 doi:10.20944/preprints202001.0348.v1

Article

Correlation between Functional Group and Formation of Nanoparticles in PEBAX/Ag Salt/Al Salt Complexes for Olefin Separation

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Abstract: PEBAX-2533/metal salt/Al salt membranes were prepared for mixed olefin/paraffin separation. PEBAX-2533 with 80% ether group and 20% amide group was suggested as the polymer matrix for comparison of separation performance according to the functional group ratio in copolymer PEBAX. In addition, Al salts were used to stabilize metal ions for a long time as additives. High permeance was expected with the proportion of high ether groups since these functional groups provided relatively permeable regions. As a result, the PEBAX-2533 composite membrane showed a selectivity of 5 (propylene/propane) with 10 GPU. However, the permeance of membrane was not unexpectedly improved and the selectivity was reduced. The result was analyzed by SEM, FT-RAMAN and TGA, including FT-IR. The reduction in separation performance was determined by FT-IR. From these results, in order to stabilize the metal ions interacting with the polymer through $Al(NO_3)_3$, it was concluded that specific ratio of amide group was needed in PEBAX as polymer matrix.

Keywords: olefin; paraffin; copolymer; facilitated transport; nanoparticles

1. Introduction

Olefins are one of the important raw materials in the petroleum industry.[1] Olefins have been acquired by the Fischer-Tropsch reaction of coal or the catalytic cracking of petroleum.[2, 3] Light olefins have been commonly produced together with the corresponding paraffins, but extremely high purity olefins (>99.9%) have been required to produce polymers. Therefore, olefin/paraffin separation has been so important process in petrochemical industry.[4, 5] The olefin/paraffin separation has been accomplished nowadays by cryogenic distillation.[6-8] However, distillation processes demand large amounts of energy and equipment costs due to the chemical similarity between the vapor pressure of olefin and paraffin gas.[9, 10]

In order to save huge costs in the olefin separation process, several separation methods have been proposed in recent years.[11] Several attempts have been made to develop various separation methods such as hybrid membrane-distillation, adsorption, absorption and membranes.[12, 13] Hybrid membrane-distillation aims to remove C2 splitters or C3 splitters by installing parallel membrane modules with distillation columns.[11] Adsorptive separation utilizes a method in which one component is selectively adsorbed to an adsorbent particle layer and the other component is passed through. The adsorbed components could later be recovered by either temperature swing adsorption (TSA) or pressure swing adsorption (PSA).[12] Adsorbents including zeolite 5A, NaX,

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highly porous MIL-100(Fe) were investigated for their olefin/paraffin separation performance.[14, 15] The membrane technology has offered the advantages of low energy requirements, capital investment, installation space and operating costs.[4] In particular, polymer membranes have become an attractive alternative to traditional separation methods because of several advantages such as good mechanical stability, low cost and ease of processing [4, 12]

Among them, the membrane method using facilitated transport concept has been concentrated. [10, 16-18] Ag ions could coordinate reversibly with olefins such as propylene and were known as effective olefin carrier.[19, 20] However, Ag ions were readily reduced to metal nanoparticles (NPs), and generated NPs have a disadvantage of acting as active barrier.[21] In our group, studies were performed using $Al(NO_3)_3$ to prevent the reduction of Ag ions. [22, 23] The performance of specific polymer/$AgBF_4$/$Al(NO_3)_3$ complex membrane was maintained for 14 days, and the white color of the membrane remained for 3 months, indicating the stable metal ions.[22] Furthermore, polymer to have hydroxyl groups/$AgBF_4$/$Al(NO_3)_3$ complex membrane showed the propylene/propane selectivity of 17 and mixed gas permeance of 11 GPU (1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg)) for 145 hours.[23]

On the other hand, poly ether-block-amide (PEBAX) was known as thermoplastic elastomer with the good physicochemical stability and has been interested due to their permeable property to various gas molecules.[24] To compare the permeance performance according to the monomer ratio of copolymer, we used two types of PEBAX-1657 and PEBAX-5513 as the membrane matrix. Previous study showed that PEBAX-1657 showed a selectivity of 8.8 and permeance of 22.5 GPU.[25] In the case of the PEBAX-5513, the performance achieved selectivity of 7.7 and permeance of 11.1 GPU.[26] Unfortunately, the separation performance by proportion of functional groups has not been yet clear. In this study, PEBAX 2533 was used as a new polymer matrix for facilitated olefin transport. PEBAX -2533 comprises of 80 wt% poly(tetramethylene oxide) (soft polyether segments) and 20 wt% nylon-12 (hard polyamide segments).[24] Since polyether groups in polymer could show the high permeability, this study was expected to have higher permeance than previous studies.

2. Materials and Methods

2.1 Materials

Poly(ether-block-amide)-2533 (PEBAX-2533) was manufactured by Arkema Inc. Silver tetrafluoroborate ($AgBF_4$, 98%) was purchased from TCI Fine Chemicals. Aluminum nitrate nonahydrate ($Al(NO_3)_3 \bullet 9H_2O$, ≥98%) was purchased from Aldrich Co. All Chemicals were used as received without further purification.

2.2 Preparation of membrane

The PEBAX-2533/Ag salt/$Al(NO_3)_3$ complex membrane was prepared using 3 wt% PEBAX-2533 solution. PEBAX-2533 was dissolved in a co-solvent with a 7:3 weight ratio of ethanol:water. $Al(NO_3)_3 \cdot 9H_2O$ were added to the PEBAX-2533 solution in 0.1 molar ratio relative to Ag salt and stirred for 20 minutes. Ag salt was dissolved in ethanol at a weight ratio of 1: 9.33 to PEBAX-2533. Then, each solution was mixed and stirred for 10 minutes. The solutions were then coated on polysulfone microporous supports (Toray Chemical Korea Inc.) using an RK Control Coater (Model 202, Control Coater RK Print-Coat Instruments Ltd., UK). The composite membrane was placed in a vacuum oven and dried for at least 15 hours.

2.3 Gas separation experiments

PEBAX-2533/metal salt/$Al(NO_3)_3$ complex membrane was tested under propane/propylene (50:50 vol%) mixed gas conditions. The gas permeation rate was measured through a bubble flow meter. The flow rate of the mixed gas was controlled by a mass flow controller (MFC). Gas

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chromatography (Young Lin 6500 GC system) was used to measure propane/propylene selectivity. The unit of gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2s cmHg).

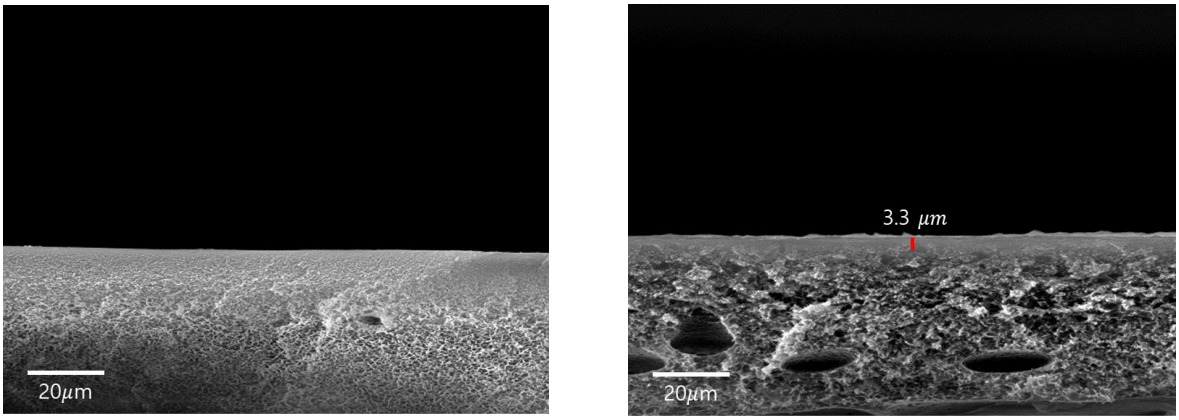
2.4 Characterization

The cross section of the composite membrane was confirmed using scanning electron microscopy (SEM, JEOL JSM-5600LV). Raman spectra were collected using a Bruker Optics Ram II Raman module with a resolution of 4 cm^{-1}. The IR peak shift was measured by a VERTEX 70 Fourier transform infrared (FTIR) spectrometer; 32 scans were signal-averaged with a resolution of 4 cm^{-1}. The thermal stability of the membranes was confirmed by thermogravimetric analysis (TGA; Universal V4.5 A, TA Instruments).

3. Results

3.1 SEM

The SEM image showed the cross section of the membrane. As shown in Figure 1, PEBAX-2533/metal salt/Al salt solution was coated on the porous polysulfone support. The thickness of the selective layer was approximately 3.3 μm. The structure of the polysulfone support was observed as the sponge-like and the structure remained constant after coating of membrane solution.



(a) **(b)**

Figure 1. SEM images of (a) neat polysulfone support and (b) PEBAX-2533/metal salt/Al salt membrane coated on polysulfone support.

3.2 FT-IR

The interaction between the functional groups and Ag cations such as ether group and amide group in PEBAX polymer chains was analyzed through infrared spectroscopy. Figure 2. showed C-O stretching bands of PEBAX-2533 and the free C-O stretching bands of the neat PEBAX-2533 were observed at 1103 cm^{-1}. After incorporation of the Ag salt, the C-O stretching band shifted from 1103 to 945 cm^{-1}. This shift was generated by the weakening of the C-O bond with donating electrons from the C-O bond to metal ions. When Al salt was added, the C-O peak shifted to 1003 cm^{-1}. As a result of the interaction of the NO_3^- of Al salts with Ag ions, the strength of C-O stretching bonds increased. The C=O stretching bonds of amide group was shown in Figure 3. The stretching bond of the carbonyl group shifted from 1639 (observed in neat PEBAX) to 1620 cm^{-1}. However, unlike ether group, there was almost no change of peak when Al salts were added. This indicated that Ag ions to interact with C=O were not interacted with NO_3^-. Thus, most of the NO_3^- was shown to interact with the ether group, which accounts for a large part of PEBAX-2533.

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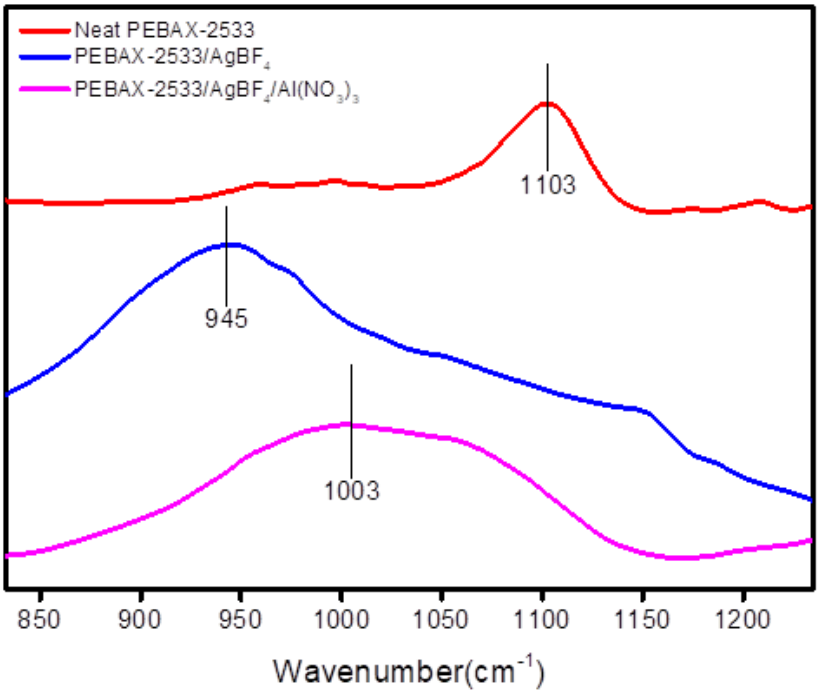

Figure 2. FT-IR spectra of ether group of neat PEBAX-2533, PEBAX-2533/metal salt, and PEBAX-2533/metal salt/Al salt.

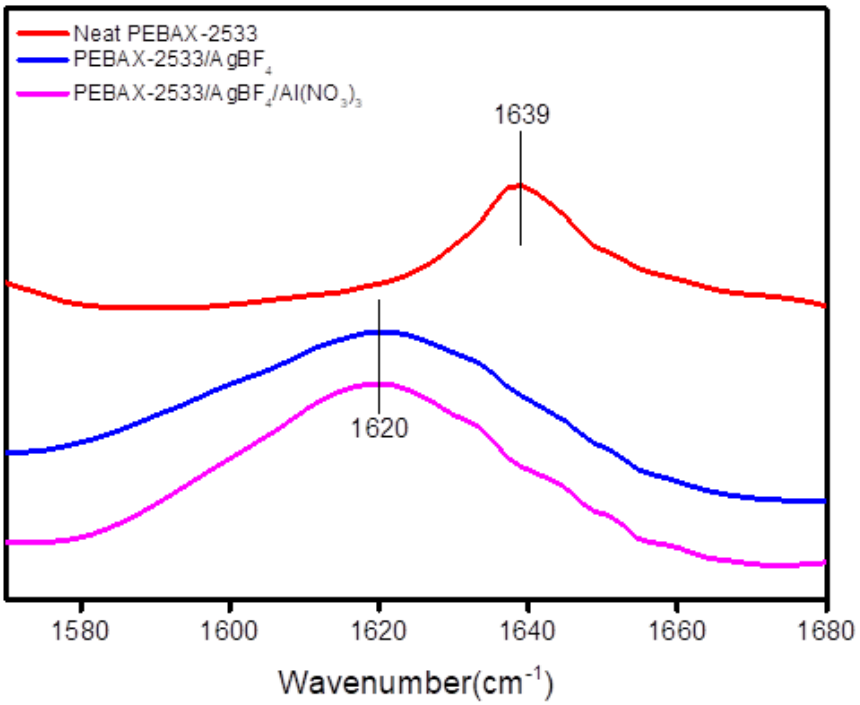

Figure 3. FT-IR spectra of carbonyl group peaks of neat PEBAX-2533, PEBAX-2533/metal salt and PEBAX-2533/metal salt/Al salt.

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3.3 Separation performance

Figure 4 showed the gas permeation test of PEBAX-2533/metal salt/Al salt as facilitated transport membrane for more than 100 hours. The selectivity of propylene/propane mixture remained as approximately 5 steadily. On the other hand, permeance decreased from initial 15 to 10 GPU after 20 hours. These decrease of permeance could be explained that the removal of the remained solvents in membranes to reduce the polymer's flexibility, thereby decreasing membrane's permeance. In the previous experiment, the permeation performance of the PEBAX-1657/metal salt/Al salt and The PEBAX-5513/metal salt/Al salt showed selectivity of 8.8 with 22.5 GPU and selectivity of 7.7 with 11.1 GPU, respectively. [22,23] Compared to the previous results, PEBAX-2533/metal salt/Al salt composite membrane showed relatively low performance. Note that amide groups have the better facilitative effect than ether groups due to the polarizing effect on metal nanoparticles. However, in the case of PEBAX-2533, ether groups accounted for high proportion of 80%, resulting in the low effect of amide groups on separation performance.

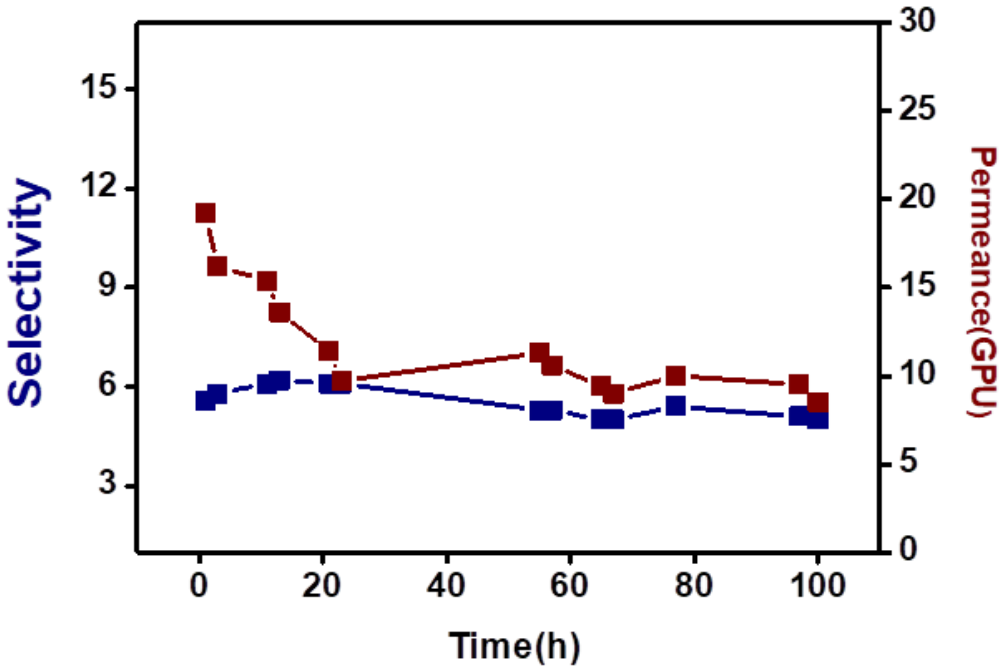

Figure 4. Gas separation performance of PEBAX-2533/metal salt/Al salt composite membrane over time

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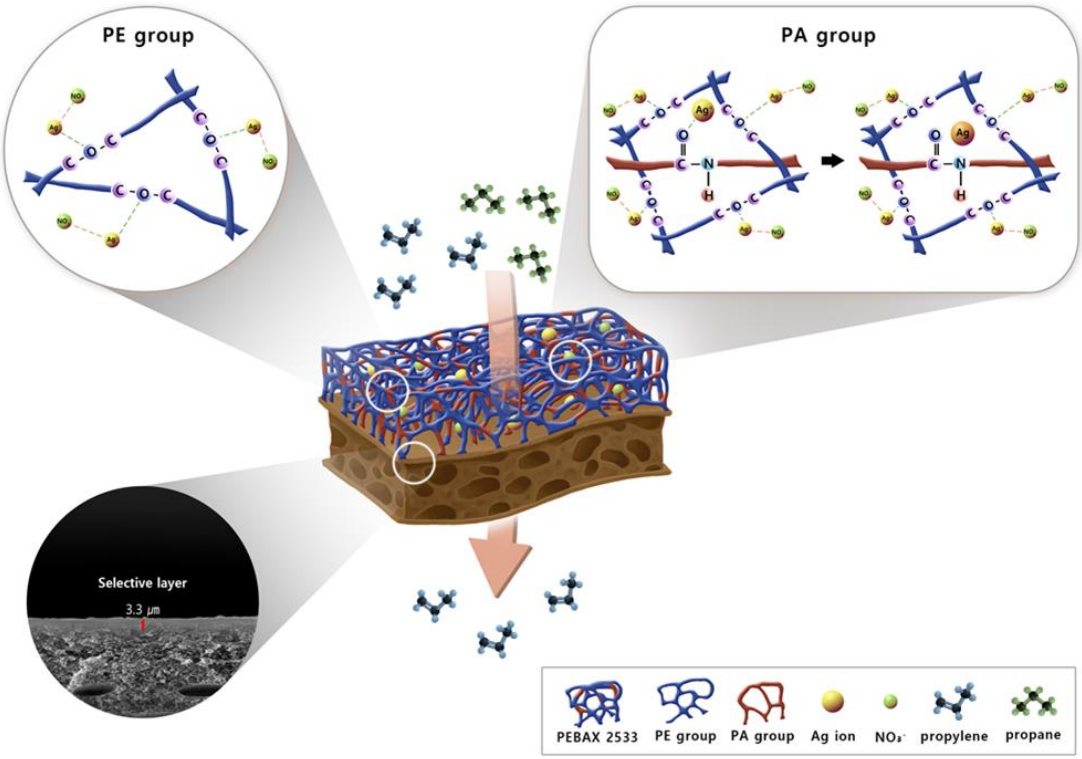

Scheme 1. Facilitated propylene transport in PEBAX-2533/metal salt/Al salt.

3.4 RAMAN

Figure 5 showed raman spectra to investigate the state of NO_3^- of Al salts. The state of NO_3^- ions was shown in Figure 4 and showed the free ions (1034 cm^{-1}), ion pairs (1040 cm^{-1}) and ion aggregates (1045 cm^{-1}). NO_3^- in neat Al salts was existed almost as ion aggregates state at 1055 cm^{-1}. In PEBAX-2533/metal salt/Al salt complex, the ion state of NO_3^- was appeared at 1031 and 1044 cm^{-1}. These results indicated that NO_3^- ions were existed mostly free ions. Thus, abundant free NO_3^- ions from countercation Al^{3+} could easily interacted with metal ions, preventing the reduction to metal nanoparticles.

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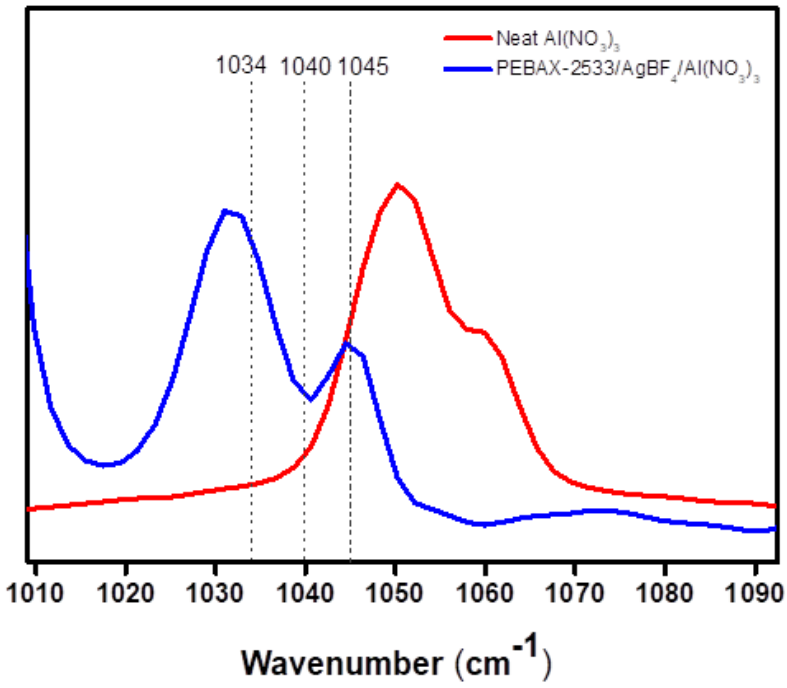

Figure 5. Raman spectra of NO_3^- ions in neat Al salt and PEBAX-2533/metal salt/Al salt complex

3.5 TGA

Thermal properties of PEBAX-2533, PEBAX-2533/metal salt and PEBAX-2533/metal salt/Al salt composite membranes were confirmed by TGA from the room temperature to 600 °C. As seen in Figure 6, pure PEBAX-2533 showed one weight loss at 330 °C. The high thermal stability of PEBAX-2533 was due to the intermolecular hydrogen bonding. When metal salts were added, the thermal stability was reduced at low temperatures. This weakening was thought that the incorporated metal ions prevented the intermolecular interactions by interacting with amide and ether groups in the polymer. Similarly, when Al salts were added, the intermolecular interactions were disturbed, leading to plasticization of the polymer. However, Figure 5 showed that after 400 °C, it was more cross-linked than neat PEBAX-2533. The increase in thermal stability could be attributed to the transient crosslinking effect of metal ions and generated metal metals.

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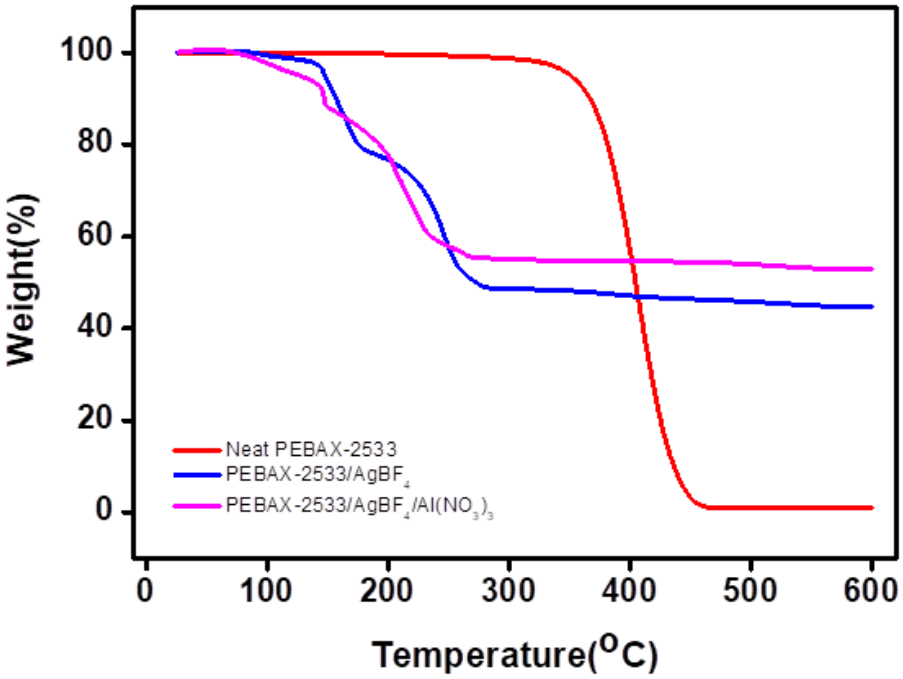

Figure 6. TGA curves for neat PEBAX-2533, PEBAX-2533/AgBF4 and PEBAX-2533/metal salt/Al salt complex

4. Conclusions

The higher permeance was expected by using PEBAX-2533 with higher ether ratio compared to PEBAX-1657 and PEBAX-5513 utilized as polymer matrix in previous studies. However, the permeance of the membrane unexpectedly was not improved, and the selectivity was reduced due to the decrease in the ratio of the amide group, which was the selective segment of PEBAX. Furthermore, even though Al salts were known to stabilize the Ag ions, it was confirmed by FT-IR that Al salts did not stabilize the metal ions interacting with the amide group due to the high ether group ratio in PEBAX-2533. Thus, higher ether groups in the copolymer matrix could interfere with the stabilizing effect of Al salts on metal ions in the polymer/metal salt/Al salt complex membrane as shown in Scheme 1. The study of the performance change according to the copolymer ratio of ether group and amide group in block-copolymer was expected to be helpful for the design of polymer structure for facilitated olefin transport membrane in petroleum industrial field.

Author Contributions: S. W. K and Y. Cho led the project, conducted the data analysis and reviewed the manuscript. S. Y. Kim performed the experiments, collected the data and wrote the paper.

Funding: This work was funded by Korea Environment Industry & Technology Institute (KEITI) as "Technology Program for establishing biocide safety management". (RE201805019). This work was also supported by the Soonchunhyang University Research Fund.

Conflicts of Interest: The authors declare no conflict of interest.

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