

Formation of Porous Poly(tetrafluoroethylene) Using a Partially Gasified Porogen

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Abstract: A method has been developed to form porous Poly(tetrafluoroethylene) (PTFE) using a partially gasified porogen. Sodium hydrogen carbonate (NaHCO_3) was selected as a porogen. The standard process for the production of porous materials including mixing, pressing, thermal treatment, porogen leaching, and drying was employed. The formation of porous PTFE structures was studied in a broad concentration range of NaHCO_3 . The mechanism for the formation of such structures has proposed. Besides, it is shown that NaHCO_3 porogen creates permeable porous structures with porosities less than 50%, compared with the lowest porosity of 70% attainable with the standard NaCl porogen. The airflow rate characteristics and the permeability of the two porous PTFE samples were determined through pressure difference measurement. The obtained flow rate characteristic was linear, which suggested a laminar airflow in the pores. The use of NaHCO_3 porogen has allowed a five-fold cut of the leaching time, a more than three times enhancement of the permeability, and an increase in the hydraulic pore diameter by a factor of 1.8, as compared to the corresponding NaCl porogen data.

Keywords: Porous polymers, Poly(tetrafluoroethylene), NaHCO_3 porogen, NaCl porogen, Porous structure, Permeability.

1. INTRODUCTION

Porous materials have various applications such as filtration and separation, fiber optics, biomedical implants, tissue engineering, catalytic substrates, thermal and sound insulations, ion exchangers, fuel cells, aerators, sorbents, silencers, shoes, and clothing, etc [1-4]. Among them porous polymers are gaining increased interest in several areas due to their unique physicochemical properties [5-8]. Various applications require special pore structures, each of which can be obtained by its method [9].

Numerous methods based on chemical, physical, and chemical-physical processes have been developed to produce porous polymers [6, 10-14]. Bulk porous polymers are often prepared by adding various porogens and considering their subsequent dissolution, evaporation, or burning out [15, 16]. A controllable porous structure is often formed using soluble inorganic materials as porogens [15, 17, 18]. However, such porogens are usually inefficient in forming open porosity (ϕ) less than 70% [19].

The present work aimed to study the effect of a porogen that is partially gasified, helps to form bulk porous polymers. This method may allow us

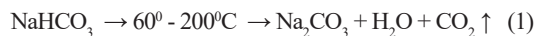
to obtain a polymer with a low ϕ value. The unreacted solid porogen fraction that remained in the pores can be removed by leaching. Such a porogen has never been in use before. The microstructure of the porous polymer formed by the partially gasified porogen was compared with the microstructure of the one formed by the leached porogen. The microstructures of partially gasified porogen and the leached porogen-derived porous polymers were compared with each other. Also, the permeability of these materials was studied.

2. EXPERIMENTAL PROCEDURE

Porous polymers were produced from a mixture of porogen-polymer powder that was subjected to pressing, thermal treatment, porogen leaching, and drying. The base of the porous polymer was PTFE with the particle size $<100 \mu\text{m}$ and density $2.19 \times 10^3 \text{ kg/m}^3$. The PTFE used was a commercial-grade F-4PN supplied by HaloPolymer Perm, OJSC.

NaHCO_3 served as a partially gasified porogen. Previously, the NaHCO_3 porogen has been subjected only to leaching [20, 21]. The density of NaHCO_3 ($2.159 \times 10^3 \text{ kg/m}^3$) is close to that of PTFE, which is favorable for preparing a quali-

tative mixture of the components [22]. On heating above 60°C, NaHCO₃ transforms into sodium carbonate (Na₂CO₃), releasing water and carbon dioxide, according to (eq.1).



Na₂CO₃ has a high melting temperature (852°C) and is well soluble in water reaching the highest solubility at T=40°C.

The mixtures of different PTFE - NaHCO₃ proportions were prepared in a laboratory blender with a rotation frequency of the grinding knives 1200 rpm, a duration time of 60 s, and at T < 19°C. The resulting mixtures were pressed in a form (40 mm ID, exposure time 30 s, and pressure 155 ± 5 MPa) to produce 12 ± 0.1 mm thick disks. The semimanufactures were then heated together with a furnace up to T = 385 ± 5°C (NaHCO₃ was partially gasified in the temperature interval T = 60 - 200°C), kept at this temperature for an hour and then cooled together with the furnace. The solid fraction Na₂CO₃ of the porogen that remained in the semimanufactures after partial gasification NaHCO₃ was removed through solving in water at T = 40°C. Drying at T = 100°C during 12 hours was the final stage of preparation of porous PTFE.

It is known [19, 23, 24] that NaCl is a water-soluble porogen that is most widely used to produce porous polymer materials. It is therefore expedient to compare the results of this study and the data taken with the NaCl porogen. The density of NaCl is 2.16 × 10³ kg/m³, which affords qualitative mixing with PTFE. The technologies of preparation of porous PTFE with NaCl and NaHCO₃ as porogens are quite similar.

The masses of the mixture components, the semimanufactures, and porous PTFE were measured with the accuracy ± 0.05 g. The sizes of the semimanufactures and porous PTFE were measured to within ± 0.01 mm.

There are several procedures for determining porosity [25]. In this study the porosity of the materials was estimated employing a calculation technique [19]:

$$\varphi = \left(1 - \frac{m}{V\rho_{\text{ptfe}}}\right) \cdot 100\% \quad (2)$$

where m is the porous material mass, kg; V is

the porous material volume, m³; ρ_{ptfe} is the PTFE density, kg/m³.

Micrographs of porous structures were obtained with BIOLAM-70 optical microscope and DV-300 digital camera.

The flow rate characteristics were estimated from the pressure difference (ΔP) at fixed rates of air filtration (V_f) through the porous material. The filtration rate is described by the equation,

$$V_f = \frac{Q}{S}, \quad (3)$$

where Q is the flow rate of the filtered medium, m³/s; S is the area of the filtering material, m².

The measurement accuracy of the pressure difference was ±0.5 kPa. The airflow rate was measured to within ±3 × 10⁻⁵ m³/s.

Permeability is an important property of a porous material. It is characterized by the permeability coefficient (K) measured in Darcy units (D) and accounts for the structural characteristics of a porous body [6, 26]:

$$K = \frac{\mu V_f L}{\Delta P}, \quad (4)$$

where L is the porous material thickness, m; μ is the coefficient of dynamic viscosity of the filtered medium (the dynamic viscosity of air at T = 20°C is 18.1 × 10⁻⁶ Pa·s).

The hydraulic pore diameter (d) was determined through a combined solution of the Darcy and Poiseuille equations under laminar flow conditions of filtration [24]:

$$d = \sqrt{\frac{32K}{\varphi}}, \quad (5)$$

Each measurement run was performed on no less than three samples of porous materials and the arithmetical mean value was taken as the final result.

3. RESULTS AND DISCUSSION

The goal of the experiment was to substantiate the possibility of using NaHCO₃ as a porogen for the production of porous PTFE. For this purpose a NaHCO₃ – PTFE mixture prepared in equal weight proportions of the components was subjected to pressing and thermal treatment. After

the porogen leaching and drying, porous PTFE was obtained, its final porosity being 52.37%. Note that PTFE with porosity below 70% was unattainable with a NaCl porogen because a part of the porogen particles were completely covered with the polymer, which prohibited their removal by leaching.

The density and porosity of different PTFE specimens were calculated after pressing, thermal treatment, leaching, and drying steps (see Table 1).

It is seen (Table 1) that after pressing the increase of the NaHCO_3 contents in the mixture causes growth of the ϕ from 0.04 to 9.41%. This is because the antifrictional properties of the mixture degrade as the PTFE content is decreasing in the mixture. As a result, the semimanufactures suffer increasing under pressing.

After thermal treatment, the porosity of the semimanufactures is a total of the after pressing porosity, and the porosity formed due to the partial porogen gasification (CO_2 liberation and H_2O evaporation). A 50-to-90 % growth of the porogen contents raises the porosity induced by partial gasification from 23.6 to 28.4%.

On leaching the porosity increases due to the dissolution of Na_2CO_3 . After leaching and drying, the growth of the porogen – PTFE ratio in the mixtures from 50 to 80% changed the porosity of the PTFE products from 52.37 to 78.50%. After leaching the porous PTFE formed with 85 and 90% of NaHCO_3 porogen turned highly elastic and were unable to hold the shape in the course

of measurements. The attempts to estimate their density and porosity by the calculation technique were unsuccessful.

A special experiment was performed on two combined samples to test the expected significance of partial porogen gasification to the formation of a porous structure.

Two powders NaHCO_3 and NaCl were compressed in a press form 25 mm ID to form two 4 mm thick disks, the pressure being 155 ± 5 MPa. Each disk was then placed into a press form of 40 mm ID where it was uniformly surrounded with PTFE and kept under the pressure 155 ± 5 MPa. After pressing, the height of the combined samples was 12 mm. The samples obtained were thermally treated at $T = 385 \pm 5^\circ\text{C}$ for an hour and then cooled down with the furnace.

The surface of the combined sample with the NaCl core remained unaffected (Fig. 1a) while that of the combined sample with the NaHCO_3 core was deformed, cambered, and had cracked (Fig. 1b).

A transverse cut of the combined sample which had the NaHCO_3 core is illustrated in Fig. 1c. It is seen that after partial gasification a gap (less than 0.1 mm) appeared between the outer surface of Na_2CO_3 (the product of partial gasification) and the inner surface of PTFE. As a result of partial gasification, the Na_2CO_3 volume decreased by 16% in comparison with the initial volume of NaHCO_3 . Also, it had a porous structure of 26% porosity.

Table 1. Density and porosity at different stages of treatment for mixtures with different NaHCO_3 contents.

Contents NaHCO_3 in mixture, % in mass	Treatment stages					
	After pressing		After thermal treatment		After leaching and drying	
	ρ , kg/m^3	ϕ , %	ρ , kg/m^3	ϕ , %	ρ , kg/m^3	ϕ , %
50	2200	0,04	1680	23,64	1050	52,37
60	2130	3,18	1630	26,09	860	60,76
65	2110	3,98	1590	27,74	760	65,28
70	2110	4,08	1540	29,80	660	70,16
75	2100	4,64	1510	31,25	550	75,06
80	2070	5,89	1470	33,38	470	78,50
85	2000	8,98	1400	36,48	-	-
90	1990	9,41	1370	37,81	-	-

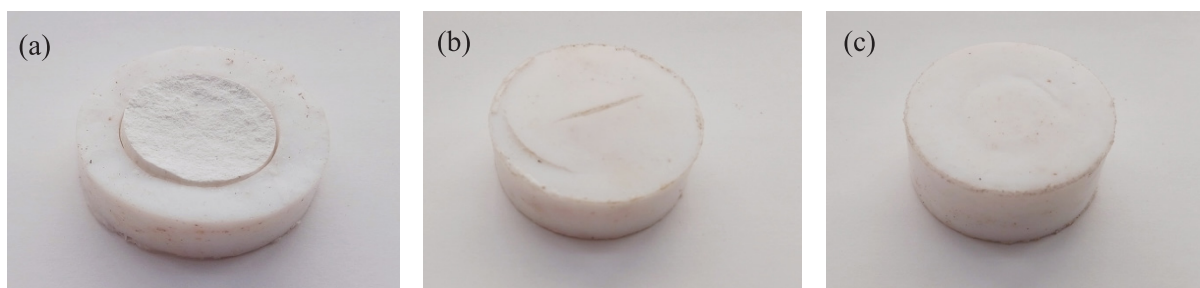


Fig.1. The combined samples after thermal treatment:
 a – NaCl core;
 b – Na_2CO_3 core (product of partial gasification of NaHCO_3);
 c – a transverse section of the combined sample (Na_2CO_3 core)

The experimental investigation shows that partial gasification of NaHCO_3 is capable of breaking down not only the thin porous partitions but also the bulk layer of PTFE.

However, the porous Na_2CO_3 particles produced by partial gasification of NaHCO_3 hold the geometry of the porous channels in the process of thermal treatment.

The permeability of porous PTFE materials formed with the NaHCO_3 and NaCl porogens was further investigated on disks 12 mm thick and 40 mm in diameter. Their porosity was 70%, which is the minimum open porosity of porous materials formed with the NaCl porogen.

After pressing and the subsequent thermal treatment, the semimanufactures were immersed in water at $t = 40^\circ\text{C}$ to leach the porogens. Here, the outer surface of the porous PTFE formed with the NaHCO_3 porogen was almost fully covered with air bubbles (Fig. 2a) while only individual small-size air bubbles appeared on the surface of the porous PTFE formed with the NaCl porogen (Fig. 2b)

The bubbles on the outer surface of porous PTFE suggest that the air is forced out by the water penetrating the pore channels. The almost complete air bubble coating of the surface of porous PTFE (the NaHCO_3 porogen) is evidence of the homogeneity of the porous structure. The porous structure of PTFE formed with the NaCl porogen was extremely inhomogeneous.

The time of complete Na_2CO_3 leaching has appeared to be five times shorter than in the case of NaCl. (The complete NaCl leaching from a disk semimanufacture of 40 mm in diameter and 12 mm high took ≈ 20 h).

The porosity of the Na_2CO_3 porogen and the formation of a clearance between the inner surface of a pore and the porogen along with the rupture of solid partitions between pore and the increasing connectedness of the porous structure due to the partial NaHCO_3 gasification assist the penetration of water into the semimanufacture and thus accelerate leaching.

After subsequent drying, the flow rate charac-

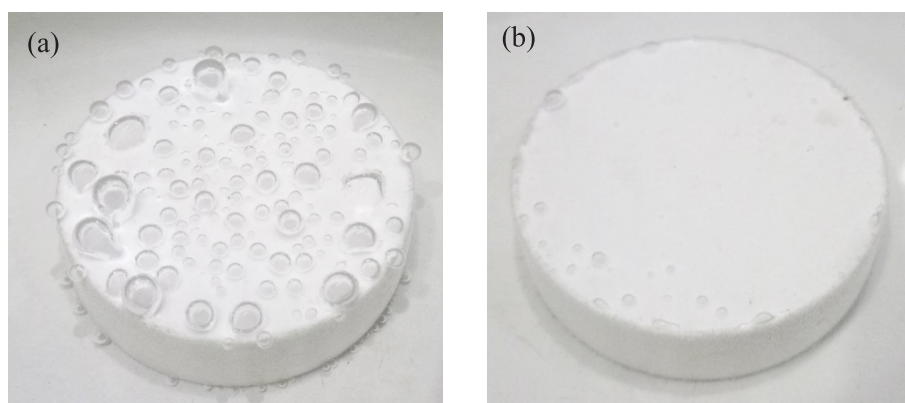


Fig. 2. Generation of air bubbles on the outer surface of porous PTFE with the porosity $\phi = 70\%$ at the starting stage of the leaching process: a – NaHCO_3 porogen; b – NaCl porogen

teristics $\Delta P(V_f)$ of porous PTFE were estimated (see the results in Fig. 3).

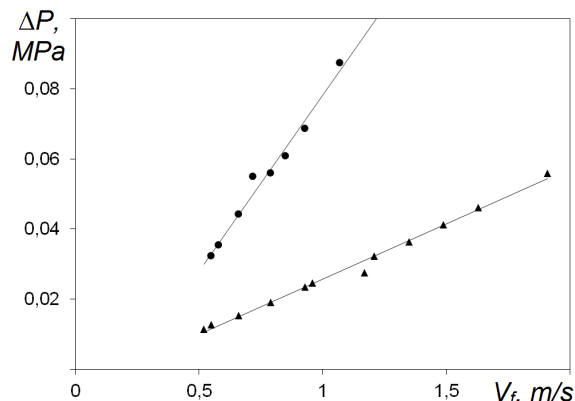


Fig. 3. The flow rate characteristics $\Delta P(V_f)$ of porous PTFE ($\phi = 70\%$) formed with porogens: ● - NaCl, ▲ - NaHCO₃

The dependences $\Delta P(V_f)$ are linear, which suggests a laminar flow of air in the pores.

The permeabilities of both types of materials were estimated numerically to be 6.9 D (NaHCO₃ porogen) and 2.22 D (NaCl porogen). It is seen that the partially gasified porogen NaHCO₃ allows a more than threefold increase in the permeability of porous PTFE. The K values were used to estimate the hydraulic pore diameters: 18 μm (with NaHCO₃ porogen) and 10 μm (with NaCl porogen).

Micrographs of pore structures formed by the NaHCO₃ and NaCl porogens were made at the same magnification (Fig. 4).

Fig. 4 had been shown a sharp difference between the porous structures formed by the NaHCO₃ and NaCl porogens. The porous structures formed with the NaHCO₃ porogen have torn porous partitions (Fig. 4a). The partitions of the porous PTFE formed by the NaCl porogen have not such changes (Fig. 4b). Thus, the significant permeability increase of the pore structure formed with the NaHCO₃ porogen is due to an increase in the interconnection of the pore channels. This is due to the rupture of porous partitions as a result of partial gasification of the porogen.

4.CONCLUSIONS.

In this study a technique of formation of porous PTFE using a partially gasified NaHCO₃ porogen was advanced and substantiated. It was shown that the NaHCO₃ porogen is highly efficient in preparing permeable porous structures. The formation of porous PTFE structures was investigated in a wide interval of NaHCO₃ concentrations. The use of the NaHCO₃ porogen allowed us to obtain porous PTFE with the porosity down to 50%, while the lowest open porosity of porous PTFE materials obtained with the NaCl porogen was 70%.

The data on the microstructure of porous PTFE formed with partially gasified and leached porogens were obtained. The porous structures formed with the NaHCO₃ porogen have torn porous partitions. The partitions of the porous PTFE formed by the NaCl porogen have not such changes.

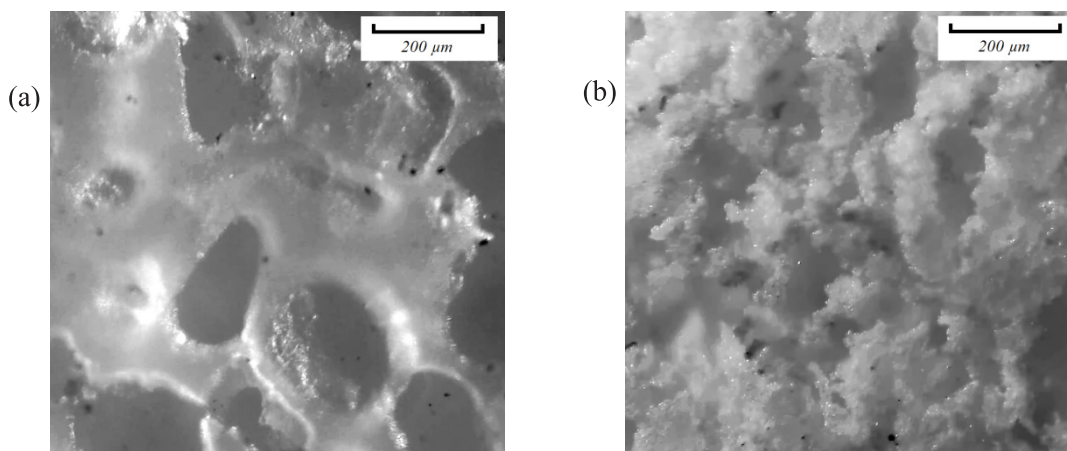


Fig. 4. PTFE porous structures with $\phi = 70\%$: a – NaHCO₃ porogen; b – NaCl porogen

The flow rate characteristics of porous PTFE ($\phi = 70\%$) formed with the different porogens were estimated. The dependences were linear, which suggests a laminar flow of air in the pores. The data on the permeability of porous PTFE structures formed with partially gasified NaHCO_3 and leached NaCl porogens were derived. The use of NaHCO_3 as a porogen has significantly improved the characteristics of the porous structure of PTFE (as compared to the results obtained with the NaCl). The leaching time was cut five-fold, the permeability of the porous structure enhanced more than three times and the hydraulic pore diameter increased 1.8 times.

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Compliance with ethical standards

Conflict of interest

The authors declare that they has no conflict of interest.

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