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# Gas permeability and permselectivity properties of ethylene vinyl acetate/sepiolite mixed matrix membranes

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ABSTRACT

Ethylene vinyl acetate (EVA) mixed matrix membranes (MMMs) were prepared by incorporating fibrous sepiolite modified by 3-aminopropyltrimethoxysilane (3-APTMS). Gas transport through the prepared MMMs was investigated in detail. Permeabilities of $O_2$, $CO_2$, $CH_4$, and $N_2$, gases were significantly increased by the addition of 3 wt.% of sepiolite. At the same sepiolite loading, the $CO_2/CH_4$ and $CO_2/N_2$ selectivity of the MMMs at 5 bar were respectively enhanced by 9% and 28.2%, while the $O_2/N_2$ selectivity did not notably change and their values remained nearly constant around 2.5–3. The enhanced permeation was attributed to the decreased crystallinity percentage, confirmed by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). Moreover, XRD results and microscopic images demonstrated that sepiolite fibers were uniformly dispersed in the EVA matrix due to the presence of hydrogen bonding between amino groups of modified sepiolite and carbonyl groups of EVA. Also, upon the incorporation of 3 wt.% sepiolite, the tensile strength and elongation at break were simultaneously enhanced by 46% and 76%, respectively.

## 1. Introduction

Over the last years, polymer/clay hybrids as mixed matrix membranes (MMMs) have drawn a great deal of attention for gas separation and gas barrier applications [1–3]. Up until now, two-dimensional (2D) clay minerals such as montmorillonite and its different derivatives have attracted the attention of the majority of researchers. Regardless of the type of the host polymer, almost in all cases, the sheet-like morphology of these types of clay materials has functioned as a barrier to the penetrant, and as a consequence, has reduced the permeability.

To exhibit the improved properties, clay-based MMMs should benefit from homogenous dispersion of clay in the matrix. Reaching a homogenous and thermodynamically stable state of clay dispersion requires the host polymer to have favorable interactions with clay surface, unless neither mixing methods nor pre-exfoliation of clay can guarantee good level of dispersion [4]. In general, depending on the host polymer, an appropriate organic modifier for 2D clay minerals is chosen to establish a strong interaction and to improve exfoliation.

One-dimensional (1D) clay minerals, in contrast to 2D ones, have drawn less attention, despite the fact that they are believed to disperse well due to their special morphology and surface characteristics. Among 1D clay minerals, sepiolite is a promising choice since it has shown to greatly improve the level of properties of polymer composites [5]. Sepiolite is a magnesium hydrosilicate composed of two tetrahedral silica sheets sandwiching a central sheet of magnesium oxide–hydroxide with $Si_{12}O_{30}Mg_8(OH)_4(H2O)_4 8H_2O$ as the unit cell formula [6]. The surface area of as large as about 300 $m^2/g$, along with a very high density of surface silanol groups makes this clay mineral as a highly promising candidate for improving mechanical, thermal, permeability properties of MMMs. It should be mentioned that high density of silanol groups provides reactive sites for surface treatment in condition that the host polymer is not compatible enough with sepiolite [7,8].

Copolymers of ethylene–vinyl acetate (EVA) are a class of widely used polymers, which have recently been used as matrix in MMMs by several researchers [9,10]. Employing silica, Sadeghi et al. [11] prepared EVA/silica MMMs and showed the enhanced permeation. On the other hand, Shafiee et al. [12] reported that the addition of clay in EVA greatly increases gas barrier properties. Kumar et al. [13] indicated that gas permeation of EVA/clay MMMs decreases as the amount of clay increases. Apart from its geometry,

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when a filler is added in a polymer, the change in percentage and morphology of crystallites, chain segmental dynamic, free volume fraction, membrane polarity, etc., greatly affect gas permeability and permselectivity [14]. The surface functional groups of fillers may also have desirable interactions with polar gases and/or with polymer chain segments. The former interactions enhance the solubility of penetrant in the composite. The latter ones, however, may either rigidify polymer segments around the filler in the case of amorphous polymers, resulting in the decreased permeation, or disrupt chain packing in the case of semicrystalline polymers, contributing to increasing free volume, and providing available voids for diffusive jumps.

Despite the extensive investigations on clay-based MMMs, to our knowledge, there is no study assessing the effect of 1D clay minerals such as sepiolite on mechanical and gas permeation properties of EVA MMMs. Thereby, in the light of the above discussion, this study reports the preparation of EVA MMMs based on amino-functionalized sepiolite to establish a strong interaction with carbonyl groups of EVA. Then, it discusses the permeability and permselectivity behavior of the MMMs with respect to structural changes induced by the incorporation of fibrous sepiolite.

## 2. Experimental

### 2.1. Material

EVA copolymer, 18% vinyl acetate content by melt flow index of 8 g/10 min, was purchased from Tane elf Atofina, China. Unmodified sepiolite with the average length of 44 μm and the average diameter of 100–150 nm was supplied from LingshouJiali Mineral Products Processing Factory, China. 3-aminopropyltrimethoxysilane (3-APTMS) was purchased from Fluka. Co. Ethanol and acetic acid were also purchased from Merck Co. All the materials were used without further purification.

### 2.2. Modification of sepiolite fibers

Surface modification process of sepiolite has thoroughly been discussed in the literature [15,16]. Briefly, the hydrolysis/condensation processes were carried out as follow: 0.05 g 3-aminopropyltrimethoxysilane (3-APTMS) (5 wt.% with respect to sepiolite) was mixed with 50 g of water/ethanol (40:60 w/w) and vigorously stirred for 1 h to disperse sepiolite, while pH had already been adjusted to 4 with acetic acid. The reaction was performed at room temperature with a gentle agitation for 3 h. Finally, the modified sepiolite (m-sepiolite) was washed by water three times. The schematic illustration of modification of sepiolite is shown in Fig. 1.

### 2.3. Preparation of mixed matrix membranes

MMMs were prepared as follows: first, m-sepiolite was dispersed in tetrahydrofuran (THF) for 30 min using a sonicator (Model FB15053, Fisher Scientific Co., Germany). Then, EVA granules were added to the prepared dispersion in glassware with a condenser and the mixture was stirred at 45 °C for 20 h for complete dissolution of EVA, followed by ultrasound sonication for 30 min. The solution was cast on a glass plate, and was dried at room temperature for 3 days. The thickness of the EVA/m-sepiolite films was measured with a digital micrometer and found to be 80 ± 5.5 μm. All the dried films were stored in a moisture controlled desiccators for further testing. All the solution used for film preparation had 12.5 wt.% solid content. The abbreviation which will be used for the prepared MMMs are as follows: samples containing 1, 3, and 5 wt.% of m-sepiolite were respectively named as EVA/m-sepiolite1, EVA/m-sepiolite3, and EVA/m-sepiolite5.

### 2.4. Characterization

X-ray diffractometry (XRD) was carried out by using a RigakuMiniflex II X-ray diffractometer with Cu Kα radiation. The X-ray diffraction data were recorded from $2\theta = 3–70°$ with the step size of 0.05° and scanning speed of 0.02° $\text{min}^{-1}$. The wavelength of X-ray beam was 0.15406 nm. The d-spacing of sepiolite fibers was calculated by the following equation (Eq. (1)):

$$\text{d-spacing} = \lambda/2\sin\theta \tag{1}$$

where $\theta$ is the diffraction angle giving the primary diffraction peak, and $\lambda$ is the wavelength of X-ray radiation. In these experiments, $\lambda = 0.15406$ nm (Cu Kα) was used.

In order to study the morphology of EVA and EVA/sepiolite MMMs, field emission scanning electron microscopy (FESEM) was performed using a JEOL JSM-6701F at acceleration voltage of 10 kV. The EVA/m-sepiolite films were fractured in liquid nitrogen, and sputter-coated with a thin layer of gold. Also, transmission electron microscope (TEM) was performed with a JEM-2200 FS operating at an accelerating voltage of 200 kV. For TEM observation, the samples underwent a microtome process using a Power Tome XL. The samples were embedded in resin and left to dry before it was cut with a diamond knife at a thickness of about 100 nm. The film was positioned on a copper grid for the observation.

The tensile characteristics of the membrane samples with dimensions of $60 \times 13 \times 0.3\ \text{mm}^3$ were investigated using a LRX Tensile Testing Machine (Lloyd, USA) at room temperature according to ASTM D882-10. The strain rate, and load cell were 10 mm/min, and 100 N, respectively. In order to make the data reliable, for each sample, 5 measurements were performed and the average value was reported.

Fourier transform infrared spectra (FTIR) of the membrane samples were obtained using an Equinox 25 Bruker (Canada). Typically, 1–2 mg of samples was mixed with 100 mg of KBr powder and pressed into pellets. All the spectra are the average of 32 scans taken in the wave number range of 4000–400 $\text{cm}^{-1}$.

Melt and crystallization behavior of the nanocomposites were performed on a differential scanning calorimetry (DSC) Q100 DSC (TA Instruments, New Castle, DE). About 5 mg of a sample was sealed in an aluminum pan and heated from 15 to 120 °C at a

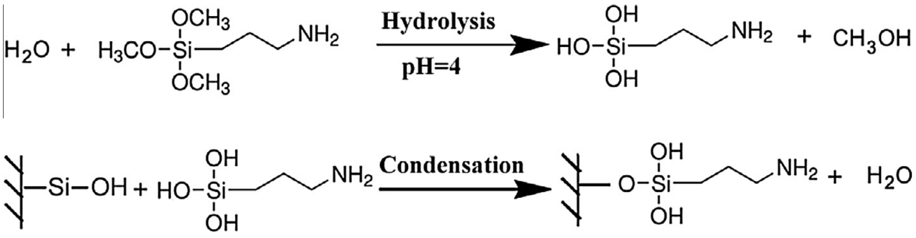

**Fig. 1.** Schematic illustration of the modification process of fibrous sepiolite.