применение пластификаторов облегчает переработку полимера, снижает хрупкость материала, значительно повышает морозостойкость, огнестойкость и улучшает многие другие эксплуатационные свойства пластикатов. В работе приводятся результаты исследования методов получения и физико-химические свойства бутоксиалкилфеноксиалкилфталатов. Приведены результаты испытаний пластифицирующих свойств бутоксиалкилфеноксиалкилфталатов в рецептурах ПВХ-пленок. Отмечено, что пленки, полученные с введением в ПВХ-рецептуру разработанных пластификаторов, по всем показателям удовлетворяют требованиям действующих стандартов и даже превосходят стандартные пластикаты. Полученные результаты

свидетельствуют о перспективности использования бутоксиалкилфеноксиалкил-фталатов в качестве пластификаторов поливинилхлорида.

Key words: butoxyalkylphenoxyalkylphthalates, butoxypropanol, butoxyethanol, dibutylphtalate, phenoxypropanol, phenoxyethanol, PVC plasticiser, PVC formulation.

Ключевые слова: бутоксиалкилфеноксиалкилфталаты, бутоксипропанол, бутоксиэтанол, дибутилфталат, феноксипропанол, феноксиэтанол, пластификаторы ПВХ, ПВХ-рецептура.

Compositions for the obtaining different polymeric materials on the base of polyvinylchloride (PVC) usually consist of fillers, stabilizers, modifiers, lubricating agents and plasticizers. In recent times the importance of plasticizers which use in processing of polymeric materials increased, because plasticizing is the simplest, the cheapest and the most available method of modifying of different properties of polymer. Introducing of plasticizers in the structure of PVC composition allow to obtain materials with desired elasticity which remain unchanged in a wide range of temperature, with high-impact under bending and with high breaking elongation. Using of plasticizer simplify the processing of polymer, increase the fire-resistance, cold-resistance and improve another service properties of plasticizes.

Ester plasticizers which able to plasticize almost all kind of polymers, particular PVC, are most functional in using. Take into account exclusive standards for PVC's characteristic: length of service, technical-and-economic, ecological indexes and many others characteristic, industry acquired production of more than three hundred kinds of plasticizers, the most part of which are phthalate esters. Phthalates occupy more than 80% of market and more than 90% of produced phthalates are used for plasticizing [3].

The most large-scale of them are di(2-ethylgexyl)phthalate (dioktylphthalate, DOP) and dibutylphthalate (DBP). These are esters of orthophthalic acid and 2-ethylgexanol and butanol. Plasticizers DOP and DBP are used for plasticizing of soft cable compound, linoleum, structural polymeric shapes, finishing materials, artificial leather, technical films, products for food, medicine, paint and coatings industries.

Dioktylphthalate which the most abundant among others industrial plasticizers, is expensive and deficit. More accessible dibutylphthalate is high volatile and this prevents wide using of DBP [3-8].

Esters of aromatic alcohols [9,10], in particular butylbenzilphthalates (BBP) can be used for the plasticizing of PVC and its copolymers. This plasticizer provides polymers with raised water resistance and resistance to activity of organic media. Also BBP prevents to formation of pollution at the surface of materials. But butylbenzilphthalate is produced in limited quantities, because benzyl alcohol is deficit.

Possibility of using of phenols in the quality of plasticizers of some polymeric materials, for example, polyamides, acetyl cellulose, is known for a long time [10,11]. But they are unsuitable for plasticizing of PVC. For this reason, in spite of a large

variety of plasticizers, the quantity of plasticizers is insufficient for complete satisfaction of modern industrial requirements.

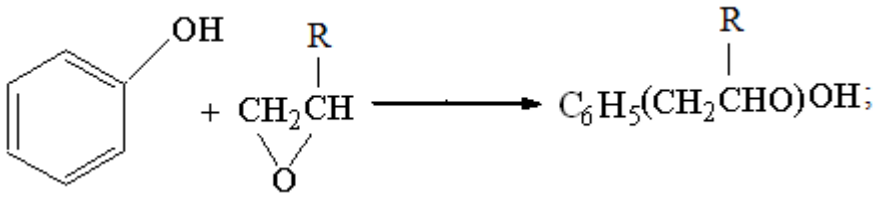
In this connection development of new plasticizers for composition of PVC materials for finishing operations is currently important and practically significant problem.

In this work the results of investigation of methods for producing and physic-chemical properties of butoxyalkylphenoxyalkylphthalates and the results of examination of plasticize properties of synthesized esters in formulation of PVC-films are shown.

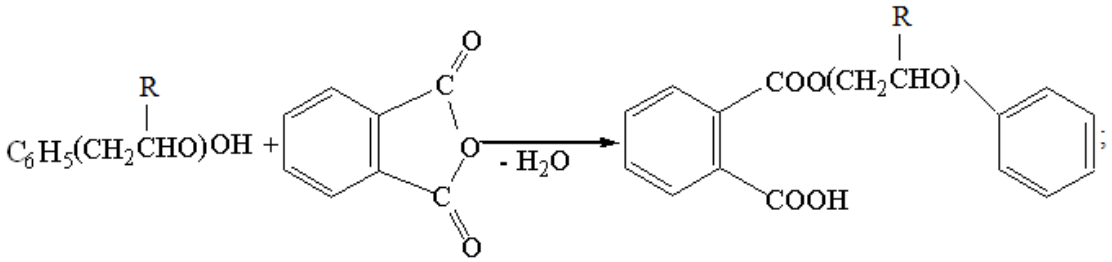
We synthesized butoxyalkylphenoxyalkylphthalates on the base of phenoxyethanol and phenxypropanol.

Butoxyalkylphenoxyalkylphthalates were obtained in four steps:

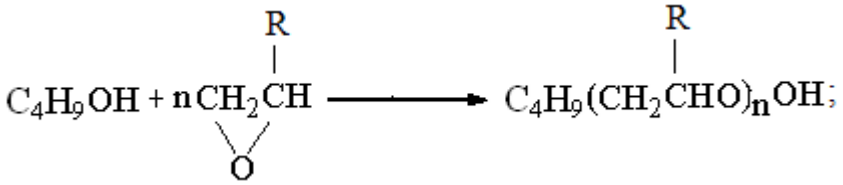
- Oxyalkylation of phenol with formation of phenoxyethanol and phenxypropanol:



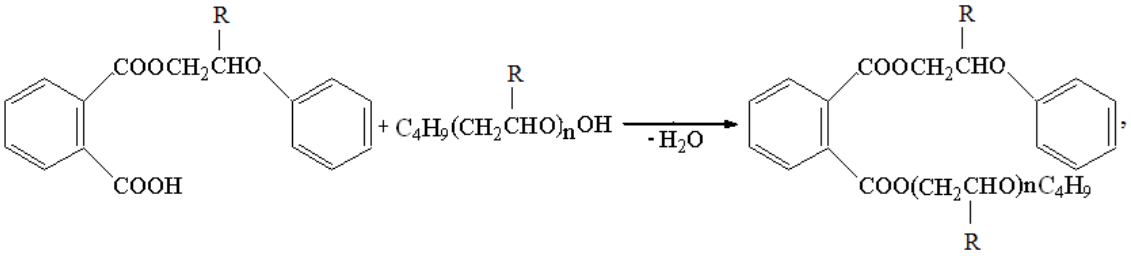
- Esterification of phthalic anhydride with phenoxyethanol and phenxypropanol with obtaining corresponding monoester of phthalic acid:



- Oxyalkylation of butanol with formation of butoxyethanol and butoxypropanol (degree of oxyalkylation range from 1,0 to 2,6):



- Esterification of monoester of phthalic acid with butoxyethanol and butoxypropanol with obtaining corresponding butoxyalkylphenoxyalkylphthalates:



where R = H (compounds 1-5 – butoxyethylphenoxyethylphthalates, BOEPOEP), CH_3 (compounds 6-10 – butoxypropylphenoxypropylphthalates, BOPPOPP).

Butoxyalkylphenoxyalkylphthalates were obtained by esterification of phthalic anhydride with oxyalkylated alcohols (phenol, butanol) in the presence of p-toluenesulfonic acid (PTSA).

Conditions, which allow to obtain desired product with more than 80% yield, were determined: first step – molecular ratio of reagents phenol: ethylene oxide (propylene oxide) 1:1, temperature 100 – 180°C, quantity of sodium hydroxide 0,5 – 3% (mass from loading); second step - molecular ratio of reagents phthalic anhydride: phenoxyethanol (phenxypropanol) 1:2,5, temperature 110 – 140°C, quantity of PTSA 0,1-2 % (mass from loading); third step molecular ratio of reagents butanol: ethylene oxide (propylene oxide) 1:2-1:4, temperature 110 – 140°C, quantity of potassium hydroxide 1% (mass from loading); fourth step - molecular ratio of reagents phthalic anhydride: butoxyethanol (butoxypropanol) 1:2, temperature 120 – 170°C, quantity of PTSA 0,1-2% (mass from loading).

Butoxyalkylphenoxyalkylphthalates are yellow, translucent, slightly hygroscopic oleaginous fluid, very soluble in organic solvents, but insoluble in water.

Physicochemical characteristics of butoxyalkylphenoxyalkylphthalates are presented in the Table 1.

Table 1. Physicochemical characteristics of butoxyalkylphenoxyalkylphthalates

Characteristics	Butoxyethylphenoxyethylphthalates					Butoxypropylphenoxypropylphthalates					DBP
	1	2	3	4	5	6	7	8	9	10	
Oxyalkylation degree of butanol, n	1,0	1,4	1,7	2,0	2,5	1,1	1,5	1,8	2,2	2,6	0,0
Refraction index, n^{20}_{D}	1,5190	1,5183	1,5180	1,5176	1,5170	1,5183	1,5179	1,5174	1,5170	1,5165	1,4904
Density, d^{20}_{4}	1,1054	1,1081	1,1110	1,1119	1,1145	1,1004	1,1032	1,1050	1,1064	1,1079	1,0432
Acid number, mg KOH/g	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,1
Ester number, mg KOH/g	293	272	261	251	237	262	249	239	228	218	401
Molecular mass, found	391	412	429	446	473	427	450	468	492	514	279
Molecular mass, calculated	386	404	417	430	452	421	444	461	485	508	278
Solidifying point, $^{\circ}C$	-39	-40	-40	-40	-39	-35	-38	-37	-37	-36	-40

According to investigations obtained butoxyalkylphenoxyalkylphthalates are less volatile than industrial plasticizer dibutilphtalate.

The most important characteristic of ester plasticizers are index of refraction and density, which mainly determine physico-mechanical characteristics of plasticizers of polyvinylchloride's composition for finishing operations. These characteristics firstly depend on structure of ester [4]. Our experiments showed that with increasing of oxyalkylation degree of butanol refraction index of butoxyalkylphenoxyalkylphthalates decrease, density of butoxyalkylphenoxyalkylphthalates grow up (Figure 1,2).

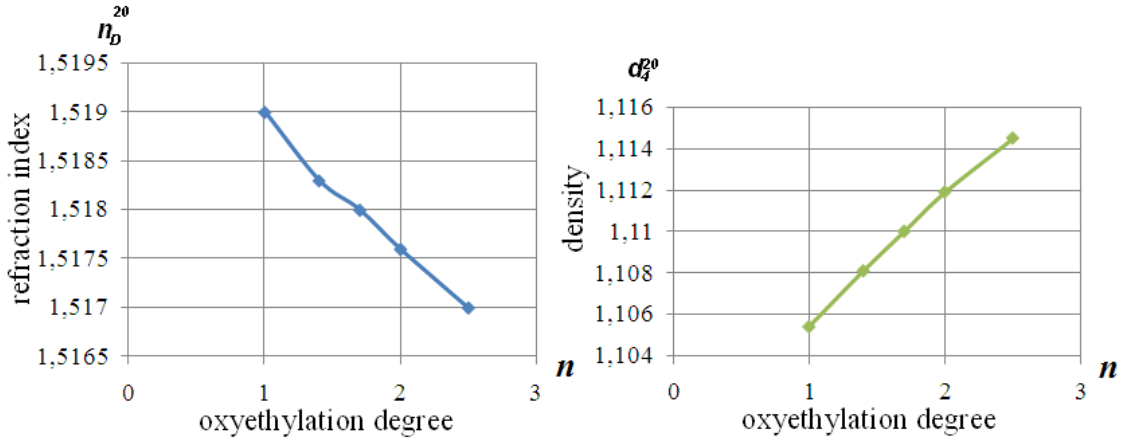


Figure 1. Dependence of refraction index and density from oxyethylation degree

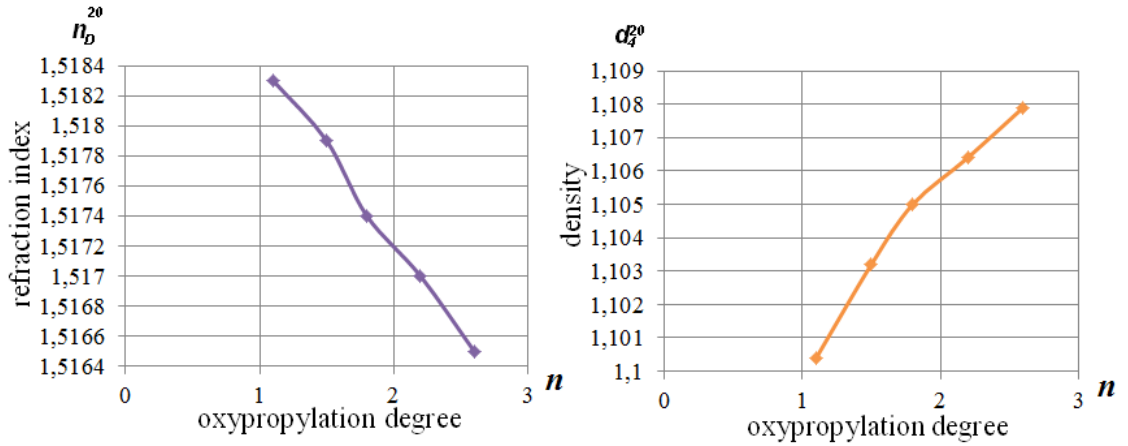


Figure 2. Dependence of refraction index and density from oxypropylation degree

In the following, butoxyalkylphenoxyalkylphthalates were tested in the quality of plasticizers in the formulation of PVC-films. The test models of plasticizers were added in the PVC-formulations instead of commercial analogue – DBP.

The results of examination of developed plasticizers in the industrial formulation of PVC-films are presented in the Table 2 (Formulation (mass number): PVC – 100; plasticizer – 50; barium stearate – 1,5; calcium stearate – 1,5).

Table 2. The results of examination of butoxyalkylphenoxyalkylphthalates in the formulation of PVC-films

Characteristics	DBP	Test models	
		BOEPOEP	BOPPOPP
Modulus at 100 %, MPa	8,6	11,8	10,7
Critical stress, MPa	18,5	22,8	24,3
Breaking elongation, %	300	285	275
Extractibility with petrol, %	4,95	1,48	1,53
Extractibility with oils, %	15,2	10,8	10,2
Long-term storing of films at 25°C during 4 months	films are good		

It is evident from table 2, that films obtained by introducing of our developed plasticizers in the formulation comply with requirements of current standards and even better than test models.

Conclusion

Obtained results give evidence that using of butoxyalkylphenoxyalkylphthalates in the quality of PVC's plasticizer is attractive.

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Information about authors
Сведения об авторах

G.F. Aminova, Post Graduate Student, FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Аминова Г.Ф., аспирант ФГБОУ ВПО УГНТУ, г. Уфа, Российская Федерация

A.I. Gabitov, Doctor of Technical Sciences, Professor of the Chair "Building Construction" FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Габитов А.И., д-р техн. наук, проф. кафедры «Строительные конструкции» ФГБОУ ВПО УГНТУ, г. Уфа, Российская Федерация

A.R. Maskova, Candidate of Technical Sciences Senior Teacher of the Chair "Applied Chemistry and Physics" FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Маскова А.Р., канд. техн. наук, ст. преподаватель кафедры «Прикладная химия и физика» ФГБОУ ВПО УГНТУ, г. Уфа, Российская Федерация

G.G. Yagafarova, Doctor of Technical Sciences, Professor of the Chair "Applied Ecology" FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Ягафарова Г.Г., д-р техн. наук, проф. кафедры «Прикладная экология» ФГБОУ ВПО УГНТУ Уфа, Российская Федерация

L.Z. Rolnik, Doctor of Chemical Sciences, Professor of the Chair "General and Analytical Chemistry" FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Рольник Л.З., д-р хим. наук, проф. кафедры «Общая аналитическая химия» ФГБОУ ВПО УГНТУ, Уфа, Российская Федерация

M.S. Klyavlin, Doctor of Chemical Sciences, Professor of the Chair "Water Supply and Water Disposal" FSBEI of HPE "Ufa State Petroleum Technological University", Ufa, the Russian Federation

Клявлин М.С., д-р хим. наук, проф. кафедры «Водоснабжение и водоотведение» ФГБОУ ВПО УГНТУ Уфа, Российская Федерация

e-mail: asunasf@mail.ru