

# Structure and Gas Selectivity Of PE/Zeolite Composite Film

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## ABSTRACT

Zeolite-filled polymeric film, currently, has been extensively developed for the applications of gas separation and purification. Molecular sieve characteristics of zeolite are contributed to an improvement of gas selectivity of polymeric film. The present work is the part of the research study aiming to develop flexible composite film of zeolite-filled PE as a packaging material with selective permeation. Structure of the composite films was investigated by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) and gas transport properties of the films was analysed at ambient condition. Hydrophobic zeolite used was found to impede transportation of non polar gases across the film, indifferently to impermeable particles, perhaps due to the presence of voids at the interface. An addition of elastomeric materials, e.g., Kraton G1657, into the composite, surprisingly improves gas transport property.

## 1. INTRODUCTION

The development of polymeric membranes for the separation and purification of gases based on the selective permeation of one component of a mixture has attracted a great deal of interests during the last decades. Intensive investigation of gas separation characteristics of polymeric membranes has resulted in rapid improvements in the properties of such membranes. The effect of zeolite particles incorporated into polymers on transport properties of the membranes has been received much attention recently. Generally, permeabilities were found to be increased but selectivities decreased or maintained when zeolite was added into the polymer, which may be resulted from interfacial voids due the poor adhesion of the polymer and zeolite surface (Hu *et al.*, 2001).

Nowadays, polymer blends or composites offer an attractive alternative in developing new polymeric materials, in which specific properties are desired. In general, property of multi-component polymeric materials depends upon the resulting morphology and interfacial adhesion between each component (Tack *et al.*, 2001). In this study, polymer-based zeolite composite membrane was studied. Effect of characteristics of polymeric matrix was investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

Two polymers used in this study were low density polyethylene (LDPE, MFI = 5.5 from TPI) as a main component and Kraton G1657 (SEBS block co-polymer from Kraton Polymer) as elastomeric minor component. Hydrophilic zeolite, i.e., ZSM5-50, from zeolyst International was used as an absorbing particle incorporated into polymeric matrix. Elastomeric component, Kraton G1657, was mixed with LDPE with the ratio of 70/30 (LDPE/Kraton) in the system of bi-component matrix. 0.2 wt% Anti-blocking agent was added if necessary.

### 2.2 Compounding

Composite film was prepared with zeolite content of 10wt%. All the components were mixed together in an internal mixer machine, Haake Rheomix 3000P, with roller rotors at 190°C and 60 rpm for 10 min. The compounds were then fabricated by blow film extrusion process using single screw extruder, 19mm with 25 L/D. A temperature gradient in the single screw extruder was

maintained in the range of 160-200°C with 200°C in a die zone. The films obtained have a thickness of 30-35 µm.

### 2.3 Characterization and materials testing

Thermal properties and transition temperatures of polymeric films were determined using a differential scanning calorimeter (Mettler Toledo DSC 822<sup>e</sup>) with temperature range of 0 to 130°C and heating/cooling rate at 10°C/min, and dynamic mechanical thermal analyzer (DMTA, Mettler Toledo DMA/SD TA 861<sup>e</sup>) with in the temperature range of -140 to 100°C and heating rate of 4 °C/min on a film sample, using the tension mode with deformation frequency of 1Hz.

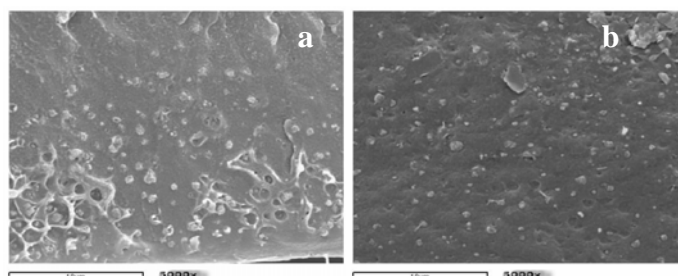
The microscopic morphology and distribution of particles in the polymeric matrix was observed on the gold coated cryo-fracture surface using scanning electron microscope (SEM - JSM 5410).

Measurement of oxygen, carbon dioxide, ethylene transmission rate and permeability were performed using a Mocon Oxtran (OTR Model2/21), Mocon Permatran (CO<sub>2</sub>TR Model 4/41) and GC-FID detector with permeation cell, respectively. Flat films of similar thicknesses (30 ± 5 µm) were tested at pressure of 1 atm, and temperature of 23°C for OTR, CO<sub>2</sub>TR and room temperature for ethylene permeation.

## 3. RESULTS AND DISCUSSION

### 3.1 Distribution of zeolite particle in PE matrix

All the composite films in this study contained 10 wt% hydrophobic zeolite particles with average particle size of 0.5 µm (measured by Mastersizer). The SEM images of LDPE and LDPE/Kraton G1657 blend containing zeolite particles are shown in Figure 1. SEM micrographs revealed that in all systems the zeolite particles showed considerably uniform distribution throughout the polymer matrix. However, voids at the interface were observed.



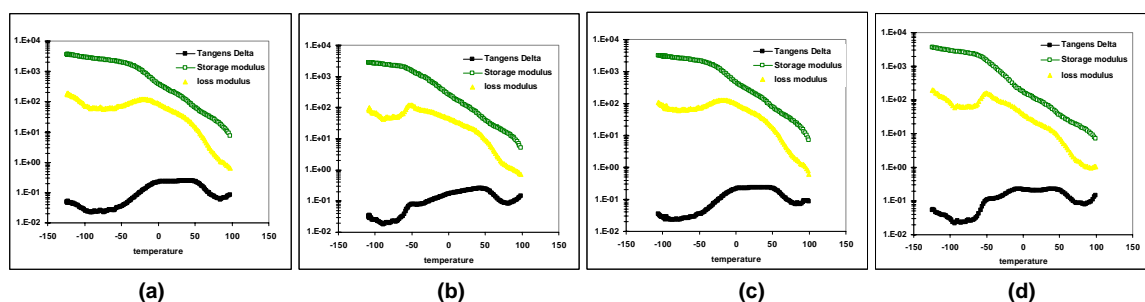
**Figure 1.** SEM images of cryo-fracture surface of composite films:

(a) LDPE + 10 wt% ZSM5-50 and (b) 70LDPE/ 30Kraton G1657 + 10 wt% ZSM5-50

### 3.2 Thermal properties

#### 3.2.1 Glass transition temperature of composite film characterized by DMTA

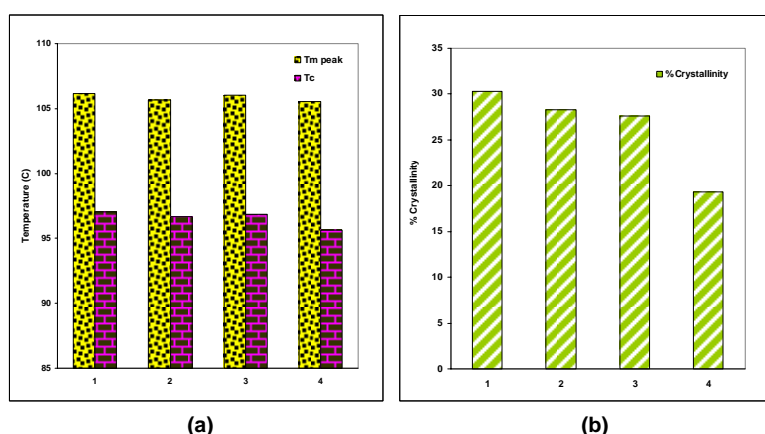
Storage modulus and loss tangent as a function of temperature of the composite films are shown in Figure 2. Loss tangent, which is defined as the ratio of the dynamic loss modulus to the dynamic storage modulus, is related to the molecular motions and phase transitions. Loss tangent is sensitive to all molecular movements occurring in polymers. It can be seen that the value of loss tangent shows in similar fashion for all the specimens between -50 to 100°C. This was believed to be due to temperature dependence of mechanical properties of the blends rather than transition temperature. An addition of zeolites to the LDPE/Kraton blend system, did not have a significant effect on the glass transition temperature of Kraton G1657 as small shoulder around -50°C was shown (see Figure 2(b) vs. (d)). However, loss modulus or energy dissipation characteristic of the blend system was more pronounced around -20°C.



**Figure 2.** Storage modulus, loss modulus and loss tangent ( $\tan\delta$ ) as functions of temperature at 1 Hz of the film of (a) LDPE, (b) 70LDPE/30Kraton G1657, (c) LDPE + 10%ZSM5-50, and (d) 70LDPE/30Kraton G1657 + 10%ZSM5-50

### 3.2.2 Transition temperature and a degree of crystallinity by DSC

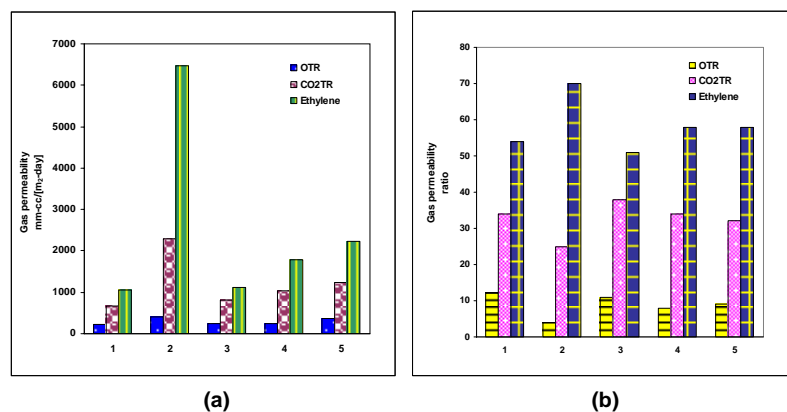
Melting temperature ( $T_m$ ) and Crystallization temperature ( $T_c$ , at cooling rate  $10^\circ\text{C}/\text{min}$ ) of LDPE containing either zeolite or Kraton G1657 were found to be indifferent from that of the pure LDPE. (see Figure 3(a)), LDPE Composite film containing 10 wt% zeolite showed slightly decrease of degree of crystallinity (see Figure 3(b)). An addition of Kraton G1657, into LDPE did not affect a degree of crystallinity of LDPE considerably; however, a significant decrease in the degree of crystallinity of LDPE/Kraton system was observed in the presence of the fillers.



**Figure 3.** (a) Melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$  at cooling rate at  $10^\circ\text{C}/\text{min}$ ) and (b) degree of crystallinity of specimens designated in the numbers corresponding to: 1) LDPE, 2) 70LDPE/30Kraton G1657, 3) LDPE + 10%ZSM5-50, and 4) 70LDPE/30Kraton G1657 + 10%ZSM5-50. Data presented is an average of 3 replicated tests.

### 3.2.3 Gas transport properties of the films

Permeation of gases involved in the packaging system of respiring fresh produce, i.e., oxygen, carbon dioxide and ethylene, was investigated as shown in Figure 4. Selective permeation of zeolite-filled polymeric composite films should perform effectively if the polymer matrix facilitated the transportation of the gas species. Gas permeation of pure LDPE was found to be rather low, while pure Kraton G1657 showed very high gas permeation, especially ethylene permeation. Poor gas permeation of LDPE as well as voids presented at the interface (see Figure 1 (a)) may lead to a relatively low gas permeation and poor selectivity in LDPE-based composite films. An addition of elastomeric component, i.e., Kraton G1657, into the composite, however, significantly improved gas permeation and slightly improved gas selection while the blend matrix did not improve such properties. This may be facilitated by a reduction of degree of crystallinity of LDPE (see Figure 3 (b)). Nevertheless, the further investigations should be carried out to clarify the findings.



**Figure 4.** Gas transport properties: (a) Gas permeability (b) Gas permeability ratio of composite films. The numbers correspond to; 1) LDPE, 2) Kraton G1657, 3) LDPE +10%ZSM5-50, 4) 70LDPE/30Kraton G1657, and 5) 70LDPE/30Kraton G1657 + 10%ZSM5-50. Data presented is an average of 3 replicated tests.

#### 4. CONCLUSION

In this study, the ZSM5-50 zeolite exhibited a good distribution in polymeric matrix. An addition of Kraton G1657, an elastomeric material, improved the gas transport property, especially permeation of ethylene which could be significant to the development of the packaging film for fresh produces.

#### REFERENCES

- Kljusurić, J.(2003), *Sādhanā*, **28**, 991- 998.
- Pötschke, P. and Paul, D.R. (2003), *J. macro.sci.*, **43**,**(1)** ,84 -141
- Hamdan,S., Hashim, D.M.A., and Yusop, M. (2003), *AJSTD*, **21****(1)**, 69 -79.
- Hu, C.,Liu, T.,Lee, K.,Ruan, R.,and Lai, J., (2006), *J. Desalination* **193**, 14-24
- Hyum Kim, S. D., Kim, D., and Sung Lee, D. (1997), *J. Membrane Sci.*, **127**, 9 – 15.
- Poshyachina,S.,Edwards, H.G.M.,and Jonson, A.F. (1996),*IRC in Polym.Sci.*,**37****(23)**, 5171– 5177.
- Tack, O.H., Ryong Kim, H.,Kon Kim, J., and Young Park, J. (2001), *Korea-Australia J. Rheology*, **13****(2)**, 83 – 87.