

Polyolefinic Fibrous Ion-Exchange Materials: Properties and Applications (Review)

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Abstract

Ion exchangers based on polyolefinic filaments remain poorly studied, though they are rather promising with regard to their well developed surface, good sorption capacity, mechanical strength, chemical and osmotic stability, *etc.* Moreover, there is a wide base of raw materials for their synthesis, and advanced modification methods may impart them quite unique properties. This review summarizes the most interesting data related to the properties and practical application of fibrous ion-exchange materials based on polypropylene and polyethylene.

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1. INTRODUCTION

Intensively growing production of nonwoven filamentous materials (NFM) is provided by the simplicity of production technology (materials are produced as wool, sheet wadding, needle-punched fabric, cloth-piercing linen) and practical application efficiency [1–5].

For NFM production one may use filaments based on various materials such as viscose, polyamide, polyethylene (PE), polypropylene (PP), polyesters, polyacrylonitrile (PAN), polyurethane, polyvinyl chloride, polysiloxane, polyvinyl alcohols (PVA), *etc.* [1, 6–10]. Moreover, filaments are made from chitin [11], crab chitin and sulphite cellulose or their mixtures [12], from wood cellulose exposed to sulphite or sulphate cooking, cotton lint [13], *etc.*

Production of mass consumption goods and wares of medical and technical purposes (geotextile, separation and membrane materials, technique filters for cleaning of dyes, spinning solution, oil-containing emulsions, *etc.*) is the prime area of NFM application [14–25].

Nonwoven fibrous materials are used in the filters of various advanced dust and gas collectors [15, 16], and in the cartridges of water purifying filters [17, 18].

Filtering cartridge of a universal water purifying device contains preliminary filter made from porous ceramic fibrous material [19], while any express analyser uses chemical indicators based on solid carriers (reactive test paper, ion-exchange cloth and filaments saturated with ion exchangers) [20].

New flocculants based on "Nitron" waste fibre efficiently clean dye wastewater [21]. Flow porous anodes based on carbon filamentous material (CFM) are used for the electrochemical oxidation of organic complexing reagents [22].

Filamentous adsorbents TIOPAN, which are PAN based copolymers with grafted polyglycidylmetacrylate modified by various nitrogen and sulphur containing reagents [23, 24], may serve for evolving chlorine complexes of platinum (II) from their solutions [23]. Other filamentous materials applied as adsorbents are shown to be selective towards platinum group metals and gold [3].

There is also a tendency of using composite NFM being combined layers of various type and structure materials [13, 26–32].

Ion-exchange fibres (IEF) and cloths may simultaneously work as mechanical filters and ion exchangers. They are mostly promising for continuous counter flow process technologies. Fibres have a more developed surface than granules, thus providing higher ion-exchange rates. Moreover, IEF may provide ion exchange in small-scale devices like filter presses allowing ions extraction from the pulp and mechanical filtering, which is practically non available in ion-exchange columns. Ion-exchange fibres may be also used for preparing carcasses for heterogeneous membranes. Ion-exchange paper (including that made of polypropylene filaments) may be applied in analysis, especially for the chromatography of biochemical objects such as proteins, enzymes, nucleic acids, *etc.* [33, 34].

For example, there are well known sulphocationite exchanger based on carbon FM [35], a weakly acid cation exchanger VION KN-1 obtained *via* a chemical modification of industrial fibre "Nitron" [36], chemisorption carbonyl-containing material based on PAN filaments [37] and many others.

There is a method involving wastewater passing through the bed of ion-exchange carbon fibre material at adjusted filtration rate. For the purpose carbon cloths "Busofit" and "Viskumak" are preliminary treated with acid and/or calcined [38].

Glass, asbestos and basalt filaments are used for producing highly efficient ion-exchange acid-resisting filtering materials capable of working in aggressive media and possessing long service

life. Their filamentous base is covered by two functional layers to attain a higher sorption capacity and bifunctional operation; in this case the upper layers holds polyacrylic acid, whereas the additional lowermost layer is comprised of polymetacrylic acid hydrazide [39].

Decorative absorbing nonwoven materials are suggested for human respiration organs protection. They are made as textile carcass covered by a fibrous layer. The latter consists of a mixture of ion-exchange and thermoplastic fibrous bundles drawn through the carcass and forming a fleecy surface [40].

A cloth consisting of ion-exchange viscose fibres containing iron ferrocyanide is suggested as a filtering material meant for liquid food purification from cesium radionuclides [41].

Natural fibres substitution for synthetic ones is a main tendency in the nonwoven materials production. Polyolefines, mostly polypropylene filaments and fibres are widely used for the purpose. Since the middle 80s of the last century, polypropylene fibres are at the popularity top with regard to their consumption, since they are considered as leaders with respect to their quality/price ratio, small density, high strength, good resistance to attrition, *etc.* [1, 42–44].

On the other hand, at present polyethylene (PE) and polypropylene (PP) are the most widely produced thermoplasts. Their production volume grows continuously, thus expanding the market of raw for various application materials, including fibres. Polyolefinic materials modification with various methods [45–56] enlarges their application fields.

Therefore, ion exchangers based on the modified polyolefinic fibres appear to be rather promising due to their chemical and thermal resistance as well as due to their negligible swelling capacity on operation, good mechanical strength, accessibility of starting materials, *etc.* At the same time polyolefinic fibre ion exchangers are poorly studied owing to the chemical inertness of starting PE and PP being indeed hard to modify. Most studies are dedicated to ion exchangers based on the cellulose, PVA and PAN fibres [25, 34].

Among the studies, devoted to polyolefinic ion exchangers, one may notice the works of V. S. Soldatov and co-workers designing new materials of FIBAN series. As we have already

mentioned filamentous PE and PP materials are used for a starting matrix of FIBAN materials. Styrene and divinylbenzene are used as monomers for the first modification. Radiation with ^{60}Co is applied for grafting polymerisation.

In the present study we review the most interesting reference data describing the properties and possibilities of polyolefinic filaments and fibres being used as ion-exchange materials.

2. PROPERTIES OF POLYOLEFINIC ION-EXCHANGE FIBRES

Ion exchangers' estimation is not an easy task. Some researchers estimate their newly synthesized materials solely by their exchange capacity. However, some new materials, though showing a rather high ion-exchange capacity, appear to be poorly resistant to high temperatures, mechanical impact, aggressive media, *etc.*, and thus can not be widely used in industrial practice. Apparently, in each particular case a certain material is demanded, possessing definite properties and meeting a definite set of requirements provided by its application field. With this regard we would like to consider the properties of polyolefinic filamentous ion-exchange materials, without classifying them as "principal" or "secondary".

Sorption, solvation, mechanical, electrochemical and other properties of ion exchangers, as well as their thermal, radiation and chemical resistance, are discussed elsewhere [2, 25, 34, 45, 57–61].

2.1. Sorption properties

Real structure of ion exchangers. Potentiometric investigation of filamentous ionites FIBAN has shown that strong-acid FIBAN K-1 and strong-base FIBAN A-1 and A-2 are closely related to the monofunctional ion exchangers. Weakly acid groups content in FIBAN K-1 and weakly base groups content in FIBAN A-1 and A-2 do not exceed 0.21 mg-eq/g, while total exchange capacity of these ion exchangers attains 3–4 mg-eq/g (Table 1). When polyfunctional amines [ethylene diamine (FIBAN A-3) or tetramethyl ethylene diamine (FIBAN A-4)] are used for amination, and carboxylic ion exchanger FIBAN K-2 is synthesized, one may obtain polyfunctional ion exchangers [62].

Total static exchange capacity (SEC) exceeds that of the strong-acid groups, when PP fibres are grafted with styrene, and then sulphonated by the sulphur (VI) oxide solution in carbon tetrachloride and by the chlorosulphonic acid solution in dichloroethane (DCE) (Table 2). Severe sulphonation conditions intensify this tendency, which is likely to be evidence of a partial formation of weakly acid carboxyl groups owing to oxidation of grafted polystyrene (PSt) chains with sulphonating reagents. Moreover, a real SEC of sulphonated PP fibres appears to be less than that calculated from the sulphur content. Most probably, some sulphur atoms are spent on the formation of nonionic groups (for example, sulphonic bridges

TABLE 1

Properties of fibrous FIBAN ion exchangers [62]

FIBAN type	Main functional groups	Ion form	OE, mg-eq/g		W, g H ₂ O/g	K, mmol H ₂ O/mg-eq
			E_1	E_2		
K-1	R-SO ₃ ⁻	H ⁺	3.44	0.19	1.23	18.5
A-1	R-N ⁺ (CH ₃) ₃	Cl ⁻	3.01	0.21	0.74	12.7
A-2	R-N ⁺ (CH ₃) ₂ C ₂ H ₄ OH	Cl ⁻	2.56	0	0.56	12.4
A-3	R-N ⁺ CH ₂ CH ₂ NH ₂	Cl ⁻	0.31	3.39	0.32	4.8
A-4	R-N ⁺ (CH ₃) ₂ (CH ₂) ₂ N(CH ₃) ₂	Cl ⁻	1.95	1.75	0.70	10.6

Note. E_1 is capacity by strong-acid (K-1) and strong-base (A-1–A-4) groups; E_2 is capacity by weakly acid (K-1) and weakly base (A-1–A-4) groups; W is moisture capacity coefficient; K is equivalent moisture capacity coefficient.

TABLE 2

Sulphonation conditions influence on the properties of PP fibres with grafted polystyrene [63]

Sulphating reagent	Sulphonation conditions			SEC, mmol/g		Strong-acid groups content, %
	C, mass %	T, °C	τ , min	total	by strong-acid groups	
Chlorosulphonic acid	0.3	30	150	0.62	0.58	92.3
	0.7	30	150	0.64	0.57	90.1
	1.1	30	150	0.91	0.75	72.5
	2.1	30	150	0.83	0.64	70.8
	0.7	40	150	0.80	0.72	88.4
	0.7	80	150	1.19	0.90	67.7
	0.7	40	60	0.65	0.63	96.2
	0.7	40	180	0.85	0.73	84.0
	0.7	40	360	0.98	0.76	71.3
Sulphur (VI) oxide	0.4	40	360	1.14	0.95	79.6

Note. C is sulphonating reagent concentration; T is temperature; τ is sulphonation duration.

between the aromatic nuclei of grafted polystyrene units) [63].

Ion-exchange capacity. Considering the ion-exchange capacity of polyolefinic fibres, one may notice a wide variety of its estimations by various researchers. Some authors declare the high SEC values of synthesized materials comparable to those of granular and powdery industrial ionites. Others report the lower capacity values appealing primarily to the high rates of ion-exchange processes and to other advantages of ion exchangers. This disagreement is probably explained by the novelty of fibre exchangers and by the variety of approaches to their investigation, as well as by the absence of standard unified procedures for their characterization.

Thus reported SEC for the polyolefinic fibre ion exchangers vary over wide limits (mg-eq/g): 0.62–1.19 (see Table 2); 0.8–1.7 [64]; 0.88–2.88 (Table 3); 2.56–3.7 (see Table 1); 0.35–8.30 (Ta-

ble 4), *etc.* SEC value for fibre PE-PAA attains ~8.5 mg-eq/g, that for sulphonated fibre PE-PSt is approximately 3 mg-eq/g (with respect to 0.1 M NaOH), and that for PE-PMVP is about 3 mg-eq/g (with respect to 0.1 M HCl) [67].

Obviously the ion-exchange capacity is influenced by many factors, among them the grafted component amount (see Tables 3, 4 for methylvinylpyridine data), synthesis conditions [68–75], *etc.*

Thus ion exchanger based on PP fibres with PMVP overweight (~120 %) is characterized by capacity equal to that of anion exchanger AN-25 (6.20 mg-eq/g by 0.1 M HCl) obtained by 2-methyl-5-vinylpyridine co-polymerisation with DVB (see Table 4). PP-PAA fibre (100 % PAA addition) is characterized by capacity equal to 4.35 mg-eq/g (by 1 M NaOH) [66].

TABLE 3

Ion-exchange capacity of grafted polyethylene copolymers with polymethylvinylpyridine (PMVP) [65]

Grafted PMVP content*, mass %	Nitrogen content, %		Ion-exchange capacity, mg-eq/g	Ion-exchange capacity after 10 sorption-desorption cycles, mg-eq/g
	by Dumas	by ion-exchange reaction		
12.1	2.2	1.23	0.88	0.85
18.7	–	1.78	1.27	1.21
36.8	3.0	3.33	2.38	2.32
56.0	–	4.01	2.88	2.84

*Determined by weighing (hereafter overweight).

TABLE 4

Influence of grafted poly-2-methyl-5-vinylpyridine content on the ion-exchange capacity of PP-PMVP filaments [66]

PMVP overweight, mass %	Ion-exchange capacity by 0.1 M HCl, mg-eq/g
2.9	0.35
3.2	0.48
11.8	0.87
16.5	1.01
22.8	1.85
61.4	4.75
101.0	5.02
120.1	6.20
147.0	7.96
275.0	8.30

The largest capacity is shown by the ion-exchange PP fibres grafted with acrylic acid or styrene (afterwards sulphonated) from solutions with monomer (AA or St) concentration no greater than 20–25 mass %. In this case grafting is more efficient, and it seems reasonable to propose that this effect is due to suppression of monomer homopolymerisation and its attendant increase in medium viscosity (so called gel effect). As a result the share of monomer used for graft co-polymerisation increases, and thus grafting becomes more efficient [72, 74].

Following procedures are found to improve the SEC of ion exchangers synthesized with PP fibres: preliminary oxidation of the initial PP fibre; grafting performance in reaction medium, providing moistening and swelling of the starting material for better monomers diffusion inside the polymer; grafted product previous storage in dichloroethane before sulphonation, providing the polymer matrix swelling allowing the better sulphonating reagent diffusion inside the matrix filaments (in the case of sulphonated cation exchangers); single washing (to prevent homopolymerisation) of PP fibres grafted with acrylic acid or styrene; grafting performance in the presence of radical polymerisation initiators. Let us note that with initiators a part of monomers is likely to be grafted through peroxides, formed by preliminary PP fibres oxidation, while another part is grafted via the chain transfer reactions. Note that benzoyl peroxide application appears to be more

efficient than that of azobisisobutyronitrile peroxide [68–75].

A two-stage grafting procedure has been also suggested in order to obtain ion exchangers with better capacity. At the first stage starting material is impregnated with the monomer at elevated temperatures. At the second stage it is heated with initiator [69].

Exchange kinetics at the ion-exchange fibres. Fibrous ion exchangers provide higher rate of exchange than the granular ones. On FIBAN fibres typical half-time of exchange is 2–10 s, while on industrial resins it ranges from 20 to 200 s (Fig. 1). Such a high rate is attained at the expense of a short path of ions diffusion inside the exchanging material. Gas or liquid pressure drop in the filtering bed may be adjusted by changing the bed density. Owing to high exchange rate, FIBAN exchangers may be arranged as thin filtering beds (7–20 mm), linear flow rates being rather high, *i.e.* up to 40 cm/min for liquids and up to 12 m/min for gases [58, 76].

2.2. Solvation properties

Polyolefinic fibre ion exchangers are characterized by a high osmotic stability (up to 99 %, [64]), allowing many times repeated acid-alkali treatment, drying-wetting, freezing-thawing

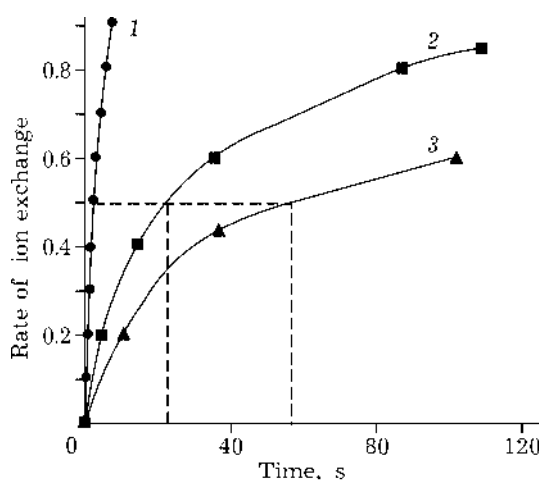


Fig. 1. Rate of Cl^- exchange for SO_4^{2-} on strong-base anion exchangers: fibrous FIBAN A-1 (1), granular Amberlite IRA 458 (2) and granular Castel A 102 (3) with dispersity 20–30 mesh. Experiment conditions: 0.9 M Na_2SO_4 solution, pH 3, $T = 25^\circ\text{C}$, intensive ionite mixing in solution; $t_{0.5}$, s: 2 (1), 26 (2), 56 (3).

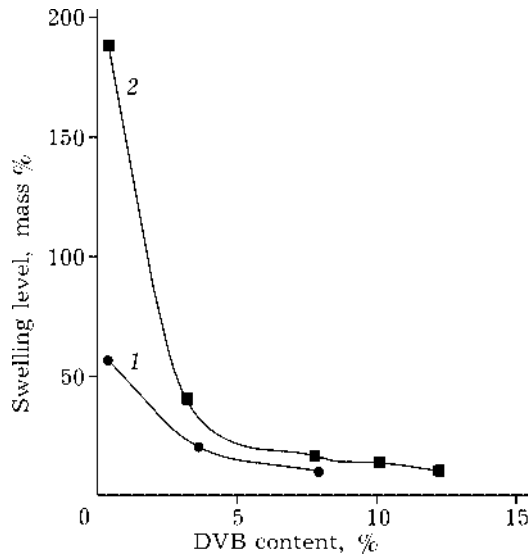


Fig. 2. Ionite swelling in water: 1 - fibrous SPS, 2 - granular KRS-10p.

[77]. They also demonstrate unessential swelling on operation (see Table 1 [62], Figs. 2 [78] and 3 [64]).

PP-based fibre ion exchangers SPS swell far less than the KRS-10p grains (see Fig. 2). Therefore, hydrophobic PP, along with DVB, is considered to decrease the equivalent moisture capacity of synthesized SPS. If necessary, 1–2 % DVB containing fibres are recommended to produce IEF with moisture capacity similar to that of granular ion exchangers. Besides, grafting points on SPS fibres serve as additional linkage places [62, 78].

Owing to the hydrophobic character of PP filaments, IEF swelling is provided by the swelling of polymer matrix formed on the surface and in the bulk. In the case that the filaments

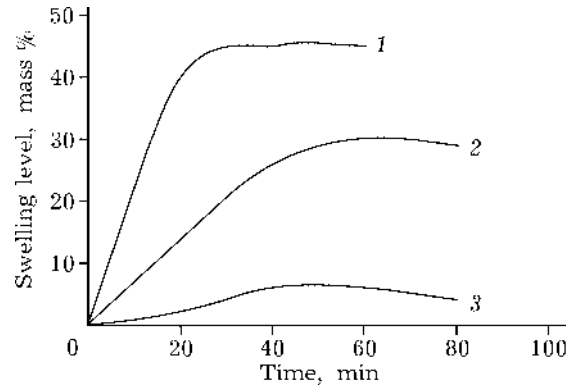


Fig. 3. Swelling kinetics characterizing fibrous cation exchangers based on profiled PP filaments (1), industrial PAN cords (2), and round PP filaments (3).

of circular section with smooth glass-like structure are used, the contribution of derived polymer matrix is lower than in case that the profiled filaments are applied. As a consequence (Fig. 3), the round PP-based IEF show the low swelling degree (not higher than 10 mass %). If one changes the profile of PP filaments by pressing their melt through filters with profiling holes followed by drawing, then the contribution of synthesized polymer matrix in IEF increases and it becomes more readily available for interaction with the solvent. The latter factor increases the swelling rate and constant as well as a limiting value of swelling, which attains 45 mass % for the profiled PPF based cationite. Moreover, its osmotic stability is 99 %, which exceeds that of industrial cationite KU-1, which is 92 % [64].

The stability studies of staple fibres and needle-punched nonwoven cloths of strong-base

TABLE 5

Osmotic stability of anion exchanger FIBAN A-1 (PP_{gr}-100 % PSt-2 % DVB) in cycles [77]

Parameter	Number of treatment cycles				
	initial	150	450	750	1000
Exchange capacity, mg-eq/g:					
total	2.81	2.78	2.80	2.80	2.82
by strong-base groups	2.59	2.53	2.54	2.51	2.47
by weakly base groups	0.22	0.25	0.26	0.29	0.35
Moisture capacity coefficient, mol H ₂ O/g-eq	9.70	9.70	8.99	8.93	8.78
Tensile strength, N	0.185	0.180	0.175	0.170	0.162
Ultimate elongation, %	30.2	31.5	37.7	34.1	32.7

Note. PP_{gr}-100 % PSt 2 % DVB - polypropylene fibres with grafted polystyrene (100 mass %) and DVB (2 mass %).

FIBAN A-1 [77] reveal their high resistance to cycles 1 M HCl–1 M NaOH, drying–wetting, freezing–thawing, which far exceeds that of conventional granular ion exchangers.

At the acid–base treatment (1 M HCl–1 M NaOH) one observes the small decrease of ion-exchange capacity of strong–base groups (Table 5) due to the partial dealkylation of quaternary functional groups while not accompanied by deamination. Many times repeated drying–wetting and freezing–thawing cycles as well as considerable moisture content changes do not lead to significant changes in anionite capacity. Thus after 100 drying–wetting cycles the average length of filaments remains sufficient to use them for nonwoven material production. At the same time granular anionites AB-17 are destroyed by more than 90 % under the same conditions [77].

In going from the fibrous Na–sulphocationite FIBAN K-1 to Mg–, Ba– and La–forms, moisture capacity decreases from 17.8 to 16.2, 11.4 and 10.7 mol H₂O/g–eq, respectively [79].

2.3. Mechanical properties

Vinyl monomers grafting to polyolefinic filaments somewhat elongate the filaments but decrease their strength by 10–20 % [67].

Grafted PMVM polymer amount determines mechanical properties of the modified fibres based on PE. Grafting up to 10 mass % of PMVP has no significant effect, but higher PMVP content (up to 40 mass %) elongates the fibres and decreases their strength. Moreover, kink strength increases, and double bending number slightly decreases. It is pertinent to note a much higher resistance to attrition: number of attrition cycles till the rupture of PE–PMVP fibres containing 25 and 40 mass % of grafted material is nearly an order of magnitude greater than that of the starting PE fibre material [65].

Materials change their mechanical properties at the each stage of the IEF synthesis (Table 6). Thus the 63 mass % of PSt to PPF grafting decreases the ultimate tensile stress by about

TABLE 6

Properties of grafted, chloromethylated and strong–base anion-exchange fibres based on polypropylene [80]

Fibre	SEC _{Cl}	$S \cdot 10^9$	d	$\sigma_t \pm \Delta\sigma$	$\epsilon_u \pm \Delta\epsilon$	$E \pm \Delta E$
PP initial	–	0.35	21	600 ± 50	40 ± 4	4.8 ± 0.5
PP irradiated (2 Mrad)	–	0.35	21	540 ± 40	32 ± 4	4.7 ± 0.4
PP _{gr} –42 % PSt	–	0.53	26	370 ± 3.5	40 ± 6	3.6 ± 3.0
PP _{gr} –63 % PSt	–	0.60	28	330 ± 2.4	52 ± 11	3.8 ± 0.2
PP _{gr} –106 % PSt	–	0.75	31	310 ± 2.1	48 ± 7	3.8 ± 0.2
PP _{gr} –144 % PSt	–	0.91	34	260 ± 20	39 ± 7	3.5 ± 0.2
PP _{gr} –173 % PSt	–	1.02	36	210 ± 15	50 ± 7	3.9 ± 0.2
PP _{gr} –212 % PSt	–	1.13	38	220 ± 42	49 ± 13	3.7 ± 0.8
PP _{gr} –233 % copolymer (99.9 % styrene and 0.1 % divinylbenzene)*	–	1.38	42	200 ± 11	46 ± 6	4.4 ± 0.3
PP _{gr} –42 % PSt, chloromethylated	–	1.02	36	300 ± 47	39 ± 8	3.8 ± 0.1
PP _{gr} –173 % PSt, chloromethylated	–	1.60	45	130 ± 11	37 ± 8	3.0 ± 0.5
PP _{gr} –34 % PSt, anion-exchange	1.8	0.91	34	300 ± 2.8	43 ± 8	2.1 ± 0.2
PP _{gr} –42 % PSt, anion-exchange	2.6	1.20	39	160 ± 22	41 ± 5	2.4 ± 0.3
PP _{gr} –106 % PSt, anion-exchange	2.4	1.50	44	150 ± 13	51 ± 5	2.1 ± 0.4
PP _{gr} –173 % PSt, anion-exchange	3.6	2.60	58	70 ± 3	19 ± 2	2.4 ± 0.1
PP _{gr} –212 % PSt, anion-exchange	3.8	3.20	64	63 ± 7	20 ± 3	2.2 ± 0.2
PP _{gr} –233 % copolymer (99.9 % styrene and 0.1 % divinylbenzene), anion-exchange	4.0	5.00	80	68 ± 14	21 ± 5	1.7 ± 0.2

Note. SEC_{Cl} is static exchange capacity of Cl[–] form of anion-exchange fibres, mg–eq/g; S is area of cross section of monofilaments, m²; d is average diameter, mm; σ_t is tensile strength, MPa; ϵ_u is ultimate elongation, %; E is elastic modulus, GPa.

*Polypropylene fibre with grafted (233 mass %) copolymer St and DVB.

1.8-fold, elastic modulus – by 25 %, and increases somewhat elongation. As PSt content increases, elastic modulus and ultimate elongation remain essentially unchanged, whereas the ultimate tensile stress progressively decreases. Chloromethylation and amination of grafted PSt chains increases fibres rigidity, however it is necessary to increase the grafted polymer amount to reveal this effect. In view of this experimental evidence it is concluded that the tensile strength and elastic modulus decrease is explained by increasing linear density of the fibres [80].

With progressing PP and PE modification, the fibre diameter increases, while strength and ultimate elongation decreases [62]. Fibres with modified PP matrix show then least elongation (Table 7). FIBAN fibres' properties are explained by their supramolecular structure peculiarities. Thus the X-ray patterns of PPF with the content of grafted polystyrene up to $\Delta = 173$ mass % show, when the great angles of incidence are used, that reflexes responsible for the crystal monoclinic oriented PP structure typical for the starting filaments taken for the grafting are still retained. Meridian and equatorial SAXS curves for the starting and modified filaments also prove that even at a high content of ionogenic grafted styrene copoly-

mer with DVB PP matrix retains its crystal structure. Meanwhile the grafted chains form their own discrete microstructures of shape and size that may change on following chloromethylation and amination. As a result, FIBAN fibres are characterized by the less swelling in comparison to fibre materials, in which grafted PSt forms a macrophase. Moreover, they retain satisfactory (see Table 7) strength and elasticity, allowing textile materials preparation on their basis [62, 81].

Some authors [71–73, 82] note that as initial PPF decrease in diameter, their mechanical properties get worse (fibres do not withstand the chemical modification procedure, being partially or totally destroyed). Modified fibres strength also decreases, as copolymer grafting reaction condition become more severe.

In order to study the effect of grafting on the structure and mechanical strength of synthesized materials, IEF samples with IEC ranging within 0.85–2.3 mg-eq/g were tested. XRS curves show that as grafting degree increases, material structure ordering decreases due to the growing number of defects. This phenomenon appears in the continuous decrease of peaks corresponding to the far order, which are clearly shown in the X-ray diffraction curve of the

TABLE 7

Mechanical properties of modified PP and PE fibres [62]

Sample No.	Fibre	d , μm	F , cN	σ , GPa	ε , %	E , GPa
1	PP initial	25	21.7	360	62	2.46
2	PP washed with benzene	26	13.3	240	105	1.76
3	PP _{gr} -120 % St + 2 % DVB	35	14.1	145	52	1.75
4	FIBAN K-1 based on sample 3	39	8.1	67	11	2.82
5	Chloromethylated sample 3	35	8.0	82	17	2.58
6	FIBAN A-1 (aminated sample 5)*	42	12.2	87	30	2.48
7	FIBAN A-2 (aminated sample 5)	37	10.1	87	26	1.93
8	FIBAN A-3 (aminated sample 5)	40	9.1	72	10	2.49
9	FIBAN A-4 (aminated sample 5)	38	7.7	67	13	1.89
10	PE initial	23	6.7	159	112	–
11	PP _{gr} -120 % St + 0.5 % DVB	34	6.0	72	78	–
12	FIBAN K-1 based on sample 11	41	4.3	32	63	–
13	FIBAN K-1 based on sample 11	40	4.1	32	63	–

Note. d is monofilament diameter; F is breaking stress, σ is tensile strength; ε is ultimate elongation; E is elastic modulus.

*Material was prepared through amination of sample 5.

initial PPF sample. As a result samples with high grafting degree have lower mechanical strength. However, reaction conditions optimisation may allow the wanted strength parameters of final products at a rather high grafting degree [73].

2.4. Thermal and chemical stability

Fibres based on grafted PE and PMVP copolymers well resist-aggressive media, their capacity remaining practically unchanged after several treatments by 3 % alkali and 1 % hydrochloric acid solutions. Essentially thermostability of PE filaments does not change after PMVP grafting, and ultimate tensile deformation does not increase at elevated temperatures at a rather high content of grafted component [65].

Temperature dependence of loading deformation of initial polypropylene, grafted filaments and anion exchangers shows that thermal and mechanical resistance of modified fibres depends on the grafted polymer nature. Grafting of PSt, which is less thermostable than PP matrix, makes final product less heat-resistant. However, the softening temperature of anion exchangers based on grafted fibres with $\Delta m = 63$ mass % is by 80–100 °C higher than that for the softening of initial PPF. Apparently, at temperature higher than that of PP melting the aminated polystyrene domains add thermostability to the anion-exchange fibres [80, 81]. Since chemical stability of PP and of functional benzyltrimethyl ammonium groups is rather high, and cross-

linked ionogenic grafted copolymer is hard to wash out from the PP matrix, physicochemical properties of strong-base fibrous anion exchangers FIBAN A-1, such as exchange capacity, moisture content and mass, are rather stable [77]. These properties were studied regarding the chemical resistance of chloride and hydroxyl forms of FIBAN A-1 on its treatment with the solutions of NaOH, H₂SO₄, HNO₃ and H₂O₂ (Table 8).

Tensile strength of mentioned anion exchangers decreases not lower than by 12 % after the treatment with the listed reagents, but ultimate elongation somewhat increases due to the washing out of some portion of low-molecular products from the inner amorphous domains and from the fibres surface [77].

Cation exchanger FIBAN K-4 was exposed to the action of solutions of 0.25 M H₂SO₄ and 5 M NaOH (30 min in boiling water bath), and of 10 mass % H₂O₂ (48 h at the room temperature). This sample slightly changes its exchange capacity and strength σ in concentrated acids and alkalis, yet essentially lowers its ultimate elongation ϵ , especially after treatment with acid and hydrogen peroxide (Table 9). With this regard it is necessary to improve the chemical and mechanical resistance of FIBAN K-4 for its repeated application in aggressive media [83].

Thermal resistance of FIBAN K-1 depends on the nature of exchanged cation and increases with the growing ionic potential of the latter [84].

As conditions of initial PPF formatting become severe to obtain the filaments with smaller diameter, their resistance to chemical reagents

TABLE 8

Properties of fibrous anion exchanger FIBAN A-1 before and after treatment in aggressive media [77]

Grafted filament composition and ion form of anionite	E_{IF}	Fibre after treatment							
		5 M NaOH		0.25 M H ₂ SO ₄		1 M HNO ₃		10 % H ₂ O ₂	
		E	Δm	E	Δm	E	Δm	E	Δm
PP _{gr} -100 % PSt-2 % DVB, Cl ⁻ -form	2.72	2.74	-0.9	2.70	-0.5	2.71	-0.6	2.74	+8.5
PP _{gr} -100 % PSt-2 % DVB, OH ⁻ -form	3.00	2.93	+3.7	3.00	+5.3	3.01	+3.2	2.91	+11.2
PP _{gr} -180 % PSt-2 % DVB, OH ⁻ -form	3.74	3.65	-1.3	3.60	-0.1	3.68	+3.0	3.57	-5.1

Note. IF is initial fibre; E is static exchange capacity, mg-eq/g; Δm is fibre mass change, %.

TABLE 9

Chemical resistance of cation exchanger FIBAN K-4 [83]

Treatment conditions	SEC, mg-eq/g	σ , GPa	ϵ , %
Non-treated cationite	6.2 (100)*	16.8 (100)	31 (100)
0.25 M H ₂ SO ₄	5.4 (87)	15.8 (94)	12 (39)
5 M NaOH	5.1 (82)	14.6 (87)	18 (58)
10 mass % H ₂ O ₂	3.6 (58)	10.9 (65)	11 (36)

Note. σ is tensile strength; ϵ is ultimate elongation.

*The bracketed parameters are given in percent of starting values.

decreases. Therefore, sometimes fibres do not withstand modification conditions, and are partially or totally destroyed [71, 72, 82].

Ionites based on PO fibres and films possess high thermal and mechanical resistance, and therefore withstand many times repeated regeneration cycles. Their exchange capacity after 10–20 sorption–desorption cycles decreases only by 1–4 % (see Table 3). Besides, regeneration of fibrous ion exchangers goes with considerably higher rate than that of granular ion exchangers [85].

3. APPLICATION OF POLYOLEFINIC ION-EXCHANGE FIBRES

All properties of ion-exchange fibres determine the field of their possible practical application. Since fibre ion exchangers demonstrate the high rate of ions sorption and desorption, their application may be rather efficient even with comparatively small capacity. Ion-exchange fibres and cloths are more convenient in operation, than resins, and allow less sophisticated technologies and apparatuses for ion exchange. Apparently, they will find wide application in the future practice [65].

Thus, sulphuric acid, being used as catalyst for esters production, provides aggressive wastewater. Fibrous sulphocationite in H⁺-form may act as a highly efficient acidic catalyst instead of sulphuric acid at isobornyl acetate synthesis from the commercial camphene and acetic acid [86].

Fibrous cation and anion exchangers have found application in the design of sorption elements in respirators for protection against sulphur dioxide, hydrogen halides and ammonia [87]. They are also used for gas cleaning from sulphur dioxide [88].

The kinetics of copper ions absorption by the PP-based fibrous cation exchanger and by granulated KU-2×8 shows that Cu²⁺–H⁺ equilibrium is attained 10-fold faster on fibres than on grains. Total exchange capacity (TEC) of synthesized IEF was 1.5–2.8 mg-eq/g, while that of KU-2×8 was 4.9 mg-eq/g. Meanwhile fibre working dynamic capacity (WDC) with respect to copper ions at a solution flow rate of 0.1 ml/min attained 1.0–1.7 mg-eq/g, which was 52–66 % of TEC. For granulated KU-2×8 these values were ~0.6 mg-eq/g and 13 %, respectively.

WDC of fibrous ion exchanger with respect to mercury ions at a solution flow rate of 0.1 ml/min is 1.2–2.2 mg-eq/g (77–88 % TEC), while for KU-2×8 these values are ~1.1 mg-eq/g and 22 %, respectively. As solution flow rate is increased to 0.5 ml/min, WDC decreases to 0.8–1.7 mg-eq/g (53–68 % TEC) for the fibrous ion exchanger, and to 0.6 mg-eq/g (12 % TEC) for granulated KU-2×8, respectively. Apparently, PP-based IEF may be successfully used for non-ferrous metals extraction from diluted solutions, such as wastewater hydrometallurgy waste products, etc. Their exchange capacity is better realized than that of granulated materials at the same loading of ion-exchange columns, especially at high flow rates [85].

When fibrous ion exchangers SPS were studied with regard to their application as sorbents in ion-exchange chromatography, varied were such parameters as degree of PPF grafting with PSt divinylbenzene content, column packing density and filling method (in the form of finely divided lengths or bundles of parallel filaments). KCl + CsCl solutions were used as system tests. Data were compared with those for Cs⁺ and K⁺ separation in the similar col-

umn filled with cationite Dowex-50×2 mesh 100–200. Data comparison shows that SPS ion exchangers are quite competitive to Dowex with regard to their ability for separation. SPS fibres demonstrate some additional advantages: constancy of bed size, reproducibility of column package. They also allow the regulation of filling degree and pressure drop. Therefore, they seem to be quite promising for application in the ion-exchange chromatography [78].

IEF advantages may be used for developing efficient purification of dye works solutions. SPS fibres are proved to adsorb up to 0.8 g/g of methylene blue dye under equilibrium conditions [78].

Fibre ion exchangers may be used to extract metals from water. Thus, for synthesized sulphocationite (SPC) dynamic capacity with respect to iron was 62.4 mass %. In static conditions, within 1 h of interaction, sorption capacity attained 76.8 and 65.6 mass % towards iron and nickel ions, respectively. Within 25 h, sample capacity for iron and nickel extraction increases to 92.4 and 74.0 mass %, respectively [70].

PP-based materials grafted with acrylic acid and containing certain dyes (malachite and methylene greens) are suggested for radiation control within the in a range of (5–400 kGy) [89].

Most studies are focused on ion exchangers FIBAN based on PP and PE fibres and obtained using radiation grafting polymerisation with isotope ^{60}Co . Their basic properties are given in Table 10. These fibres were meant for cleaning water and air from various pollutants such as acids, bases, amines, hydrogen sulphide, acid anhydrides, mercaptans, heterocyclic compounds, Cl_2 , Br_2 , H_2S , etc.). Moreover, they may be used for water purification from metal ions [Pb(II), Hg(II), Cu(II), Zn(II), Fe(II), Fe(III), Mn(II), etc.), viruses, bacteria, as well as for water softening and deionisation.

It is possible to apply high-molecular FIBAN for removing acids, alkalis and aggressive reagents from human skin and working surfaces, for protecting respiratory organs from toxic gases and vapours, for manufacturing protecting clothes, preventing human skin contact with spray, aerosols, vapour of acids and alkalis.

Fibrous ion exchangers FIBAN enter into the composition of substrates “Biona” together with natural (clinoptilolite) and synthetic (KU-2, EDE-10P, AN-2F) ionites saturated with biogenic macro- (K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Fe^{3+} , NO_3^- , SO_4^{2-} , H_2PO_4^-) and micro- (Mn^{2+} , Cu^{2+} , Zn^{2+} , MoO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$, Co^{2+} , Na^+ , Cl^-) elements. Ion-exchange substrates “Biona” (ionite soils)

TABLE 10
General properties of fibre materials FIBAN

Fibre	Functional groups	Type	SEC*	S**	WR	T_{\max}
FIBAN A-1	$\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	Monofunctional strong-base	2.7	0.8	0–14	50 (OH^-) 100 (Cl^-)
FIBAN K-1	$-\text{SO}_3^- \text{H}^+$	Monofunctional strong-acid	3.0	1.0	0–14	100 (H^+)
FIBAN K-1-1***	$-\text{SO}_3^-(\text{K}^+, \text{Co}^{2+})$ $\text{K}_x\text{Co}_y[\text{Fe}(\text{CN})_6]$	Strong-acid modified with potassium-cobalt ferrocyanide	3.0	0.7	0–11	100
FIBAN K-4	$-\text{COOH}$	Monofunctional weakly acid	5.0	1.1	5–13	80

Note. SEC is static exchange capacity, mg-eq/g; S is swelling, g H_2O /g ionite; WR is working pH range; T_{\max} is maximum temperature of operation for ion exchanger in form OH^- , Cl^- , and H^+ ($^\circ\text{C}$).

*Materials with larger or lesser ion-exchange capacity may be prepared.

**Materials with larger or lesser swelling may be prepared.

***Adsorbent of radiocesium.

are synthetic alternative to humus, developed at the Institute of Physical and Organic Chemistry, NAS of Belarus. "Biona" was developed for growing plants in outer space, at arctic stations, on atomic ice-breakers, and other objects, where it is not possible to use ordinary soils. Besides, "Biona" is recommended for many applications in agriculture for plants growth, adaptation, and fertilizing as well as for restoring fertility of exhausted and arid soils, and so on [90–92].

FIBAN K-1 is a sulphocationite based on PPF with radiation-grafted copolymer of St and DVB. It is a needle-punched nonwoven cloth with a surface density of 250–1000 g/m², and a staple fibre with 40 µm in diameter. Colour is light brown, cloth width is up to 160 cm, and cloth thickness ranges from 3 to 12 mm. Volume density is 0.1 kg/dm³, and yet it may run to 0.25 kg/dm³. Flow resistance of FIBAN K-1 depends on the packing density, determined by the type of textile and by additional forced packing. For air cleaning optimal bed density is 0.1 kg/dm³, and its thickness is 3–10 mm. In respirators bed thickness is 3 mm.

FIBAN K-1 is used as a support for catalysts for hydrogen oxidation, and in H⁺ form it may act as a highly efficient acid catalyst for producing high-octane fuel additives such as methyl *tert*-butyl (MTBE) and methyl *tert*-amyl ethers. It is also a catalyst for olefines isomerisation and alcohol dehydration [93–96]. Besides, FIBAN K-1 may be used for sorption, extraction and separation of antibiotics, dyes, vitamins, *etc.*,

and for concentrating ions at diluted solutions analysis.

Fibrous sulphocationites FIBAN K-1 may serve as the carriers for supported metal catalysts for acid-base and redox reactions [93, 95]. Varying conditions for fibre synthesis, one may regulate the character of functional groups distribution. Transferring synthetic ionites from H⁺-form to Ba²⁺-form, and then changing Ba²⁺ for cations [Pd(NH₃)₄]²⁺, one may obtain palladium catalysts for hydrogen oxidation. Different functional groups distribution provides regulated behaviour of catalytic active phase across the fibre section. In the samples with exchange capacity equal to 0.27 and 0.57 mg-eq/g the reduced palladium is distributed over the subsurface layer of fibres, layer thickness being up to 5 µm. In the samples with EC equal to 4.0 mg-eq/g the palladium-containing layer thickness attains 10–15 mm. Since palladium content in all samples is nearly the same, and degree of palladium reduction from Pd(II) to Pd⁰ in the hydrogen flow is also very similar, samples with higher EC seem to show a lower catalytic activity. Most likely, exchange rate decreases owing to diffusion hindrances provided by the palladium containing layer growth. As a result, catalysts with palladium distribution in the subsurface layer with a thickness less than 5 µm show highest activity in the reaction of hydrogen oxidation [93].

FIBAN K-1 catalytic activity in the MTBE synthesis via methanol interaction with isobutylene essentially exceeds that of industrial

TABLE 11

SEC effect on the catalytic properties of sulphocationite FIBAN K-1 in MTBE synthesis (temperature 75 °C, molar ratio CH₃OH : *i*-C₄H₈ = 1 : 1) [96]

SEC, mg-eq/g	Catalyst mass, g (V = 7.6 ml)	MTBE yield, %	Selectivity, %
<i>Catalyst FIBAN K-1</i>			
0.57	0.7	29	99
1.3	0.7	51	98
2.2	0.7	64	98
3.7	0.7	24	93
<i>Catalyst KU-2×8</i>			
4.8	0.7 + quartz	3	75
4.8	5.8	21	69

granulated cationite KU-2×8 (Table 11) [96]. More favourable reaction conditions are likely provided by the less thickness of polymer matrix and less cross-linkage degree in FIBAN. When FIBAN K-1 with small EC is used (0.57 and 1.3 mg-eq/g), MTBE yield decreases by virtue of catalytic activity decrease. Obviously in this case FIBAN has insufficient concentration of active proton sites. On the other hand, FIBAN K-1 with the highest capacity (SEC = 3.7 mg-eq/g) also provides lower product yield owing to the relatively large thickness of the grafted layer of copolymers St and DVB, which provide diffusion limitations for mass transfer in the reaction course. FIBAN K-1 with EC around 2.2 mg-eq/g, most likely providing the optimum combination of active sites concentration and grafted layer thickness, demonstrates the highest catalytic activity [96].

Ionite bed thickness, bed packing density, volume exchange capacity and solution flow rate are the main parameters affecting the efficiency of calcium ions extraction from the model solutions of hard water [97]. The most optimum conditions for the practical FIBAN K-1 application in the apparatus for water softening are the following: high density of filtering material packing, adsorbent bed thickness – 20–30 mm, water flow rate 16–37 cm/min. Granular ionites with such parameters (*e.g.* KU-2 used for comparison) demonstrated immediate breakthrough of calcium ions. One may use granular ion exchangers for high water softening only if filtering bed thickness is not less than 40 mm.

The exit curves of Ca^{2+} sorption on FIBAN K-1 and on KU-2 *versus* the rate of liquid flow through the 10 mm filtering bed are evidence for the good kinetic properties of fibre sulphocationites, allowing the high degree of water softening in thin filtering beds at relatively high liquid flow rates. Comparison with KU-2 shows that standard granular ionites arranged in thin beds (10–20 mm) allow Ca^{2+} breakthrough even in the first portion effluent, even at the lowest flow rate [97].

Ammonium and amine complexes of copper fixed in the bed of FIBAN K-1 catalyse turpentine oxidation [98]. Besides, in the wetted state these catalysts show higher efficiency.

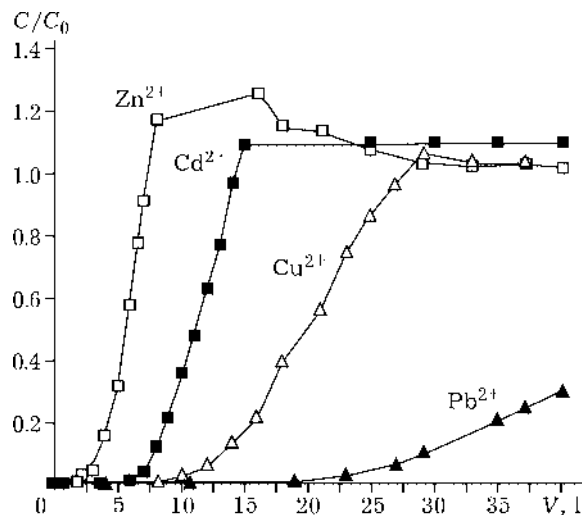


Fig. 4. Dynamics characterizing the sorption of heavy metals ions by cation exchanger FIBAN K-4 from model Me^{2+} -containing solutions. Experimental conditions: C_0 – Me^{2+} concentration in starting solution equal to 0.04 mg-eq/l; C – Me^{2+} concentration in eluate; pH 6; flow speed of model Me^{2+} -containing aqueous solution in adsorption column 9.5 cm/min; cationite bed thickness 3 cm, column diameter 1.25 cm, cationite mass 0.6 g.

FIBAN K-1 and obtained from which impregnated with potassium-cobalt ferrocyanide (FIBAN K-1-1) are used for extracting cesium, strontium and americium from natural waters [62].

Fibrous weakly acid cationite FIBAN K-4 contains groups $-\text{COOH}$, and it is a nonwoven needle-punched cloth with a surface density of 300–600 g/m². It may be prepared as staple fibre as well. Pressure drop on the filtering bed of FIBAN K-4 depends on the density of its packing, which in its turn is determined by the cloth type or additional thickening. Bed (2–6 cm thick) with a density of 0.16–0.20 kg/dm³ is found to be optimum for water purification.

Material FIBAN K-4 may be used for air purification (for example, for purifying industrial exhausts from ammonia, amines, alkali aerosols, *etc.*) and for water purification from heavy metal ions, including those of lead, copper, zinc, cadmium, as well as from iron ions (Fig. 4) [76].

Strong-base fibrous anionite FIBAN A-1 may be used efficiently for iron extraction from water as colloid-dispersed suspensions and in the plants for water purification (water pipe, basins, baths, *etc.*). It may also be used for the treatment of drinking water from municipal

water pipe and autonomous reservoirs. Besides, synchronous with the iron extraction, this material considerably reduces free chlorine content [99, 100].

4. CONCLUSIONS

In summary the essential advantages of fibrous ion exchangers are the following: high sorption rate and purification degree; wide variety of forms (nonwoven needle-punched, canvas-sewn, and other cloths, staple, fibres, filaments, *etc.*) allowing the use of diversified technologies and apparatus for numerous processes; capacity to withstand many times repeated sorption-desorption cycles and to provide low-pressure drop, *etc.*

At present ion exchangers based on polyolefinic fibrous materials are poorly understood, though they show considerable promise. Polyethylene and polypropylene are thermoplasts produced at the most scale, and their growing market allows development of new various purpose materials. Advanced modification methods may provide unique properties to these materials.

Polyolefinic ion-exchange fibres have highly developed surface, good sorption parameters, high mechanical strength, and demonstrate high chemical and osmotic stability. They may be used for various research and practical purposes ranging from analytical separation and preparative synthesis of organic substances to metals extraction from ores and liquids purification from various pollutants, *etc.*

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