

Superficial Acid-Base Properties of Polymer Fibres

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Abstract. Protolytic properties of fine fibre plastics based on polypropylene, polyethyleneterephthalate and polycarbonate were investigated. Acidic (carboxylic, hydroxyl) and basic Lewis sites (esters, carbonates, epoxies) were discovered on fibres surface using IR spectroscopy. The number of active groups of various nature and their pKa values were evaluated by potentiometric titration in aqueous and non-aqueous media. The tested fibres possess a low capacity for both acidic and basic sites on it. The results indicate that all the polymer fibre materials (PFM) due to the presence of carboxyl groups on the surfaces, enable modification of their surfaces with metal nanoparticles, thereby giving them unique properties, e.g., photocatalytic and bactericidal.

INTRODUCTION

Nowadays, polymer fibre materials (PFM) are used extensively in a variety of fields: medicine, bioengineering, electronics, gas and liquid filtering, in composite materials (for the reinforcement of polymeric matrix) [1-6]. Spheres of its application are determined by physical properties, chemical constitution of polymers, structure and acid-base properties of the surface, which depend on the way of material obtaining [7]. Furthermore, in such processes as liquids and gases purification from oil, petroleum, heavy metals, organic and biological contaminants along with developing catalytic and bactericidal systems, it is necessary to use fibre materials possessing a wide range of physical-chemical properties as well as presence of active sites on its surface, which are difficult to obtain using conventional methods of forming polymer fibre materials.

Currently, for the production of polymer fibre materials used methods of spinneret drawing, less melt blowing and spunbond. The centrifugal-blowing method is not widely used probably due to an operational properties instability of produced fibrous material [8]. At the very beginning of its development are methods of fibre formation by the direct impact of the working fluid flow (air, vapour, aerosols) on the freely outflowing stream of the polymer melt, using an ejector device [9]. In such devices, the melt of fibre-forming materials is sprayed at the expense of the blowing air stream energy, is usually at transonic velocities, and the subsequent solidification in the form of fibres. Using this method, fibrous materials may be formed with a given set of properties. In addition, the method of direct melt spraying using ejective spray heads (DMSE), by virtue of its technological features, is more suitable for processing of contaminated and non-homogeneous melts than other, which is especially important when using secondary raw materials.

The efficiency and application of polymer fibre material, obtained using ejector devices, depends on the protolytic properties of the surface, the nature and number of active sites. As a rule, protolytic properties of PFM superficial sites are bland so it is necessary to use non-aqueous media for its studying [10,11]. Investigation of

protolytic properties of fibres surface, as well as nature and a number of active sites, is necessary for realising the adsorptive capacity and selectivity of PFM. However, monitoring of surface energy and acid-base properties of PFM using surface analysis method based on the study of the phenomena of wetting test fluid, it is difficult due to the heterogeneity and the high degree of dispersion of these materials. Methods of spectroscopy and temperature-programmed desorption yield is mainly about the quality characteristics, since largely, determined by the bulk properties of the substance. Adsorption-chemical method, which is based on adsorption phenomena investigation from aqueous and non-aqueous solutions, is highly reliable, express, simple and mobile in hardware design [12]. At present, it is mainly used to determine the acidity of the surface of fine materials [13]. In order to study the surface of the polymer fibre materials, this method is not widely applied. Since the active sites of the polymer fibres surface are characterised by weak protolytic properties to assess their numbers and power indicators (pKa) it is advisable to use the method of potentiometric titration with non-aqueous or mixed solvents, which can enhance donor-acceptor properties.

Thus, the goal of this work is to investigate the superficial active groups of PFM, produced by the direct melt spraying method via an ejector device using polypropylene (PP), polyethyleneterephthalate (PETF) and polycarbonate (PC) as raw materials, and to evaluate of their protolytic properties by potentiometric titration with non-aqueous media.

EXPERIMENTAL PART

An analysis of the PFM samples obtained by DMSE method had been carried out. As raw materials for PFM producing was used melts of commodity polypropylene of 21080-16 grade issued in accordance with engineering specifications TU 2211-016-05796653-95 ed.3 by holding company «Sibur» (Russia), secondary polyethyleneterephthalate as fractured particles of plastic packaging and commodity polycarbonate of Makrolon-2456 grade produced by Bayer (Germany). The selection of samples was provided according to the Russian state standard GOST 10213.0-2002. "Staple fibre and tow chemical. Acceptance rules and the method of sampling" [14]. The chemical composition of the PFM sample surface was studied by IR spectroscopy using Fourier transform spectrometer Nikolet 6700, USA. The protolytic properties of the samples surface active sites was studied by potentiometric titration using pH-metre/millivolt metre PP-15, Germany, in aqueous and non-aqueous media. To intensify acidic properties of PFM samples surface was used dimethylformamide (DMF) (high grade, Russian state standard GOST 20289-74) as an organic solvent. That is why DMF is characterised with greater basicity and wider scale span (24.7) than water [15]. Titration of PFM acidic sites was provided in water and mixed water-DMF media (H₂O:DMF = 40:60), last was used for investigation of weakly acidic properties of carboxyl cationites [16]. Solutions of NaOH in relevant solvent were used as the titrant. Titration of PFM basic sites was provided in acetic acid, which is a strong protogenic solvent and possible to protonate even very weak basic groups in water, such as aldehydes and epoxides. As the titrant was used a perchloric acid ethanoate solution.

Potentiometric titration technic: 0.1 g PFM was filled with a solution with different ratios of titrant with concentration 0.1-0.01 M and pure solvent, the total volume was maintained constant (10ml). Upon reaching equilibrium, in the aqueous solution was measured the pH, in the organic solvent - E , then $\text{pH}(E) - V$ diagrams were plotted. In order to determine the titrant volume at the point of equilibrium (V_{EP}) differential curves were plotted in the coordinates $\Delta\text{pH}/\Delta V - V$ ($\Delta E/\Delta V - V$), which illustrate the dependence of pH (ΔpH) of solution or voltage potential (ΔE) on the volume of added titrant. Full exchange capacity (FEC) was calculated from the titration curves by alkali (acid) amount, added when (m) sample weight titrated until the point of equilibrium had been reached, as

$$\text{FEC} = (V_{\text{EP}} \cdot c_{\text{T}}) / m, \quad (1)$$

where c_{T} is titrant concentration.

The value of power parameters of active sites (pKa) in water was determined by linearized titration curves in the coordinates of the Henderson–Hasselbalch equation

$$\text{pH} = \text{pKa} + n \lg \left(\frac{\alpha}{1 - \alpha} \right), \quad (2)$$

where α is PFM neutralisation degree at the given moment of titration. In non-aqueous media – by the equation

$$\text{pKa} = \frac{E^0 - E_{0.5}}{0.059}, \quad (3)$$

where E^0 is the true value of electrode system potential in a given solvent using HClO_4 which was determined from the Nernst equation using step-by-step approach

$$E^0(\text{H}_2\text{O} : \text{DMF}) = 0.5V, \quad (4)$$

where $E_{0.5}$ is the half- neutralisation potential of active sites, was determined from titration curves.

The diagrams analysis was provided using the Origin 8.0 software.

RESULTS AND DISCUSSION

Investigation of PFM active groups by IR spectroscopy

The functional groups of studying fibrous and raw materials were identified using IR spectroscopy (table 1).

TABLE 1. The results of PFM superficial groups identification using IR spectroscopy

No	Polymer	v, cm^{-1}		Absorbing group
		Raw material	PFM	
1	PP	3250–3500	miss	OH ($-\text{COOH}$, H_2O)
		2966 (weak); 2918 (weak)	2966; 2918	C-H ($-\text{CH}_2-$, $-\text{CH}_3$)
		1740 (weak); 1650 (weak)	1717	C=O ($-\text{COOH}$)
		1376; 1456	1376 (weak); 1456 (weak)	C-H; C=C
			1241; 1094	C-O-C
2	PETF	3250–3650	3402 (weak)	OH ($-\text{COOH}$, H_2O)
		2983; 2890	2983; 2890 (weak)	C-H ($-\text{CH}_2-$, $-\text{CH}_3$)
		1718	1718	C=O ($-\text{COOH}$, $-\text{COO}-$)
		1259; 1118; 1097	1259; 1118; 1097	$-\text{COO}-$
3	PC	2988; 2870	2988; 2870	C-H ($-\text{CH}_2-$, $-\text{CH}_3$)
		1771	1771	C=O ($-\text{O}-\text{C}-\text{O}-$)
		1504	1504	C=C
		1221; 1107; 1079	1221; 1107; 1079	$-\text{O}-\text{C}-\text{O}-$

The results shows a slight difference in the IR spectra of the polyethylenterephthalate fibrous material (PETF PFM), polycarbonate fibrous material (PC PFM) and their raw materials samples. This provides an evidence that polymer degradation during melt forming fibres by spraying does not occur. It should be emphasised that PETF and PC chemical constitution characterised by the combination of aliphatic, aromatic and carbonyl fragments, which can impart specific properties of materials. All the samples have absorption bands in the $2800\text{--}3000\text{ cm}^{-1}$ range due to stretch vibration of the $-\text{CH}_3-$ and $-\text{CH}_2-$ groups. The wide absorption band in the PETF and PC IR spectra in the range of $3250\text{--}3650\text{ cm}^{-1}$ with the maximum of absorption at 3410 and 3335 cm^{-1} is due to phenolic and OH groups in carboxyl group, which contain the absorbed water [17]. Moreover, this absorption band is absent in the IR spectra of PP PFM or recognizable decreased in the PETF PFM spectra. Both raw polymer and PFM IR spectra of PETF and PC have absorption band in the range of carbonyl group vibrations: 1718 cm^{-1} (PETF) corresponds to the stretch vibration of C=O of the ester group, 1771 cm^{-1} (PC) corresponds to the stretch vibration of C=O of the carbonate group ($-\text{O}-\text{C}-\text{O}-$). The reason for carbonate group identification is the presence in PC PFM IR spectra of bands with maximum at 1221 , 1107 and 1079 cm^{-1} , which correspond to the antisymmetric bending vibration of this group, on the other hand, PETF – maximum at 1259 , 1118 and 1097 cm^{-1} , which correspond to the bending vibration of ester group. The sample of raw PC practically does not absorb in this range. The absorption band at 1717 cm^{-1} is appeared in the spectra of PFM based on PC and corresponds to the C=O bond in carboxyl group, at the

same time, absorption bands at 1241, 1094 cm^{-1} – to the bending vibration of simple ethers and/or epoxides bonds. Since the fibrous material is blown from the PP melt, ketone, aldehyde and other Lewis basic sites are formed at the fibres surface. Furthermore, it is possible harder PP PFM surface oxidation to a carboxyl group. Thus, all the samples of PFM possess the acidic (carboxyls) and the basic Lewis sites (ethers, epoxides) on their surface, which is characterised by weak protolytic properties.

Investigation of PFM protolytic properties by potentiometric titration

Studying of Acidic Sites in Water

The curves of PFM potentiometric titration in water with NaOH are presented in figure 1.

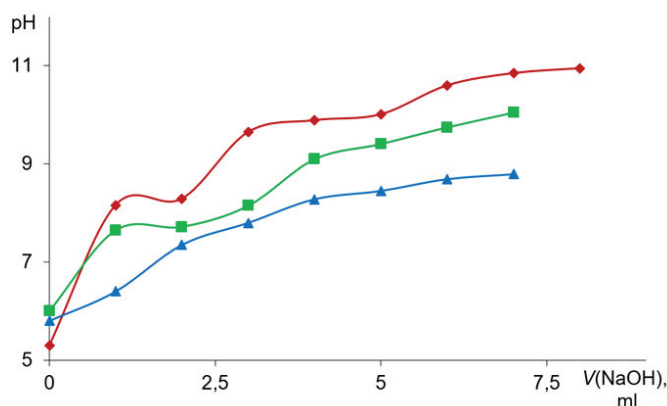


FIGURE 1. The curves of PFM potentiometric titration with varying concentrations of NaOH in aqueous medium:
◆ – PP PFM (0.01 M); ■ – PETF PFM (0.01 M); ▲ – PC PFM (0.05 M)

As it may be seen from the graph (fig. 1), potentiometric titration curves of PP and PETF PFM have inflections, which are considerably shifted to a basic area; it provides an evidence for a weakly acid type of these fibrous materials superficial active sites. Moreover, the graph for PP sample has two inflections and plainly indicates two types of acidic sites. Due to easy oxidation of polypropylene Bronsted acidic sites – carboxyl and hydroxyl groups is available to be formed.

The samples based on PC demonstrate a hydrophobic property: it practically does not turgescence in the water floating on the surface this is why PC PFM could not be titrated in water. The hydrophobicity of the PC fibrous material may be explained by the fact that when the sample in contact with aqueous solutions PC hydrolysis reaction proceeds, leading not only to an ester bond cleavage but also to a complete separation of the carbonate groups. Such process was described in work [18], which is devoted to an investigation of PC surface modification with titanium oxides in aqueous solutions.

Table. 2 shows the values of PFM capacitance, which are determined from titration curves (fig. 1) and active sites acid dissociation constants values, which, in their order, are calculated from Henderson–Hasselbalch equation (2).

TABLE 2. Capacitance values and pKa of acidic sites of PFM in water

PFM	pKa	<i>E</i> , mmol/g	FEC, mmol/g
PP	9.87 ± 0.02	0.033	0.061
PETF	7.56 ± 0.12	0.035	0.035
PC	can't be titrated		

The results in table 2 provide an evidence for weakly acid surface property of PFM. More powerful acidic properties of PETF PFM may be related to Lewis basic sites influence.

Figure 2 shows PFM potentiometric titration curves with NaOH in water-dimethylformamide medium.

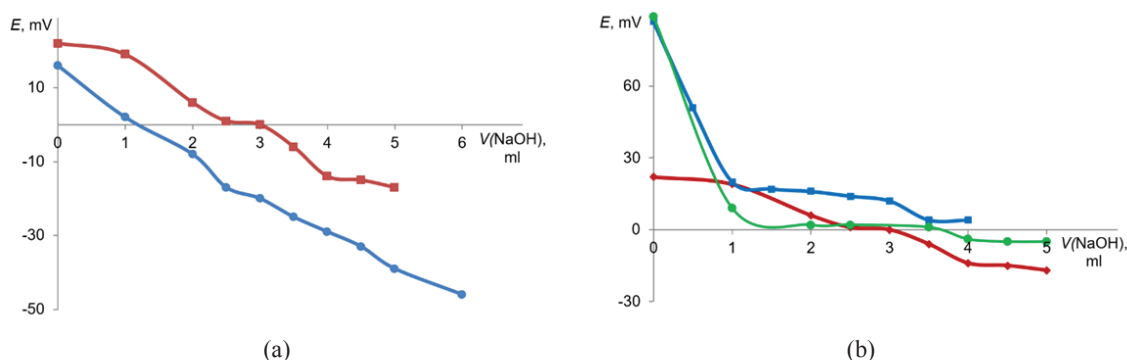


FIGURE 2. The curves of PFM potentiometric titration with solution of NaOH in H₂O:DFM medium:

a – PP PFM at holding time: — 1 day; — 1 week;
b – holding time is 1 week: — PP PFM; — PETF PFM; — PC PFM

To determine the time to reach equilibrium the potential in vessels with varying amounts of titrant was measured every day during a week. Figure 2a presents the PP PFM titration curves with potential measurement in a day and a week. It is shown that the equilibrium of PP PFM titration in the mixed solvent is established for a long time (up to 7 days). Figure 2b illustrates that in the water-organic solvent are titrated all tested fibres. Consequently, using water-organic instead of water medium is suppressed the PC PFM hydrolysis reaction and make it possible to titrate its superficial acidic sites. The titration curves of the fibrous materials based on PETF and PC have only one inflection, besides it is shown a significant decreasing of the capacitance at the initial stage ($\Delta E=70-90$ mV), which indicates a change in conformational state of the fibres when turgescence in a solvent associated with rupture of intermolecular bonds. At the titration curve of PP PFM in water-DMF medium (fig. 2b), there are two inflections, as when titrated in water (fig. 1).

Values of different acidic sites: capacitance (E), full exchange capacity (FEC) of PFM and power parameters, which are determined from titration curves (fig. 2b) are presented in table 3.

TABLE 3. The results of PFM acidic sites dissociation constant (pKa) and their number determination using potentiometric titration with H₂O:DMF medium

PFM	E , mmol/g	FEC, mmol/g	pKa	pKa [19]	
				CH ₃ COOH	cation exchange resin CBR
PP	0.036	0.053	8.47 ± 0.11	8.30	8.41
PETF	0.037	0.037	8.41 ± 0.21		
PC	1.30	1.30	8.36 ± 0.16		

The results in table 3 provide an evidence for a weakly acidic surface property of PFM. Acidic properties of PETF PFM are more powerful, it may be related to Lewis basic sites influence.

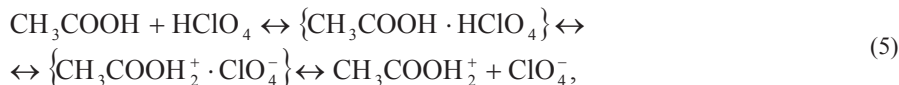
Moreover, the results indicate that the capacitance value of PFM samples based on PET and PP, determined from titration curves in water and in a mixed solvent, are well correlated. The capacitance of PC PFM value is significantly higher, therefore, this material is promising for use in sorption processes in mixed and non-aqueous solvents. Comparison of pKa values indicates that the use of a water-DMF medium is offsetting the difference in power of acid sites of the samples due to the DMF solvent is more basic than water. Reduction of the dissociation constant value of PETF PFM acidic sites in H₂O:DMF medium, compared with water, related, apparently, to a decrease of the dielectric constant of the mixed solvent ($\epsilon(\text{DMF}) = 37.2$, $\epsilon(\text{H}_2\text{O}) = 80.4$), resulting in suppression of the dissociation. Evidence of this is the pKa values, determined in [19] for a monomeric analogue of the carboxyl

groups - acetic acid and carboxyl cationite of CBR type in the water:DMF medium with DMF mass fraction of 60% (Table 3).

Thus, it is shown that the investigated fibers have on their surface weakly acidic active sites (carboxyls, hydroxyls). Replacement of water to the mixed solvent of H₂O:DMF suppresses hydrolysis of PFM based on PC. It was found that the H₂O:DFM medium has a leveling effect on the PFM active sites.

Studying of Basic Sites in Acetic Acid

As titrant in an acetic acid medium, most commonly using the perchloric acid, which dissociates according to the equation



forming ion pairs predominantly [12], since the acetic acid permittivity ($\epsilon(\text{CH}_3\text{COOH}) = 6.2$) is much less than that of water ($\epsilon(\text{H}_2\text{O}) = 80.4$).

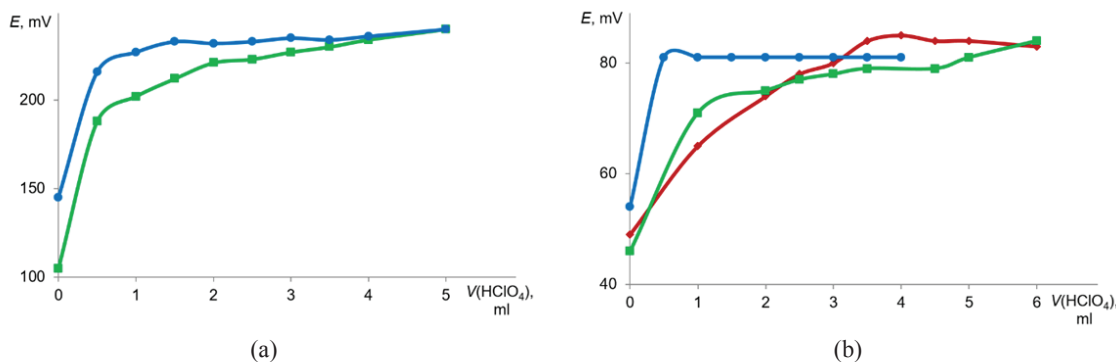
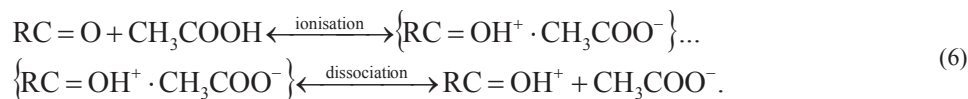


FIGURE 3. The curves of PFM potentiometric titration with solution of HClO₄ (holding time is 1 week): a – in water; b – in acetic acid: ◆ – PP PFM ; ■ – PETF PFM; ● – PC PFM

As it is evident from fig. 3, in the PFM titration curves in both media water and acetic acid, inflections are virtually absent. In water electron-donating Lewis groups (esters, carbonates, epoxides), found on the surface of PFM by IR spectroscopy, are not protonated, apparently due to their extremely low basicity.

The absence of inflections in the graphs, when titrated in a protogenic solvent, may be related to the fact that in acetic acid processes of association and ion pairs formation are prevailed due to the low polarity non-aqueous solvent, i.e. dissociation of electron-donating protolytic groups is suppressed. Thus, dissociation of carbonyl in acetic acid can be represented as follows:



In this regard, the use of non-aqueous titration is not possible to evaluate the number of PFM basic sites and power parameters of their dissociation constants (pK_b).

CONCLUSION

The potentiometric titration method was used to study the dissociation constants of active sites of PP, PETF and PC fibrous materials, obtained by the method of direct melt spraying using ejective spray heads. Found constants values indicate that the PFM, regardless of the chemical composition of raw material, characterized by a very weak acidic properties (pK_a ~ 8). Using IR spectroscopy was studied the chemical constitution of the PFM surface, based

on PP, PETF and PC. It is shown that all the fibrous materials possess the acidic (carboxyls, hydroxyls) and the basic Lewis sites (ethers, carbonates, epoxides). Since there are carboxyl groups on the surface of the polymer fibrous materials, this groups when dissociation produced one macromolecular polyvalent ion complex and a large number of simple ions. Due to the hydrogen ions, dissociation of the carboxyl groups does not occur at low pH. Thus, PFM via ionised carboxyl groups enable to bind metal-modifiers to complexes, and, at low pH, to stabilise them by the formation of hydrogen bonds between the hydrogen of the hydroxyl and the oxygen atom located at the particle surface. Despite that, the energy of the hydrogen bond is small, undissociated carboxyl groups contribute to the preliminary consolidation of nanoparticles. Thus, the results indicate that all the PFM due to the presence of carboxyl groups on the surfaces, enable modification of their surfaces with metal nanoparticles, thereby giving them unique properties, e.g., photocatalytic and bactericidal. The findings agree well with earlier results [20-22].

In addition, a low amount of PFM acid sites and the low power parameters of their dissociation constants along with low basicity of Lewis electron-donating groups (ethers, carbonates, epoxides) suggest that polymer melts are not subjected to intensive thermal destruction when spraying via the ejective spray heads and forming fibres. Consequently, a minor amount of structural defects are formed in the fibrous materials, including, not typical for the raw polymer, the unsaturated oxygen-containing functional groups such as hydroperoxides, carbonyls, ethers etc.

It draws us to conclude that surface properties of PFM based on PP, PETF and PC obtained by DMSE are capable of being used to create a wide range of products based on these new competitive advantages. Especially perspective is the use of these materials as adsorbents for water purification from heavy and toxic metals, oil and petroleum, and recovery oil from the contaminated surface of water and soil. Moreover, use of PFM as carriers of active metal nanoparticles for creating the catalytic and bactericidal systems not less important.

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