Polyacrylonitrile-based ion-exchange material synthesis and combustion properties investigation

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Abstract. Many ion exchange materials have been obtained on the basis of polyacrylonitrile (PAN) fiber. It is also known from the literature that PAN is also used in the creation of hard-to-burn materials. This is achieved by introducing functional active groups into PAN. Therefore, polyacrylonitrile was modified with triethanolamine (TEA) in order to synthesize an ion exchange material in this work. The reaction mechanism of the synthesized ion exchange substances, their structure, physicochemical properties, stability in different environments and sorption properties were studied. A flame retardant material containing nitrogen and phosphorus was obtained by attaching phosphoric acid to the resulting ion exchange material. The resulting ion exchange PAN fabric was treated with phosphoric acid to produce flame retardant PAN fabrics (FR-PAN). The incorporation of triethanolamine and phosphorus into PAN fabric was investigated using Fourier transform infrared spectroscopy (FTIR). In order to evaluate the thermal stability and fire resistance of the obtained FR-PAN, limiting oxygen index (LOI) and thermo gravimetric analyzes (TGA) were performed. Thermal analysis showed that the newly obtained FR-PAN had higher thermal stability than the original PAN fabric, produced 21 wt.% more char, and increased the limited oxygen index from 18% to 31.5%.

1 Introduction

Today, polyacrylonitrile fiber is one of the most widely used synthetic fibers, and it is widely used in the textile industry due to its good heat retention and resistance to physical and chemical effects [1]. However, since PAN fiber has an oxygen index of 17%, it burns quickly and emits harmful gases such as toxic hydrogen cyanide along with smoke. This severely limits its widespread use. Creating flame retardant PAN fiber helps overcome these challenges. One of these methods involves the synthesis of phosphorus-containing acrylonitrile polymers to improve the flame resistance of PAN fiber or fabric [2]. This is

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achieved by adding more than 3.5 wt.% phosphorus to PAN fiber and its fabrics [3]. Therefore, environmentally friendly and effective fire-resistant synthetic fibers containing phosphorus and nitrogen are widely used [4]. Addition of phosphorus has become one of the most reliable methods to ensure fire resistance of PAN fibers [5]. But in most cases, the incompatibility of additives added to acrylonitrile polymers increases fire resistance and the deterioration of the mechanical properties of PAN fibers. Materials based on synthetic and natural fibers containing phosphorus, it is of great interest due to their environmental friendliness, low smoke and gas emission, as well as high fire resistance. Complex combustible materials containing phosphorus contribute to forming a char layer in the condensed phase and are effective flame-retardants for polymer fibers [6].

Two main methods are used to improve the flame resistance of PAN, firstly, surface modification by grafting different flame retardant groups, and secondly, incorporating flame retardant materials into the polymer composition, including mixing flame retardant materials with polymer and forming composites or nanocomposites, as well as a synthesis of polymer chains containing fire-resistant groups [7].

In one work aimed at obtaining a fire-resistant material [8], polyacrylonitrile was first modified with hydroxyethyl methacrylate, then phosphoric acid was attached using a urea catalyst to produce a fire-resistant polymer containing phosphorus. In this work, the limited oxygen index is 32%. In another work [9], to obtain FR-PAN, polyacrylonitrile was first modified with ethylenediamine, and then phosphoric acid was added under a urea catalyst. To create the corresponding FR-PAN fabric by researchers [10], phosphoric acid was bonded to the PAN fabric and aminated using triethanolamine. In this study, polyacrylonitrile was grafted onto the surface of polyacrylonitrile fabric in a novel way to create FR-PAN fabric containing nitrogen and phosphorus using triethanolamine and phosphoric acid. Based on PAN fabric and triethanolamine, an anion exchange material with basic properties was synthesized. The reaction mechanism of the obtained anion exchange substances, their structure, physicochemical properties, stability in different environments, sorption characteristics and fire resistance properties were studied. It shows that slightly better results were obtained than the obtained urea-based refractory material (PAN-KDM). The limited oxygen index did not exceed 30% in difficult combustible material obtained based on PAN-KDM.

2 Materials and methods

It is known that temperature and time are the main factors affecting the course of chemical reactions. The influence of temperature and time on the reaction of nucleophilic addition of triethanolamine and modification of PAN fibers was studied. The modification process was initially carried out at different temperatures for a fixed period of 3 hours. The research results showed that the favourable temperature for modification of PAN with triethanolamine was 175-180°C. It was also observed that the process has a negative effect on the mechanical strength of the PAN fiber at temperatures higher than those selected at this fixed time for modification.

Changes in the physicochemical and sorption properties of anion exchange materials formed during the modification process were monitored by checking the value of the static exchange capacity (SEC). Values of SEC ranging from 0.78 to 4.1 meq/g were obtained according to the temperatures mentioned (Table 1).

Table 1. Effect of temperature during modification of PAN with triethanolamine (reaction time 3 hours)

№	Reaction temperature, °C	Weight of PAN, g	Weight of modified PAN, g	Weight gain, %	Exchange capacity: meq/g
1	150	5.02	5.77	14.94	0.8
2	160	5.07	5.91	16.57	2.06
3	170	5.12	6.20	21.09	3.9
4	180	5.05	6.31	24.95	4.1
5	190	5.03	6.19	23.06	4.0

The effect of time on the modification process of PAN with triethanolamine was also investigated. Also, experimentally, a reaction time of 4 hours at 175°C was found to be sufficient and optimal (Table 2). Apparently, after a certain immobilization of triethanolamine molecules in the polymer matrix, the further possibility of the reaction is hindered by the large conformation of the modifying reagent.

Table 2. The effect of time on the static exchange capacity of the modification process (temperature of reaction 175 °C).

№	Reaction time, h	Weight of PAN, g	Weight of modified PAN, g	Weight gain, %	Exchange capacity: meq/g
1	1	5.12	6.07	18.55	2.4
2	2	5.11	6.23	21.91	3.2
3	3	5.19	6.46	24.47	4.02
4	4	5.06	6.61	30.63	4.41
5	5	5.14	6.63	28.98	4.4

To find out the grafting percentage of triethanolamine, the modified fiber (PAN-TEA) was dried in a drying oven at 50°C for 6 hours, and the grafting percentage was found using the following equation:

$$GP = \frac{W_2 - W_1}{W_1} \times 100\%,$$

where W_1 is the mass of PAN and W_2 is the mass of modified PAN.

2.1 Preparation of FR-PAN fabric from ion exchange material

The phosphorylation of anion-exchange materials and changes in their combustion properties were studied at this stage of the research. The modified PAN fabric was properly washed with deionized water before being dried in a 60°C oven. The dried fabric was placed in a 500 ml conical flask and immersed in a 5 wt.% phosphoric acid solution at room temperature for 24 hours.

3 Results and discussion

3.1 Thermo gravimetric analysis of PAN and FR-PAN

Figure 1 shows the TG analysis curves of PAN fabric and FR-PAN fabric. In this picture, the PAN fabric showed a different decomposition curve than the FR-PAN fabric, i.e. a slow first and then a sharp mass loss curve with increasing temperature.

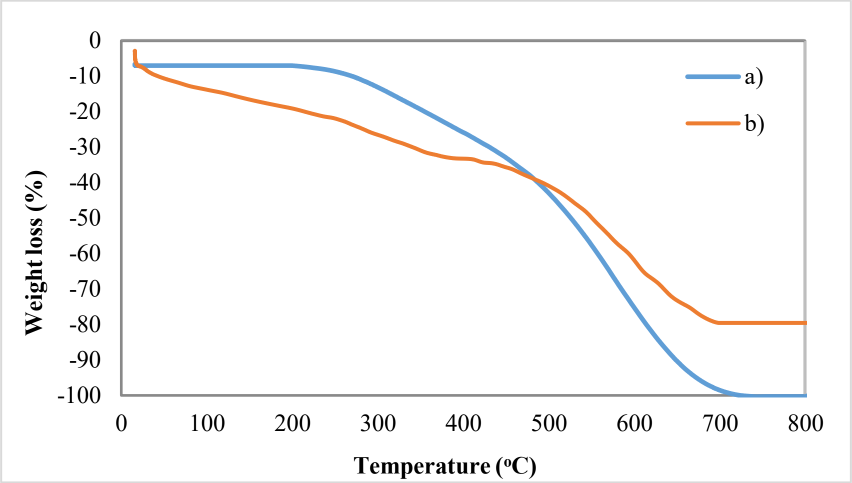

Fig. 1. TG curves of PAN (a) and FR-PAN (b) fabrics.

If the decomposition of initial PAN is divided into phases, a small mass loss was detected in the first stage of the decomposition curve in the temperature range up to 258°C. This phase has been reduced slightly due to the cyclization process. The cyclization process happens mostly for neighboring cyano groups [10], and the mass falls as a result of gas release from subsequent decomposition. There is a loss of mass and a minor drop in the curve as a result of gas separation. The rate of weight loss increases between 260°C and 482°C. The carbon-carbon structure degrades in this zone. As a result, various gases, including light gases like hydrogen, hydrogen cyanide, and ammonia, are emitted during this step [11]. Thermal decomposition happens during the following weight loss, resulting in a higher weight loss than the prior ones. As a result, hydrogen gas is one of the primary emitted gases during this stage of decomposition. When the thermal analysis of the original PAN is compared to the thermal analysis of the FR-PAN, it can be shown (Fig.1, b) that the weight loss curve is slightly higher at the beginning temperatures. If the weight loss process for FR-PAN is broken down, the first stage occurred at temperatures ranging from 44.9°C to 395.4°C, with a mass loss of around 24.38 wt.%. This loss is caused by the changed fabric's bound water and partially bound amino acids. Furthermore, this stage is one of the primary stages of mass loss. The second stage occurred between 395.4°C and 513.8°C, resulting in a 5.29 wt.% mass loss. This could be owing to the mass loss caused by the breakdown of the flame retardant PAN's ammonium and phosphate groups [12]. Phosphoric acid, ammonia, polyphosphoric acid, and other chemicals may increase at this stage [13]. The second step of fabric weight loss began at 513.8°C and proceeded to 692.4°C, the main degradation stage of FR-PAN, resulting in a weight loss of approximately 35.9 wt.%. The carbonized layer transmits heat very poorly in this process, which serves to slow down the combustion process, lower the flame temperature, and prevent burning [14]. The final stage started at 692.4°C and ended in the temperature range of 785.4°C, with a mass loss of around 0.5 wt.%.

3.2 IR spectrum analysis of PAN and modified PAN

The analysis of the IR spectrum of polyacrylonitrile fabric revealed (Fig. 2, a) that in the IR spectrum of unmodified polyacrylonitrile (a), there are peaks corresponding to -CN groups in the 2241 cm^{-1} area, corresponding peaks for CH_2 groups in the 2920 cm^{-1} area, and deformation vibrations of CH_2 groups in the 1450 cm^{-1} regions. It was also discovered that C=O groups in methyl acrylate and itaconic acid have deformation vibrations in the 1729 cm^{-1} range.

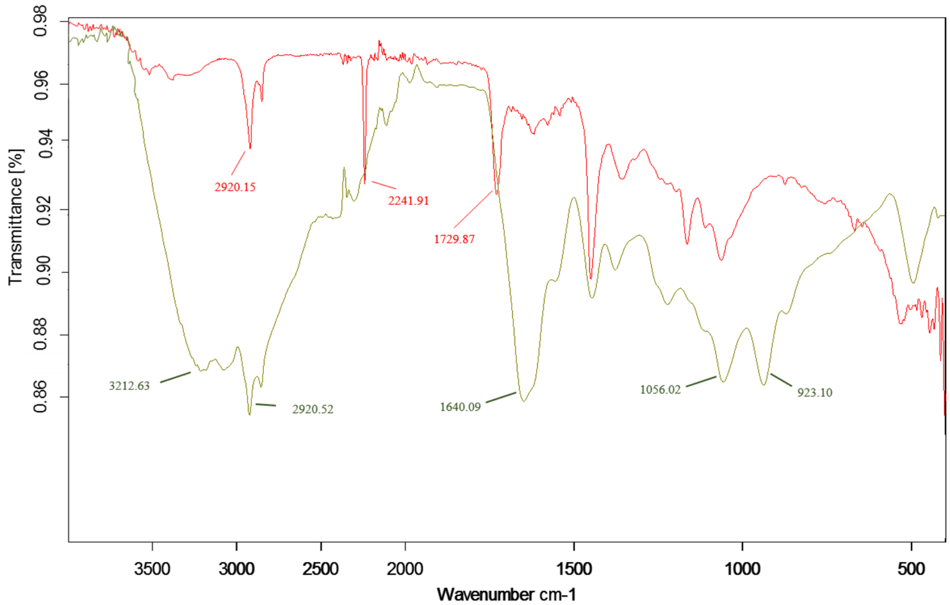

Fig.2. FTIR specters of PAN (a), and FR-PAN (b) fabrics.

As can be seen from the IR-spectrum of modified PAN (Fig. 2, b), a decrease in the intensity of the absorption line was observed in the region of 2241 cm^{-1} belonging to the -CN group. This indicates a decrease in the amount of –C≡N groups in the sample. Also, in the IR-spectrum of FR-PAN, new extended absorption lines corresponding to -OH and $-NH_2$ groups appeared in the regions of 3303 cm^{-1} and 3214 cm^{-1}, vibrations corresponding to the groups -C=NH in the region of 1246 cm^{-1}. The wavelength of 923 cm^{-1} in the modified sample was found to belong to the O-P-O groups in phosphoric acid.

The limiting oxygen index values of the original PAN and FR-PAN are presented in Table 3. The limited oxygen index value of FR-PAN (31.5%) was shown to be significantly higher than that of the original PAN fabric (18%) even after 20 washing cycles.

Table 3. The limiting oxygen index values of different fabrics before and after washing.

Samples	LOI (%)					
	Cycles	**0**	**5**	**10**	**15**	**20**
PAN	18		18	18	18	18
FR-PAN	31,5		30,2	29,8	29,2	29.0

The main disadvantage of modified PAN cloth is that its dyeing qualities deteriorate after alteration. Furthermore, modified PAN loses transparency [15] and turns yellowish-brown in color.

4 Conclusion

A new ion exchange material was created by chemically modifying PAN with triethanolamine. From the acquired ion exchange material, a method for creating difficult flammable compounds comprising phosphorus and nitrogen was created. The composition and qualities of the resulting non-flammable polyacrylonitrile fabric were studied using TGA, FTIR analysis, and limited oxygen index testing. According to the TG study, the thermal stability of FR-PAN is higher than that of the original PAN fiber, and the char residue is 21 wt.% higher than that of the original PAN. The limited oxygen index value of FR-PAN grew to 31.5% after 20 washing cycles, indicating that hard-to-burn materials based on PAN have been created.

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