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ION-EXCHANGE PROPERTIES OF MATERIALS OBTAINED BY RADIATION GRAF--ETC(U)  
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# FOREIGN TECHNOLOGY DIVISION



ION-EXCHANGE PROPERTIES OF MATERIALS OBTAINED BY RADIATION  
GRAFTING POLYMERIZATION ACRYLIC ACID AND STYROL  
FROM GAS PHASE ON POLYPROPYLENE FIBERS AND FABRICS

by


M. I. Boldyrev, A. V. Vlasov, et al.



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ION-EXCHANGE PROPERTIES OF MATERIALS OBTAINED BY RADIATION GRAFTING POLYMERIZATION ACRYLIC ACID AND STYROL FROM GAS PHASE ON POLYPROPYLENE FIBERS AND FABRICS

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<b>А а</b>	A, a	Р р	<b>Р р</b>	R, r
Б б	<b>Б б</b>	B, b	С с	<b>С с</b>	S, s
В в	<b>В в</b>	V, v	Т т	<b>Т т</b>	T, t
Г г	<b>Г г</b>	G, g	У у	<b>У у</b>	U, u
Д д	<b>Д д</b>	D, d	Ф ф	<b>Ф ф</b>	F, f
Е е	<b>Е е</b>	Ye, ye; E, e*	Х х	<b>Х х</b>	Kh, kh
Ж ж	<b>Ж ж</b>	Zh, zh	Ц ц	<b>Ц ц</b>	Ts, ts
З э	<b>З э</b>	Z, z	Ч ч	<b>Ч ч</b>	Ch, ch
И и	<b>И и</b>	I, i	Ш ш	<b>Ш ш</b>	Sh, sh
Й й	<b>Й й</b>	Y, y	Щ щ	<b>Щ щ</b>	Shch, shch
К к	<b>К к</b>	K, k	Ъ ъ	<b>Ъ ъ</b>	"
Л л	<b>Л л</b>	L, l	Ы ы	<b>Ы ы</b>	Y, y
М м	<b>М м</b>	M, m	Ь ь	<b>Ь ь</b>	'
Н н	<b>Н н</b>	N, n	Э э	<b>Э э</b>	E, e
О о	<b>О о</b>	O, o	Ю ю	<b>Ю ю</b>	Yu, yu
П п	<b>П п</b>	P, p	Я я	<b>Я я</b>	Ya, ya

\*ye initially, after vowels, and after ъ, ь; e elsewhere.  
When written as ě in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh <sup>-1</sup>
cos	cos	ch	cosh	arc ch	cosh <sup>-1</sup>
tg	tan	th	tanh	arc th	tanh <sup>-1</sup>
ctg	cot	cth	coth	arc cth	coth <sup>-1</sup>
sec	sec	sch	sech	arc sch	sech <sup>-1</sup>
cosec	csc	csch	csch	arc csch	csch <sup>-1</sup>

Russian	English
rot	curl
lg	log

**ION-EXCHANGE PROPERTIES OF MATERIALS OBTAINED BY RADIATION GRAFTING  
POLYMERIZATION OF ACRYLIC ACID AND STYRENE FROM GAS PHASE ON  
POLYPROPYLENE FIBERS AND FABRICS**

**M. I. Boldyrev, A. V. Vlasov, Ye. V. Yegorov, Ye. S. Kolesnik, S. B.  
Makarova, L. I. Malakhova, L. G. Tokareva, B. L. Tsetlin**

**Ion-exchange fibers and fabrics which contain certain functional groups have a number of advantages over standard resins: They can serve simultaneously as ion-exchange and mechanical filters; their use is particularly promising in formulating continuous processes; since they have a developed surface, they are characterized by high exchange rates.**

Usually cation- and ion-exchange materials are obtained either directly from fiber-forming polymers which contain ion-exchange groups or polymer-analogous conversions. The production of ion-exchange fibers and fabrics by the radiation-chemical method [1] also appears very promising. Until now these were obtained by radiation grafting polymerization from the liquid phase [2-4].

The object of the present article is to study the exchange processes of ion-exchange grafting materials based on polypropylene fiber which are obtained by the method of radiation graft polymerization from the gas phase during irradiation of the original fibers and fabrics directly in the vapors of the monomer. As we know, this grafting method eliminates homopolymerization and makes it possible to obtain two-layered fibers, the outer portion of which is the layer of the graft polymer [5, 6]. In the proposed variation the graft polymer chains are connected directly to the substrate by C-C-bonds, which causes the high resistance of ion-exchange materials under conditions of repeated action by corrosive media and long-term use.

#### Experimental Part

Here we studied specimens of propylene fabric (article 25337) on

which the gas-phase method was used to graft polyacrylic acid or polystyrol. The radiation grafting polymerization reaction was achieved on a pilot device where  $\gamma$ -radiation of  $Co^{60}$  was used as the source [7].

When acrylic acid was used as the original monomer, synthesis of the ion-exchange fabrics consisted only of a single graft stage. In order to impart the ion-exchange properties to specimens of polypropylene fabric containing a graft polystyrol, these were subjected to sulfonation by concentrated sulfuric acid in the presence of a catalyst (aluminum trichloride) or phosphorylation by phosphorus trichloride in this presence of aluminum trichloride with subsequent oxidation of the product by nitric acid. An ion-exchange fabric with strong-alkaline groups was produced as the result of chloromethylation of the grafted polystyrol by monochloromethyl ether (ester) in the presence of a catalyst (stannous tetrachloride) and further amination of the chloromethylated copolymer by an alcohol solution of trimethylamine.

An investigation of the properties of ion-exchange fabrics revealed that the capacity of the studied specimens was high and close to the calculated value (Table 1).

One of the main advantages of ion-exchange of fabrics

synthesized by the described method is that such materials are stable during use. Thus, in a fabric with graft polyacrylic acid, after 30 sorption-desorption cycles (0.1 normal NaOH-H<sub>2</sub>O-0.1 normal HCl), the original capacity decreased by only 5-10%. For graft fabrics containing the groups -SO<sub>3</sub>H, -PO<sub>3</sub>H<sub>2</sub> and -CH<sub>2</sub><sup>+</sup>N(CH<sub>3</sub>)<sub>3</sub>, this treatment is accompanied by losses of 3-10% of the original capacity. At the same time in ion-exchange of fabrics obtained by the usual chemical grafting there is frequently a 15-30% decrease in the exchange capacity after several cycles. This difference is apparently a result of the fact that under conditions of gas-phase radiation grafting strong chemical bonds of the C-C-type between macromolecules of the original fiber and the graft copolymer are formed, as was noted above.

Generally ion-exchange materials are described by significant heterogeneity. The method of gas-phase radiation graft polymerization made it possible to synthesize an ion-exchange fabric with a high degree of homogeneity:

Specimen number	1	2	3	4	5	6	7	8
Capacity, mg-equiv/g	4.3	4.4	4.1	4.2	4.1	4.7	4.3	4.3



Due to the fact that functional groups of synthesized ionites are located on the surface and that the exchange of ions is not limited by diffusion in the phase of the sorbent, the rate of ion-exchange on synthesized fabrics is significantly higher than on standard resins (figure). The capacity of graft two-layer (particularly those based on graft polyacrylic acid) cation-exchange materials to react with replacement of the hydrogen ion of the acid groups by cations of different metals with formation of salts of polymer acids can be used to obtain fibrous materials with a high concentration of bound metal. The introduction of significant quantities of a certain metal into the two-layered material may lead to a substantial change in the physical and physicochemical properties of the material, for example, the thermal properties of fibers with a graft layer of polyacrylic acid and its salts (Table 2). Polyethylene and polypropylene fibers with a graft layer of polyacrylic acid retain a high degree of strength up to temperatures on the order of 150°, although above 170-200° they lose their strength entirely as a result of the thermal decarboxylation reaction.

Fibers with a graft layer of salts of polyacrylic acid, obtained by treating the oxygen form of graft copolymers with solutions of appropriate metals, retain their mechanical strength at such higher temperatures. This is the result of the greater thermal resistance of

salts of polyacrylic acid as compared to the polymer acid itself.

For absorption of large quantities of cations of certain metals (for the purpose of achieving complete exchange capacity of the fibers) conditions for conducting the exchange reaction must be selected in each specific case. This can be illustrated using as an example the introduction of lead into graft fabrics.

If an ion-exchange fabric containing groups  $-COOH$  is treated by 0.1 normal solutions of lead acetate or nitrate, then only 10% is substituted. If, however, the fabric has been pretreated with a 6% solution of ammonia and rinsed in water, then after contact with 0.1 normal solution of lead salts, then lead can be introduced up to 25% of the original capacity. Finally, if after the ammonia treatment the fabric is dried and the lead absorbed, then the capacity with respect to  $Pb^{2+}$  may constitute more than 100% of that which is theoretically possible. For example, we can use this method to introduce into a fiber with a total exchange capacity of 6 mg-equiv/g up to 7-8 mg-equiv  $Pb^{2+}$ /g from a saturated (at room temperature) solution of lead acetate or nitrate. Here the obtained capacity is above the total exchange capacity. This is caused by the fact that lead is sorbed on the fabric not only in the form of  $Pb^{2+}$ , but also in the form of complex ions of  $Pb(CH_3COO)^+$ . The use of basic lead acetate makes it possible to introduce 11-12 mg-equiv  $Pb^{2+}$ /g into

the fabric. Treatment of the fabric with sorbed lead by hot (60-70°) water or washing it with standard cleaning agents (soap, detergent powders, etc.) does not lead to desorption of the absorbed lead (loss of capacity with respect to lead does not exceed 2-3%, and is within the error range of the experiment).

It should be mentioned that ion-exchange fabrics can also be obtained both by grafting appropriate monomers to finished fabrics or by grafting to fiber and filaments with subsequent processing into fabric. The selection of a certain system for producing these materials depends on their purpose and the technical and economic production indices.

#### Conclusion

1. Gas-phase radiation grafting polymerization of acrylic acid or styrol (with subsequent sulfonation, chloromethylation, and amination) onto polypropylene fabrics is used to synthesize ion-exchange materials with the following groups:  $-\text{COOH}$ ;  $-\text{SO}_3\text{H}$ ;  $-\text{PO}_3\text{H}_2$ ;  $-\text{CH}_2\overset{+}{\text{N}}(\text{CH}_3)_3$ .

2. Ion-exchange fabrics are characterized by a high exchange capacity, excellent kinetic characteristics, thermal and chemical

stability, and homogeneity of composition.

3. The introduction into such fabrics of ions of metal greatly increases their heat resistance and makes it possible to use these fabrics at temperatures above 200°.

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Table 1. Exchange capacity of ion-exchange fabrics. KEY: (1) Graft polymer, (2) Concentration of graft polymer, % (3) Functional group, (4) Calculated capacity, mg-equiv/g, (5) Capacity for 0.1 normal solutions, mg-equiv/g, (6) or, (7) Polyacrylic acid, (8) The same, (9) Polystyrol, (10) \*Capacity for 0.1 normal HCl.

(1) Привитой полимер	(2) Содержание привитого полимера, %	(3) Функциональная группа	(4) Расчетная емкость, мг-экв/г	(5) Емкость по 0,1 н. растворам, мг-экв/г		
				NaOH	NaCl	(6) Pb (NO <sub>3</sub> ) <sub>2</sub> или Pb (CH <sub>3</sub> COO) <sub>2</sub>
(7) Полиакриловая кислота	32	-COOH	4,5	4,2	0,5	2,3
(8) То же	43	-COOH	6,0	5,7	0,6	2,6
.	54	-COOH	7,5	7,3	0,7	3,4
(4) Полистирол	70	-SO <sub>3</sub> H	4,3	3,9	3,1	1,5
.	70	-PO <sub>3</sub> H <sub>2</sub>	8,7	6,0	0,8	4,1
.	70	-CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>	2,3	2,1*	1,7	—

(10)\* Емкость по 0.1 н. HCl.

Figure. Exchange kinetics between  $H^+$ -(OH)-form of ionite and 0.1 normal NaOH (HCl): 1 - propylene fabric with grafted polystyrol-sulfuric acid; 2 - resin KU-2-8; 3 - propylene fabric with grafted polyacrylic acid; 4 - resin KB-4; 5 - propylene fabric with grafted polystyrol which has been chloromethylated and aminated; 6 - resin AV-17-8; 7 - propylene fabric with grafted polystyrol which has been phosphorylated; 8 - resin KRF-5p resins with granularity of 0.25-0.5 mm used; solution not mixed. KEY: (1) Depth of exchange, % (2) Time, min.

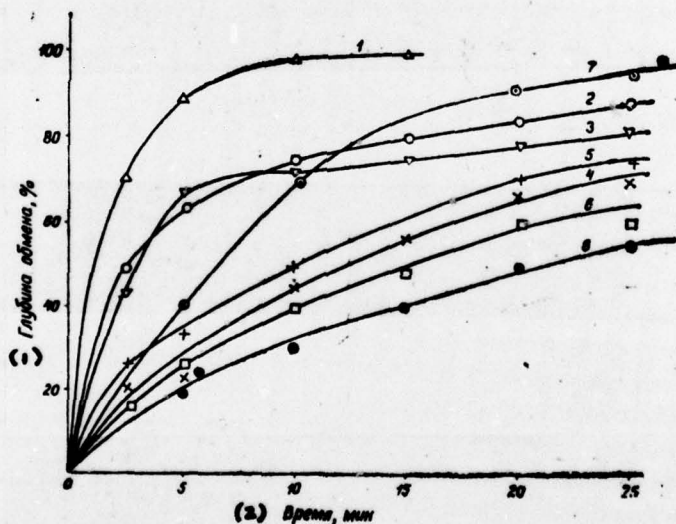


Табл. 2.

(1) Образцы	(2) Прочность на разрыв при температурах, °C								
	20°		150°			250°			P <sub>3</sub>
	P	P <sub>1</sub>	P	P <sub>1</sub>	P <sub>2</sub>	P	P <sub>1</sub>	P <sub>2</sub>	
(3) Исходное полиэтиленовое волокно (ПЭ)	210	42	0	0	—	0	0	—	
(4) ПЭ с привитой полнакриловой кислотой (ПАК)	200	17	160	14	25	0	0	0	
(5) То же после обработки аммиачным раствором уксуснокислой меди	220	19	180	16	28	150	13	23	
(6) То же после обработки раствором гидрата окиси бария	230	20	150	13	23	120	10	19	
(7) То же после обработки раствором уксуснокислого кобальта	230	20	—	—	—	130	11	21	
(8) Исходное полипропиленовое волокно (ПП)	1600	54	240	8	—	0	0	—	
(9) ПП с привитой ПАК (59%)	1500	21	700	10	—	0	0	0	
(10) То же после обработки аммиачным раствором уксуснокислой меди	1500	21	900	13	—	60	8	15	
(11) ПП с привитой ПАК (25%)	1400	35	—	—	—	—	0	0	
(12) То же после обработки аммиачным раствором уксуснокислой меди	1400	35	—	—	—	300	8	30	

(3) Условные обозначения: P — прочность выражена в граммах; P<sub>1</sub> — прочность выражена в разрывных километрах в расчете на всё волокно; P<sub>2</sub> — прочность выражена в разрывных километрах в расчете на привитой слой.

Table 2. Change in strength of fibers (P) containing grafted polyacrylic acid and its salts at different temperatures. KEY: (1) Specimens, (2) Tensile strength at temperatures, °C, (3) Original polyethylene fiber (PE), (4) PE with grafted polyacrylic acid (PAK), (5) The same after treatment by ammonia solution of copper acetate, (6) The same after treatment by solution of hydrate of barium oxide, (7) The same after treatment by a solution of cobalt acetate, (8) Original polypropylene fiber (PP), (9) PP with grafted PAK (59%), (10) The same after treatment by ammonia solution of copper acetate, (11) PP with grafted PAK (25%), (12) The same after treatment by ammonia solution of copper acetate, (13) Nomenclature: P - strength expressed in grams;  $P_1$  - strength expressed in fracture kilometers, calculated for entire fiber;  $P_2$  - strength expressed in fracture kilometers, calculated for grafted layer.



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C510 AIR MOBILITY R&D LAB/FIO	1	E413 ESD	2
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C535 AVIATION SYS COMD	1	CCN	1
		TOIS	3
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