

EFFECT OF NANOFILLER ON THE GAS PERMEABILITY OF
EPOXY NANOCOMPOSITE

By

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CHAPTER 1

INTRODUCTION

Polymer composites have a wide range of application in aircraft, automobile, sport, construction, fuel and especially in packaging industry. The overgrowing demands have given rise to a significant amount of interest in manufacturing packaging films with greatly improved barrier properties. Again the permeability is related to environmental degradation property of polymer composite. Polymers with lower permeability creates opportunity for new application like transportation vehicle of gasses like hydrogen and nitrogen. Typical approach to decrease permeability of polymer is to apply barrier coating such as aluminum metallization on polymer surfaces [1] and to laminate high barrier material, such as ethylene vinyl alcohol [2] and polyvinyl alcohol (PVA) [3] which is usually too expensive and cannot achieve desired long-term barrier properties [2]. The emergence of polymer nanocomposites introduced a new opportunity to improve barrier properties of polymers.

Clay is conventionally used as nanofiller to improve barrier property of nanocomposite. It is reported that gas permeability can be reduced by 5–50% using as little as 3% nanoclay dispersion [4]. Moreover, clay has high stiffness, high aspect ratio, cost effectiveness and provides superior mechanical, thermal properties at low levels of loading when compared to neat resin [5, 6]. However, processing of clay nanocomposite is difficult mainly due to the high viscosities of the clay and the need to keep a homogeneous dispersion throughout the process [7]. Also higher percentage of clay creates agglomeration, decreases the mechanical property of the composite and makes it impossible to use in some manufacturing technique in case of composite like Vac-

cum Assited Resin Trannsfer Molding (VARTM). This brings the concept of another nanofiller Polyhedral Oligomeric Silsequioxane (POSS). It is a kind of hybrid material that possess both organic and inorganic properties, having a size between 1–3 nm and have several advantages over conventional inorganic fillers including monodispersity, low density, high thermal stability and controllable functionalities. Uniform dispersion of POSS in a polymer matrix at nanoscale level can create synergistic effect on improving the bulk properties [8, 9, 10]

Recently POSS has been widely used in manufacturing nanocomposite due to good thermal stability, abrasion resistance, chemical resistance, environmental friendliness and controllable functionalities [11, 12, 13]. Surprisingly, there has not been significant amount of investigation on the permeability of POSS, specially epoxy POSS system. There has been few studies like O₂ and N₂ permeability of polystyrene/POSS by Rios dominguez *et al.*[14], CO₂ transport property of poly(bispanol A coarbonate)/POSS by Ning hao *et al.*[15] and gas diffusivity of poly(methyl methacrylate)/POSS by molecular simulation by Zhang *et al.*[16].

Focus of this study is to compare the helium gas permeability of POSS and clay nanocomposite respectively with two different kinds of epoxy and to have a clear understanding about the permeation behavior of POSS nanocomposite. The reason for choosing helium gas is due to the fact that the molecular size of helium is close to hydrogen. As a result determining helium gas permeability coefficient will enable us to utilize this composite in various new applications with hydrogen.

1.1 Nanocomposites for reducing permeability

Polymer nanocomposites are nanoscale materials, in which at least one of the components has a dimension smaller than 100 nm. The incorporation of nanoparticles with huge surface area and often anisotropic geometry in a polymer matrix leads to increased particle-matrix interactions and decreased interparticle distances with con-

sequent changes in morphology and performance without degrading density of the material[17, 18]. Significant improvements in permeability, thermal stability, flame retardancy and mechanical and dielectric properties have been observed at low filler volume fraction compared to conventional polymer[19, 20, 21, 22, 23, 24] .

These improvements in the gas barrier properties result from two separate phenomena. Firstly, the change in the solubility of the permeant gas, within the nanocomposite followed by diffusion through it. This occurs due to the incorporation of inorganic phase resulting in modifying the polymer chain flexibility and the polymer matrix itself, which ultimately lowers the penetrant mobility [25]. Secondly, the impermeable inorganic phase forces a more tortuous pathway for permeant molecules by presenting a physical barrier and resulting in affecting the diffusion through adventitious pores and free volumes.

1.2 Epoxy resin

Amine cured epoxies are one of the most commonly used matrix material for fiber reinforced composite having superior mechanical property, chemical resistance due to their high degree of crosslinking [26, 27] . Recently, there has been a lot of investigation in improving their property by adding filler material. With addition of the filler there are significant changes in curing kinetics, local stoichiometry, curing reaction, curing temperature of neat resin resulting in changes in mechanical property. In particular nano size fillers have unique properties, show uniform dispersion without agglomeration and small amount is needed to cause significant changes. Again, for POSS epoxy resin is the one with higher compatibility. They offer potential for better cross linking opportunities with POSS with strong hydrogen bonding along with inorganic silica core incorporation [28]. The principal reason for choosing SC79 and Epon862 is their compatibility with clay and POSS. These resins are well understood, readily available and amenable to nanoparticulate blending.

1.3 Clay

Clay is a montmorillonite mineral belonging to the smectite family, obtained from the volcanic eruptions of bentonite. This montmorillonite clay is of special interest due to their high surface area and high aspect ratio which influence barrier property of nanocomposite. The unit layer of clay has an octahedral sheet of aluminum or magnesium hydroxide sandwiched between two tetrahedral sheets of silicon oxide figure 1.1. The layers become negatively charged by replacement of silicon by aluminum or of aluminum by magnesium ion and attracts cations such as sodium, potassium etc. The layers are connected by Van Der Waals creating galleries. It was discovered by Toyota that, incorporating low volume fractions of clay (such as 2%) with nylon fibers, improved the strength, modulus and heat distortion temperature of the composite compare to neat resin. [29, 30]

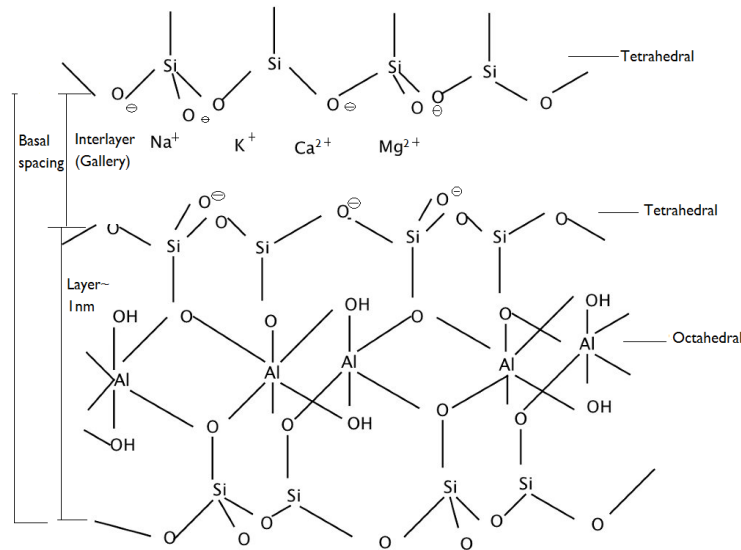


Figure 1.1: Clay structure

In general, clays are commercially modified with surfactant to achieve less surface energy of the clay layers and to match their surface polarity to polymer polarity to

have better dispersion. Dispersion is classified into three terms: phase separation, intercalation and exfoliation. Phase separation or agglomeration is breaking of clay tactoids in the resin with no monomer particle or polymer matrix present in layers as shown in Fig. 1.2a. Intercalation is breaking of clay stacks into groups of smaller stacks with polymer chain inserted between the layers and platelets move apart but are still exhibiting in a regular ordered structure[Fig1.2b]. Exfoliation is the separation of the clay platelets into individual platelets in the polymer resin as shown in fig. 1.2c and it gives the best mechanical and barrier properties [31].

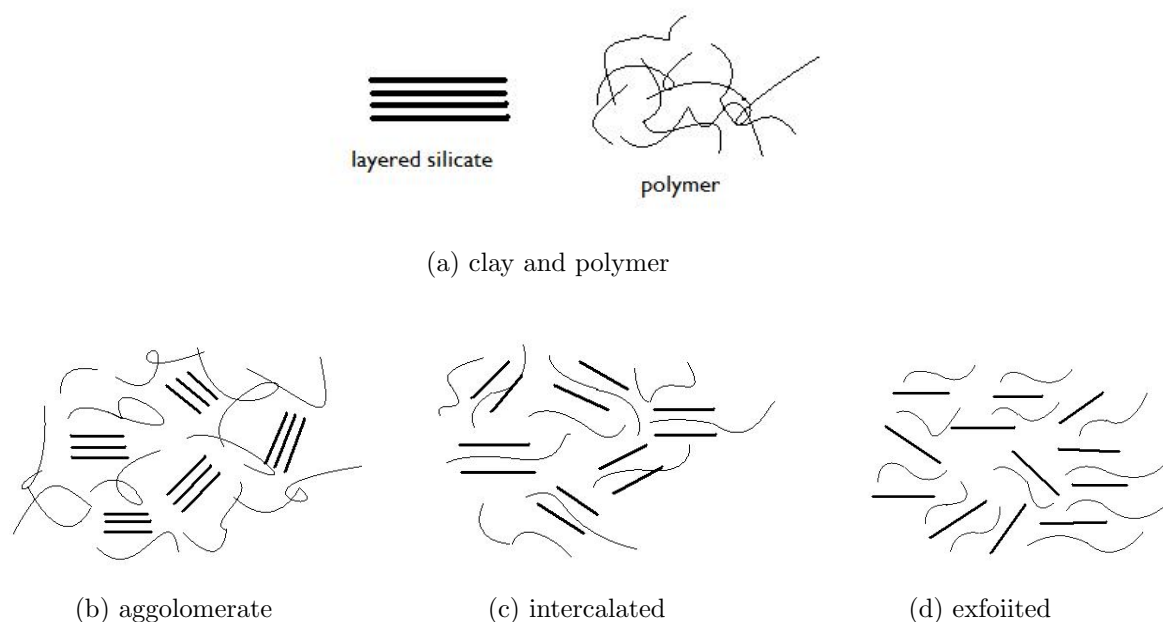


Figure 1.2: (a) Clay and polymer, clay layers (b) agglomerate(c) intercalated (d) exfoliated

Factors that influence the permeability of nanocomposite are the volume fraction of nanoplatelet, their aspect ratio and their orientation relative to the diffusion direction. For clay the decrease in solubility coefficient is lower than the diffusion coefficient as the volume of nanoclay is low in polymer matrix. On the other hand, decrease in diffusion coefficient is the result of introducing more tortuous pathway by clay. However, tortuosity is dependent on the shape and degree of dispersion of

clay.[32, 33] Fully dispersed (exfoliated) clay in polymer will have higher values of tortuosity factor and aspect ratio in comparison to partially dispersed (intercalated) clay composite making it impermeable to gas.

1.4 Polyhedral Oligomeric Silsequioxane

The POSS molecule contains both organic and inorganic part with the formula $(\text{RSiO}_{1.5})_n$. The inorganic part consists of silicon cage containing silicon and oxygen atom and organic part consists of the substituents on the inorganic cage [fig. 1.3].

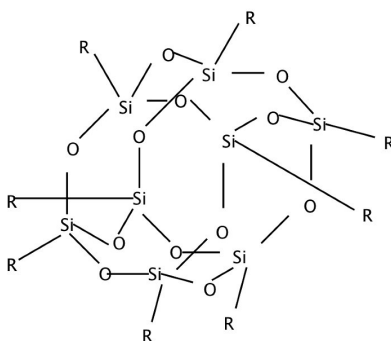


Figure 1.3: POSS structure

The POSS molecule was first reported in 1946 [34] and have been successfully incorporated into polymers by scientists from the Air Force Research Laboratory [35]. POSS with an average size of 1–3 nanometer can be considered as the smallest possible particle of silica. However, unlike silica, silicon or any filler the reactive or unreactive organic part of POSS makes it more compatible with polymer. Studies have shown that POSS have enhanced mechanical strength, reduced flame reterdancy, higher glass transition temperature[36].

Dispersion of POSS depends on the interaction of the organic part with polymer. Generally there are two kinds of interaction based on the reactivity of the organic

substituent:

1. Reactive organic substituent reacts with polymer chain forming covalent bond.
2. The non reactive organic substituent shows compatibility either by similarities in chemical structure or by specific polar interaction between itself and the polymer chain.

Usually positive reinforcement is obtained if there is good interaction between the polymer and POSS. The main difference between clay and POSS as a nanofiller is that clay is physically incorporated in polymer whereas POSS is chemically incorporated. Also POSS can be dissolved into other monomer and copolymerized. So the dispersion of POSS is more easily achievable compare to clay which influences the permeability by affecting the diffusivity factor. The silicon cage of POSS is the impermeable part of the substituent. However for POSS the key factor is the compatibility between the resin system and POSS.

In this study, we compared the permeability of POSS and clay reinforced polymer respectively. We analyzed the interaction between the nanofiller and resin to comprehend a total understanding about their permeability characteristics.

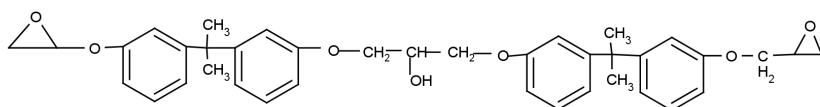
CHAPTER 2

MATERIALS AND METHODS

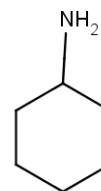
2.1 Materials

2.1.1 Resin System

Two types of resin system have been used in this study. The first one is SC79 Part A (Applied Poleramics, Benificia, CA) a diglycidyl ether of bisphneol A which was cured with SC79 Part B, a cycloaliphatic amine. The second one is EPON 862 (Hexion speciality chemicals, Columbus, OH) which was cured with Epikure 3274, an aliphatic amine having low viscosity. Figure 2.1 and Figure 2.2 shows the chemical structure of both the resin and curing agent.



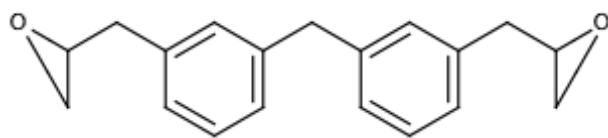
(a) SC79



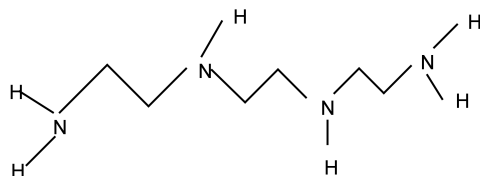
(b) Monomer of cycloaliphatic amine

Figure 2.1: Chemical structure of (a) SC 79 and (b) Curing agent

These resins were selected for this study as these are well studied in literature, show superior mechanical property, chemical resistance and also easy to fabricate. Both of these resins have high cross linking density.



(a) Epon 862



(b) Epikure 3274

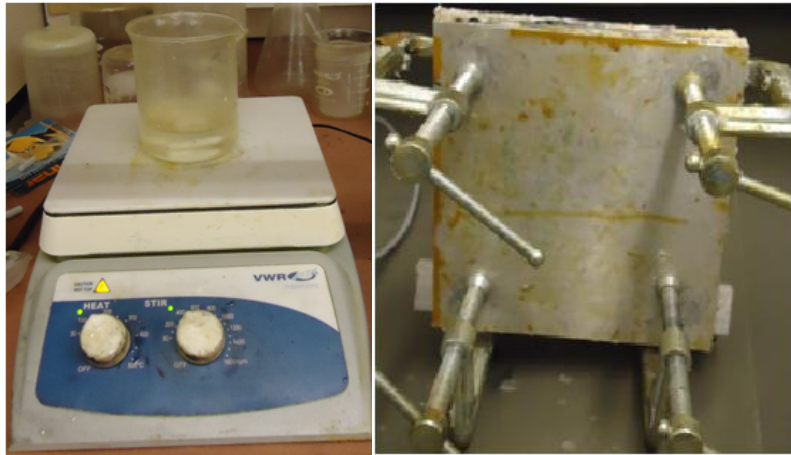
Figure 2.2: Chemical structure of (a) Epon 862 and (b) Epikure 3274

2.1.2 Nanofillers

Two types of nanofiller were used in this work. One is the conventional nanofiller nanoclay. We used Nanomer I28E (Southern Clay Products, Gonzales, TX, USA) due to its compatibility with the resins and high temperature resistance. It has an average particle size of 8–10 μm and an aspect ratio of 75-120. This clay is modified with quaternary trimethylsterayl ammonium salt.

The second one is Polyhedral oligomeric silsesquioxane(POSS). For SC79 we used three different functionalities of POSS which are trisilanol phenyl, methacryl and glycidyl. These POSS were purchased from Hybrid Plastics, Hattiesburg, MS. For Epon862 we used only glycidyl and methacryl POSS. Figure2.3 shows the chemical structure of these POSS.

Based on the presence of the functional group on silicon atom and interaction with epoxy resin these POSS were selected among different types of POSS. All these POSS are compatible with our resin system. Trisilanol phenyl has the appearance



(a) magnetic stirrer

(b) Mold

Figure 2.4: Sample preparation of POSS (a) Magnetic stirrer and (b) Prepared mold
min for both the resins.

As shear mixing induces large amount of bubbles, degassing was done before adding hardener. After all the bubbles were removed from the mixture, hardener was added at the same ratio like POSS, followed by hand mixing. Subsequently degassing was done to remove the entrapped bubble in the mixture. Then mixture was poured into the mold followed by the same curing cycle.

2.3 Determination of gas Permeability

The standard test method for determining gas permeability is documented in ASTM D14382 (re-approved in 1997) “Standard Test Method for Determining Gas Permeability Characteristic of Plastic Film and Sheetting ”[37]. The permeability can be measured by two experimental methods. Volumetric determination method has been adopted for this investigation.



Figure 2.5: Shear mixer

2.3.1 Gas permeation apparatus

The gas permeation apparatus basically consists of three chambers. The permeant gas is pressurized in upstream chamber, permeates through the sample in middle chamber and escapes through the downstream chamber. Two pressure transducers (model:PX01C1-075G5T, Omega Dyne Inc.) are connected to inlet and outlet to acquire precision pressure of upstream and downstream chamber. The data of the pressure was obtained with the help of an oscilloscope (Tektronix TDS 460 A).

In order to evacuate the chambers two valves are connected with inlet and outlet section. Figure 2.6 shows all the parts of the setup. It also includes a high capacity gas purifier (Agilent Technologies, Palo Alto, CA, USA), as shown in fig. 2.6, to prevent any impurity present in the helium gas coming from the gas tank.

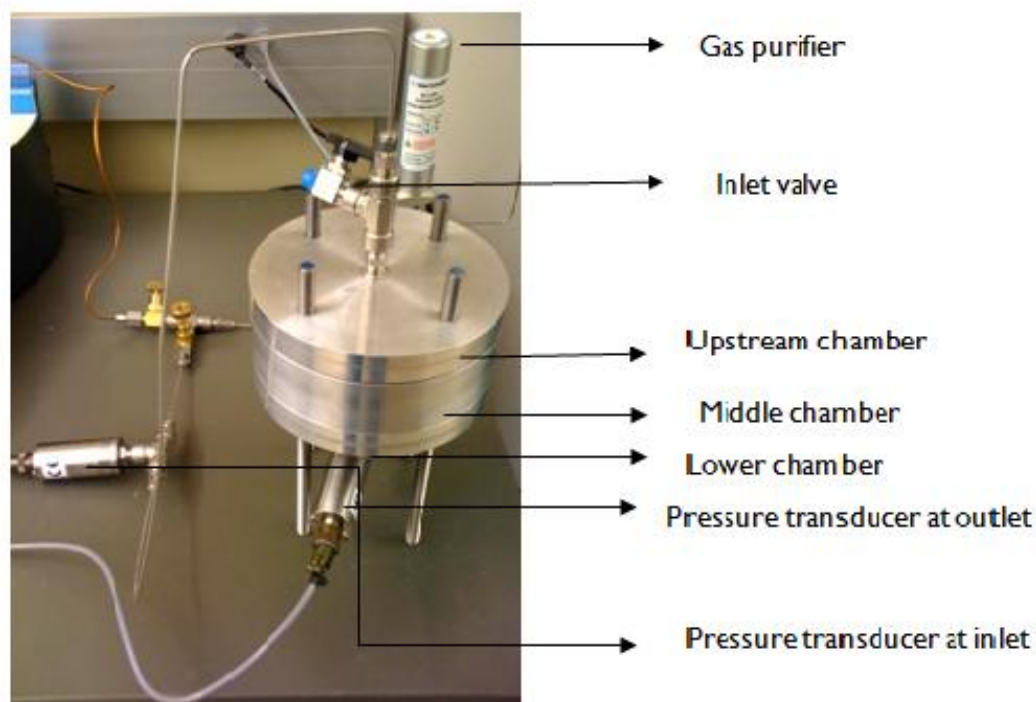


Figure 2.6: Gas permeability setup

2.3.2 Calibration of the setup

Volume of the cavity in the downstream chamber was calibrated. A plastic pipe was connected with the outlet valve and filled with water. Subsequently, the inlet valve was opened to allow the gas for permeation at 20 psi. When there was enough pressure in the lower chamber the outlet valve was opened and the permeant gas (helium) was allowed to pass through the pipe. From the deflection of water in the pipe calibration was done and it has about 10% error with the geometric dimension. These data are summarized in Table 2.1.

| PressureP1 (V) | P2 (mV) | P1 (psi) | P2 (psi) | h | V (m ³) | V (Avg) (m ³) | error | V(geometric) (m ³) | error |
|-------------------|------------|-------------|-------------|-----|------------------------|------------------------------|--------|-----------------------------------|--------|
| 1.04 | 760 | 15.6 | 11.4 | 155 | 5.3294E-05 | 5.13E-05 | 6.7% | 5.71E-05 | 10.18% |
| 1.04 | 758 | 15.6 | 11.37 | 150 | 5.1075E-05 | | 10.61% | | |
| 1.04 | 758 | 15.6 | 11.37 | 157 | 5.346E-05 | | 6.45% | | |
| 1.042 | 776 | 15.63 | 11.64 | 140 | 5.173E-05 | | 9.46% | | |
| 1.042 | 776 | 15.63 | 11.64 | 140 | 5.173E-05 | | 9.46% | | |
| 1.042 | 776 | 15.63 | 11.64 | 130 | 4.804E-05 | | 15.93% | | |
| 1.042 | 778 | 15.63 | 11.67 | 135 | 5.039E-05 | | 11.81% | | |
| 1.044 | 776 | 15.66 | 11.67 | 139 | 5.15E-05 | | 9.88% | | |
| 1.042 | 772 | 15.63 | 11.58 | 140 | 5.0708E-05 | | 11.26% | | |
| 1.042 | 774 | 15.63 | 11.61 | 132 | 4.82E-05 | | 15.5% | | |

Table 2.1: Data for volume calibration

The setup was calibrated using a standard mylar film. In this process the permeability coefficient was evaluated under steady state condition using the following expression [38]

$$P = \frac{273VL}{76ATP_0} \frac{dp(t)}{dt} \quad (2.1)$$

here, P= Permeability(bar), V=volume of the downstream chamber(cm³), dp(t)/dt= rate of pressure change in downstream chamber(cmHg/s)(fig 3.3), L=thickness of the flim(cm), A=area of the film(cm²), P₀ = inlet pressure(cm Hg), T=temperature(K).

Permeability for three different pressures with a time interval of 90 minute and also for another two different time interval was evaluated and the error came out to be around 30%-38%. The calibration was done for three different inlet pressure with differnt time interval and for each acse ten reading were taken. So the error actually ranges from 30%-38% for all these cases which also accounts the errorof 10% in downstream chamber. As a summary this error includes systematic error and for particular sample the result can vary within 2-3% from actual value excluding this systematic error. These results are shown in Table 2.2 and Table 2.3 respectively.

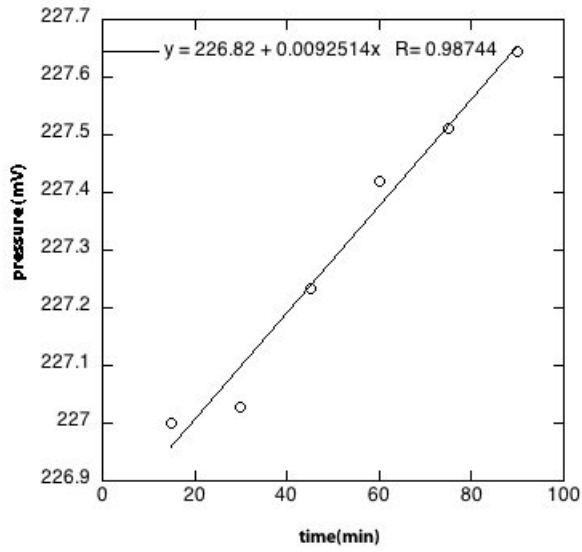
| P (cm Hg) | Slope (cmHg/ min) | Slope (cm Hg/s) | Thickness (cm) | T (K) | V (cm ³) | A (cm ²) | P (Barrer) | P (cc/100in ² /24hr/ atm/mil) | P (mylar) | Error |
|-----------------|-------------------------|-----------------------|-------------------|----------|-------------------------|-------------------------|---------------|--|--------------|-------|
| 103. | .009 | 1.202 | .002 | 314 | 51.3 | 1.25 | 1.27 | 203. | 150 | 35. |
| 40 | 3 | E-05 | 337 | | | 41 | E-10 | 3977 | | 598% |
| 129 | .011 | 1.447 | .002 | 314 | 51.3 | 1.25 | 1.2248 | 195. | 150 | 30. |
| .25 | 2 | E-05 | 337 | | | 41 | E-10 | 9616 | | 64% |
| 155 | .013 | 1.78 | .002 | 314 | 51. | 1.25 | 1.25 | 201. | 150 | 34. |
| .10 | 8 | E-05 | 337 | | 3 | 41 | 7E-10 | 2106 | | 14% |

Table 2.2: Data for different pressure in 90 minute

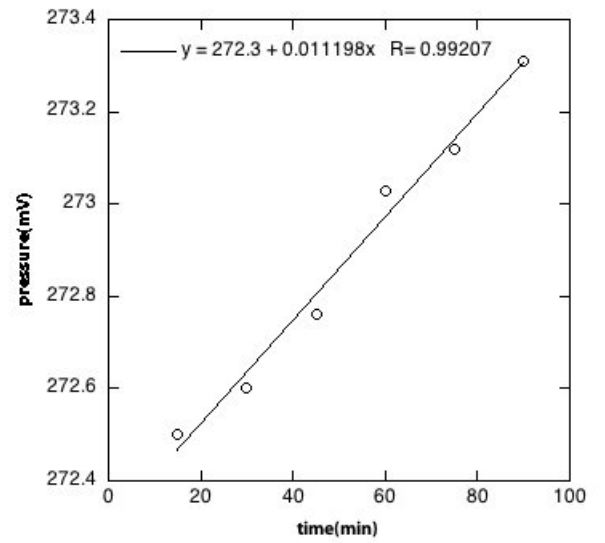
2.3.3 Evalutaion of Permeability coefficient

Permeability of the nanocomposite was evaluated based on Darcy's equation:

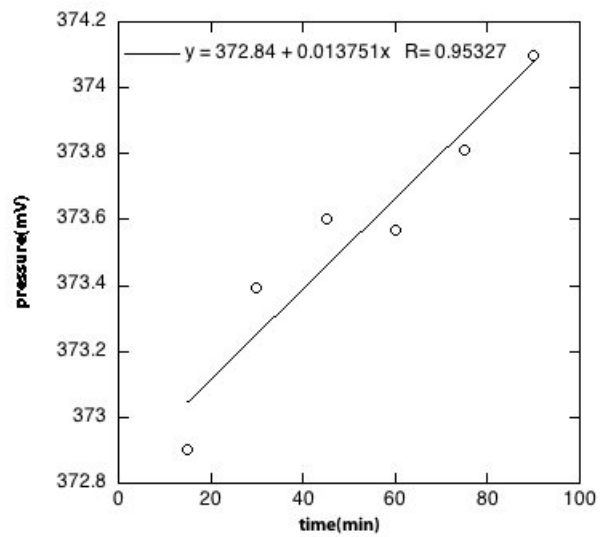
$$Q = \frac{kpA}{\mu x} \quad (2.2)$$



(a) 20 psi



(b) 25 psi



(c) 30 psi

Figure 2.7: Different pressure graphs

| P (cmHg) | P1 (mV) | P2 (mV) | delp (cmHg) | V (cm ³) | A (cm ²) | T (K) | del t (sec) | L (cm) | P (bar) | P | P mylar | Error |
|-------------|------------|------------|----------------|-------------------------|-------------------------|----------|----------------|-----------|------------|------|------------|-------|
| 51. | 148 | 148 | .01 | 51.3 | 1.25 | 314 | 1800 | .002 | 1.276 | 204. | 150 | 36.08 |
| 7 | .1 | .24 | 0857 | | 41 | | | 337 | E-10 | 127 | | 47% |
| 10 | 216 | 216 | .003 | 51.3 | 1.25 | 314 | 300 | .002 | 1.285 | 205. | 150 | 37 |
| 3.4 | .37 | .416 | 567 | | 41 | | | 337 | E-10 | 5848 | | .06% |
| 10 | 216 | 216 | .003 | 51.3 | 1.25 | 314 | 300 | .002 | 1.276 | 201. | 150 | 34 |
| 3.4 | .54 | .587 | 567 | | 41 | | | 337 | E-10 | 2106 | | .14% |
| 129 | 265 | 265 | .003 | 51.3 | 1.25 | 314 | 300 | .002 | 1.2904 | 206. | 150 | 37 |
| .25 | .626 | .685 | 567 | | 41 | | | 337 | E-10 | 4596 | | .64% |
| 129 | 265 | 265 | .003 | 51.3 | 1.25 | 314 | 300 | .002 | 1.2685 | 202. | 150 | 35 |
| .25 | .34 | .398 | 567 | | 41 | | | 337 | E-10 | 9603 | | .31% |

Table 2.3: Data for different pressure for different time

here, Q= volume flow rate of gas, k=permeability, p= pressure change in both sides, μ = dynamic viscosity, x=thickness of the medium, A=area

Pressure change was known from pressure transducers. By applying ideal gas law the volume flow rate Q was evaluated

$$PV = nRT \quad (2.3)$$

here, P= Pressure in downstream chamber(Pa), V=volume of the downstream chamber(m³), n=amount of gas(mol), R=universal gas constant, T=temperature(K)

Getting the value of n from this equation and using the molar weight and density of helium the volume of the gas was calculated. Subsequently, flow rate was evaluated taking time into consideration.

2.4 Physical Characterization

The morphology of the samples were analyzed using the scanning electron microscope (SEM) (Hitachi S-4800 FESEM, Dallas, TX). Since the samples were nonconductive they were sputtered using the gold-palladium alloy before any imaging was done. The samples were also analyzed by energy dispersive X-ray analysis (EDX) to identify the Si composition in the specimen.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Permeability coefficient

3.1.1 Nanocomposite of Diglycidyl Ether of Bisphanol-A (SC79)

For this epoxy system three kinds of POSS and I28E clay are used as nanofiller. The permeability was evaluated at room temperature and at a constant pressure of 20 psi. For each percentage of nanofiller five samples were tested and error was determined.

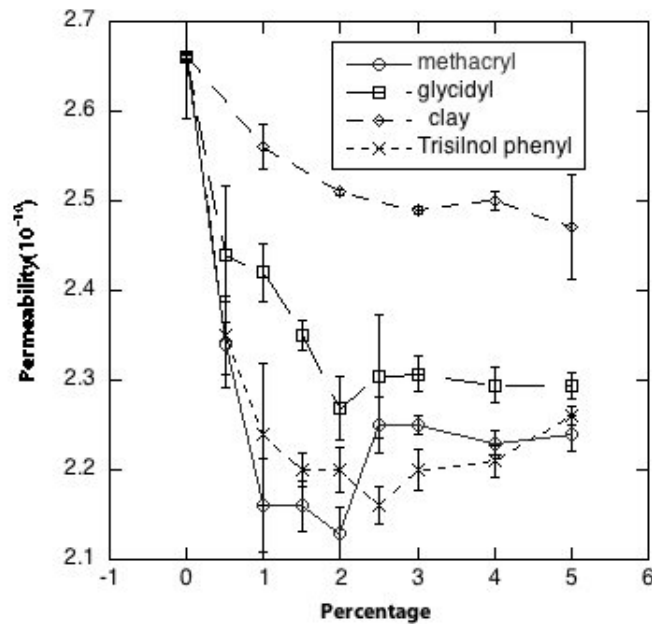


Figure 3.1: Permeability coefficient of DGEBA resin with methacryl, glycidyl, trisilanol phenyl and clay

From fig. 3.1 we can observe that the incorporation of POSS resulted in better barrier property compared to clay. The permeability decreases approximately 20% for methacryl whereas it only decreases upto 7% for clay in comparison to neat resin. All three functionality of POSS showed the same trend where lower permeability coefficient at 2%. Among three POSS methacryl showed the lowest permeability.

For POSS the permeation can occur by two methods as follows:

1. through the Si-O cage of POSS
2. through the polymer matrix

Tejerina *et al.* computationally showed that high energy barrier exists in Si-O cage which may prevent the permeation of the penetrant gas through it [39]. So the permeation of helium gas occurs through the polymer matrix only which depends on the excess free volume.

Free volumes act as sites for gas sorption. Basically free volumes are disconnected packets that slowly exchange position because of thermally activated chain motion. Activated diffusional jump of permeant gas takes place through this process. Dispersion of POSS in the polymer matrix will cause reduction of the free volume and restriction of the polymer chain motion. Therefore, will decrease the diffusivity and solubility of penetrant. This phenomenon explains the decrease in permeability compared to neat resin in case of POSS that we observed in our experiment. Also the specific trend that we see in all the POSS curves could be attributed to the fact of uniform dispersion of POSS which was further clarified with help of SEM and EDX analysis.

For clay like POSS the factor that affects the permeability is the dispersion. Due to the high aspect ratio clay itself works as an impermeable barrier to the penetrant gas, forcing them to follow a longer or tortuous pathway. So with better dispersion or exfoliation the effective surface area of clay increase which results in increasing the tortuosity factor. Also the restriction of polymer motion is a function of the

interaction of the polymer with the surface of clay. As a result, by adding clay a decrease in solubility is expected due to the reduction in matrix free volume as well as decrease in diffusivity by increasing tortuosity factor. This is the reason for observing a decreasing trend for clay in fig. 3.1 with higher percentage. However, clay tends to agglomerate easily causing large scale of holes in the matrix. This holes act as a lower resistance path for gas and results in higher permeability. This explains the reason of epoxy/clay nanocomposite having higher permeability compare to epoxy/POSS in DGEB-A resin system which is verified by SEM images.

3.1.2 Nanocomposite of Diglycidyl Ether of Bisphenol-F

For this epoxy system the experimental condition is same as DGEB-A. Figure3.2 shows the experimental evaluation of permeability of DGEB-F. In case of this system only methacryl and glycidyl POSS were used.

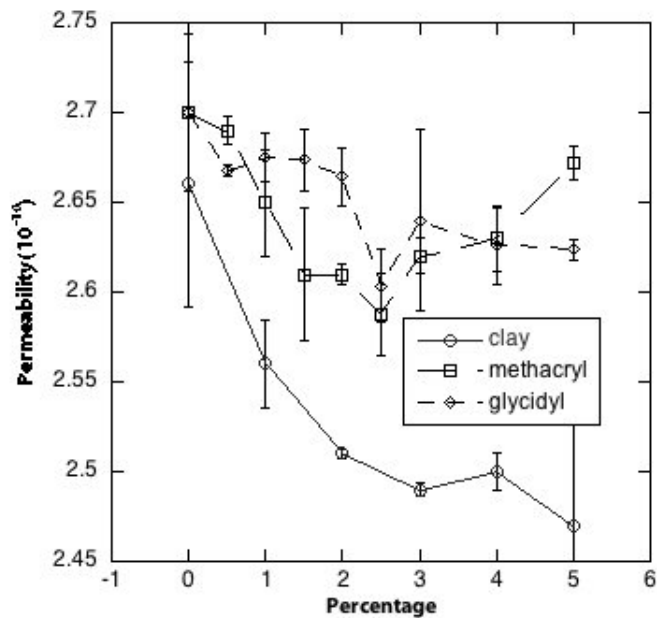


Figure 3.2: Permeability coefficient of DGEBA resin with methacryl, glycidyl and clay

Surprisingly for this resin system we can see that the epoxy/clay nanocomposite showed better barrier property compared to epoxy/POSS nanocomposite. For clay the decrease in permeability coefficient is upto 12% whereas it is only 3.33% for methacryl compared to neat resin. However, for POSS we observed the same trend as DGEBA and methacryl showing lower permeability compared to glycidyl.

The dispersion of any nanofiller in any resin system depends on their compatibility. The reason of this resin system showing higher permeability with POSS can be attributed to this fact. And this can also be the reason for clay to have lower permeability. This hypothesis is further investigated by SEM and EDX.

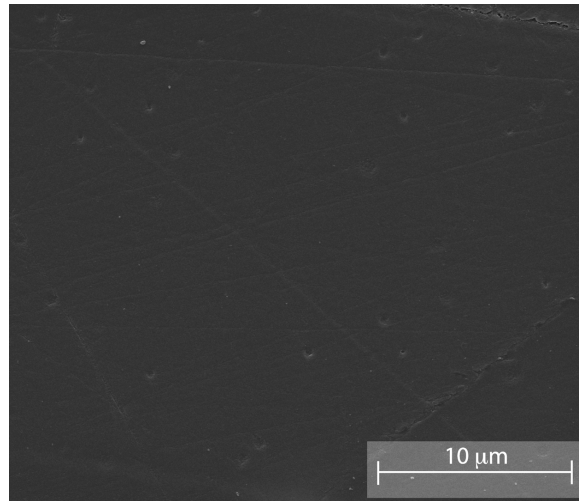
3.2 SEM and EDX

3.2.1 DGEB-A

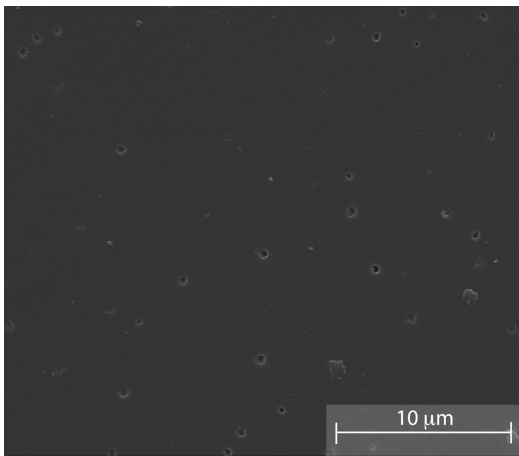
The SEM images showed hole like structure for all of the POSS compared to neat resin. All the holes have high percentage of silica which is confirmed by EDX. So it can be concluded that these holes are created due to POSS molecules. As POSS has a lot functional groups, it is possible that during the polymerization process some volatile material was created. These volatile materials created holes during degassing of the samples. From the images of methacryl we can observe that the hole number increases with decreasing permeability for upto 2% of methacryl and then again reduces when permeability increases for higher percentage (fig.).

POSS was physically incorporated to the resin where they got molecularly dispersed within the resin. However, when amines are added as hardener several POSS molecules get attached with amine chain. Basically POSS molecules form a homogeneous hybrid polymer network with silicon caging dispersed in epoxy matrix. This dispersion is actually indicated by the hole numbers. The numbers of these holes vary for different percentage and for different POSS. All these data from SEM and EDX are summarized in table 3.1.

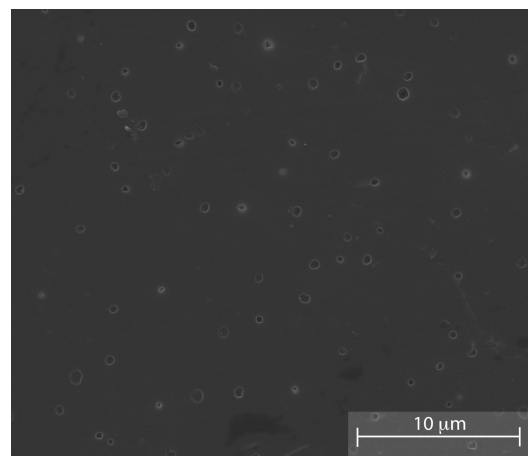
From the table it can be said that these holes govern the permeability property of POSS. Large number of holes indicates better interaction of POSS and epoxy system providing better dispersion of impermeable silicon caging. These silicon cages decreased the free volume and created more tortuous pathway for permeant gas. All these incidents resulted in lower permeability. Also this explains the specific trend of POSS of having the increase in the number of holes upto 2% and then the decrease in the number of holes. Among three POSS, methacryl shows the higher hole numbers and lower permeability and for glycidyl this phenomenon is just reversed. Methacryl has more compatibility with epoxy resin and hardener due to the existence of more



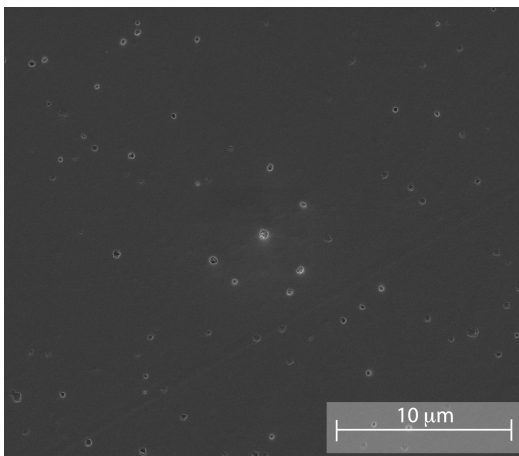
(a) Neat SC79 (DGEBA)



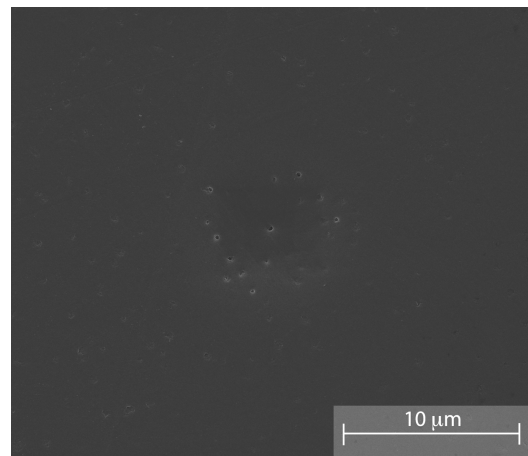
(b) 1% methacryl



(c) 2% methacryl



(d) 3% methacryl



(e) 4% methacryl

Figure 3.3: Surface image of (a) DGEBA resin and epoxy/methacryl (c) 1% (d) 2% (e) 3% and (f) 4% by SEM

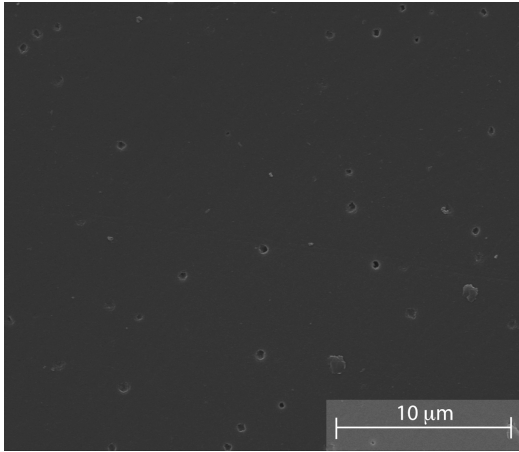
| Percentage | Average hole dia (micrometer) | hole number | Si in hole | Silicon in smooth surfae | Average Si |
|--------------|----------------------------------|-------------|---------------|-----------------------------|---------------|
| methacryl 1% | 0.321 | 26 | 0.4 | 0.36 | 0.2 |
| 2% | 0.364 | 65 | 0.5 | 0.365 | 0.3 |
| 3% | 0.2395 | 56 | 0.49 | 0.355 | 0.4 |
| 4% | 0.158 | 10 | 0.46 | 0.565 | .6 |
| glycidyl 1% | 0.354 | 17 | 0.55 | 0.4 | 0.4 |
| 2% | 0.3691 | 21 | 1 | 0.8 | 0.73 |
| 3% | 0.323 | 18 | 1.4 | 1.6 | 1.7 |
| 4% | 0.3368 | 15 | 3.35 | 2.5 | 2.65 |

Table 3.1: Data of holes of methacryl and glycidyl POSS

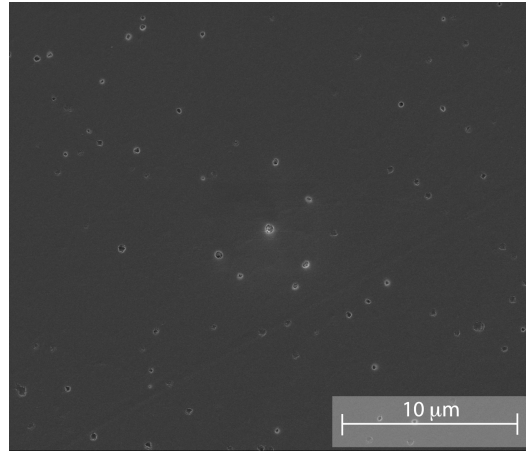
double bonds which has higher reactivity than any other functional group. Therefore, methacryl shows higher number of holes and better dispersion of silicon cage with better barrier property. Glycidyl interacts with epoxy by substituting the epoxy ring. It has lesser compatibility than methacryl which is the reason for less dispersion and lesser number of holes. This comparison is shown in fig. 3.4. Again, all the POSS shows larger number and better dispersion of aggregates at 2% which can be due to the reason of having better stoichiometric ratio at this percentage only.

Another POSS, trisilanol phenyl which we used with this epoxy system showed their permeability coefficient in between methacryl and glycidyl. Because it is more compatible with DGEBA compare to glycidyl by having phenyl group for substitution and hydroxyl group for hydrogen bond in epoxy. However, still it showed higher permeability than methacryl. For both glycidyl and trisilanol phenyl we can assume that steric hindrance is another reason to have less compatibility with DGEBA compare to methacryl.

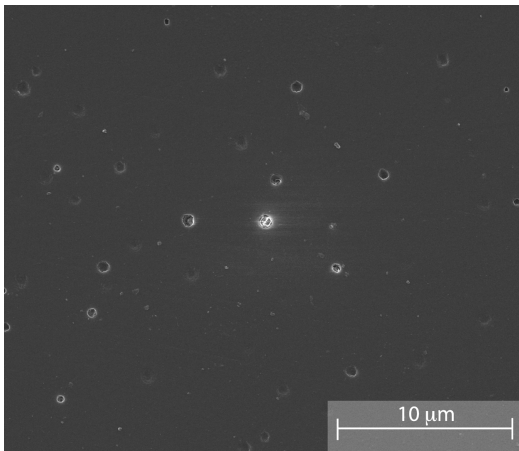
Surprisingly, we can also observe the holes in epoxy/clay nanocomposite with increasing number of hole with the increasing percentage (fig. 3.5). As a result it can



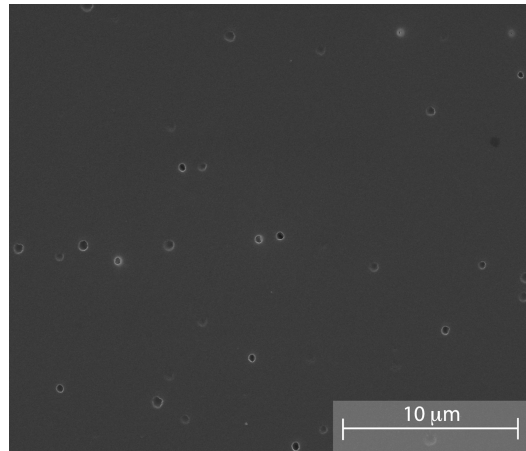
(a) 1% methacryl



(b) 3% methacryl



(c) 1% glycidyl



(d) 3% glycidyl

Figure 3.4: Surface image of epoxy with (a) methacryl 1% (b) glycidyl 1% (c) methacryl 3% and (d) glycidyl 3% by SEM

not be concluded for sure that the epoxy/POSS interaction is the reason for creation of holes. There is also a possibility that there were bubbles inside the samples which were not removed and both the nanofillers clay and POSS were cluttered with bubbles which gives high percentage of silica. .

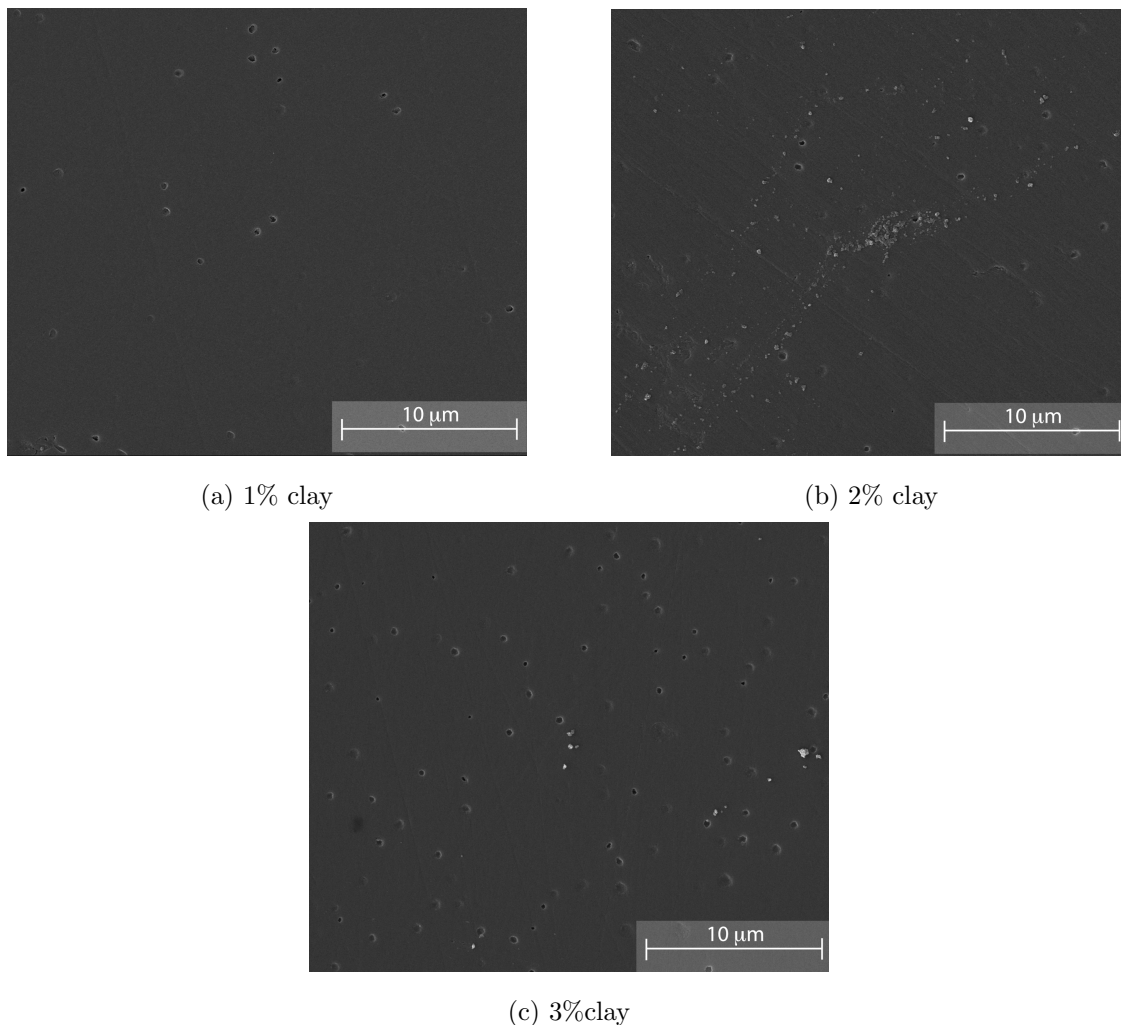


Figure 3.5: Surface image of DGEBA resin and clay(a) 1% (b) 2% (c) 3% by SEM

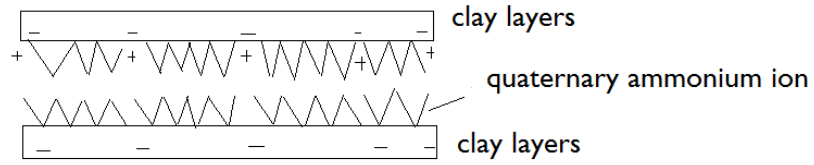
However, the interaction of clay with epoxy and the process of affecting permeability by clay is different. Clay is a layered silicate where the functional group is present due to the surface modifier. The interaction of clay with epoxy has several steps with numerous parameters at each step. The first step is the swelling of clay which depends on the physico-chemical interaction between the clay and neat resin.

The next step is reaction with hardener which has different interaction and swelling kinetics with clay compare to neat resin. At this step there is a competition between intra and extra gallery due to different stoichiometric ratio. During polymerization the elastic energy between the layers can increase and can push apart the layers and this force is balanced by the viscosity of the monomer outside the gallery. This affects the intercalation or exfoliation process and it is represented pictorially in fig. 3.6 and all the data from SEM and EDX are summarized in table 3.2.

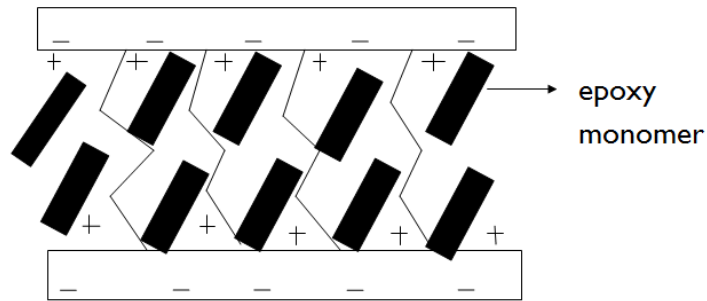
| Percentage | Average hole dia (micrometer) | hole number | Si in hole | Silicon in smooth surfae | Average Si |
|------------|----------------------------------|-------------|---------------|-----------------------------|---------------|
| 1% | 0.293 | 12 | 0.7 | 0.7 | .7 |
| 2% | 0.2878 | 15 | 1.41 | 1.417 | 1.452 |
| 3% | 0.263 | 25 | 0.997 | 1.062 | 1.46 |
| 4% | 0.255 | 33 | 5.421 | 7.441 | 3.743 |

Table 3.2: Data of nanoaggregation of DGEBA and clay

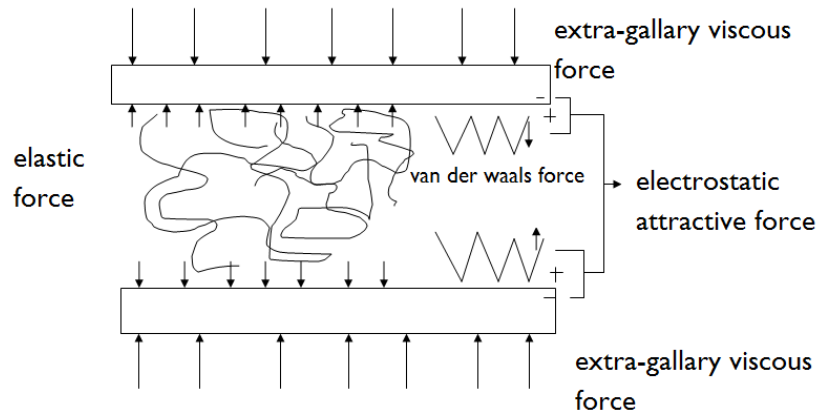
From the table we observe that though the hole number increases with percentage. This can be attributed to the fact that, clay has more attraction to the aromatic part of the resin and create areas with high silicon and also without silicon. With higher percentage it had better interaction with high number of holes, higher percentage of silicon and lower permeability. However, for clay another prime factor is the high aspect ratio which can be achieved through exfoliation. With the high interaction it cannot be concluded that clay has higher dispersion as the dispersion or exfoliation depends on numerous parameter as discussed earlier. From the SEM images we can conclude that though with higher percentage there were higher nuber of holes it was not good enough to create exfoliation and may be also the state of intercalation which results in higher permeability than POSS.



(a) modified clay



(b) intercalated state



(c) exfoliated state

Figure 3.6: Schematic illustration of intercalated and exfoliated state showing forces on a pair of clay layers (a) modified clay (b) intercalated (c) exfoliated

3.2.2 DGEB-F

The SEM images of DGEB-F and methacryl showed a very little amount of aggregate compare to neat resin (fig. 3.7). The SEM images presented in fig. 3.7 are in higher magnification than the images for DGEB-A as in lower magnification we were not able to see any kind of aggregate for this epoxy.

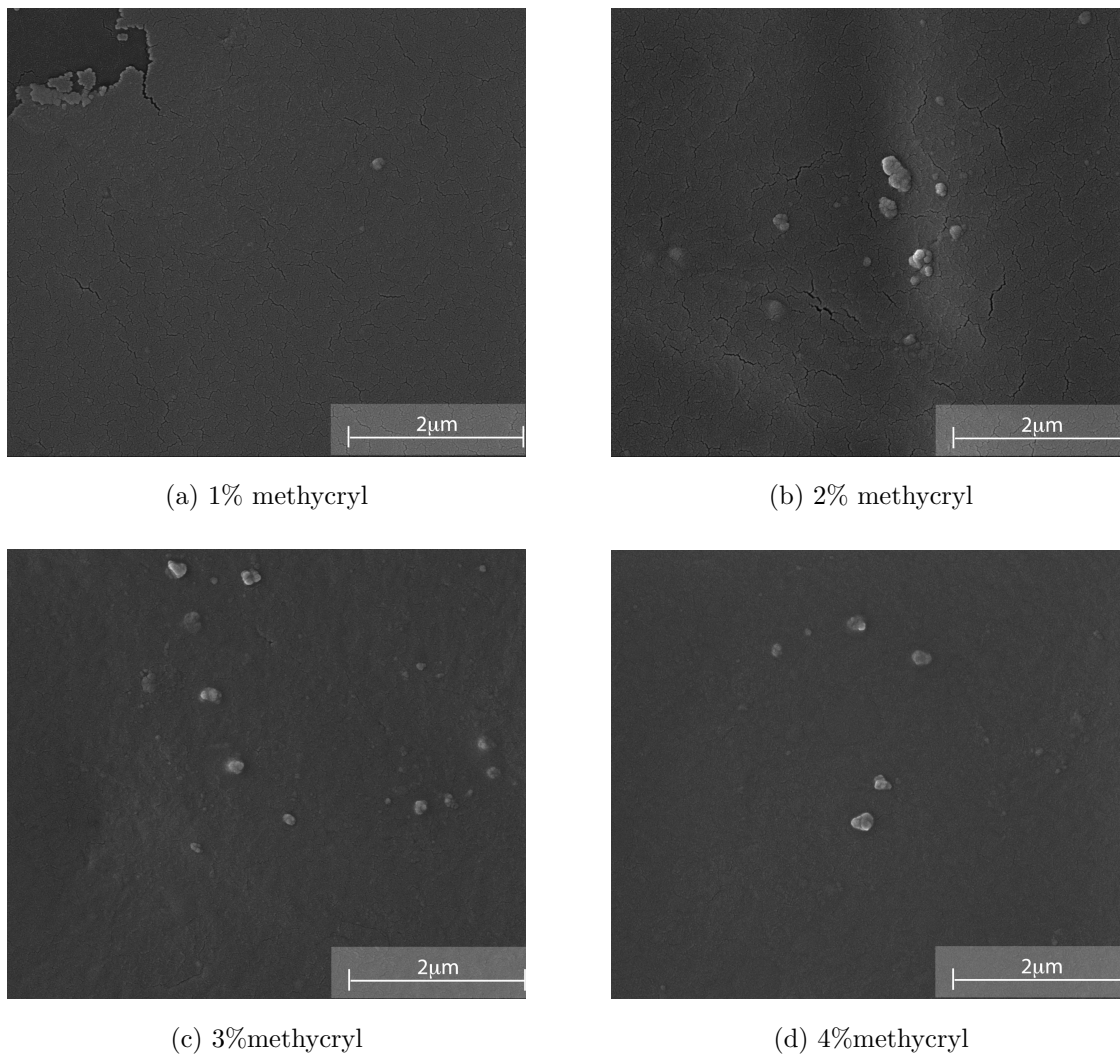


Figure 3.7: Surface image of DGEB-F resin and methacryl (a) 1% (b) 2% (c) 3% and (d) 4% by SEM

From these images we can conclude that methacryl has less compatibility with DGEB-F. So initially it remained unreacted in the epoxy/POSS system before hard-

ener was added. We used aliphatic amine as a hardener for this epoxy system which has the highest reactivity towards epoxy. For amine the reactivity will follow this pattern: aliphatic amine>cycloaliphatic amine>aromatic amine. As a result in the polymerization process the POSS remained unreacted and aggregated[40]. Therefore, it had less affect on the free volume of polymer as well as in permeability. This phenomenon exactly explains our experimental finding of having only 3.33% reduction in permeability for Epon862/methacryl samples compared to neat resin. For this resin system both POSS have close values of permeability coefficient. So the same explanation justifies the permeability behavior of glycidyl also. Similarly, the lowest value of permeability at 2% could be explained by perfect stoichiometric ratio.

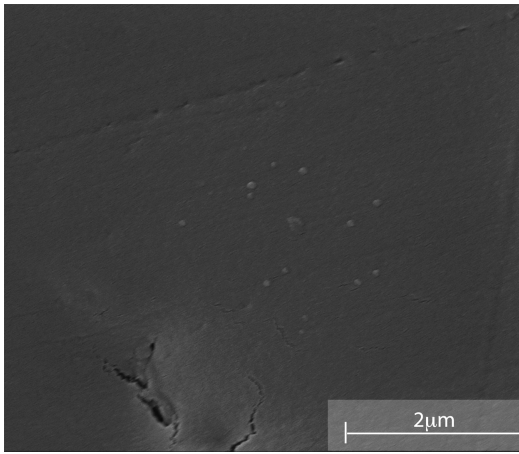
The SEM images for clay (fig. 3.8) clearly revealed the reasons for better barrier property. With the higher percentage, the clay is well dispersed and clay appeared almost everywhere on the surface. As clay has higher aspect ratio this well dispersion decreased the free volume of polymer matrix and more importantly created more tortuous pathway for penetrant molecule resulting in lower permeability.

From the images and permeability data it can be concluded that clay had better compatibility with this epoxy resin system which resulted from a good stoichiometric ratio, the balanced intra/extra gallery reaction and being the extra gallery reaction not too fast providing good inter gallery reaction leading to exfoliation.

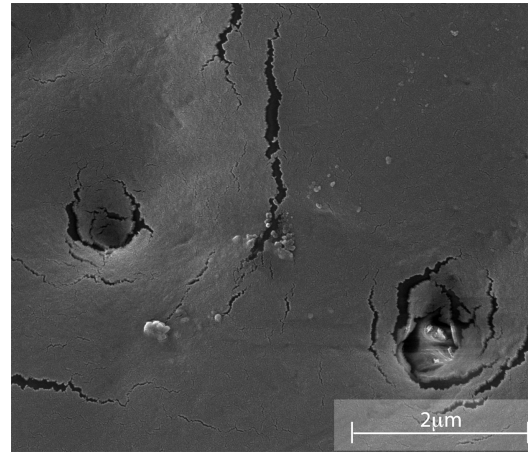
3.2.3 Comparison between DGEB-A and DGEB-F

POSS

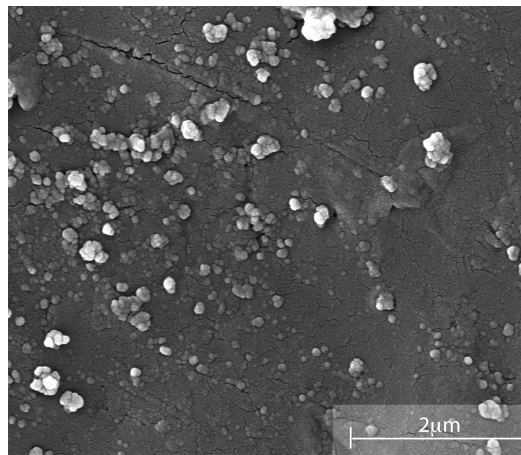
The POSS with DGEB-A showed better barrier property compared to DGEB-F. The decrease in permeability is upto 20% in case of DGEB-A and methacryl where it was only upto 3.33% for DGEB-F and methacryl compared to neat resin respectively. The only reason behind this is the compatibility between the POSS and epoxy system. For DGEB-F it is possible that for this system there was more steric hindrance so



(a) 1% clay



(b) 2% clay



(c) 3% clay

Figure 3.8: Surface image of DGEBA-F resin and clay(a) 1% (b) 2% (c) 3% by SEM

POSS could not interact with resin properly. Also the hardener we used for DGEBA was cycloaliphatic amine where as it was tertiary amine for DGEB-F having higher attraction to resin itself rather than POSS.

For clay DGEB-F resin showed better result having upto 12% decrease in permeability where it was 7% for DGEB-A system. This is also due to same reason that for clay, DGEB-F provided better interaction which leads to better dispersion and higher barrier property. Figure3.9 shows the visual difference between the two system in case of clay.

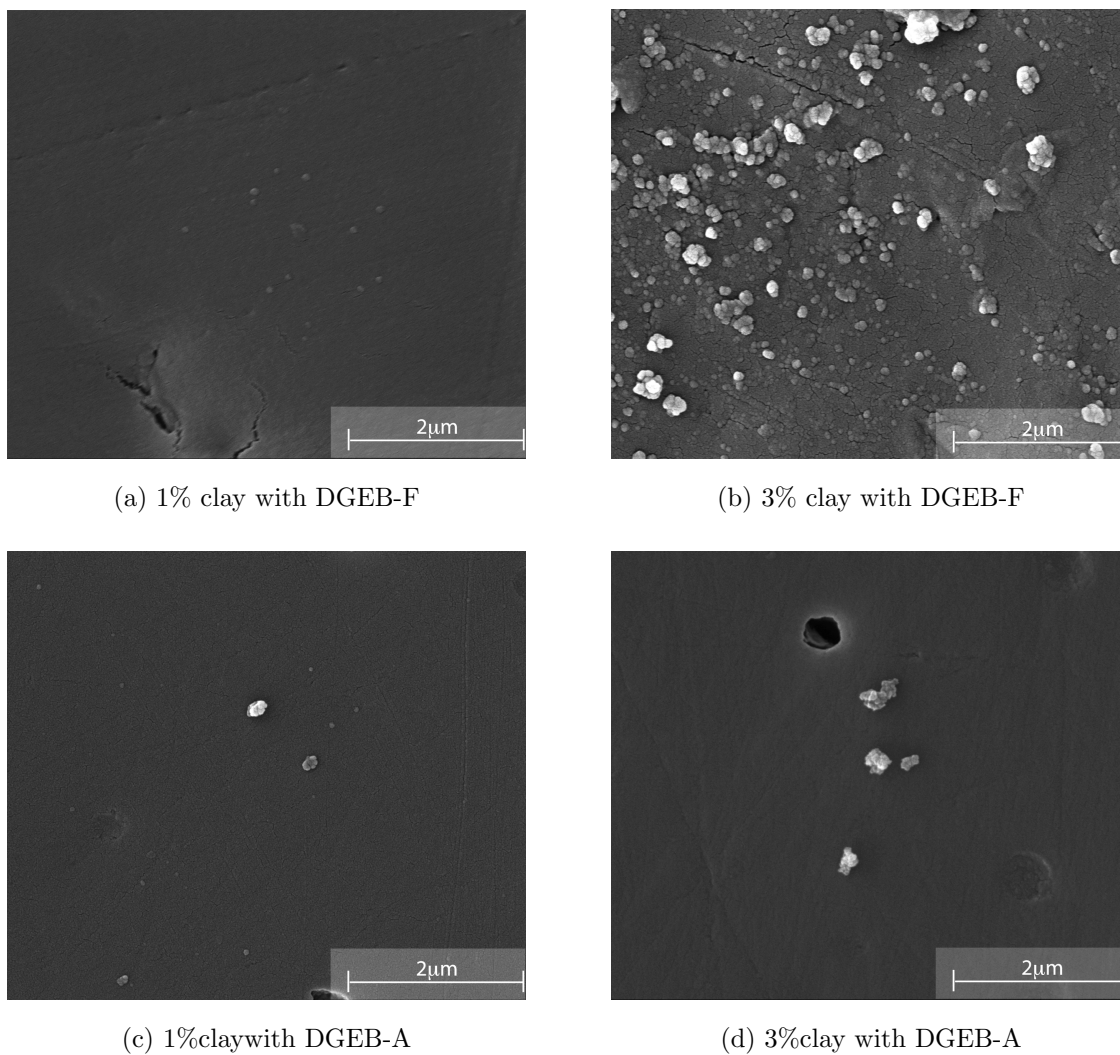


Figure 3.9: Surface image of (a) DGEB-F resin and clay1% ,(b) 3% and DGEB-A and clay(c) 1%, (d)3% by SEM

As a summary we can say that the creation of holes is mainly due to the resin system as we did not observe any kind of holes in DGEBA-F system for any nanofiller. These holes are related with the dispersion of nanofiller which affects the permeability in case of POSS. However, for clay the dispersion is a complex process involving several parameters including mixing technique which can be the reason for showing different permeability in case of different epoxy resin though there is less decrease in permeability compare to POSS.

CHAPTER 4

CONCLUSIONS

Epoxy nanocomposites were synthesized by physical incorporation of nanofiller. There were significant reductions in permeability in nanocomposite compare to neat resin. Permeability was measured by an experimental setup following ASTM Standard D1434. We obtained specific trend for all kind of POSS with both epoxy system. For DGEBA, POSS nanocomposite samples showed less permeability in comparison to clay and for DGEBF this was reversed. These experimental findings were analyzed using SEM and EDX. Among three POSS used methacryl showed the lowest permeability compare to neat resin.

From our result we can conclude that permeability of nanocomposite depends on the compatibility between the nanofiller and the epoxy system. For POSS the creation of holes is the principal reason for reducing permeability which is confirmed by SEM and EDX. We assume that these holes indicated better interaction of POSS with epoxy as well as dispersion of silicon cage causing decrease in volume fraction, creating more tortuous pathway and resulting in lower permeability. However, the interaction depends on the reactivity of POSS functionality. Because with increasing number of existing covalent bonds between the POSS and polymer the compatibility becomes more efficient and produces more stable network. As a result Epon862 does not show good barrier property due to insufficient compatibility with the POSS used. But this hypothesis can not confirmed as we also observe holes in case of clay and DGEBA nanocomposite, which again helps us to conclude that the creation of holes depends on particular epoxy system and this phenomenon could have been more

effectively analyzed with the help of FTIR and TEM images of clay nanocomposites. For clay the dispersion is the prime factor in addition with the orientation of the clay platelets influencing permeability. Dispersion depends on the interaction of resin, hardener and clay itself. It is evident from SEM images that DGEBA-F has better dispersion of clay resulting in lower permeability. As a summary we can conclude that the conventional nanofiller clay does not show better barrier property with each type of epoxy system. Alternatively for a specific epoxy system a particular POSS can achieve lower permeability compared to clay. But the selection of any kind of nanofiller entirely depends on the interaction of resin and nanofiller.

It will be worth to investigate the permeability as well as mechanical property of epoxy nanocomposite in cryogenic condition. This will create opportunity towards new industrial application of epoxy nanocomposite. Also developing a mathematical model to compare the permeability with experimental result to obtain more effective analysis is a good scope for future work.

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Candidate for the Degree of Master of Science

Major Field: Mechanical Engineering

There is an increasing demand of advanced materials with better property to meet new requirements of the present time and nanocomposite is such a material. It has better surface area per unit volume and high aspect ratio. So the reinforcing efficiency is greater than any other conventional polymer film. In recent times the barrier property of the nanocomposite has drawn a significant amount of interest. The conventional nanofiller that is used to achieve high barrier property is clay. Because apart from good barrier property clay also possesses high mechanical and thermal property. With higher percentage of clay the barrier property improves, however the improvement in the mechanical property diminishes. This brings the concept of using an alternative nanofiller polyhedral oligomeric silsesquioxane to decrease permeability of nanocomposite. POSS is a unique material having both inorganic and organic part and having better property as nanocomposite. The aim of this study is to compare the permeability of two different epoxy systems with POSS and clay respectively. Epoxy is a general used resin system for most of the nanocomposites due to their higher crosslinking ability. The permeability was measured using a gas permeability setup and acquired data from this system was analyzed. Results showed that the permeability of a nanocomposite is mainly dependent on the interaction of the resin and filler instead of filler itself.

ADVISOR'S APPROVAL: _____