CHAPTER IV
RESULTS AND DISCUSSION

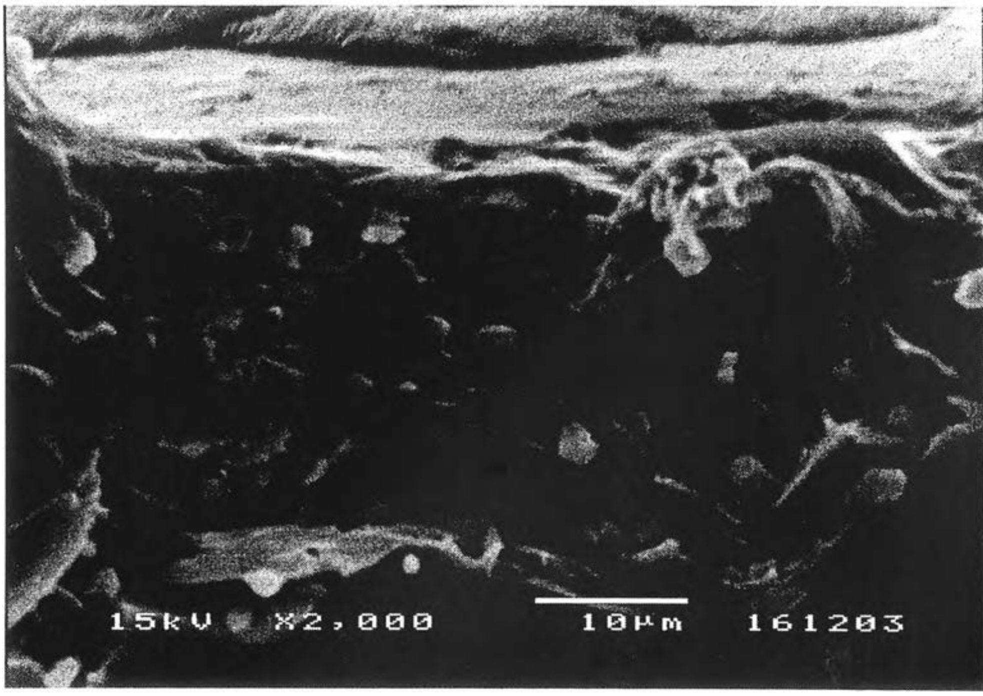
4.1 Properties of Silicalite-1

Silicalite-1 was used in this study. The silicon/aluminum (Si/Al) ratio of silicalite-1 is infinity. The (Si/Al) ratio indicates the hydrophobicity of zeolite. In general, A high value of the Si/Al ratio value relates to the hydrophobicity of the material. Therefore, Silicalite-1 used in this study can be considered hydrophobic. The pore size of silicalite-1 is in the range of 5.1-5.6 Å.

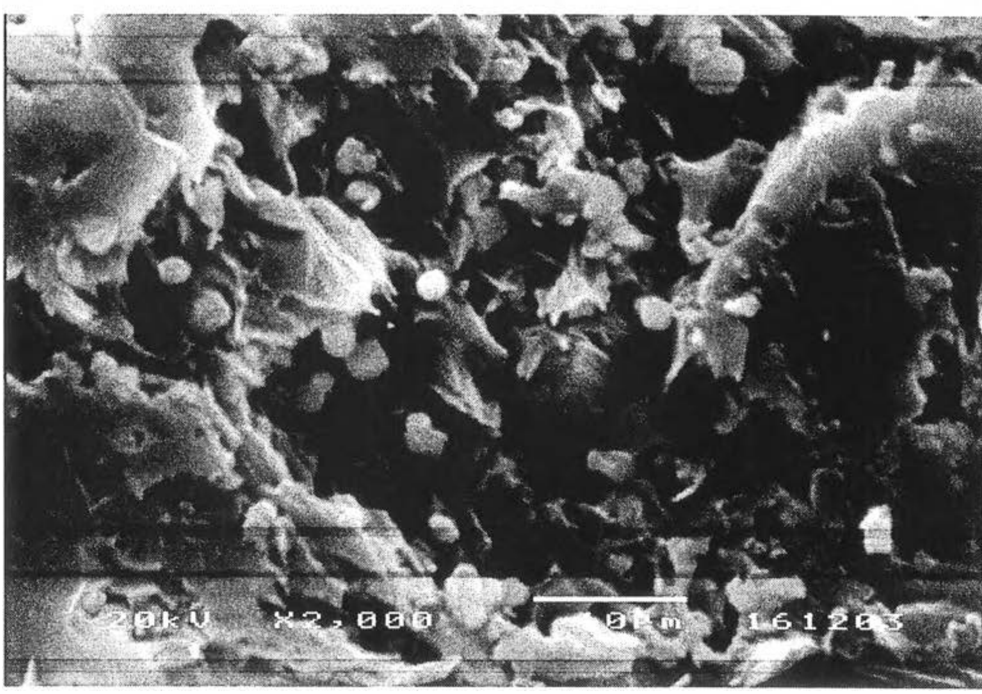
4.2 Morphological Change of MMM's

The SEM images are shown in Figure 4.1 for the cross-sectional of MMM's included polyimide incorporated with 10, 20, and 30 wt% silicalite-1 loadings. As shown in the figure, MMM's contain many interfacial voids around silicalite-1 particles. The round shape particles are silicalite-1, and the continuous phase is polyimide. The dark area between silicalite-1 particles and polyimide is empty space, i.e. interfacial void. The interfacial voids decreases with an increase in silicalite-1 loading.

(a)



(b)



(c)

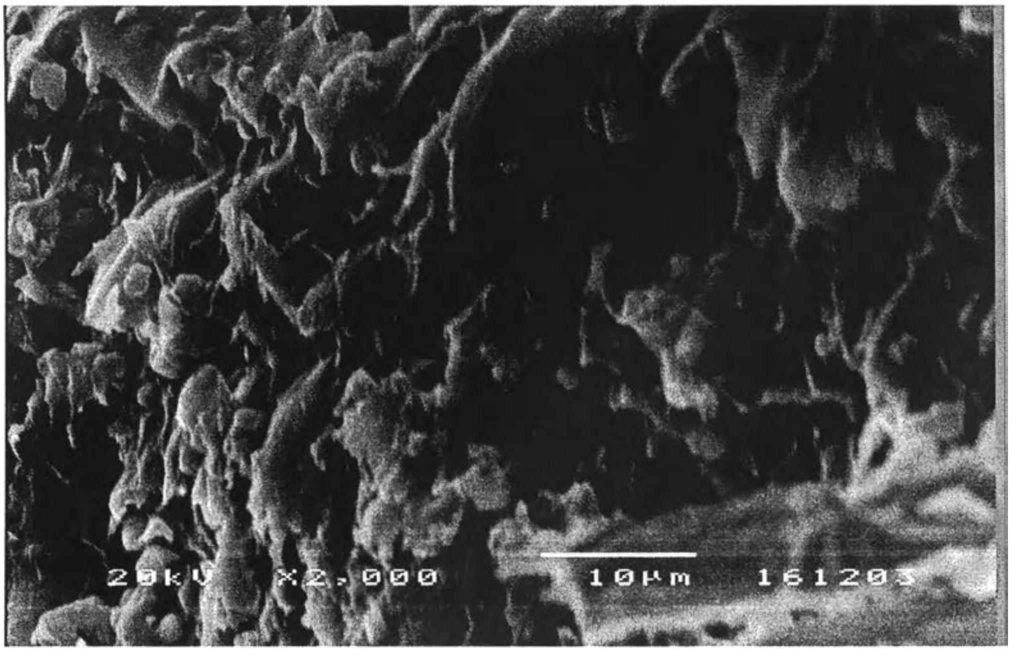


Figure 4.1 SEM images showing cross-sectional morphologies of MMM's: (a) 10 wt% silicalite-1/polyimide MMM; (b) 20 wt% silicalite-1/polyimide; (c) 30 wt% silicalite-1/polyimide.

4.3 Pervaporation

The polyimide membrane and polyimide-based MMM's were prepared by solution casting and solvent evaporating methods. They were evaluated for their ability to separate *p*-xylene from a 1:1:1:1 mixture of *p*-xylene, *o*-xylene, n-heptane and 1-hexene. The membrane pervaporation was carried out. Although pervaporation can be performed at low temperatures, preferred temperatures should be 80°C or higher. The maximum upper limit is typically the temperature at which the membrane is physically damaged (Miller *et al.*, 2002). Three MMM's including polyimide and polyimide incorporated with different loadings of silicalite-1 (10, 20 and 30 wt%) were prepared. Membranes with significantly high zeolite/polymer ratios tend to be brittle (Miller *et al.*, 2002). Selctivities of *p*-xylene were calculated with respect to *o*-xylene and n-heptane. The permeabilities and selectivities of the polyimide and silicalite/polyimide MMM's are shown in Figures 4.2, 4.3 and 4.4.

As shown in Figure 4.2, the permeabilities of *p*-xylene and *o*-xylene increase with the increase in the silicalite-1 loading. In contrast, the permeabilities of n-heptane and 1-hexene show the opposite trend. These results may be due to the membrane solubility parameter and effect of silicalite-1. The xylenes present in the feed dissolve into the membranes because of similarity between membrane solubility parameter and those of xylenes. The xylenes diffuse through the membrane with *p*-xylene permeating at a higher rate than *o*-xylene. Moreover, silicalite-1 is more selective to xylenes than paraffins and olefins, so the permebilities of n-heptane and 1-hexene decrease with increasing the silicalite-1 loading.

Figures 4.3 and 4.4 show the *p*-/*o*-xylene selectivity and C_8 aromatics/paraffins selectivity, respectively. Figure 4.3 shows that all membranes are selective to *p*-xylene over *o*-xylene. The *p*-/*o*-xylene selectivity for the polyimide membrane, 10, 20 and 30 wt% silicalite/polyimide MMM's are 1.042, 1.032, 1.288 and 1.858, respectively. Figure 4.4 shows that all membranes are selective to *p*-xylene and *o*-xylene over n-heptane. This result is consistent to that from Santiworawut (2003) who reported that polyimide and polyimide-based MMM's were selective to C_8 aromatics over paraffins. The *p*-xylene/n-heptane and *o*-xylene/n-heptane selectivities are shown in Table 4.1.

Table 4.1 Selectivity of polyimide and polyimide-based MMM's

Membrane	**Selectivity**	
	***p*-xylene/n-heptane**	***o*-xylene/n-heptane**
Polyimide	1.275	1.224
10 wt% silicalite/polyimide	7.029	6.809
20 wt% silicalite/polyimide	39.072	30.344
30 wt% silicalite/polyimide	27.02	25.636

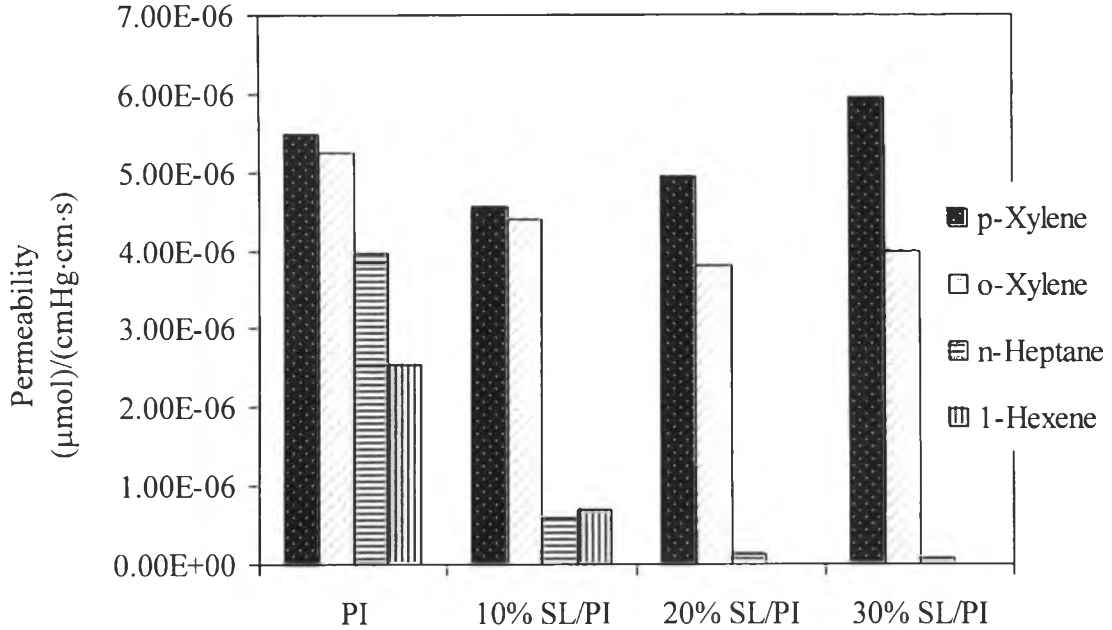


Figure 4.2 Permeability of each component through polyimide and polyimide-based MMM's.

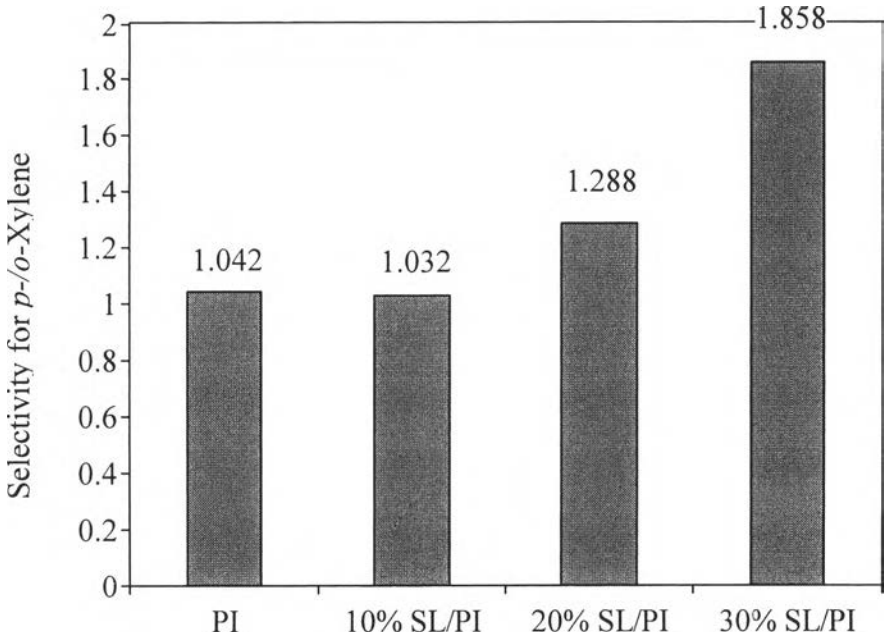


Figure 4.3 Selectivity for *p*-/*o*-xylene of the polyimide and polyimide-based MMM's.

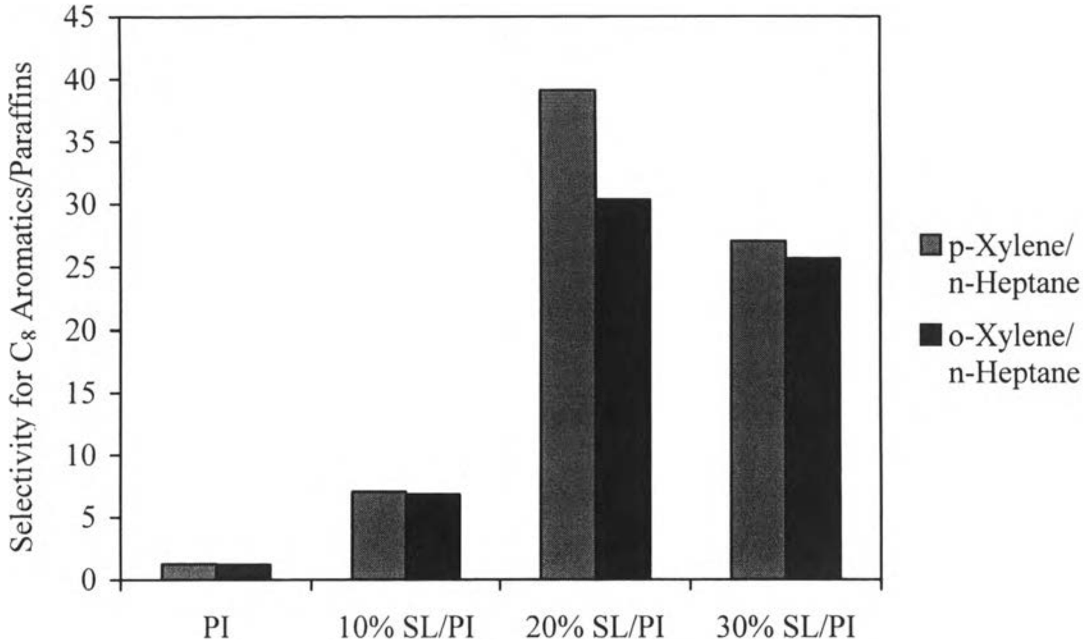


Figure 4.4 Selectivity for C_8 aromatics/paraffins of the polyimide and polyimide-based MMM's.

Some MMM's have high permeabilities but low selectivities. This result must be related to the interfacial void formation between silicalite-1 particles and polyimide matrix. When voids are formed, the molecules can pass through the voids without any resistant against permeation. Therefore, the permeability of membranes containing empty voids must be high.

4.4 Single Component Adsorption Experiment

Single component adsorption capacity on silicalite-1 was measured for n-hexane, *p*-xylene and *o*-xylene at room temperature. This result is shown in Table 4.2. The amount of xylenes and n-hexane adsorbed are expressed in gram of the adsorbed species per gram of silicalite-1. The data demonstrates that silicalite-1 has a much higher adsorption capacity for n-hexane than it does for *p*-xylene and *o*-xylene. The silicalite-1 possesses two channel systems, a straight and a sinusoidal with a window size of 0.53×0.56 and 0.51×0.55 nm, respectively. According to the critical molecule dimensions of *o*-xylene (≈6.8 Å), *o*-xylene has little chance to access to the pores of the silicalite-1. On the other hand, n-hexane (≈4.3 Å) and *p*-xylene (≈5.8 Å) can be adsorbed into the channels, so silicalite-1 may adsorb n-hexane and *p*-xylene at equilibrium.

Table 4.2 Adsorption capacities of n-hexane, *p*-xylene and *o*-xylene on silicalite-1

Component	Adsorption capacity (g/g)
n-hexane	0.073
p-xylene	0.029
o-xylene	0.011

From the adsorption experiments, the results show that silicalite-1 is selective to n-hexane over *p*-xylene, which contradicts the results from the MMM's experiments. Because of its hydrophobicity, silicalite-1 has higher capacity and selectivity to n-paraffin than *p*-xylene. However, the equilibrium capacity and selectivity are not necessarily applied to the kinetic capacity and selectivity such as the membrane operation. Hence, the results from the MMM's experiments are possible that silicalite-1 in MMM's adsorbs n-heptane and slows down the diffusion rate. This allows *p*-xylene to diffuse through the membrane at a faster rate than n-heptane.