

NANOCARBON-BASED CELLULOSE ACETATE MEMBRANES FOR CO₂ SEPARATION APPLICATIONS

T. Esser^{1*}, T. Wolf¹, T. Schubert¹, J. Benra², S. Forero², G. Maistros³, A.A. Sapalidis⁴, E.P. Favvas^{4,**}

¹Institute of Chemical Process Engineering and Plant Design, TH Köln, Köln, Germany

²Future Carbon GmbH, Ritter-von-Eitzenberger-Str. 24, 95448 Bayreuth, Germany

³ADVISE, 17, Gymnasiarchou Madia St., 82100 Chios, Greece

⁴Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Aghia Paraskevi 153 41, Athens Greece

(*tobias.esser3@smail.th-koeln.de & **e.favvas@inn.demokritos.gr)

ABSTRACT

The main scope of this work is to develop highly selective cellulose acetate based membranes, for the efficient separation of carbon dioxide (CO₂) from binary gaseous mixtures. For this purpose a variety of mixed matrix membranes, consisting of cellulose acetate polymer and nano-carbon materials (NCM) as additives were prepared, characterized and tested. Multiwalled carbon nanotubes (M-CNTs) were used as membranes' filler material using diacetone alcohol (DAA) as the common solvent. For the physicochemical characterization of the M-CNTs numerous techniques such as scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and nitrogen adsorption isotherms at 77K were used. The first main objective towards highly efficient composite membranes was the proper preparation of agglomerate-free NCM-dispersions.

INTRODUCTION

Membrane systems possess many advantages such as small footprint, low capital and operating costs, being environmentally friendly, no moving part for the separation as such and exhibiting process flexibility [1]. However, there are several drawbacks of commercially available polymeric membranes (cellulose acetate (CA), cellulose triacetate (CTA) and polyimide (PI), etc), especially when they are used for high pressure natural gas sweetening. The relatively low separation performance (i.e., low CO₂/CH₄ selectivity) and low CO₂ permeances, due to membrane compaction and plasticization, are the two major disadvantages. These issues lead to high costs due to a large required membrane area and a short lifetime, which indicates the need of development on novel, high performance membrane materials.

Recently, mixed matrix membrane materials ("MMMs") provided positive outcomes to the researchers of the membrane science & technology field, mainly thanks to their improved properties regarding CO₂ selectivity, increased mechanical stability, plasticization and degradation phenomena [2]. From various nanomaterials proposed as membrane fillers nano-carbon materials (*are also referred as "carbon nanomaterials"*) are reported to provide new advanced properties on the final mixed matrix produced membranes. Carbon nanotubes (CNTs), both single and multi-walled (SWCNTs & MWCNTs), graphite and graphene based nanostructured (GO, NGPs) are currently on the first line of membrane technology [3, 4]. This new type of carbon based mixed membranes in principle provide excellent CO₂ permeabilities and selectivities versus CH₄, H₂ and N₂ even in harsh conditions.

Carbon nanomaterials (CNTs, Graphenes, Graphene Oxide, NGPs, Fullerene) are a fascinating class of materials thanks to their special properties [5, 6]. The interest of using nanoparticles as fillers in membrane structures focuses mainly on their beneficial effect on fluxes and fouling resistance [7]. Significant improvement in separation properties compared to neat polymers is expected for the resultant MMMs [8,9]. Especially the nano-carbon based materials, added to a polymer matrix can have the following three effects on the permeability: i) they can act as molecular sieves altering the permeability, ii) they can disrupt the polymeric structure increasing the permeability and iii) they can act as barriers reducing the

permeability [10, 11]. Moreover, they provide better thermal and mechanical behaviour of nanocomposite materials.

In current work high purity carbon nanotubes, cellulose acetate and γ -butyrolactone were used for preparing the flat sheet mixed matrix membranes; whereas the investigation of the best dispersion method (ultrasonic and rotor-stator systems) was also investigated compared to the final structural characteristics and gas permeability performance of the prepared membranes.

RESULTS AND DISCUSSION

High purity carbon nanotubes were produced by catalyst assisted chemical vapor deposition [12, 13].

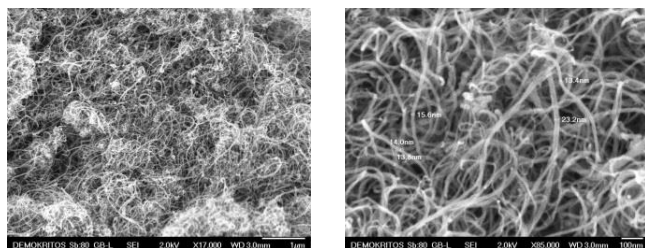


Figure 1. SEM images of M-CNTs.

In Figure 1 SEM images are displayed showing the M-CNT morphology and their interwoven and entangled arrangement. The outer diameter of the carbon nanotubes range is between 12 to 22nm and the length is in between 10-50 μ m.

Total pore volume, specific surface area and pore size distribution characteristics were determined by using nitrogen adsorption measurements at 77K. The sample, before was measured, was degassed overnight at 250 °C. The shape of the adsorption isotherm (Figure 2) is classified as type II with a close to type H3 a mild adsorption hysteresis loop according to IUPAC classification [14]. The isotherm is similar to typical N₂ isotherms and hysteresis for CNTs, mesoporous materials with broad pore size distribution, and aggregated plate-like pore structures. The calculated specific surface area (s.s.a) is 200m²/g according to the BET method.

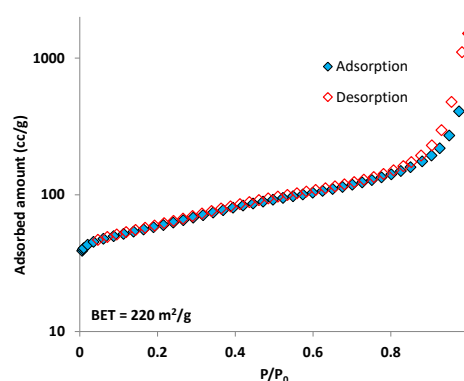


Figure 2. N₂ adsorption isotherm at 77K of M-CNTs.

The above M-CNTs nanostructures were used as filler materials in order to prepare mixed matrix cellulose acetate flat sheet membranes. M-CNTs in diacetone alcohol (DAA) can be dispersed using combined techniques with high shear rates leading to stable dispersions, but during long-term storage and especially when added to polymer solutions (which is necessary for membrane manufacture) M-CNTs tend to re-agglomerate. Therefore, a secondary dispersion step becomes necessary. The secondary dispersion of the M-CNTs into the solvent took place by using both ultrasonic and rotor/stator techniques and the results were compared and discussed.

For both systems the critical parameter is the energy input and transmission, which was systematically changed under the consideration of different treatment durations and equipment performances.



Figure 3. Comparison membrane (a) 2.5 wt% CA (low viscosity) (b) 10 wt% CA (high viscosity).

Furthermore, the parameter of the polymer concentration into the M-CNTs/Polymer/Solvent mixtures was determined as a long-term stability factor of the M-CNTs dispersions and an influencing factor for the drying process as well as for the associated tendency of re-agglomeration during the drying of membranes. Figure 3 depicts two membranes prepared with two different

polymer concentrations and thus by different solution viscosities within a primary study.

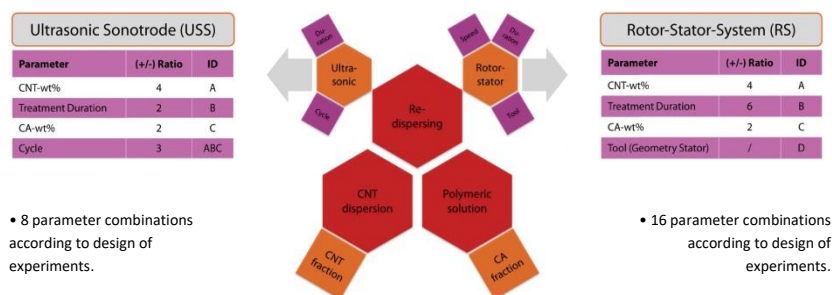


Figure 4. Summary of analyzed influencing factors in the parametric study.

In the conducted parametric study the parameters of each redispersing method varied between two settings labelled with (-) for the lower interval boundary and (+) for the upper interval boundary. According to DoE, 16 parameter combinations for the RS and 8 parameter combinations for the USS are required for determining the significance of each parameter.

The above-mentioned dispersions were used for the production of mixed matrix membranes via dry cast which are characterized by scanning electron microscopy, thermal analysis, electrical and mechanical properties in regard with their CO₂/CH₄ and CO₂/N₂ separation performance. Based on the above methodology a large number of mixed matrix membranes were prepared and the mechanical behavior concerning their ultimate tensile strength was investigated [15]. In Figure 5 a comparison diagram between selected sample which were prepared by using the ultrasonic sonotrode (USS) and rotor-stator-system (RS) it is presented.

By combining these results with the preparing conditions it is obvious that:

I) In USS system: 1) any increase of M-CNTs concentration leads to weakening of the material by more poorly-dispersed M-CNTs, 2) the decrease of cycle causes in poorly dispersing conditions and conclude at more agglomerates, 3) this method generates more inhomogeneous zones, which cause the material weaker, and 4) USS is the less suitable method.

II) In RS system: 1) the increase of the M-CNTs concentration leads to a reinforcement of the material by well-dispersed CNTs, 2) the decrease of CA concentration results in thinner, less stable membranes, 2) a weak interaction is recorded between CNTs-wt% and CA-wt%, 3) as smaller is the CA concentration so higher is the effect of the CNTs concentration, and 4) finally RS seems to be the more suitable method for the CNTs dispersion.

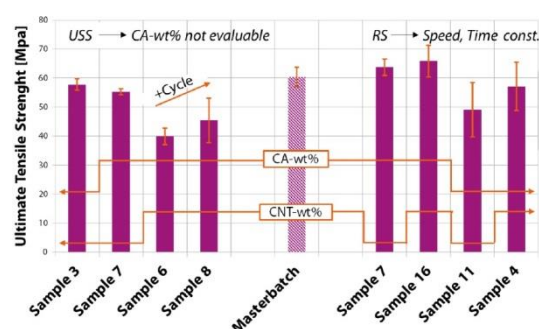
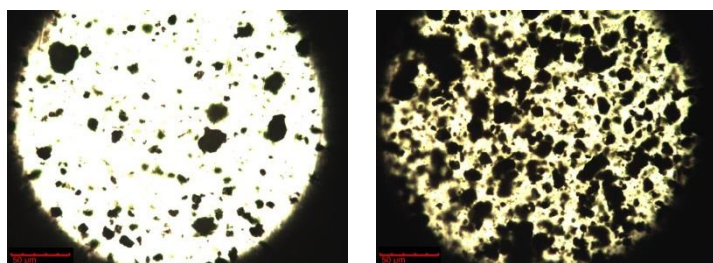


Figure 5. Mechanical analysis – ultimate tensile strength.



(a) sample 7

(b) sample 6

Figure 6. Comparison of microscopic pictures for USS with (a) 0.5 wt% and (b) 2.0 wt% CNTs.

The comparison shows that the number and size of the agglomerates increases significantly as the CNTs concentration increases. This complies with the assumption that the increase in CNTs concentration leads to weakening of the material by more poorly-

dispersed CNTs. It is plausible that the increased amount of particles leads to an increased attenuation of the ultrasonic waves and thus significantly reduces the energy transmission.

The mixed matrix cellulose acetate flat sheet membranes were tested by impedance spectroscopy in order to evaluate the effect and the quality of the dispersion of M-CNTs. For these tests the membrane samples were positioned on flat interdigital dielectric sensors thus facilitating single-side electric field application on the samples. The membranes were pressed on the sensor surface and a bias voltage of 10 V AC at frequencies from 1 Hz to 10 kHz was applied at the sensor terminals [16]. The impedance vector was estimated and it was expressed in the form of impedance amplitude, Z , and phase angle, θ . A typical result is shown in Figure 7 which demonstrates a capacitive/resistive (C-R) behaviour of the membrane (the phase angle ranges between -90° and 0°) due to the effective dispersion of the CNTs in the matrix. In this behaviour certain relaxation regions can be identified. In Figure 7 the main relaxations (where the phase angle undergoes steep drop) occur under 3 Hz and between 10 and 100 Hz. The frequency of the relaxations is indicative of the time scale of the process and therefore of the mean distances between the CNT entities in the membrane. It is believed that this parameter can be used for the quality check of the membrane condition during operation in gas cleaning.

The impedance vector will be modelled in the future steps of analysis through equivalent circuit models (i.e. branches of capacitors, resistors and inductances), where each circuit element corresponds to a physical parameter, such as size of CNT agglomerates and average distance between CNT particles in the matrix. Such analysis is feasible due to the sensitivity of the impedance spectra of the membranes on the CNT content and the dispersion time. This is demonstrated in Figure 7 where the increased dispersion time (from 2.5 min to 5 min) has led to decrease of the impedance values (the membranes become more conductive) and to the increase of phase angles towards 0° in the given frequency range (more dominant resistive behaviour). This trend is expected since the longer dispersion time leads to breaking down of the agglomerates to smaller entities and the effective distance between the entities is decreasing (hence the increase in conductivity).

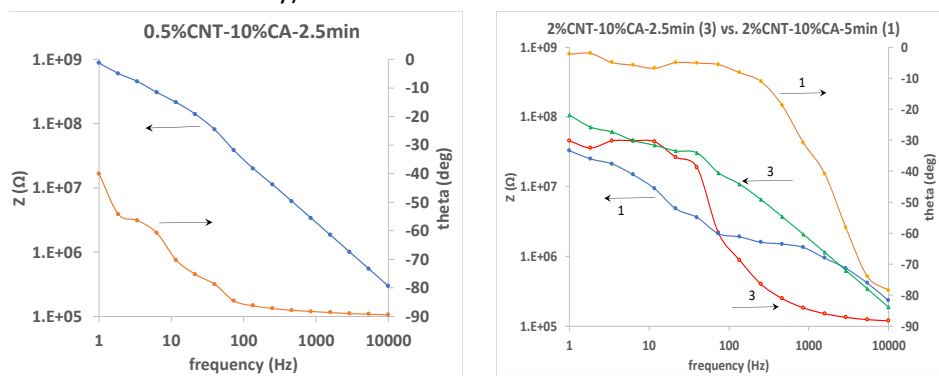


Figure 7. Left: Impedance spectrum of membrane sample containing 0.5% of CNT in the DAA matrix after dispersion time of 2.5 min; **Right:** Effect of dispersion time (2.5 and 5 min) on the impedance vector of membranes containing 0.5 % CNT in the DAA matrix.

The preliminary analysis of the impedance scans indicate that increased polymer concentration, increased concentration of CNTs in the membrane and increased time of dispersion contribute to higher conductivity values of the membranes. While the

quality of dispersion will be assessed through the equivalent circuit modeling of the spectra, it can be observed that the membranes are below the conduction percolation threshold and their resistive behaviour can be used as a quantitative measure of the above contributions.

CONCLUSIONS

By using M-CNT a large number of mixed matrix cellulose acetate flat sheet membranes were prepared and characterized. Ultrasonic sonotrode (USS) and rotor-stator-system (RS) were used for the dispersion of nanostructured carbon materials into DAA solvent. The parametric study of the effect of numerous parameters of both USS and RS techniques took place by concluding that the RS method seems to be the more suitable method for the CNTs dispersion. Mechanical properties investigation of the prepared

membranes took place by determining the ultimate tensile strength. Due to the correlation of results of mechanical tests and microscopic pictures of the membranes it was shown, as expected, that the number and the size of the agglomerates increases significantly as the CNTs concentration increases. Furthermore the prepared membranes were tested by impedance spectroscopy in order to evaluate the effect and the quality of the dispersion of M-CNTs. The results obtained indicate that increased polymer concentration, increased concentration of CNTs and increased time of dispersion lead to higher conductivity values of the prepared membranes. Finally, the membranes present good properties for carbon dioxide separations from both nitrogen and methane. An extended experimental analysis is required for these gas mixture measurements and the numerical results will be reported in our next work.

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