Chapter - 6

The Effect of Nanoclay on the Moisture Absorption Behaviour of Vinylester Composites

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6.1 Introduction

Polymer composites are increasingly used in civil and marine structures due to their corrosion resistance, light weight, high strength and durability [1–2]. The drawback of polymer composites is their inherent time-dependent nature of the mechanical properties. This implies that strength and stiffness are time-dependent due to the viscoelastic properties of polymers. The reasons for the degradation of strength and stiffness of a polymer include: micro-structural and compositional changes, time-dependent deformation and resulting damage accumulation, environmental attack and the synergistic effects among all of these. Sander et al reported degradation in mechanical properties, cracking and flaking of polymers exposed in high pH environment [3-5].

There is an increased interest in polymer nanocomposites using nanoclays due to their high modulus, large surface area, high aspect ratio and have been successfully used to improve the mechanical, thermal, barrier and Fire Retardant properties [6-9]. These are considered for applications in a wide variety of areas, such as aerospace, marine, electronics, sports gadgets, automotive industries etc., [10-12]. Commercially different types of organomodified nanoclays are available with varied interlayer gallery spacing with different organomodifications. It is common in open literature to find the diffusion reports on treated nanoclay.

H.K. Rana et al [13] studied diffusion of moisture through neat resin as well as glass-fiber reinforced vinylester samples, both containing up to 5 wt % Montmorillonite clay. Transient and steady state diffusion experiments were carried out with both neat resin as well as glass-fiber reinforced samples in saline and alkali solution. The authors observed that diffusivity decreased due to the presence of nanoclay in polymer. Shu-Kai Yeh [14] studied two kinds of GFRP materials. One was e-glass / vinylester (plain GFRP) and the other was nano-GFRP prepared with the addition of 1wt. % of Cloisite 10A nanoclay. These samples were aged in an alkaline solution with different sustained load. Time to failure or tensile strength reduction was measured and used to determine the durability of the samples in terms of Aging Index, which was proposed as the tensile strength reduction per day. The failed cross sectional areas of samples were examined by using
optical microscopy. Pavlidou et al [15] conducted study to determine the effect of clay content in GFRP (glass-fiber-reinforced polymer) samples and without clay content composite samples are aged in an alkali solution. The alkaline solutions produce an embrittlement of the matrix and damage at the fiber-resin interface level due to chemical attack and growth of hydration products, this effect lead to a loss in tensile strength and interlaminar transverse properties.

Many studies reported one dimensional moisture diffusion [16-17]. Moisture diffusion through polymer composites can be classified as Fickian or non-Fickian [18-21]. Fickian behavior is represented in polymers that have enough chain mobility to allow water ingression [22]. Aouatef et al [23] showed agreement of Fick’s law only in the initial region. The Langmuir-Adsorption model considers two dimensional diffusion to explain the diffusion mechanism and accounts for the non-Fickian behavior. In this the diffusion process is described by separating the diffusing molecules into two phases, mobile and bound. Vinylester is preferred in marine applications due to their lower moisture absorption and mechanical property degradations than other resins such as epoxy, polyester and iso-polyester which are traditionally used for marine vehicles [24].

Review of literature [1-24] on moisture diffusion through polymer nanocomposites indicated that such studies are mainly focused on Fick’s Law of Diffusion and the application of the Langmuir Model for their diffusion behaviour is scarce. The influence of basal spacing of the nanoclay on the diffusion behaviour of nanocomposites is also not reported. The aim of this research was to examine the moisture diffusion through nanoclay/vinylester employing unmodified and organomodified nanoclay and to study the diffusion behaviour using both Fick’s Law of diffusion and the Langmuir Model. The nanoclay was dispersed in vinylester using a combination of ultrasonication and twin screw extrusion. The effect of diffusion on the microhardness of the nanocomposites was studied.
6.2 Experimental

6.2.1 Materials

The superior quality vinylester resin (Polyflex GR 200-65) used in study was supplied by Naphtha Resins and Chemicals, Bangalore. The curing agents used were cobalt naphthenate, di-Methyl acetamide and methyl ethyl ketone peroxide supplied by MP Corporation, Bangalore. The nanoclay used were Cloisite-Na and Cloisite-15A supplied by Southern Clay Products, USA. Potassium hydroxide, Sodium hydroxide and calcium hydroxide were supplied by Sigma Aldrich, Bangalore.

6.2.2 Nanocomposites preparation

Two types of composites i.e. Cloisite-Na/vinylester and Cloisite-15A/vinylester specimens were prepared for comparative studies. Nanoclays in 2 - 5 wt% were dispersed in vinylester by ultrasonication at 37 kHz for one hour using tip sonicator followed by co-rotating twin screw extruder. The screw extrudent was mixed with 2 wt% each of di-Methyl acetamide as promoter, cobalt naphthalate as accelerator and methyl ethyl ketone peroxide as catalyst at room temperature to initiate the cross-linking process.

After dispersing the nanoclay in the resin system using all the above instruments. Finally the mixture is added with promoter, accelerator and catalyst stirred manually. Then it is poured into the Teflon mould as shown in Fig. 6.1. The thickness of the mould is 1 mm. The mould is kept on a mylar sheet to prevent any resin adhering to its bottom surface. The resin/nanoclay mixture is poured into the mould and left to curing for 24 hours. Once the specimens are cured it is taken out of mould and used for the experiment.

The same procedure is repeated to both Cloisite Na and Cloisite 15A with the loading level up to 5 wt %. Fig.6.2 shows the cured neat samples of Vinylester, Vinylester/Cloisite Na and Cloisite 15A.
6.3 Alkaline solution ageing

6.3.1 Alkaline solution preparation at room temperature

Diffusion process of vinylester nanocomposites is studied in alkaline solution by varying the temperature. Alkaline solution is prepared according to ASTM D6942 using the composition shown in Table 6.1. The pH of alkaline solution is maintained to be 13.5 as per the ASTM standard; this operation is performed using the pH meter. The specimens immersed in room temperature shown in Fig. 6.3. Alkaline solution is used to resemble the concrete solution. Hence, studying the diffusion in this solution helps us to use the composite in civil application. The Chemicals are listed in Table 6.1 is added to distilled water. The chemicals are stirred after addition to obtain a better alkaline solution. However, some chemical particles are found to be deposited in the bottom which is common in alkaline solution. The solution checked for pH using pH meter and it was found to be 13.5 as shown in Fig. 6.4.

6.3.2 Alkaline Solution Preparation at 50° C Temperature

The preparation of alkaline solution is same as explained in Section 6.3.1 also the pH of the solution is maintained to be 13.5. The solution is poured into a serological water bath in which the desired temperature is maintained using the temperature controller. The water bath heater is shown in the Fig.6.5 and the specification of the same is given in Table 6.2. About 10 liters of alkaline solution is prepared and some amount of solution is kept in reserve since, the alkaline solution evaporates due to higher temperature.

6.3.3 Sample immersion

Before immersing the samples the following procedure should be followed.

- Each sample is numbered and their weights are noted.
- The Micro Hardness of all the samples are determined
- Some samples are taken for morphology studies to determine the clay dispersion in the samples.
6.4 Diffusion Studies

6.4.1 Alkaline solution at room temperature

The experiment in alkaline solution is conducted for the duration of 100 days. Fig.6.6 and Fig.6.7 show the water uptake curves for vinylester/Cloisite Na and Cloisite 15A in alkaline solution at room temperature. In alkaline solution the water uptake of vinylester is 0.739% and that of 5wt% Cloisite Na and Cloisite 15A is 1.0065% and 0.9841%. For 2 wt % Cloisite Na and Cloisite 15A the water uptake was 0.8812% and 0.7359%.

6.4.2 Alkaline solution at 50° C Temperature

In this, the samples are immersed in the alkaline solution which is maintained at 50° C and the experiment is carried for the duration of 300 hours. Water uptake curves of vinylester/Cloisite Na and Cloisite 15A is shown in Fig.6.8 and Fig.6.9 respectively. Here the diffusion of moisture into the samples is enhanced due to the temperature and pH of alkaline solution. Water uptake for vinylester is 0.8018% and that of 5 wt % Cloisite Na and Cloisite 15A is 1.5907% and 1.4313%. Water uptake for 2 wt % Cloisite Na and Cloisite 15A is 1.3433% and 1.1080%. The water uptake is more when compared to that of alkaline solution, the reason being that both the temperature and pH of the alkaline solution enhances the aggressivity of the solution. This type of experiment helps us to predict the nature of nanocomposites for a longer duration of exposure and adverse condition. Here, 5 wt% Cloisite 15A/vinylester sample is the most deviated from neat vinylester sample showing that the duration to moisture ingress is less when compared to vinylester.

6.5 Hardness studies

The specimens were immersed in saline and alkaline environment for the duration of 100 days until the value of moisture uptake is constant. Table 6.3 represents the micro hardness of the specimen determined during this period. Before immersion the micro hardness results are shown in Fig.6.10 and after immersion at room temperature shown in Fig.6.11 show the variation of micro hardness of Cloisite Na, Cloisite 15A/vinylester specimens in alkaline solution at room temperature. The VHN for 4 wt % Cloisite 15A and vinylester specimen decreased by 12.7% and 20% respectively.
Fig. 6.12 shows the variation of micro hardness of Cloisite Na, Cloisite 15A/vinylester specimens in alkaline solution at 50°C. The specimens were immersed in the solution for a period of 13 days until the moisture uptake reached equilibrium. The least decrease in VHN was seen in 4 wt% Cloisite 15A with 21.7% and highest decrease in VHN was seen in vinylester specimen with 33.5% decrease in VHN. This degradation can be attributed to the higher pH and higher temperature of the solution. The highest value of VHN before immersion was seen in 4 wt% Cloisite 15A/vinylester specimen and lowest was seen in neat vinylester specimen.

Hence, the addition of nanoclay either modified or unmodified results in increase of micro hardness. The increase in VHN due to addition of Cloisite Na is 21% corresponding to 4 wt% clay loading and Cloisite 15A is 45% corresponds to 4 wt% Cloisite 15A before immersion. The highest retention of the hardness was seen in 4 wt% Cloisite 15A specimen in both saline and alkaline solution.

6.6 Modeling of Moisture Diffusion
6.6.1 Fick’s Law of Diffusion

Fick’s law is one of the most popular model used to predict diffusion. Fick’s second law controls distribution of moisture concentration in polymers [23]. In the case of a flat specimen it can be described by the following one-dimensional equation 6.1:

\[
\frac{dC}{dt} = D \frac{d^2C}{dx^2} \tag{6.1}
\]

where:

\(C\) = concentration of diffusing species at time \(t\),
\(D\) = diffusion coefficient or diffusivity of moisture in the specimen.

The solution of equation 6.1 gives the mass uptake \(m_t\) of a thin polymer film in humid condition. This is given by Eq 6.2:

\[
\frac{M_t}{M_w} = \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp \left[-\frac{D(2n+1)^2\pi^2t}{4l^2}\right]\right] \tag{6.2}
\]
where

\[ M_t = \text{mass uptake at time } t, \]
\[ M_e = \text{equivalent mass uptake} \]
\[ l = \text{half the thickness of the polymer film.} \]

Eq 6.2 can be rewritten as Eq 6.3

\[ D = \frac{\pi}{16} \left( \frac{M_t/M_e}{\sqrt{l}/2l} \right)^2 \]

A plot of \( \frac{M_t}{M_e} \sqrt{l}/2l \) (Eq.6.3) is linear at the initial stage and the diffusivity can be calculated from its slope, but below \( M_t/M_e = 0.5 \).

The values of diffusivity obtained from Fick's law can be compared to that of Hitesh et al. [13]. It is seen that the addition of montmorillonite clay has a very significant effect on moisture diffusivity that reduces by 79.5% and 70.7% corresponding to 5 wt% Cloisite 15A specimens in alkaline solution at room temperature and 50°C respectively. Since, unmodified Cloisite Na was hydrophilic in nature the specimens with 5 wt% have increased the moisture diffusivity by 19.69% and 22.92%. This signifies that surface treatment is necessary to enhance resistance to moisture ingress. Although the diffusion coefficient reduces rapidly and progressively, there is increase in equilibrium moisture content with the clay content. The graphs of both room temperature and 50°C are shown in Fig.6.13 and Fig.6.14.

6.6.2 Diffusion coefficient

Diffusion coefficient is the rate at which the moisture ingress occurs in the specimen. Highest value of D is 12.2272x10^{-7} mm^2/s corresponding to vinylester samples immersed in alkaline solution at 50°C. Lowest value of D is 1.5321x10^{-7} mm^2/s corresponding to 5 wt% Cloisite Na/vinylester samples immersed in alkaline solution at room temperature shows the variation of diffusion coefficient with clay content in alkaline solution at room temperature and at 50°C. The results are tabulated in Table 6.4 and Table 6.5. The figures are shown in Fig.6.15 and Fig.6.16.
6.6.3 Permeability

Permeability is the amount of material (in this case weight of water) passing through unit area of a membrane or film per unit time. In the ideal case the clay is assumed to completely exfoliate and orient themselves perpendicular to the direction of the diffusing molecules. The effective path that the molecule has to traverse is then increased by $L/2$ for each clay platelet. The tortuosity ($\tau$) is then given by the relation shown in Eq 6.4,

$$\tau = \frac{1}{1 + \left(\frac{L}{2W}\right)V_f} \quad \text{(6.4)}$$

Hence the relative permeability is then written in terms of the clay platelet dimensions and content as shown in Eq 6.5,

$$\frac{P_c}{P_p} = \frac{1}{1 + \left(\frac{L}{2W}\right)V_f} \quad \text{(6.5)}$$

where,

- $P_c$ is the permeability of the nanocomposite
- $P_p$ is the permeability of the neat resin (polymer).
- $L$ is the length of the clay plates.
- $W$ is the thickness
- $V_f$ is the volume fraction of clay in the sample

Permeability ($P$) of POLYFLEX VINYLESTER 411-350 vinylester resin and nanocomposite samples were calculated as a product of diffusion coefficient and solubility shown in Eq 6.6:

$$P = DS \quad \text{.........................................................(6.6)}$$

where,

- $D$ is the diffusion coefficient, $\text{mm}^2/\text{s}$ and $S$ is the solubility of water in the resin, $\text{g/m}^3$.

Solubility of water was calculated by multiplying the equilibrium moisture content of the samples with the density of the dry sample. Density was measured by the water displacement method. The samples were accurately weighed and the volume measured by
immersing them in a measuring jar with an least count of 0.2 ml. The solubility increases as the amount of clay in the sample increases. This is because of the water molecules adsorbing onto the clay surface. The permeability coefficient mirrors the diffusion coefficient change, and reduces as the amount of clay is increased in the sample.

Increase in the value of permeability signifies that the specimen enhances the moisture ingress whereas decrease in the value signifies the opposite. The value of relative permeability of neat resin specimen is 1 if the value of the other specimen exceeds 1 then the moisture permeability increases and if the value is less than 1 then, the specimen offers more resistance to moisture ingress and is more durable when compared to neat resin specimen. Permeability is found to decrease by 45 % for 5 wt% of Cloisite 15A specimen and for 5 wt% Cloisite Na specimen the permeability doubled its value.

Fig. 6.17 and Fig. 6.18 shows variations of relative permeability with clay loading in alkaline solution at room temperature and at 50°C respectively. The relative permeability of vinylester is 1 since it is considered as the reference material. For alkaline solution the least relative permeability was 0.15 for 5 wt% Cloisite 15A specimen and the highest was 2.84 corresponding to 5 wt% Cloisite Na specimen. Similarly for alkaline solution at 50°C the least relative permeability was 0.22 for 5 wt% Cloisite 15A specimen and the highest was 1.98 corresponding to 5 wt% Cloisite Na specimen. The results are tabulated in Table 6.6 and Table 6.7

6.6.4 Langmuir Model for Moisture Diffusion

The Langmuir-Adsorption model used to explain the mechanism of diffusion of water through polymer nanocomposites seemed to fit the data well.

In the Langmuir type of model, the diffusion process was described by separating the diffusing molecules into two phases, mobile and bound. The model was also able to predict the deviation from Fickian behavior and the slow reach to equilibrium at high Organoclay contents. This could mean that water molecules exist in two phases, namely, "free" water and "bound" water which is adsorbed onto the clay. This would then not only slow down the diffusion of water molecules, but also prevent the water from
reaching the glass fibers; thereby improving the durability of a glass fiber reinforced polymer composite. However, Fickian diffusion was still observed at low Organoclay contents, for which case the model parameters became insignificant.

Hence the diffusion process may not be explained by any one mode of diffusion alone. There might be regions when one mode influences the diffusion more than another does. For e.g., in cases of very low concentrations of clay, Fickian mode of diffusion may be dominating, as the number of adsorption sites will be smaller at low clay concentrations.

Equation 6.7 is the Langmuir model for diffusion

\[ M_t = M_\infty \left[ \frac{\beta}{\gamma + \beta} e^{-\gamma} \left( 1 - \frac{1}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-n(2n+1)^2\gamma} \right) + \frac{\beta}{\gamma + \beta} (e^{-\beta t} - e^{-\gamma}) + (1 - e^{-\beta t}) \right] \]  

when \( \gamma = 0 \), the equation reduces to the simple diffusion equation obtained from Fick’s second law. The diffusion co-efficient \( (D\gamma) \) can be calculated with the formula given below 6.8

\[ D\gamma = \frac{\pi}{16} \frac{(\gamma + \beta)^2}{\beta} \left( \frac{M_t}{M_\infty} \right)^2 \left( \frac{t}{\gamma t} \right)^2 \]  

while at larger times, when \( t >> 1/K \)

\[ M_t \approx M_\infty \left[ 1 - \frac{\gamma}{\gamma + \beta} e^{-\beta t} \right] \]  

For \( t >> 1/k \), the data was fitted to equation 6.10

\[ y = (1 - a e^{-bt}) \]
the values of ‘a’ and ‘b’ are obtained from the non linear fit, these values are substituted in equation 6.11 and 6.12 to get the values of ‘γ’ and β.

\[ a = \gamma / (\gamma + \beta) \] ...............................(6.11)

\[ b = \beta \] ...............................(6.12)

Fig.6.19 and Fig.6.20 shows the Langmuir model applied to nanocomposite specimens immersed in alkaline solution at room temperature and at 50° C respectively. The Langmuir model is used to fit the experimental values obtained from diffusion. This model considers the linear and non-linear region of the moisture diffusion hence it is more compatible to nanocomposites. The Langmuir curve follows the deviation in the non-linear region which does not happen when Fick’s law is applied. 5 wt % Cloisite 15A/vinylester specimen is found more deviation from the vinylester specimen. This phenomenon is also seen in experimental diffusion studies. In the experimental water uptake the deviation increases with the clay content, which is similar with the Langmuir curves. The diffusion coefficient of the specimen increases rapidly since the nonlinear region is also taken in to account. The permeability of the specimen also increases since it is dependent on the diffusion coefficient.

6.7 Mechanism of Diffusion through Polymer-Clay Nanocomposites

Diffusion through polymer clay nanocomposites showed certain deviations from Fickian behavior, especially at high clay contents. Nanoclay is usually added to polymer to fill in the micro and nano voids or gaps that may be present in the cured polymer. Hence, the path followed for diffusion in nanocomposite is termed “Tortuous Path” shown in Fig.6.21 impedance as represented schematically. Due to the nanoclay particles dispersed throughout the resin, the effective path of the diffusing molecule is longer, leading to a decrease in the diffusion coefficient and permeability. Also, as expected, the diffusion coefficient decreased with increase in clay content. The exfoliated clay improves barrier properties by physically impeding the movement of the penetrant through the matrix. The
water molecules are believed to adsorb onto the clay surface, thereby rendering them immobile.

6.8 Conclusions

Based on the experimental and analytical studies on alkaline solution ageing of nanoclay/vinylester nanocomposites, for duration of 100 days at room temperature and at 50° C the following conclusions are drawn:

6.8.1 Alkaline solution ageing at room temperature:

Diffusion tests conducted for Cloisite Na and Cloisite15A nanoclay specimens in alkaline solution also revealed that C 15A nanoclay composites are better. When Fick’s law was applied to the experimental data the following results were obtained

- Diffusion coefficient of the specimen decreased up to 79.5 % for 5 wt % of C 15A whereas for C Na it increased to 19.68 % for 5 wt % of clay loading.
- Solubility appeared to decrease by 50 % for 5 wt % C 15A and it increased by 33.8% for 5 wt% C Na specimen.
- Permeability decreased by 85 % for 5 wt % C 15A and it increased by 184 % for 5 wt% C Na specimen.
- Confirming that Cloisite 15A which is a organo modified clay is better in reducing moisture ingress.

When Langmuir model was applied to the experimental data the following results were obtained

- Diffusion coefficient of the specimen decreased up to 70.1 % for 5 wt % of C 15A whereas for C Na it increased to 112% for 5 wt % of clay loading.
- Solubility appeared to decrease by 50.3 % for 5 wt % C 15A and it increased by 33.8 % for 5 wt % C Na specimen.
Permeability decreased by 85.12% for 5 wt % C 15A and it increased by 184% for 5 wt% C Na specimen.

6.8.2 Alkaline solution at 50° C

Diffusion tests are conducted for Cloisite Na and Cloisite15A nanoclay specimens in alkaline solution at 50° C, when Fick’s law was applied to the experimental data the following results were obtained

- Diffusion coefficient of the specimen decreased up to 70.8% for 5 wt % of C 15A whereas for C Na it increased to 22.5% for 5 wt % of clay loading.
- Solubility appeared to decrease by 40.5% for 5 wt % C 15A and it increased by 36% for 5 wt% C Na specimen.
- Permeability decreased by 78% for 5 wt % C 15A and it increased by 98% for 5 wt% C Na specimen.
- Confirming that Cloisite 15A which is a organo modified clay is better in reducing moisture ingress.

When Langmuir model was applied to the experimental data the following results were obtained

- Diffusion coefficient of the specimen decreased up to 63.4% for 5 wt % of C 15A whereas for C Na it increased to 45.4% for 5 wt % of clay loading.
- Solubility appeared to decrease by 40.5% for 5 wt % C 15A and it increased by 36.1% for 5 wt% C Na specimen.
- Permeability decreased by 78% for 5 wt % C 15A and it increased by 98% for 5 wt% C Na specimen.

Hence, it can be concluded that the organomidified clay is better than unmodified clay in diffusion aspects.
6.8.3 Micro hardness

Micro hardness increased with the addition of nanoclay. The increase in VHN is 44.87 % for 4 wt % C 15A and it is 21 % for 4 wt % C Na specimen. After immersion in alkaline solution the least decrease in VHN is 12.68 % for 4 wt % C 15A and highest decrease is 20% for neat specimen. For alkaline solution at 50° C the least decrease in VHN is 21.7% corresponding to 4 wt% C 15A, the highest decrease in VHN is 33.5% for neat vinylester specimen. This is due to the (a) voids formed by trapped air due to the increased viscosity (b) Formation of clay agglomeration in the resin due to poor dispersion.

Micro hardness test values also showed significant increase in hardness at 4 wt % of nanoclay samples. This is due to the increased surface area for the interaction between the nanoclay clusters and the vinylester resin. Therefore, it can be concluded that the nanoclay content should be kept at 4 wt % in order to get superior mechanical properties.
### Table 6.1 Composition Alkali solution

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Hydroxide</th>
<th>Quantity (g/litre water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOH</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Ca(OH)(_2)</td>
<td>1.6</td>
</tr>
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</table>

### Table 6.2 Specifications of Serological water bath

<table>
<thead>
<tr>
<th>Serological water bath</th>
<th>Supplier</th>
<th>Temperature range</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lawrence &amp; Mayo</td>
<td>0-100°C</td>
<td>10 Litre</td>
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Table 6.3 Micro Hardness of nanocomposites samples before and after immersion

<table>
<thead>
<tr>
<th>Samples</th>
<th>Micro Hardness before immersion VHN</th>
<th>Micro Hardness (Alkaline solution after 100 days) VHN</th>
<th>Micro Hardness (Alkaline solution at 50°C after 300 hours) VHN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylester</td>
<td>12.3942</td>
<td>9.91115</td>
<td>8.2456</td>
</tr>
<tr>
<td>VE + 2% C-Na</td>
<td>12.9564</td>
<td>10.7974</td>
<td>9.4321</td>
</tr>
<tr>
<td>VE + 3% C-Na</td>
<td>13.5642</td>
<td>11.5084</td>
<td>9.99567</td>
</tr>
<tr>
<td>VE + 4% C-Na</td>
<td>14.9979</td>
<td>12.8271</td>
<td>11.3071</td>
</tr>
<tr>
<td>VE + 5% C-Na</td>
<td>13.8717</td>
<td>11.6915</td>
<td>10.1925</td>
</tr>
<tr>
<td>VE + 2% C-15A</td>
<td>13.9654</td>
<td>11.8742</td>
<td>10.3578</td>
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<tr>
<td>VE + 3% C-15A</td>
<td>15.972</td>
<td>13.8143</td>
<td>12.2143</td>
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<tr>
<td>VE + 4% C-15A</td>
<td>17.9562</td>
<td>15.6791</td>
<td>14.0591</td>
</tr>
<tr>
<td>VE + 5% C-15A</td>
<td>16.9825</td>
<td>14.5987</td>
<td>12.9978</td>
</tr>
</tbody>
</table>
Table 6.4 Diffusion test results of vinylester/Cloisite Na and Cloisite 15A in alkaline solution at room temperature

<table>
<thead>
<tr>
<th>Type of specimen</th>
<th>slope</th>
<th>Diffusion co-efficient ( \times \frac{-7}{10^2} ) mm/s</th>
<th>Equilibrium moisture content wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylester</td>
<td>0.117</td>
<td>7.4664 Fig. 6.13 Fick’s model applied to ( v )</td>
<td>0.7359</td>
</tr>
<tr>
<td>VE + 2% C-Na</td>
<td>0.107</td>
<td>6.2447</td>
<td>0.8813</td>
</tr>
<tr>
<td>VE + 3% C- Na</td>
<td>0.114</td>
<td>7.0885</td>
<td>0.9086</td>
</tr>
<tr>
<td>VE + 4% C-Na</td>
<td>0.121</td>
<td>7.9857</td>
<td>0.9645</td>
</tr>
<tr>
<td>VE + 5% C- Na</td>
<td>0.128</td>
<td>8.9364</td>
<td>1.0035</td>
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<tr>
<td>VE + 2% C-15A</td>
<td>0.089</td>
<td>4.3204</td>
<td>0.8054</td>
</tr>
<tr>
<td>VE + 3% C-15A</td>
<td>0.082</td>
<td>3.6675</td>
<td>0.8620</td>
</tr>
<tr>
<td>VE + 4% C-15A</td>
<td>0.063</td>
<td>2.1648</td>
<td>0.9264</td>
</tr>
<tr>
<td>VE + 5% C- 15A</td>
<td>0.053</td>
<td>1.5321</td>
<td>0.9841</td>
</tr>
</tbody>
</table>
Table 6.5 Diffusion test results of vinylester/Cloisite Na and Cloisite 15A in alkaline solution at 50°C

<table>
<thead>
<tr>
<th>Type of specimen</th>
<th>Slope</th>
<th>Diffusion co-efficient $\times 10^{-7}$ mm/s</th>
<th>Equilibrium moisture content wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylester</td>
<td>0.15</td>
<td>12.2272</td>
<td>0.8108</td>
</tr>
<tr>
<td>VE + 2% C-Na</td>
<td>0.147</td>
<td>11.786</td>
<td>1.3433</td>
</tr>
<tr>
<td>VE + 3% C-Na</td>
<td>0.152</td>
<td>12.602</td>
<td>1.4598</td>
</tr>
<tr>
<td>VE + 4% C-Na</td>
<td>0.159</td>
<td>13.789</td>
<td>1.5277</td>
</tr>
<tr>
<td>VE + 5% C-Na</td>
<td>0.166</td>
<td>15.030</td>
<td>1.5907</td>
</tr>
<tr>
<td>VE + 2% C-15A</td>
<td>0.104</td>
<td>5.8994</td>
<td>1.1080</td>
</tr>
<tr>
<td>VE + 3% C-15A</td>
<td>0.097</td>
<td>5.132</td>
<td>1.2628</td>
</tr>
<tr>
<td>VE + 4% C-15A</td>
<td>0.087</td>
<td>4.1284</td>
<td>1.3523</td>
</tr>
<tr>
<td>VE + 5% C-15A</td>
<td>0.081</td>
<td>3.5786</td>
<td>1.4313</td>
</tr>
</tbody>
</table>
Table 6.6 Permeability studies on alkaline solution using Fick’s law

<table>
<thead>
<tr>
<th>Sample</th>
<th>M∞</th>
<th>$D \times 10^{-7}$ mm²/s</th>
<th>Density g/cc</th>
<th>Solubility g/cc</th>
<th>Permeability $\times 10^{-7}$ g·m⁻²·m⁻³·s⁻¹</th>
<th>Relative permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEAT RESIN</td>
<td>0.117</td>
<td>7.4664</td>
<td>1.11E-04</td>
<td>1.30E-05</td>
<td>1.21E-04</td>
<td>1.00</td>
</tr>
<tr>
<td>2% C Na</td>
<td>0.107</td>
<td>6.2447</td>
<td>1.28E-04</td>
<td>1.37E-05</td>
<td>1.08E-04</td>
<td>0.89</td>
</tr>
<tr>
<td>3% C Na</td>
<td>0.114</td>
<td>7.0885</td>
<td>1.33E-04</td>
<td>1.52E-05</td>
<td>1.63E-04</td>
<td>1.35</td>
</tr>
<tr>
<td>4% C Na</td>
<td>0.121</td>
<td>7.9857</td>
<td>1.36E-04</td>
<td>1.64E-05</td>
<td>1.96E-04</td>
<td>1.62</td>
</tr>
<tr>
<td>5% C Na</td>
<td>0.128</td>
<td>8.9364</td>
<td>1.36E-04</td>
<td>1.74E-05</td>
<td>3.44E-04</td>
<td>2.84</td>
</tr>
<tr>
<td>2% C 15A</td>
<td>0.089</td>
<td>4.3204</td>
<td>1.21E-04</td>
<td>1.08E-05</td>
<td>5.87E-05</td>
<td>0.49</td>
</tr>
<tr>
<td>3% C 15A</td>
<td>0.082</td>
<td>3.6675</td>
<td>1.23E-04</td>
<td>1.01E-05</td>
<td>4.09E-05</td>
<td>0.34</td>
</tr>
<tr>
<td>4% C 15A</td>
<td>0.063</td>
<td>2.1648</td>
<td>1.25E-04</td>
<td>7.88E-06</td>
<td>2.69E-05</td>
<td>0.22</td>
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<tr>
<td>5% C 15A</td>
<td>0.053</td>
<td>1.5321</td>
<td>1.22E-04</td>
<td>6.46E-06</td>
<td>1.80E-05</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table 6.7 Permeability studies on alkaline solution at 50°C using Fick’s law

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo</th>
<th>D × 10^-7 mm²/s</th>
<th>Density g/cc</th>
<th>Solubility g/cc</th>
<th>Permeability × 10^-7 g·m²/m²·s</th>
<th>Relative permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEAT RESIN</td>
<td>0.15</td>
<td>12.2723</td>
<td>1.11E-04</td>
<td>1.66E-05</td>
<td>2.20E-04</td>
<td>1.00</td>
</tr>
<tr>
<td>2% C Na</td>
<td>0.147</td>
<td>11.786</td>
<td>1.28E-04</td>
<td>1.88E-05</td>
<td>2.40E-04</td>
<td>1.09</td>
</tr>
<tr>
<td>3% C Na</td>
<td>0.152</td>
<td>12.602</td>
<td>1.33E-04</td>
<td>2.02E-05</td>
<td>3.26E-04</td>
<td>1.48</td>
</tr>
<tr>
<td>4% C Na</td>
<td>0.159</td>
<td>13.7891</td>
<td>1.36E-04</td>
<td>2.15E-05</td>
<td>4.09E-04</td>
<td>1.86</td>
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<tr>
<td>5% C Na</td>
<td>0.166</td>
<td>15.03</td>
<td>1.36E-04</td>
<td>2.26E-05</td>
<td>4.36E-04</td>
<td>1.98</td>
</tr>
<tr>
<td>2% C 15A</td>
<td>0.104</td>
<td>5.8994</td>
<td>1.21E-04</td>
<td>1.26E-05</td>
<td>1.37E-04</td>
<td>0.62</td>
</tr>
<tr>
<td>3% C 15A</td>
<td>0.097</td>
<td>5.132</td>
<td>1.23E-04</td>
<td>1.19E-05</td>
<td>1.07E-04</td>
<td>0.49</td>
</tr>
<tr>
<td>4% C 15A</td>
<td>0.087</td>
<td>4.1284</td>
<td>1.25E-04</td>
<td>1.09E-05</td>
<td>6.58E-05</td>
<td>0.30</td>
</tr>
<tr>
<td>5% C 15A</td>
<td>0.081</td>
<td>3.5786</td>
<td>1.22E-04</td>
<td>9.87E-06</td>
<td>4.80E-05</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Fig. 6.1 Teflon Mould

Fig. 6.2 Cured neat resin samples (vinylester, Cloisite Na, Cloisite 15A)
Fig 6.3 Specimens immersed in alkaline solution at room

Fig. 6.4 Setup to measure pH value of the Alkali solution
Fig. 6.5 Serological water bath

Fig. 6.6 Water uptake curves for vinylester/Cloisite Na in alkaline solution at room temperature
Fig. 6.7 Water uptake curves for vinylester/Cloisite 15 A in alkaline solution at room temperature.

Fig. 6.8 Water uptake curves for vinylester/Cloisite Na in alkaline solution at 50°C.
Fig. 6.9 Water uptake curves for vinylester/Cloisite Na in alkaline solution at 50°C

Fig. 6.10 Micro Hardness of Cloisite Na, Cloisite 15A/vinylester specimens before immersion
Fig. 6.11 Micro Hardness of Cloisite Na, Cloisite 15A/vinylester specimens in Alkaline solution at room temperature

Fig. 6.12 Micro Hardness of Cloisite Na, Cloisite 15A/vinylester Specimens in Alkaline at 50 C
**Fig. 6.13** Fick’s model applied to vinylester/Cloisite Na & Cloisite 15A in alkaline solution at room temperature

**Fig. 6.14** Fick’s model applied to vinylester/Cloisite Na & Cloisite 15A in alkaline solution at 50°C
Fig. 6.15 Diffusion Co-efficient v/s nanoclay loading in Alkaline solution at room temperature

Fig. 6.16 Diffusion Co-efficient v/s nanoclay loading in alkaline solution at 50°C
Fig. 6.17 Relative Permeability vs Clay Loading in Alkaline solution at room temperature

Fig. 6.18 Relative Permeability vs Clay Loading in alkaline solution at 50°C
Fig. 6.19 Langmuir model applied to vinylester/Cloisite Na & Cloisite 15A in alkaline solution at room temperature

Fig. 6.20 Langmuir model applied to vinylester/Cloisite Na & Cloisite 15A in alkaline solution at 50°C
Total path of a diffusing gas
\[ d' = d + d \cdot \frac{L \cdot V_f}{2W} \]
- \( d \): thickness of a film
- \( L \): length of a clay
- \( W \): width of a clay
- \( V_f \): volume fraction of a clay

Tortuousity factor
\[ \tau = \frac{d'}{d} = 1 + \frac{L \cdot V_f}{2W} \]

Equation for a permeability coefficient
\[ P_c = \frac{P_p}{\tau} = \frac{P_p}{1 + \frac{L \cdot V_f}{2W}} \]
- \( P_p \): permeability coefficient of a matrix polymer

Fig.6.21 Tortuous Path in Polymer Nanocomposites
6.9 References


