

# INFLUENCE OF NANOCCLAY ADDITION ON PROPERTIES OF UNSATURATED-POLYESTER NANOCOMPOSITE GEL COAT SYSTEM

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## ABSTRACT

This work deals with processing of nanocomposite gel coat system using unsaturated polyester resin, aerosil powder and dodecylamine treated nanoclays. Further, the work focuses on the influence of nanoclay addition on mechanical and water barrier properties of a polyester gel coat system with different weight fractions (1, 2, 3, 4 & 5 wt.%) of nanoclay. The nanocomposite gel coat system exhibits 94% improvement in tensile modulus for 5wt.% nanoclay and 24% improvement in tensile strength for 2wt.% nanoclay. Nanocomposite gel coat system exhibit a maximum of 68% improvement in barrier resistance for 3 wt.% nanoclay compared to the conventional gel coat system. At higher clay concentration (>3%) the mechanical and barrier properties decrease due to the limitation in the processing as well as the high viscosity of resin/clay/aerosol system.

**Keywords:** nanocomposite, gel coats, polyester.

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## 1. INTRODUCTION

Composites with gel coats are an essential part of many aspects of life today and include bathroom units, boats, cultured marble, airplane structures, windmills, and automotive parts. Gel coat imparts good surface finish, bears better hardness, scratch resistance and resistance to corrosion and water absorption.

Recently polymer clay nanocomposites have received considerable attention since their properties can be appreciably improved by the infusion of nanosized clay particles /1-3/. Based on this concept, a fair amount of research work has been carried out using thermoset polymer systems such as epoxies /4/ and polyesters /5-7/. Smectite layered silicate clays are normally used as basic reinforcing element, because of the high aspect ratio and platy morphology. Incorporation of nanosize clay platelets to the polymer matrix increases modulus and strength /8/. Nanosize clay platelets decrease permeability /9/, shrinkage /10/ and increases resistance to heat and flammability /11/. In thermoset polyester system, the fracture energy could be doubled even at low concentration (1.5 wt.%) of clay infusion/12/. The formation mechanism based on fabrication methods has been reported for unsaturated polyester layered silicate nanocomposites /6/. The method of mixing clay in the polyester resin, curing agents used and curing conditions influence the properties of nanocomposites /13, 14/. The effect of nanoclay on the cure kinetics of unsaturated polyester resin in the range of 35 to 65°C was investigated by Liqun *et al.* /15/. The clay polyester nanocomposites produced using reactive organoclay had better dynamic modulus /16/. Similarly, it was reported that, the incorporation of modified nanoclays improved the mechanical, barrier and tribological properties of polyester /17, 18/. Nanoclay infused polyester matrix in glass fiber reinforced composite system has improved the mechanical behavior of composites /19/. Investigation on clay polyester nanocomposites leads us to develop a new three phase composite gel coat system with nanoclay infused polyester as matrix and fine SiO<sub>2</sub> powder as filler.

It is expected that the incorporation of nanoclay in gel coat would lead to an improvement in the properties, which will make the material viable in high loading environments. In the present work nanocomposite gel coat system was prepared using nanoclay infused unsaturated polyester resin with

aerosil powder as filler. The mechanical and barrier properties were investigated.

## **2. EXPERIMENTAL DETAILS**

### **2.1. Materials**

In this study dodecylamine treated bentonite nanoclay (Southern Clay Products, USA) was incorporated into a isophthalic polyester resin (IP) system. Additionally, aerosil powder with an average size of 6  $\mu\text{m}$  was used as filler in the nanocomposite gel coat system. The aerosol powder was procured from AMT Composites, South Africa and the isophthalic polyester resin was procured from KZN Composites, South Africa. The major chemical composition is dicyclopentadiene (DCPD) of 83-88%, CPD–m CPD codimer of 2-6%, isoprene – CPD codimer of 1-5% and minor trace elements.

### **2.2. Methodology**

Nanoclay of various weight fractions (1, 2, 3, 4 and 5 wt.%) was thoroughly mixed with isophthalic polyester (IP) resin using a high shear mechanical mixer for 1 hr. 1.5 wt.% Methyl ethyl ketone peroxide catalyst and cobalt naphthanate accelerator was added to the mix. Samples of size 300x 300x3mm were cast in glass mould and were allowed to cure for 24 hr. Post curing was done at 70°C for 3 hr. The purpose of producing these nanocomposite structures was to check the level of of clay dispersion.

Nanocomposite gel coat system was prepared by mixing the nanoclay of definite weight fraction to the polyester resin for 1 hr as discussed earlier. Thereafter, 2 wt.% aerosil powder was added to the nanoclay infused resin and mixed well with a glass rod for 15 minutes. After adding the catalyst and accelerator, the nanocomposite gel coat system was cast in glass mould and allowed to cure overnight for 24 hr. Similarly conventional gel coat system was prepared with pristine polyester resin as matrix and 2 wt.% aerosil powder as the filler. The samples were cast in the glass mould after adding 1.5 wt.% of catalyst and accelerator. Post curing was done on both nanocomposite gel coat system and conventional gel coat system at 70°C for 3 hr.

### 2.3. X-ray characterization

The x-ray diffraction was performed on the nanoclay filled polyester composites to study the state of clay dispersion. It was carried out at a scanning rate of 2°/min using Cu-K $\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) using SHIMADZU, XD-DI X-ray Diffractometer.

### 2.4. Transmission electron microscopy

TEM characterization was carried out on the nanocomposite samples to correlate and confirm the XRD results. Thin films of 60-90 nm thickness were prepared using a diamond blade Philips microtome. The sliced films were taken in copper grids for further characterization using transmission electron microscope (JEOL JEM 1200EX) operated at the operating voltage of 200 kV.

### 2.5. Physical properties

The density of gel coat systems was measured using Archimedes principle. The density of samples ( $\rho$ ) was calculated using equation 1.

$$\rho = (W_a / (W_a - W_w)) \times \rho_w \quad (1)$$

$W_a$  : Weight of specimen measured in air

$W_w$  : Weight of specimen immersed in water

$\rho_w$  : Density of water

To determine the mass uptake of nanocomposite gel coat system and conventional gel coat system, coupons of dimension of 50 X 50 X 3 mm were placed in the beakers containing distilled water for thirty days. The samples were taken out of the water at specific intervals, wiped with tissue paper and the weights were measured to the accuracy of 0.1 mg using METTLER-AE 200 balance.

### 2.6. Mechanical testing and evaluation

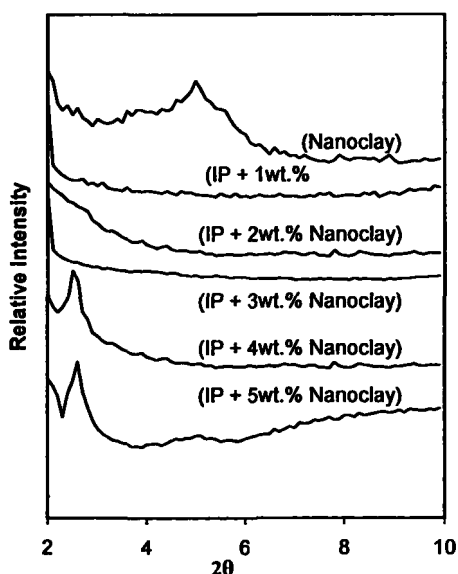
Tensile tests (ASTM D-638) were performed at room temperature on both nanocomposite gel coat system and conventional gel coat system using

Instron 4301 universal testing machine (UTM), with a crosshead speed of 2 mm/min. Five specimens of each type were tested and the average values are presented. Tensile fractured samples were analyzed using JEOL JSM 840A scanning electron microscope (SEM) with EDAX.

### 3. RESULTS AND DISCUSSION

#### 3.1.x-ray characterization

XRD patterns of modified nanoclay and nanoclay filled composites are shown in Figure 1.



**Fig. 1:** X-ray diffraction patterns of nanoclay particles and Isophthalic polyester with nanoclay

The nanoclay shows a sharp peak at  $2\theta$  values of  $5^\circ$  corresponding to the 001 basal plane diffraction. The inter-layer distance ( $d$ - spacing) of nanoclay obtained from Bragg's law is  $17.7\text{\AA}$ . It is observed that the 001 basal plane diffraction peak of nanoclay is absent in polyester filled with 1, 2 and 3 wt.% nanoclay. This reveals that the inter-layer distance of nanoclay is more than

70Å or the layers are randomly dispersed in the polymer matrix. For composites with higher nanoclay content (4 & 5 wt.%), the diffraction peak shifts towards lower  $2\theta$  value of  $2.5^\circ$ . The inter layer d-spacing of clay platelets is around 35Å. The X-ray diffraction pattern confirms the formation of exfoliated or well intercalated nanocomposites at lower clay content (1, 2 & 3 wt.%) and intercalated nanocomposites for higher clay content (4 & 5wt.%). The appearance of peaks at higher clay contents may also due to the presence of agglomerated clay tactoids. This phenomenon is verified TEM shown later.

### 3.2. Tem characterization

Transmission electron micrographs of polyester filled with nanoclay were analyzed to study the structure, since it was difficult to slice the nanocomposite gel coat samples using microtome to the thickness in the order of nanometer. Figure 2(a) shows the TEM micrograph of polyester filled with 1wt.% nanoclay.



Fig. 2(a): TEM pictures of nanocomposite samples with 1 wt.% nanoclay,

The clay platelets are moved apart by the intercalation of polymer molecules and spacing between the clay platelets is approximately 500 Å and the arrangements of clay platelets is semi parallel. This confirms the formation of well intercalated nanocomposites for 1wt.% nanoclay addition and supports the XRD data. Similarly intercalated nanocomposites were

found for nanocomposites with 2wt.% nanoclay and the d-spacing between the silicate platelets is approximately 200 – 400 Å (Figure 2b).



**Fig. 2(b):** TEM pictures of nanocomposite samples with 2 wt.% nanoclay

Figure. 2c shows more closely packed silicate platelets for composites with 4wt.% nanoclay when compared with nanocomposites with 1 and 2 wt.% nanoclays.



**Fig. 2(c):** TEM pictures of nanocomposite samples with 4 wt.% nanoclay.

The d-spacing between the silicate layers are less than 70 Å and also the parallel arrangement of the clay platelets confirms the formation of an intercalated structure. It is in agreement with the XRD data (Figure. 1) showing that the d-spacing between the clay platelets was of the order of 35 Å. TEM studies reveal the formation of intercalated nanocomposites.

### 3.3. Density of gel coat system

Density values of conventional gel coat and nanocomposite gel coat systems are shown in Figure 3. The density of conventional gel coat system is 1.32 g/cm<sup>3</sup>. The density of gel coat system is constant up to the clay content of 3 wt.% and thereafter decreases slightly to the value of 1.27 g/cm<sup>3</sup> for the nanoclay content of 5 wt.%. The decrease in density of nanocomposite gel coat system with 5 wt.% nanoclay is due to the presence of voids. Entrapped air during mixing cannot escape out of polyester matrix and remains as voids.

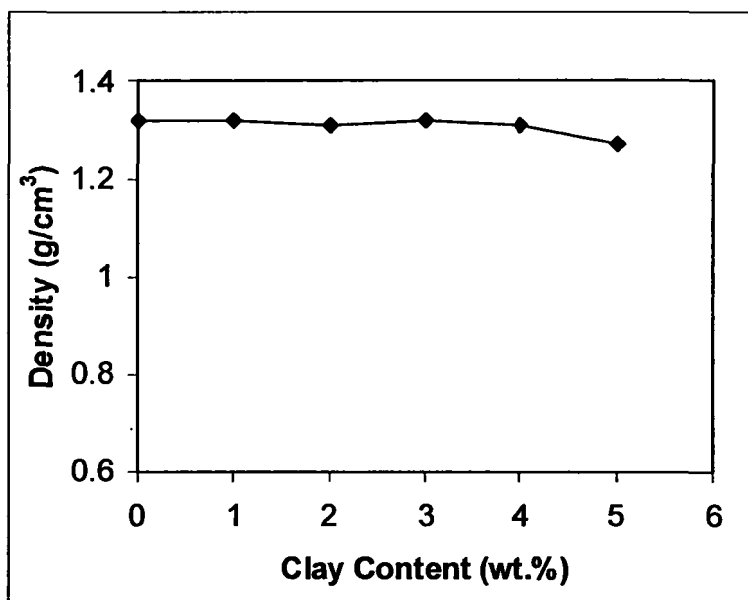
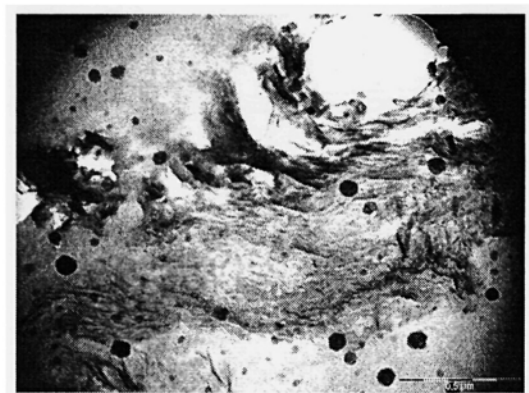


Fig. 3: Density of gel coat system

Figure 4 shows the TEM of nanocomposite sample with 5wt% clay. It is observed that the voids size range from 0.25µm to 0.4µm. The % of voids calculated from TEM by using optical imaging is approximately 3% in the



nanocomposite system. However, the voids concentration based on the density measurement is about 3.7% despite efforts in trying to minimize the voids during processing. Perhaps vacuum/controlled atmosphere/high temperature processing may minimize the voids.



**Fig. 4:** TEM picture of nanocomposite with 5wt% clay shows the presence of void

### 3.4. Barrier properties of gel coat system

The barrier properties of conventional polyester gel coat system and nanocomposite gel coat systems were studied by placing the samples in distilled water for 30 days. By keeping such nanocomposites in water medium over the extended period, it is expected that the water penetrates into the polymer medium and hence the weight of nanocomposite increases. This percentage increase in weight of the nanocomposite gel coat system kept in water is shown in Figure 5. For a period of seven days, the percentage increase in weight due to water mass uptake for conventional gel coat system was 0.41 %, whereas it is reduced to 0.20 % for the nanoclay content of 3 wt. % and then increases to the value of 0.23% for 5wt.% nanoclay. This result suggests that the addition of nanoclay lowers the water mass uptake in composite medium.

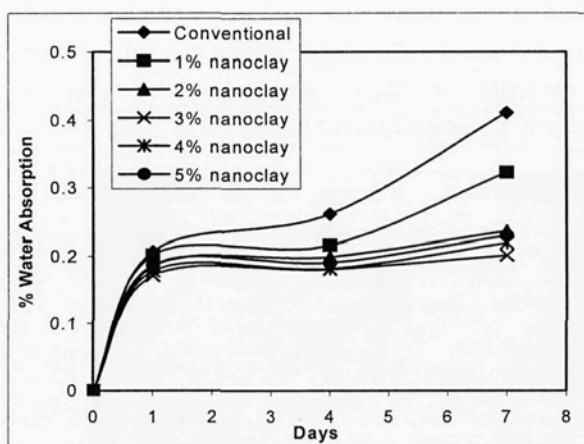


Fig. 5: Percentage weight increase of gel coat system in Water

It was found that there is an increasing trend in mass uptake for samples kept in water with respect to the number of days. To find the equilibrium mass uptake, the samples were kept for prolonged periods (30 days). It was found that after 20 days the mass uptake was almost constant and no further increase in water mass uptake was observed. The equilibrium mass uptake for the gel coat systems is shown in Figure. 6. The equilibrium mass uptake for conventional polyester gel coat system is 1.06 % in water, whereas for 3 wt% clay specimen it is 0.31%. Structures with more than 3% wt. clays results in the creation of voids. This void causes the increased mass uptake in nanocomposite system; however this mass uptake is lower than in pristine polyester-aerosil gelcoat.

This result shows that nanocomposite gel coat system has better resistance to mass uptake compared to conventional polyester gel coat system especially for the nanoclay content of 3 wt.%. The clay is basically hydrophilic in nature. The organic modification by dodecylamine makes the clay organophilic and hydrophobic. The reason for the improvement in absorption resistance is due to the dispersion of intercalated hydrophobic clay platelets in the nanocomposite gel coat system. These dispersed intercalated clay platelets increase the tortuous path for the molecules in the corrosion medium to travel and hinders the diffusion path and also decreases mass uptake in the matrix [20-21]. The presence of fully intercalated structure for

the nanoclay content of 1 and 3 wt.% in polyester matrix was confirmed earlier (Figure. 2).

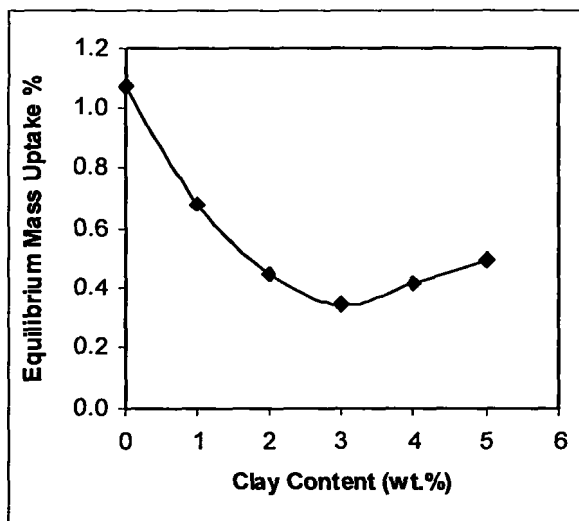


Fig. 6: Equilibrium mass uptake of gel coat system

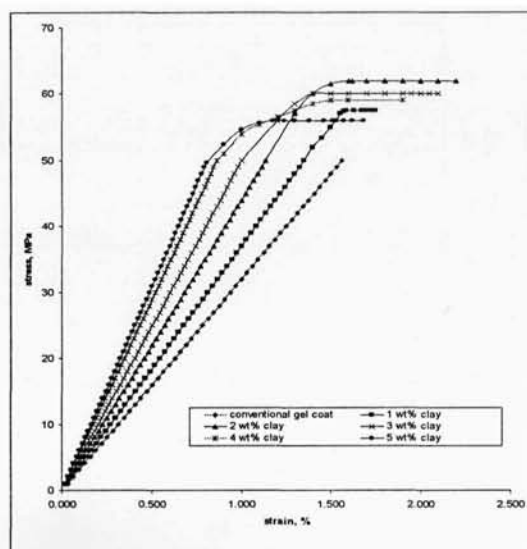
### 3.5. Tensile properties

The tensile properties of the conventional gel coat and nanocomposite systems are shown in Figure 7. The figure shows that the modulus increases as the clay content increases. However, failure strain and strength behaves differently as a function of clay concentration. The failure strain values are 1.56%, 1.75%, 2.2%, 2.1%, 1.9 and 1.68% for 0%wt., 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% clay inclusion respectively. Initially, failure strains increases with increased clay content up to 2 wt% clay. Further addition of clay decreases the failure strain values. Low strain failure may be attributed to the presence of voids as well as agglomerated clay concentration.

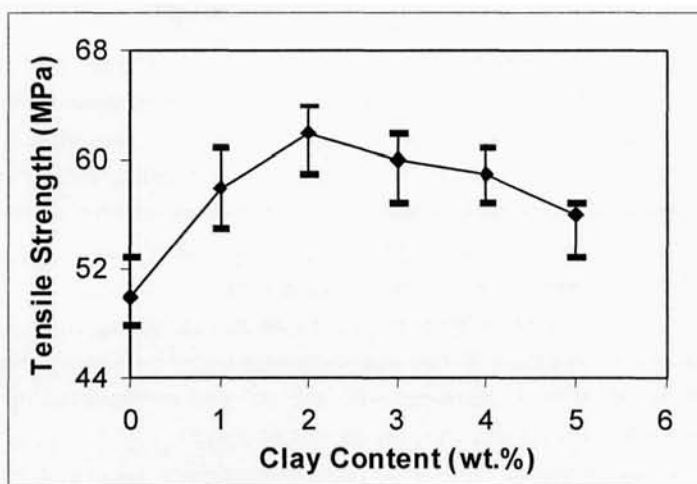
The tensile strength of conventional gel coat and nanocomposite gel coat systems is shown in Figure 8. The tensile strength of conventional gel coat is found to be 50 MPa. It increases with the addition of nanoclay up to a maximum of 62 MPa for the nanoclay content of 2 wt.%.

The tensile modulus values of conventional gel coat system and nanocomposite gel coat system is shown in Figure 9. The conventional gel coat system has modulus of 3.2 GPa. It increases to 3.7, 4.4, 5, 5.8 and 6.2

GPa for the nanoclay contents of 1, 2, 3, 4 and 5wt.% respectively. The tensile modulus increases by 94% for nanocomposite gel coat system with nanoclay content of 5wt.%.



**Fig. 7:** Tensile stress-strain curves of conventional gel coat and with different clay concentrations



**Fig. 8:** Tensile strength of gel coat systems

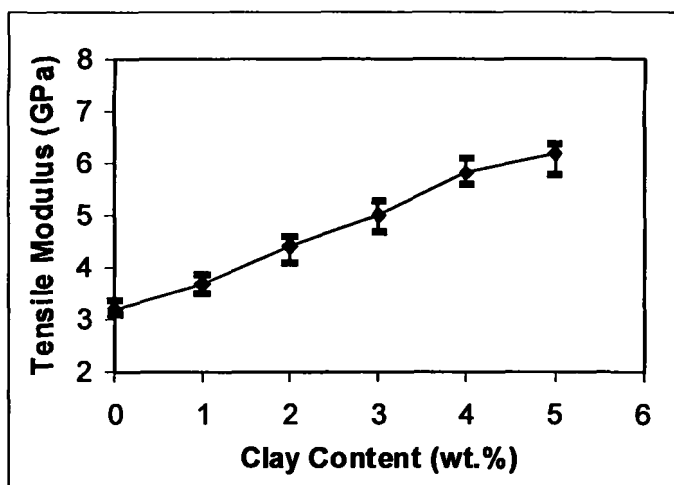


Fig. 9: Tensile modulus of gel coat systems

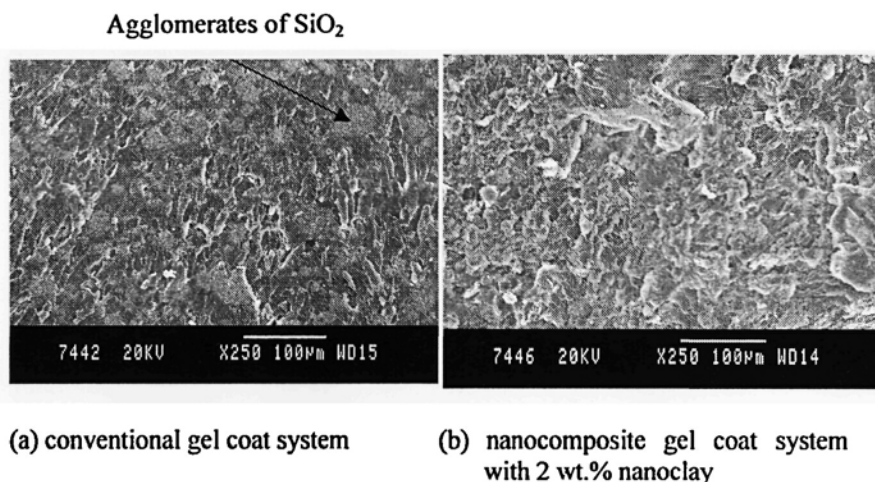
The improvement in mechanical properties was due to the presence of well-intercalated nanoclay and interaction of nanosize clay layers with the polymer matrix, as well as due to the rigid nature of the clay layers [22]. As the clay platelets are well intercalated, the surface area of clay platelets available for interaction with polymer increases and hence the reinforcing effect increases resulting in increased strength, and modulus. The improvement in strength and modulus for this system is consistent with the work reported elsewhere [23, 24]. However considering the XRD and TEM characterization (Figures. 1 & 2), it was expected to have large improvement for the nanocomposites infused with 3wt.% nanoclay. The possible reason may be the, nanocomposites might have attained the threshold tensile strength for the clay content of 2 wt.%. From Figure. 2(b), we could able to notice some agglomerated tactoids in the microstructure. The agglomerates might be hindering the improvement of tensile strength for the nanocomposites with 3 wt.% nanoclay.

Improvement in tensile strength was not significant for nanocomposite gel coat system with 5 wt.% nanoclay. Even though the nanosize clay acts as load bearing component, the dispersion of intercalated and agglomerated clay platelets hinders the cross linking of the polymer chains [7]. The decrease in tensile strength at high clay content ( $> 3\text{wt.}\%$ ) may also be due to the agglomeration effect of the nano clay and also due to the increase in viscosity of the polyester resin at higher clay content. Moreover, the air entrapped during

mixing may not escape out of the system due to high viscosity, and remains as micro-pore in the nanocomposite gel coats, as confirmed by density studies (Figure. 3) resulting in decreased strength.

### 3.6. Fracture analysis of gel coat system

The tensile strength increases with the increase nanoclays in gel coat system. Figure 10 shows the tensile fracture surface of conventional gel coat system and nanocomposite gel coat system.



**Fig. 10:** Tensile fracture surface

The fracture surface of the conventional gel coat system (Figure 10a) appears glassy suggestive of a brittle failure. But the nanoclay addition has brought some improvements in mechanical properties. It was clearly evident from the fracture morphology of nanocomposite gel coat system. The fracture surface seems to be very rough with fine facets indicating that, the resistance to crack propagation is very high, and also confirms that the nanocomposite gel coat system have better load bearing capacity. The surface roughness also suggests that nanoclay addition increases the tortuous path of crack propagation as reported elsewhere [25, 26].

Figure 10(a) show the presence of some agglomerated particles on the fractured surface. There exists a possibility of agglomeration of aerosil (fine SiO<sub>2</sub>) powder. EDAX analysis was carried out on a relatively large area viewed under microscope, and on the selected agglomerated area (Figure. 11).

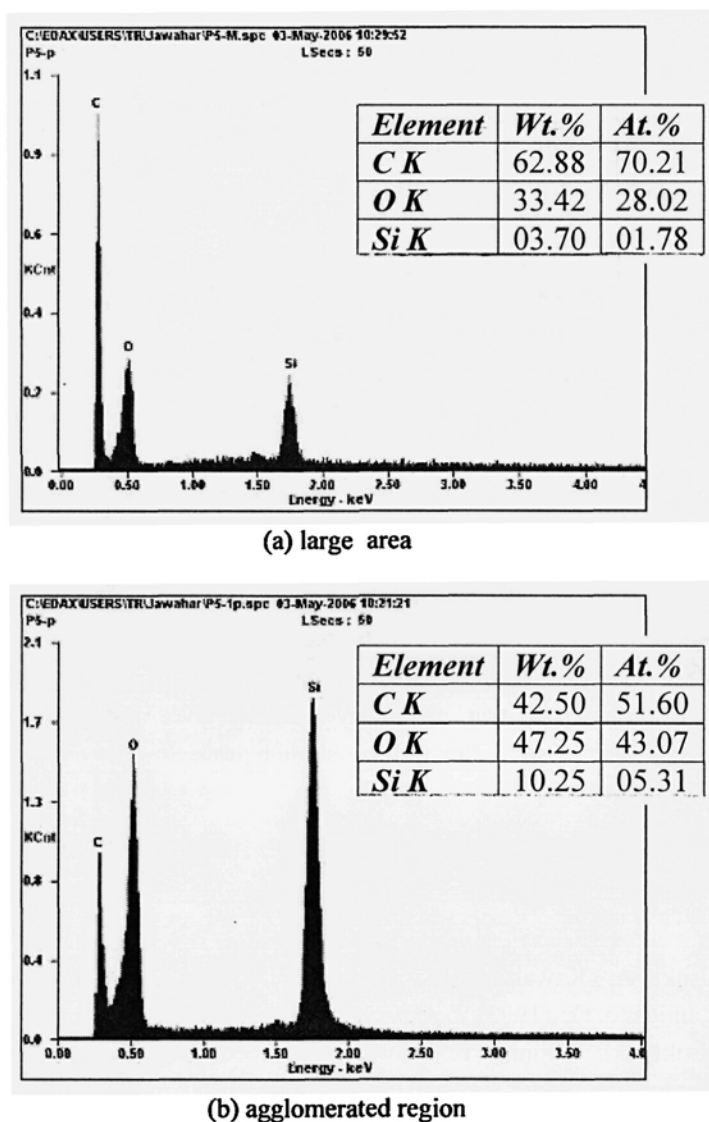


Fig. 11: EDAX analysis on conventional gel coat system

From EDAX analysis, it was confirmed that the agglomerated region consists of  $\text{SiO}_2$  particles, because the Si content of the agglomerated area is nearly 10 wt.%, whereas the average Si content is 3.70 wt.%. Surprisingly no agglomerates are found for nanocomposite gel coat systems. This suggests that, the clay platelets present in the polyester matrix might be inducing some

mechanism to prevent agglomeration of fillers. The intercalated clay platelets present in the polyester matrix might be interacting with micro fillers readily and hinder the agglomeration of micro filler. There is a possibility that the modified clay with a long chain of organic molecules can act as a deflocculant. Further studies are needed to confirm the mechanism.

## CONCLUSIONS

Nanocomposite gel coat systems were prepared using unsaturated polyester resin, aerosil powder and treated nanoclay. The incorporation of nanoclay improves the mechanical and water barrier properties of nanocomposite gel coat system. The nanocomposite gel coat system exhibits 94% improvement in tensile modulus for 5wt.% nanoclay and 24% improvement in tensile strength for 2wt.% nanoclay. Nanocomposite gel coat system also exhibit a maximum of 68% improvement in barrier resistance for 2 wt.% nanoclay. Further enhancement in properties of nanocomposites may be obtained by improving processing techniques, particularly at higher clay concentrations (>3wt.%) due to the creation of voids in gel coat system. Hence we conclude that nano clay addition gives maximum beneficial properties up to 3wt% and further addition leads to voids under present processing medium.

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