Effect of carbon nanotubes on a gases permeability of polymer PMMA

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Abstract. Mixed matrix membranes (MMMs) with unique transport characteristics can be prepared by the addition of the minor amounts of carbon nanotubes. Changes in the membrane performance are shown to be provided by the formation of a percolation cluster composed of nanotubes. For MMMs based on Poly(methyl methacrylate) (PMMA) containing carbon nanotubes (CNT), due to the formation of the CNT percolation cluster, gas permeability increases by a factor of 2.5-10.

1. Introduction

In the recent years research is being actively carried out in the field of the development of hybrid membrane materials (mixed matrix membranes) [1,2] and hybrid membrane materials by incorporation of these polymers with nanoparticles[3]. The interest in such polymer modification is connected with the improvement of the membrane properties: the increase in permeability coefficients, selectivity, mechanical properties, etc. [4]. These effects are connected with the change of the polymer chain mobility, the degree of crystallinity and the structure of polymer free volume which interacts with nanoparticles [5]. In most cases inorganic nanoparticles (TiO₂, ZnO, Al₂O₃, SiO₂, etc.), nanoporous particles with high selectivity (e.g. zeolites), nanoparticles with high aspect ratio (carbon nanotubes, carbon fibers) are used for the development of hybrid membranes [6,7]. The non-linear change of different characteristics of hybrid membranes with CNT is described in the published works: mechanical properties, electroconductivity, magnetic properties, increase in gas and liquid permeability, etc. [8,9]. The change of permeation connected with the formation of the percolation cluster in the nanostructured domains is confirmed by the decrease of the critical concentration during the orientation of MCNT in the polymer. Nevertheless, despite the well-understood connection of the change in the permeability of the polymers and the percolation structure which is formed with the incorporation of nanoparticles, the mechanism of the selective transport in such materials is still ambiguous. In this work the research was carried out on the permeability gases through the hybrid membranes based on the polymer Poly(methyl methacrylate comprising CNT (less than 3% wt.) and the critical concentration of the percolation cluster formation from the domains containing CNT was determined. And confirmed what addition of CNTs above the critical concentration leads to the formation in PMMA percolation cluster, the permeability of which is several times greater than polymer permeability.
2. Methods and materials
In this work, we used the multiwalled carbon nanotubes (CNT) (TAUNIT™), NanoTekhCenter LLC, Russia) prepared by chemical precipitation from a gaseous phase. According to technical specifications, TAUNIT™ carbon nanomaterial is composed of fibrils based on polycrystalline graphite with a length below 2 microns; their outer diameter varied from 20 to 70 nm, specific surface was 120-130 m²/g, and the bulk density was 0.4-0.6 g/cm³. After the treatment with nitric acid according to the standard procedure [10], density of the CNT samples was 2.26±0.03 g/cm³, specific volume was \( V = 0.20±0.02 \) cm³/g, and the surface area was \( S = 150±5 \) m²/g.

We used the commercial polymer PMMA sample with a density of 1.18 g/cm³; the permeability coefficients were \( P(\text{He}) = 12, P(\text{O}_2) = 0.23, P(\text{N}_2) = 0.039 \) [11]. In this experiment were obtained permeability coefficients in PMMA: \( P(\text{He})=11.3, P(\text{O}_2)=0.27, P(\text{N}_2)=0.06 \) barrier. To create hybrid PMMA / CNT, PMMA membranes were dissolved in chloroform, then a CNT / chloroform slurry was added to the PMMA / CNT solution, an ultrasonic disperser was used to disperse the CNT agglomerates to separate CNTs. In order to select the optimal concentration of CNTs in chloroform for casting membranes, to determine the optimum processing time for ultrasonic scanning and the distribution function of CNTs by dimensions, measurements were made on a laser particle size analyzer "nanotrac 150/250" and on a spectrophotometer "Hach dr 5000". In the experiments, we used the solutions containing 0.01 wt % of CNTs. According to the DSL method, the dimensions of agglomerates in the solution fit the dimensions of individual nanotubes with a diameter varying from 20 to 70 nm and with a length a length below 2 microns.

The chloroform solution of PMMA (3 wt %) was prepared under normal conditions then and filtered. Concentrations of PMMA and CNTs in the chloroform solutions was controlled by their optical density. The membranes were prepared by casting the PMMA and CNT solutions onto a cellophane support. Chloroform was evaporated under normal conditions (atmospheric pressure, \( T = 25^\circ \text{C} \)) until the constant weight was attained. Thickness of the prepared membranes was 25±2 mkm. We prepared the PMMA /CNT membranes containing 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 wt. % of CNTs.

Gas permeability of nitrogen, oxygen, methane, and propane through the PMMA/CNT membranes were measured by the Dyness-Barrer method, the pressure gradient was 1 bar. and the temperature was 30°C.

3. Results
Figure 1 presents the gas permeability of the mixed matrix PMMA/CNT membranes for nitrogen, oxygen, methane, helium, and propane plotted against the CNT concentration in the membrane, and this plot also shows three well-pronounced concentration intervals. When the CNT content in the membrane is lower than 1.5 wt %, gas permeability of the matrix mixed membranes for all gases under study is equal to the permeability of the neat PMMA. When the CNT content is changed from 1.5 to 2 wt %, gas permeability increases in the following manner: by a factor of 2 for helium, by a factor of 4 for hydrogen, by a factor of 12 for nitrogen, by a factor of 10 for oxygen, 70 for methane. When the CNT content is higher than 2 wt %, the growth in the gas permeability is ceased and this value remains virtually constant or slow degrease. This behavior was also observed for other glassy polymers. [14, 15, 16].
This nonlinear change in the permeability of the mixed matrix membranes suggests that permeability of the mixed matrix membranes is controlled by the parameters of the formed percolation cluster. Traditionally, when two different materials are mixed, any additive changes in their characteristics can be described by the mixture rule. If changes in the net membrane permeability are provided by the development of highly permeable open channels in the membrane, permeability starts to increase only when CNTs are organized into the percolation cluster; in this case, permeability should be proportional to the volume of the percolation cluster. By analogy, if permeability of the mixed matrix membranes depends on the content of nanotubes, this parameter can be described by the following relationship:

\[ P_{\text{PMM}} = P_{\text{CNT}} \cdot C_{\text{cluster of CNTs}} + P_{\text{polymer}} \cdot C_{\text{polymer}} \]

Where PMMA is the permeability coefficient of the hybrid polymer/CNT membrane, \( P_{\text{CNT}} \) is the permeability coefficient of the percolation cluster of the CNT formed, \( C_{\text{cluster of CNTs}} \) is the volume fraction of the percolation cluster formed from CNT, \( P_{\text{polymer}} \) is the polymer permeability coefficient, \( C_{\text{polymer}} \) – volume fraction of polymer. Changes in the membrane permeability and \( C_{\text{cluster of CNTs}} \) are nonlinear when concentration of nanotubes in the membrane is above the percolation threshold [16]. At low CNT concentrations, the percolation cluster does exist or, in other words, \( C_{\text{cluster of CNTs}} \) is equal to zero and the presence of nanotubes has no effect on the membrane permeability. The effect of the percolation cluster on the permeability of the mixed matrix membranes was studied according to the Monte Carlo scheme which allows one to assess the conditions providing the formation of the percolation structures composed of nanotubes in the 3D space and their characteristics [17].

Figure 2 shows the permeability coefficients of the PMMA/CNT membranes calculated after the substitution of \( C_{\text{cluster of CNTs}} \) to Eq. (1). In these calculations, we assume that there is no gas transfer through inner CNT channels, and the increase in gas permeability is solely provided by gas transport through the highly permeable layer of the modified polymer near the CNT surface. This assumption is valid only for the permeability coefficient \( P_{\text{CNT}} \) but has no effect on the threshold concentrations corresponding to the formation of the percolation cluster and related changes in permeability. As follows from Fig. 3, the calculated permeability coefficients well agree with the experimental values when the concentration of nanotubes in the matrix is below 1.5%. The development of the percolation structure and threshold changes in permeability are observed when the volume concentration of nanotubes varies from 1.5 to 2.0%. When the volume concentration of CNTs is above 2 wt %, the calculated permeability

![Figure 1: The coefficient of gas permeability (He, H₂, N₂, O₂, CH₄) through samples of hybrid PMMA.](image-url)
coefficients appear to be appreciably higher as compared with the experimental values. This disagreement can be explained by different parameters of the percolation cluster due to the agglomeration of nanotubes with increasing their content in the membrane. As follows from calculation, when the average diameter of capsules increases due to the coalescence and agglomeration of nanotubes, the volume fraction of highly permeable regions at the same concentration of the capsules in the matrix decreases.

![Figure 2. Gas permeability for model gases through the PMMA/CNT membranes with the account for agglomeration](image)

4. Conclusion
This work shows that, for the mixed matrix CNT-containing membranes, there exists the concentration interval where gas permeability dramatically increases. At high (excessive) concentrations of CNTs, due to agglomeration of nanotubes and deterioration of the percolation structure, further increase in the CNT concentration does not provide any improvement in the membrane performance. According to the experimental results, as the CNT concentration varies from 1.5% to 2 wt %, permeability of the CNT-containing membranes markedly increases: by a factor of 2 for helium, by a factor of 4 for hydrogen, by a factor of 12 for nitrogen, by a factor of 10 for oxygen, 70 for methane. However, further increase in the CNT content does to slow degrease in permeability.

This behavior (effect, phenomenon) was explained by the numerical simulation of a percolation cluster composed of capsules in the 3D matrix with the dimensions equivalent to nanotubes and membranes. Experimentally observed changes in the membrane permeability at high CNT concentrations can be explained with the account for the agglomeration of nanotubes (capsules) and related changes in the dimensions of the percolation cluster.

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