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# Effect of polymer matrix on characteristics of percolation cluster composed of MWCNT

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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. The paper presents the results of study gas permeability ( $O_2$ ,  $N_2$ ,  $CH_4$ ) for poly(vinyltrimethylsilane (PVTMS) and Poly(methyl methacrylate) (PMMA) with embedded multiwall carbon nanotubes (MWCNT). The paper shows how the choice of a polymer matrix affects the parameters of a percolation cluster from CNTs.

## 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) and hybrid membrane materials by incorporation of these polymers with nanoparticles. The interest in such polymer modification is connected with the improvement of the membrane properties: the increase in permeability coefficients, selectivity, mechanical properties, ect.. 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 [1, 13]. The non-linear change of different characteristics of hybrid membranes with CNT is described in the published works: mechanical properties, electro conductivity, magnetic properties, increase in gas and liquid permeability, etc. [2]. 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 [15].

In this work, we studied the effect of the polymer matrix on the parameters of a percolation cluster from CNTs. The gas permeability of polymer films of polyvinyltrimethylsilane and polymethylmethacrylate with embedded MWCNTs (TAUNIT<sup>TM</sup>) was studied, the thickness of film was 25  $\mu\text{m}$ . Within the framework of the percolation model described in the work [3, 4] the parameters of the percolation cluster are determined.



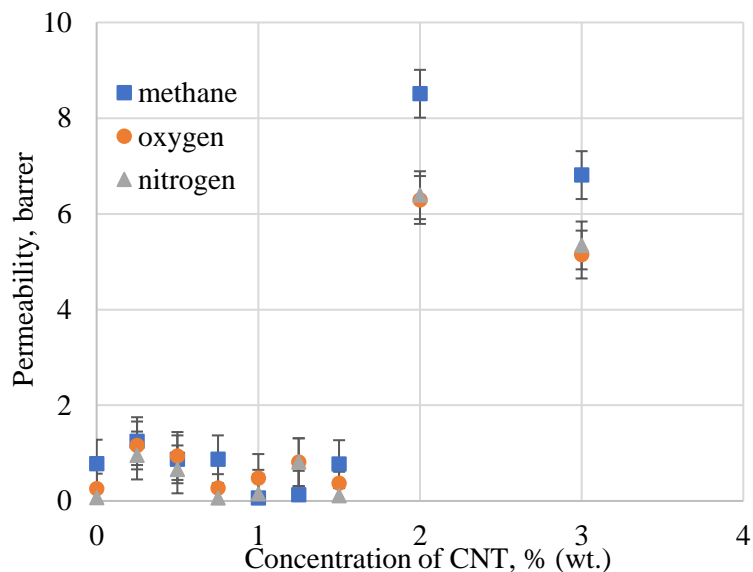
## 2. Methods and materials

In this work, we used the multiwall carbon nanotubes (MWCNT) (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 m<sup>2</sup>/g, and the bulk density was 0.4-0.6 g/cm<sup>3</sup>. After the treatment with nitric acid according to the standard procedure [5], density of the MWCNT samples was 2.26±0.03 g/cm<sup>3</sup>, specific volume was  $V = 0.20 \pm 0.02$  cm<sup>3</sup>/g, and the surface area was  $S = 150 \pm 5$  m<sup>2</sup>/g. We used the commercial polymer PMMA sample with a density of 1.18 g/cm<sup>3</sup>: the permeability coefficients were  $P(\text{He}) = 12$ ,  $P(\text{O}_2) = 0.23$ ,  $P(\text{N}_2) = 0.039$  [11] and commercial PVTMS sample with a density of 0.86 g/cm<sup>3</sup>: the permeability coefficients were  $P(\text{N}_2) = 11$ ,  $P(\text{O}_2) = 44$ ,  $P(\text{CH}_4) = 13$  barrer [6] and commercial PMMA  $P(\text{N}_2) = 0.07$ ,  $P(\text{O}_2) = 0.26$ ,  $P(\text{CH}_4) = 0.78$  barrer [7]. To create hybrids films PMMA / MWCNT and PVTMS/ MWCNT, polymers were dissolved in chloroform, then a CNT / chloroform slurry was added to the polymer / 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 %) and PVTMS (3 wt %) was prepared under normal conditions then and filtered.

Concentrations of polymers and CNTs in the chloroform solutions was controlled by their optical density. The membranes were prepared by casting the polymer/CNT/chloroform 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  $25 \pm 2$  mkm. We prepared the PMMA / MWCNT and PVTMS/ MWCNT membranes containing 0-3 wt. % of CNTs. Gas permeability of PMMA/ MWCNT and PVTMS/ MWCNT membranes were measured by the classical barometric method [8].

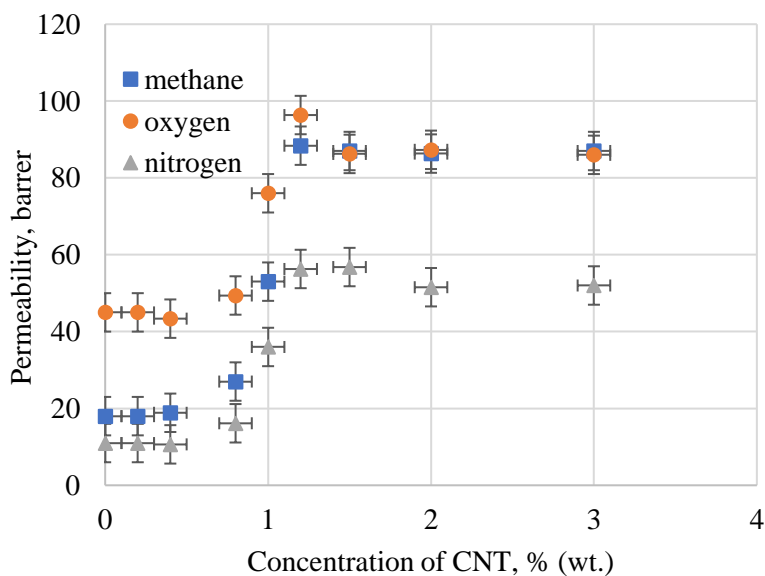
## 3. Result and discussion

Figure. 1 presents the gas permeability of the mixed matrix PMMA/CNT membranes for nitrogen, oxygen, methane 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 91 for nitrogen, by a factor of 24 for oxygen, 11 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 decrease [14].



**Figure 1.** Gas permeability of PMMA/MWCNT membrane.

Figure 2 presents the gas permeability of the PVTMS/CNT membranes for nitrogen, oxygen, and methane 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 0.4 wt. %, gas permeability of the matrix mixed membranes for all gases under study is equal to the permeability of the neat PVTMS. When the CNT content is changed from 0.8 to 1.5 wt. %, gas permeability increases in the following manner: by a factor of 5 for nitrogen, by a factor of 2 for oxygen, 4 for methane. When the CNT content is higher than 1.5 wt. %, the growth in the gas permeability is ceased and this value remains virtually constant.



**Figure 2.** Gas permeability of PVTMS/MWCNT membrane.

This increase in the gas permeability of the PVTMS/MWCNT and PMMA/MWCNT membranes can be explained by formation of the system of the connected nanostructured domains (percolation cluster). The critical concentration, at which the percolation cluster of CNTs is formed, is different: it is in the range from 1.5 to 2.0% (wt.) for PMMA / MWCNTs, in the range from 0.4 to 0.8% (wt.) for PVTMS / MWCNT. The same MWNTs were used in the work and the method for manufacturing the MWNT / Chloroform molding solutions was the same. Therefore, from the difference in the experimental data, we can conclude that the region that CNTs modifies near itself in the polymer has different characteristics such as the thickness of the interfacial layer and the permeability coefficient. The critical concentration of MWCNTs at which the percolation cluster is formed in PMMA and PVTMS is different. To determine the parameters of the percolation was used percolation model and software package as described in [3 4].

Mass transfer in polymer films with carbon nanotubes embedded in its structure is possible: through the polymer, through the polymer / CNT interfacial layer, which arises as a result of poor adhesion between the polymer chains and CNTs, through the inner cylindrical channels of CNTs.

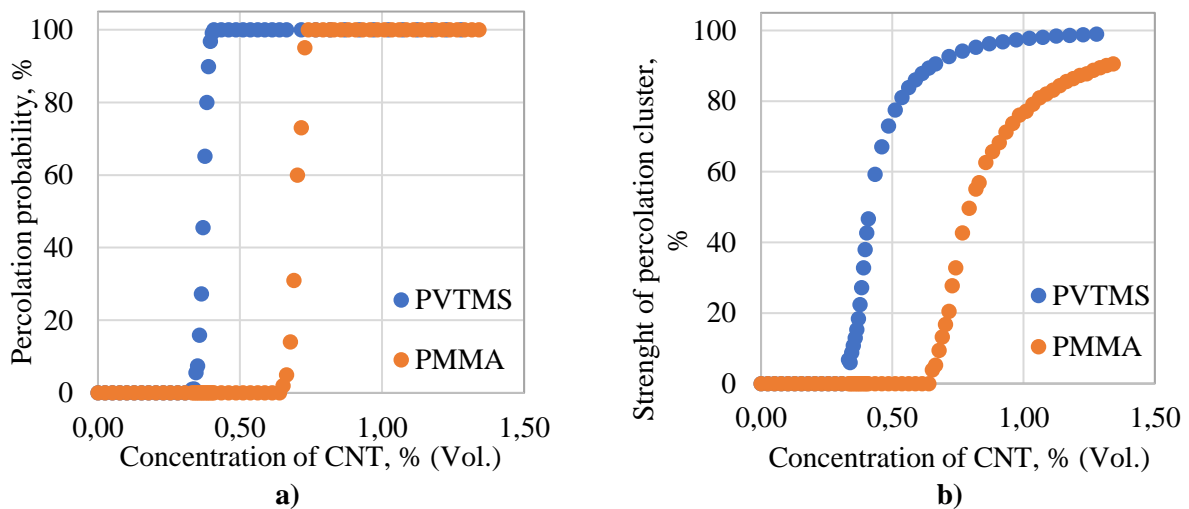
If we consider the flows through regions of polymer and cluster as independent, then we can use the rule of mixtures in which the fraction of the volume of the membrane with high permeability should be related to the volume of the percolation cluster:

$$K_{MMM} = K_{кл} \cdot C_{кл}(L, R, dR) + K_p \cdot (1 - C_{кл}(L, R, dR)) \quad (1)$$

$C_{кл}$  – the fraction of the membrane volume occupied by the percolation cluster,  $K_{кл}$  – the permeability coefficient of the percolation cluster,  $K_p$  – the polymer permeability coefficient,  $dR=R - R_0$  – the thickness of the interfacial layer. The value  $C_{кл}$  changes nonlinearly when the concentration of nanotubes is greater than the percolation threshold. At low CNT concentrations, the percolation cluster does exist or, in other words,  $C_{кл}$  is equal to zero.

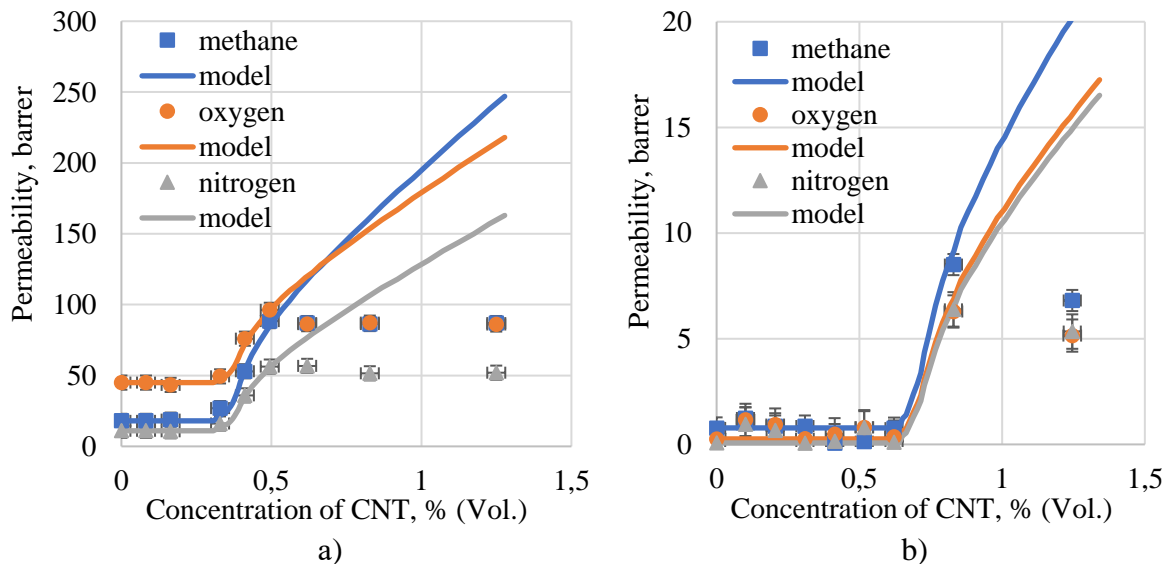
The parameters of the percolation cluster of the PMMA/MWCNT and PVTMS/MWCNT membranes was calculated according to the Monte Carlo scheme which allows one to assess the conditions providing the formation of the percolation structures composed of nanotubes in the 3D space and their characteristics. We used the standard algorithms such as the Mersenne twister for the estimation of coordinates and orientation of CNTs [9], the Hashen-Koppelman algorithm for the calculation of the CNT distribution over the clusters [10], and the method of the percolation cluster detection [11]. The main parameters of the percolation cluster: the probability of formation, it shows with what probability the percolation cluster will be formed at a given concentration of nanoparticles and the strenght of the percolation cluster, which shows how much of the embedded nanoparticles will participate in its formation, that is, to determine the volume fraction of the percolation cluster. The mass concentration of CNTs in the polymer was converted to the volume concentration, for this the densities of MWNTs, PMMA, and PVTMS determined by helium pycnometry were used.

Figure 3 shows the result of calculations of the probability of formation and power of the percolation cluster composed of MWCNTs in PMMA and PVTMS. In the calculations, the dimensions of the three-dimensional system were:  $25 \times 25 \times 25$ , MWNT length 2  $\mu$ m, diameter 50 nm, interfacial layer thickness for PVTMS 100 nm, for PMMA 54 nm. A change in the volume concentration of MWCNTs in PVTMS from 0.33 to 0.41 leads to a change in the probability of percolation cluster formation from 0 to 100%, percolation cluster power from 3% to 42%, an increase in concentration to 1.2% leads to an increase in power to 98%. In PMMA the percolation cluster forms at higher concentrations than in PVTMS. The formation probability varies from 0 to 100% when the volume concentration changes from 0.63 to 0.74, and the power increases from 42% to 92% when the volume concentration changes from 0.74 to 1.3.



**Figure 3.** Parameters of the percolating cluster at different concentrations of MWCNT (a) probability of the formation of a percolating cluster, (b) strength of a percolating cluster.

The obtained parameters of percolation clusters for MWCNTs in PMMA and MWCNTs in PVTMS and percolation model (1) were used to analyze experimental data. Between the experimental data and the percolation model there is good agreement at low concentrations, for PVTMS from 0.0 to 0.3% for PMMA from 0.0 to 0.6%, where percolation cluster has not been formed, and at concentrations where percolation cluster is formed and there is an increase in its volume fraction by increasing its strength, for PVTMS from 0.3 to 0.5%, for PMMA from 0.62 to 0.83%. A further increase in concentration does not lead to an increase in permeability and there is a discrepancy between the experimental data and the model. This is due to agglomeration of MWNTs in the polymer.



**Figure 4.** Analysis of experimental data by percolation model (a) PVTMS/MWCNT membrane, (b) PMMA/MWCNT membrane.

In the framework of the percolation model, the permeability coefficients of the percolation cluster formed in PMMA and PVTMS from MWNTs and size of MWCNTs agglomerates. The interaction of Van-der-Waals between the side walls of MWCNTs leads to the formation of agglomerates in the form of bundles [12], this leads to an increase in the diameter of the agglomerate composed of MWCNTs

due to which the percolation cluster degrades and its volume fraction decreases. The permeability coefficient of percolation cluster of MWCNTs in PVTMS from the permeability coefficient of percolation cluster of MWCNTs in PMMA differs for CH<sub>4</sub> by 3.7 times, for O<sub>2</sub> by 3.4 times, for N<sub>2</sub> by 3 times (Table 1). This is due to the different adhesion arising between the MWCNTs and PMMA, PVTMS, which is determined by the group grafted onto the surface of the MWCNTs and the structural formula of the polymer. We used the same MWCNT grafted with a carboxyl group, so the key is the difference in the structural formula of polymers. There is no silicon in the structure of PMMA and there are CO groups.

**Table 1.** Results of calculation permeability of percolation cluster of MWCNTs in PVTMS and PMMA

gas	K <sub>PVTMS</sub> , barrer	K <sub>cl.pvtms</sub> , barrer	K <sub>PMMA</sub> , barrer	K <sub>cl.pmma</sub> , barrer
CH <sub>4</sub>	18	702	0.78	190
O <sub>2</sub>	44	507	0.26	150
N <sub>2</sub>	11	429	0.07	145

#### 4. Conclusion

In this work, using two polymers as an example, it is shown that when nanotubes are added to the polymer, the gas permeability changes as a result of the formation of a percolation cluster, in the framework of the percolation model, the permeability coefficients of the percolation cluster of MWCNTs to PMMA and PVTMS were determined and the thickness of the interfacial layer, which CNT modifies near itself. It is found, that for identical MWCNT and different polymers of the same thickness critical concentration of MWCNT, at which the effect from the introduction of nanotubes will be observed, will be different. It will be determined by the adhesion between the MWCNTs and the polymer.

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