Biocomposite membranes based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and multiwall carbon nanotubes for gas separation

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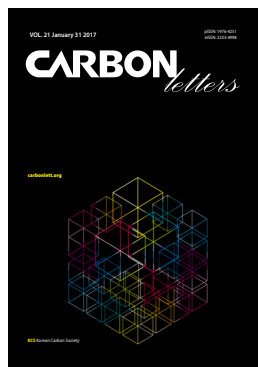
The development of gas separation membranes is currently an active research area because of the rapidly increasing interest in carbon dioxide capture and hydrogen recovery, which are two of the most important solutions for problems related to energy and the environment [1-4]. Polymer membranes show selectivity in the separation of gases due to differences in the permeability of individual gases through the polymer film [3,4]. Even though advantageous in terms of low cost, the segmental flexibility of polymers has limited the discriminating ability of polymer membranes. As the permeability increases, this typically leads to a more open structure, and the selectivity decreases. It has been shown that the trade-off between permeability and selectivity has an evident "upper-bound" [5]. The existence of this upper limit can explain the fact that the performances of polymeric membranes do not yet meet the requirements of current membrane technology. A new class of membranes based on polymer composites, namely, mixed matrix membranes (MMMs), has been proposed as an alternative approach to overcome the inherent drawbacks of polymeric membranes [6-8]. MMMs are comprised of inorganic particles embedded in a polymer matrix and benefit from the unique properties of these inorganic fillers while exploiting the low cost of processing polymers. Carbon nanotubes (CNTs) have been explored in MMM applications due to their unique capability to enhance the mechanical strength of composites even for a small amount of filler content, their potentially good control of pore dimensions at the nanometer scale, and their cavities with frictionless inner surfaces [9-14]. Generally, as-synthesized CNTs are not open ended, and one of the problems of using CNTs for MMM applications is that they must be cut either during the purification processes or in an additional processing step to shorten them [6]. Effective use of CNTs in MMMs also depends on whether the CNTs can be uniformly dispersed in the polymer matrices. The poor dispersion of CNTs largely arises from the smooth and chemically inert surface of the CNTs which is incompatible with most solvents and polymers. One of the most effective methods to overcome the dispersion problem of CNTs is to chemically functionalize the surface of CNTs to improve the interfacial attraction between CNTs and a polymer. In this study, first, nitrogen-doped multiwall carbon nanotubes (MWCNTs) were synthesized with a chemical vapor deposition (CVD) process using flowing CH_4 and NH_3 gases to create defects on the CNT surfaces. The N-doped MWCNTs were subsequently cut to shorter nanotubes during the functionalization of the CNTs by acid treatment. The short f-MWCNTs could be beneficial for gas transportation through the inner cavities of the tubes because of CNTs with an increased number of open ends and a more uniform dispersion due to their decreased length. Nitrogen doping has been proven to be an effective method to tailor the electrical properties as well as the chemical reactivity of CNTs [15-20]. However, the use of N-doped CNTs for obtaining shortened nanotubes has not been reported thus far. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a naturally derived biodegradable polyester that has better processing and mechanical properties than poly(3-hydroxybutyrate) in terms of its lower melting temperature and low brittleness due to the presence of the 3-hydroxyvalerate (3 HV) units in the former [21,22]. PHBV is an excellent environmentally friendly replacement for petroleum-derived plastics [21,22].

Membranes made of poly(3-hydroxybutyrate) and its copolymers have rarely been used in pervaporation processes [23,24]. Although the free volume of PHBV membranes was extensively studied under various thermal crystallization conditions [25,26], gas separation using PHBV or other Poly(3-hydroxybutyrate) (PHB) based copolymers has not yet been reported. In this study, we report the gas permeation properties of pure PHBV and PHBV/MWCNTs nanocomposite membranes. The incorporation of MWCNTs into the PHBV matrices enhanced the gas permeability as well as the mechanical properties of the membranes. The effects of the surface modification and length of the CNTs on the gas separation property and mechanical properties of the nanocomposite membranes are discussed.

PHBV with a 12% HV content was purchased from Goodfellow Cambridge Ltd., UK. Chloroform was purchased from Sigma-Aldrich (USA). The gases, H_2, N_2, O_2, and CO_2 with 99.999% purity used for the gas permeability experiments were purchased from Dongzin gas (Korea). MWCNTs were produced by CVD from a flowing gas mixture of CH_4 and H_2 over a Mo/Fe (0.1/0.02 mol/mol) catalyst at 950°C for 1 h [27,28]. For N-doping of the CNTs, a CH_4/NH_3 mixture gas was used in the CVD process. Nitric acid (HNO_3) was the reagent used for purification of as-produced CNTs because of its mild oxidation ability, which can selectively remove amorphous carbon and metal catalysts as described elsewhere [29,30]. The N-doped MWCNTs were easily cut by acid treatment; the experimental procedure was as follows. N-doped MWCNTs were suspended in a 500 mL mixture of HNO_3 and sulfuric acid (H_2SO_4) stirred at 80°C for 4 h. The resulting black solid was thoroughly washed with deionized water until a neutral pH was reached. Acid treated N-doped MWCNTs were sonicated in 40 mL of ethanol for 10 min. The cutting process by the acid-treatment also leads to the chemical functionalization of the MWCNTs. Hereafter, p-MWCNT and f-MWCNTs denote the purified MWCNTs without the N doping/acid-treatment and the functionalized (acid-treated) N-doped MWCNTs, respectively. Both the p-MWCNTs and f-MWCNTs were used as embedded fillers in PHBV membranes.

Commercial PHBV polymers were dissolved in chloroform (3 wt%) under stirring at 60°C and cooled down to room temperature prior to casting neat PHBV films. MWCNTs in chloroform were sonicated for 20 min. and were subsequently added to the PHBV solutions at room temperature. The composite solutions were cast onto glass plates to produce composite films. The solvent was evaporated slowly at room temperature after which the films were dried in a vacuum oven.

Raman spectroscopy was used to determine the structure and crystallinity of the MWCNTs produced by CVD with and without NH_3. The Raman spectra of the CNTs generally showed a strong band around 1585 cm^{-1} originating from the Raman active E_{2g} mode, which is referred to as the G-band, and a D band at about 1350 cm^{-1}, which is normally explained as a disorder-induced feature due to a finite particle size effect [31,32]. The D-band originates from defects in curved graphene sheets [33]. In N-doped CNTs, the formation of pentagons and heptagons due to the doping of N atoms leads to a distortion in the graphite sheets. Thus, as the concentration of the N atoms increases, the D-band becomes stronger and broader. The intensity ratio (I_G/I_D) is thus useful in estimating the defect concentration of N in N-doped CNTs. Transmission electron microscopy images were

obtained to compare the morphologies of the as-MWCNTs and f-MWCNTs using a JEM-2200 FS microscope (JEOL Korea Ltd., Korea) with an acceleration voltage of 200 kV. The tensile strength and modulus were measured by the ASTM D638–1 procedure. The permeabilities of the polymeric and composite membranes were measured with a continuous-flow technique using a previously described apparatus and methodology [34]. For the gas permeation tests, a circular membrane disc with an effective permeation area of 12.6 cm^2 was put in a constant pressure. All the runs were performed with a 3 bar feed pressure at room temperature. The permeability of the membranes was determined with the following equation:

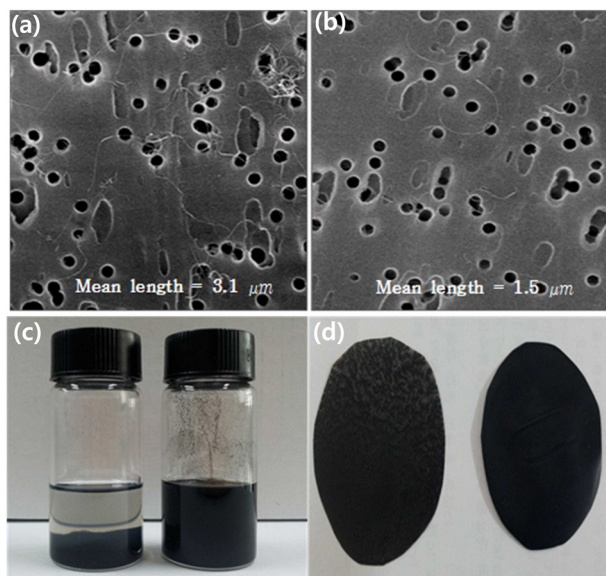$$P = \frac{Ql}{A\Delta p} \times 100 \tag{1}$$

, where Q is the measured volumetric flow rate (at standard temperature and pressure); P is the permeability; l is the membrane thickness; A is the effective membrane area, and Δp is the pressure difference across the membrane. Each gas was tested three times, and the average was reported. Permeabilities were reported as units of Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg). The selectivity was defined by P_i / P_j (P_i and P_j are the permeabilities of components i and j, respectively)

Fig. 1 shows a comparison of the scanning electron microscope image and Raman spectrum of the N-doped MWCNTs with those obtained for the as-produced MWCNTs. The CNT structure is characterized by a highly regular arrangement of carbon atoms leading to a high crystallinity. The Raman spectrum showed that the I_G/I_D decreased from 5.70 to 1.71 when the MWCNTs were doped with N; this result is in accordance with that previously reported for N-doped CNTs [18-20,31-33]. The decrease in I_G/I_D indicates a decrease in the crystallinity of carbonaceous structures, which, in this case, was due to the defects created by the N atoms. Compared to the as-produced MWCNTs, some of the nitrogen-doped CNTs agglomerated possibly due to the increased surface reactivity of the CNTs (Fig. 1). Nitrogen-doped CNTs have been extensively investigated for applications as catalysts, biosensors, and electronic devices due to their enhanced surface reactivity and electrical properties [15-
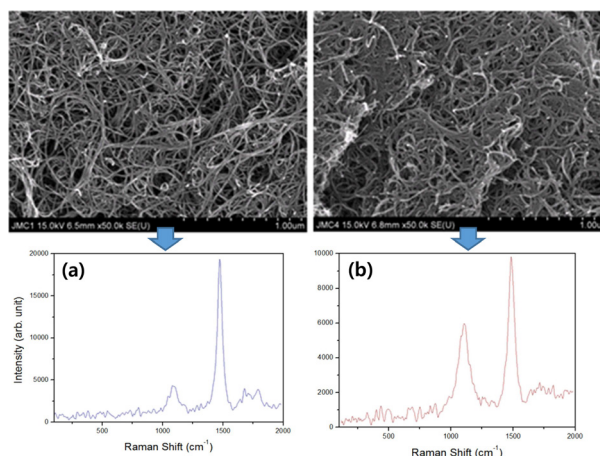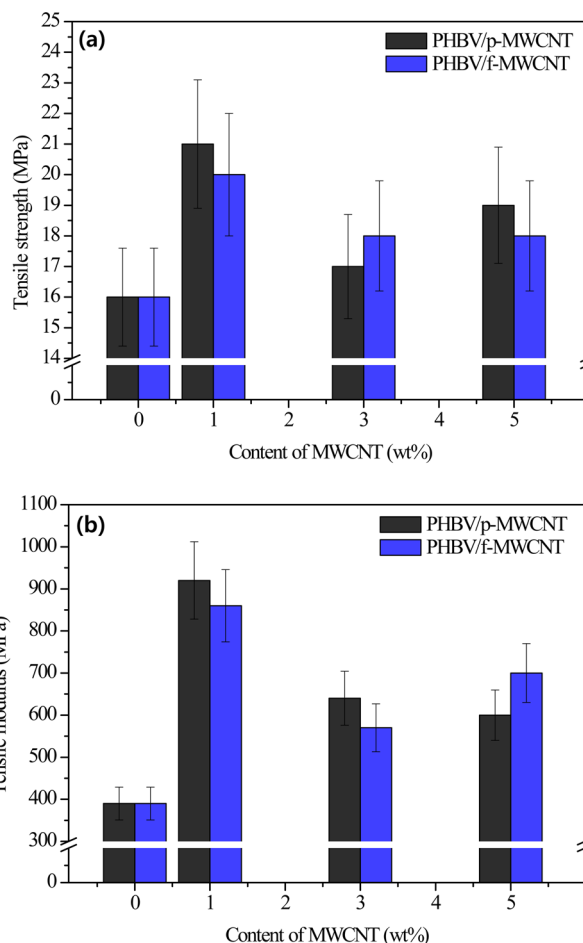

Fig. 1. The scanning electron microscope image and Raman-spectrum of the as-synthesized multiwall carbon nanotubes (a) without introducing NH_3 and (b) with introducing NH_3 gas.

20]. In the current work, N-doped MWCNTs were further treated chemically by strong acids to functionalize as well as to cut them. The acid treatment of the CNTs also resulted in a significantly decreased length for the N-doped CNTs, shown in Fig. 2a and b, indicating that these were easily cut due to the presence of the defects created by the N atoms. This result indicates that N doping is an effective method to cut MWCNTs yielding shorter tubes with more open ends. Intrinsic van der Waals attractions between the individual nanotubes in combination with a high aspect ratio and large surface area make it difficult to disperse MWCNTs in a polymer. Acid modified CNTs have hydroxyl and carboxyl groups at the open ends and at the defect sites that enable good dispersion of these CNTs in polyesters, possibly through the formation of hydrogen bonds with the C=O groups in the polyester [35]. A reduction of entanglements due to the CNT shortening could improve their dispersion. As expected, the f-MWCNTs showed better solubility both in the PHBV solutions and in the films when compared to the p-MWCNTs (Fig. 2c and d). The tensile strength and modulus were measured for pure PHBV, PHBV/p-MWCNT, and PHBV/f-MWCNTs nanocomposites, and the results are shown in Fig. 3. The incorporation of a very small quantity of CNTs significantly increased the tensile strength and modulus of the PHBV nanocomposites due to the nano-reinforcing effect of the MWCNTs having a high aspect ratio. Although f-MWCNT was better dispersed and had stronger interfacial interactions with the PHBV matrices, the decreased length of the f-MWCNTs resulted in a less effective reinforcement of the nanocomposite compared to the p-MWCNT. With a further increase in the MWCNT content to 3%, the tensile strength and modulus decreased. By increasing the concentration of the MWCNTs, large aggregates of nanotubes are formed, which may act as stress concentrators and result in


Fig. 3. (a) Tensile strength and (b) Young's modulus of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/purified multiwall carbon nanotubes (p-MWCNT) and PHBV/functionalized (acid-treated) N-doped MWCNTs (f-MWCNT) composite membranes.

Fig. 2. Transmission electron microscopy of (a) as-produced multiwall carbon nanotubes (MWCNTs) and (b) functionalized (acid-treated) N-doped MWCNTs (f-MWCNTs). Photographs of the composite solutions and films (c) (left) poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/purified MWCNTs (p-MWCNT) and (right) PHBV/f-MWCNT solutions in chloroform (d) PHBV/p-MWCNT (left) and PHBV/f-MWCNT (right) films.

degraded mechanical properties.

The permeability of H_2, N_2, O_2, and CO_2 gases through the membranes were measured at room temperature and 3 bar pressure. The permeability of pure PHBV membrane was measured to be very low and unstable for all the gases tested in this study. Fig. 4 shows the gas permeability of PHBV/p-MWCNT as a function of the p-MWCNT content for H_2, N_2, O_2, and CO_2 at 25°C and 3 bar pressure. As shown in Fig. 4a, all the gases had very low and unstable values for permeability at low p-MWCNT concentrations. However, the permeability increased substantially when the p-MWCNT concentration was increased to 2%. The highest permeability was observed for the composite membranes with a p-MWCNT concentration of 3 wt%. Compared to the other gases, the smaller H_2 gas molecules had a higher permeability (Fig. 4a). The selectivity values of H_2 over N_2, O_2, and CO_2 at different p-MWCNT concentrations are shown in Fig. 4b. The nanocomposite membrane had a significant increase in the selectivity of H_2 over all the other gases when a sufficient amount (2%) of p-MWCNT was added to the MMMs. This result proved that PHBV-MWCNT MMMs are good candidates for the fabrication of environmentally friendly membranes for
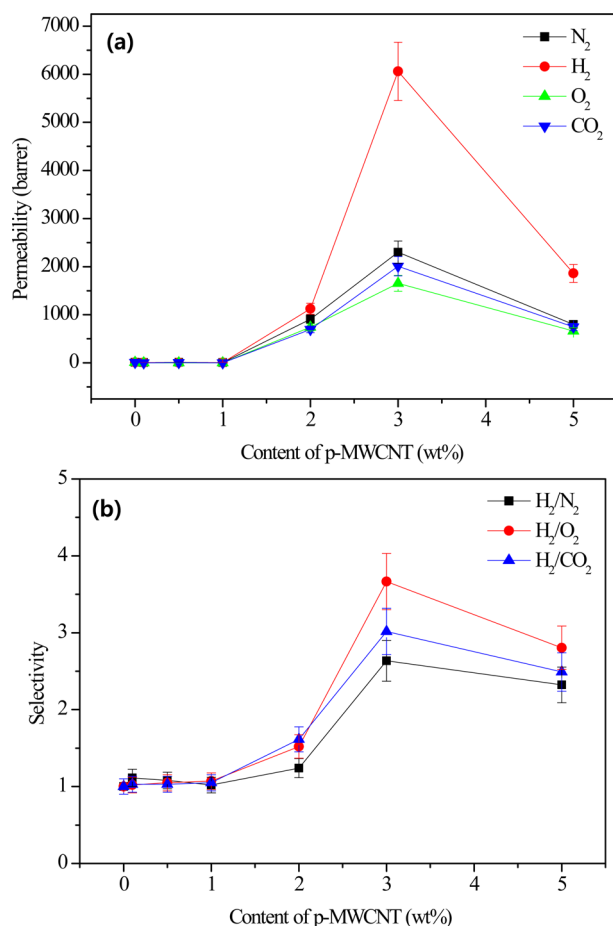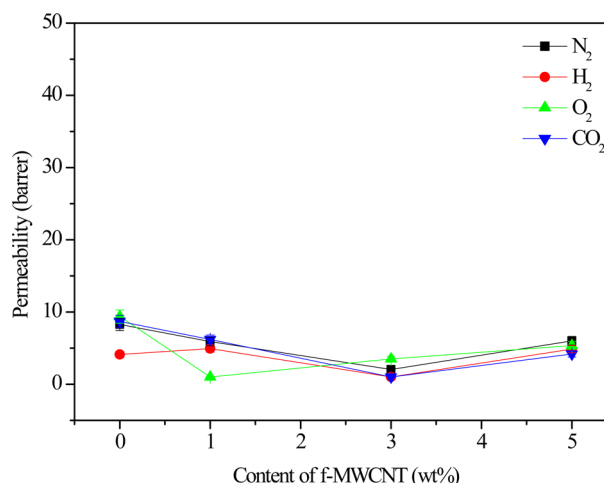
Fig. 4. (a) Permeability and (b) selectivity of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/purified multiwall carbon nanotubes (p-MWCNT) nanocomposite membranes as a function of the p-MWCNT content.

Fig. 5. Permeability of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/functionalized (acid-treated) N-doped multiwall carbon nanotubes (f-MWCNT) nanocomposite membranes as a function of the f-MWCNT content.

H_2 gas separation. It was also found that further addition (5%) of CNTs to the MMMs led to a decrease in both the permeability and selectivity indicating a less effective formation of pathways for gas transport, probably due to substantial aggregations of the CNTs.

Fig. 5 shows the gas permeability values of the PHBV/f-MWCNTs measured for H_2, N_2, O_2, and CO_2 at 25°C and 3 bar pressure. Compared to the permeability of the p-MWCNT composite membrane shown in Fig. 4, the PHBV/f-MWCNTs membrane showed a completely different gas permeability behavior. The gas permeability values show almost no difference from those measured for the pure PHBV membranes, although the f-MWCNTs have more open ends and are better dispersed in the PHBV matrices compared to the p-MWCNTs. These results indicate that the major pathway for gas transportation may not be through the inner cavities of the nanotubes. In a recent study, it has been reported that the increased gas diffusivity and permeability are not only due to gas transportation inside the channel of an inorganic filler but may also be due to the presence of narrow gaps or voids that provide a shorter alternative route for the gas molecules to easily pass through [4,9]. For example, measurements on a composite non-porous fumed silica and C_{60} mem-

brane showed that the presence of the filler disrupts the chain packing and creates interfacial voids between the two phases due to the incompatibility between the inert filler particles and the polymer chains [36,37]. The enhanced free volume due to the presence of interfacial voids resulted in the increased overall gas separation performance of the resultant membrane [36,37]. Because the interfacial interaction of the f-MWCNTs with the PHBV matrix is stronger compared to the p-MWCNTs, a smaller number of interfacial voids are likely to form in the former resulting in a lower diffusivity for the f-MWCNTs composites. The observed higher permeability for the smaller H_2 molecules implies that gas separation in this case is caused by the size difference between the permeates and the interfacial voids which act as molecular sieves. In conclusion, when MWCNTs were added to a PHBV matrix, the obtained composite membranes showed substantially improved gas permeability and were especially selective for H_2 over N_2, O_2, and CO_2. N-doped MWCNTs prepared with NH_3 in the reactive gas mixture were effectively cut to shorter tubes during the surface functionalization using an acid treatment, which led to more open tube ends. However, these short and functionalized MWCNT composite membranes did not improve the permeability of H_2, N_2, O_2, and CO_2 gases at 25°C and 3 bar even when they had more open ends and better dispersion. The stronger interfacial interaction may create substantially lower volumes of voids between the MWCNTs and the PHBV matrix resulting in decreased permeability. Our results indicate that the gas separation mechanism for PHBV/MWCNT nanocomposite membranes is through a size sieving effect by the interfacial voids or pores between the CNTs and the PHBV matrix rather than through the inner cavities of the MWCNTs. The MWCNTs also effectively reinforced the PHBV matrices.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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