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# Effect of addition of nanoclays on properties of vinyl ester

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#### Abstract

Vinyl ester resins have been used in many engineering applications such as matrix for composites used in ships, chemical reservoirs, pipes etc. It is desirable to enhance a few important properties of the resin such as flammability resistance, water absorption resistance, and fracture toughness. The addition of nanoclays has been shown to enhance these properties of epoxy resins. The work in this project is to investigate the effect of adding nanoclays on these properties of vinyl ester.

Commercial vinyl esters usually contain styrene, which serves both as a diluent and a crosslinking agent. The presence of styrene complicates the incorporation of clays into the vinyl ester. As such two types of vinyl ester were used. One is commercial vinyl ester (Derakane 411-350) which contains styrene, and the other is vinyl ester synthesized in the laboratory, which is kept free of styrene during the clay incorporation. Different types of clays were examined. Different methods of mixing the clays in the vinyl ester were investigated.

The results show that among the different clays, composites made using vinyl ester and Cloisite 20A show better performance. If the mixing conditions are right, there is significant improvement in fracture toughness. However there is some reduction in flexural strength upon the addition of the clays.

# Introduction

Vinyl ester nanocomposites belong to a relatively new class of materials obtained by dispersing montmorillonite clay in vinyl ester matrix. The addition of nanoclays has been shown to enhance properties of epoxy resins such as flammability resistance, water absorption resistance, and fracture toughness. In the nanocomposites fabrication process, there are many factors which affect their properties. It is generally believed that the improvement of properties of nanoclay composites is directly related to the complete exfoliation of silicate layers in the polymer matrix. However, a processing technique that produces complete exfoliation is still a technical challenge

[1–7]. Researchers have studied dispersion of clay platelets in polymer by the difference of temperature, pre-mixing speed, duration of time [8-10].

This project focuses on studying the effect of nanoclays addition on vinyl ester properties. In this study, the modification in mixing order of resin, styrene and Cloisite 20A, as well as three different mixing methods: Three-Roll Mill Mixing (R), High speed mixing (H) and High Pressure mixing (HP), vinyl ester nanocomposites are introduced. Two types of resin are used: synthesized vinyl ester resin (syn.VE or VE) and Derakane 411-350 (D) (commercial vinyl ester). Three types of clay (Cloisite® 10A, 20A, and 30B abbreviated as C10A, C20A, and C30B respectively) are used.

# Experimental

1- Material:

The resin selected for the synthesis of Vinyl ester is EPON<sup>TM</sup> 828 (Diglycidylether Bisphenol-A), from Miller-Stephen chemical company, Inc (Danbury, CT, USA). Commercial vinyl ester (Derakane 411-350) and Cobalt Dusyn 12% were supplied by Progress Plastics (Canada). The chemicals used for the synthesizing and curing reaction are acrylic acid (anhydrous 99%), styrene 99%, pyridine (anhydrous 99.8%), MEKP (methyl ethyl ketone peroxide), and hydroquinone. These are provided by Sigma-Aldrich. Southern Clay Products supplies nanoclay used for this study, which are Cloisite® 10A, 20A and 30B (natural montmorillonite modified with a quaternary ammonium salt). Even though three types of clays were used, previous work done (not shown in details here) showed the C20A clays gave the best performance. As such, results in the paper are shown for C20A only.

- 2- Experiments
- 2.1- Synthesis of vinyl ester

The synthesizing reaction was carried out following the conditions and the proportions of reagents: Epon 828:Acrylic acid (equivalent) = 1:1.05; Pyridine = 0.40 % total weight; Hydroquinone = 0.02 % total weight; Temp.:  $90^{\circ}$ C; Speed: 300rpm under nitrogen atmosphere (low pressure ~6.5 ml/min). The time for reaction was 4.5 hrs (270 minutes). FTIR and titration free acid were used to follow the process of reaction.

2.2- Nanocomposites

Three mixing techniques were used: Three-Roll Mill Mixing, High speed mixing and High Pressure mixing.

# -Three-Roll Mill Mixing

This technique utilizes a three-roll mill that employs shear force created by three horizontally positioned rolls rotating at opposite directions and different speeds relative to each other. All the three-rolls of the mill are firmly fixed with a gap of few microns. When the nano-clay mixed with viscous matrix are fed in between the feed and center rolls it experiences two forces: a shearing force and a compressive force while passing through the rolls. EXAKT 80E three-

roller-mill in gap mode – (a quantitative setting to a specific gap value) was used in this project. The mixture was passed through 4 times with gap settings ( $\mu$ m): 20, 10 and 5 (repeat 2 times).

#### - High speed mixing

The mixtures were mixed at  $60^{\circ}$ C by high speed mixer (ULTRA-TURRAX T25 basic IKA® - WERKE) following the steps:

- . Step 1: Mix at speed 1000 rpm for 10 min, rest for 2 hrs.
- . Step 2: Mix at speed 6500 rpm for 10 min, rest for 2 hrs.
- . Step 3: Mix at speed 9500 rpm for 10 min.

#### - High pressure mixing

The dried C20A clay was dispersed in acetone to form a pasty mixture containing about 4% wt clay with the high-pressure mixing machine, where the mixture of clay and acetone was forced with more than 15,000 psi into a very small chamber and then impinged on the wall of the chamber many times. The exact concentration of clay was measured by drying the pasty mixture for 4 hrs at 100°C. The desired amount of paste was added to the synthesized vinyl ester resin (or Derakane, which had its styrene removed by evaporator at 60°C). The mixture was mechanically stirred at 800-1000 rpm for 10 hrs. Acetone in the mixture was removed by using evaporator for 8 hrs at 60°C (amount of residual acetone was determined by weighing method). Styrene was added into the mixture for curing reaction.

The four fabrication methods are summarized as shown in Figure 1. The differences between the four methods are: In method 1, clay is mixed with synthesized VE (no styrene). After mixing to obtain the intermediate mixture M1, styrene is added and mixed with a magnetic bar. In method 2, clay is mixed first with styrene to obtain the intermediate mixture M2. After that, either syn. VE with styrene or commercial Derakane is added to complete the material. In method 3, clay is mixed directly into syn.VE with styrene or with Derakane (this is the common method most people use). In method 4, a high pressure mixing machine is used to mix acetone and clay to obtain an intermediate mixture Ma. After that either syn. VE or Derakane (styrene extracted) are added to obtain another intermediate mixture Mb. Subsequently acetone is removed to obtain yet another intermediate mixture Mc. Finally styrene is added into the mixture Mc to obtain the final product. The material resulting from each method is given a 7-digit material code. For example, the material [VE 1R 40 3 T60] has the following meaning: VE stands for syn. vinyl ester; 1 stands for method 1; R stands for 3-roll mill as the method for mixing; 40 means 40% styrene; 3 means 3% clay; and T60 means the process was done at 60°C. For other symbols, D means Derakane, H means high speed mixer, HP means high pressure mixing machine. In later figures, there is also a symbol m meaning mixing by hand.

To start the reaction, added into the final product at the end of each of the mixing method are the Cobalt Dusyn 12% (0.1% of total weight) and then the initiator MEKP (1% of total weight). The samples mentioned above were cured at room temperature for at least for 4 days before being post-cured in an oven at 140°C for one hour. After that, these samples were used for tests.

#### 2.3. Characterization of cured vinyl ester and nanocomposites

- X-ray diffraction (XRD) analysis: To evaluate the intercalation/exfoliation of the nanoclay in the polymer matrix, X-ray diffraction (XRD) patterns were obtained from the surface of the samples with a Bruker Discover 8 powder X-ray diffractometer with CuK $\alpha$  radiation. The polished surfaces of the samples were examined.

- Glass transition temperature (Tg) by differential scanning calorimetry (DSC): DSC TA Q2000 Instrument was used to conduct the dynamic scan for all the samples, following the segment description: From 20°C, heating at a rate of 10°C/min to 250°C. Cool down at a rate of  $-20^{\circ}$ C/min to 250°C. Heating again at a rate of 20°C/min to 250°C



Fig.1. Four methods used to fabricate nanocomposites from synthesized VE and Derakane

- **Flexural properties:** flexural properties of composites were determined according to ASTM D790-02, using a MTS Servo Hydraulic Testing Machine at a crosshead speed of 1.3mm/min with small load cell (max capacity 2.5 KN). Rectangular bars of nominal dimensions 13 mm x 3 mm x 55 mm were molded directly or cut from sheets. The support span is more than 16 times the thickness of the specimen. At least 5 specimens of each composition were tested.

- **Fracture tests:** fracture tests were performed on a MTS Servo Hydraulic Testing Machine at a crosshead speed of 10 mm/min according to ASTM D 5045-99 with small load cell (2.5 KN). The specimen dimensions are shown in Figure 2 and the support span is 4 times the width of the specimen. At least 4 specimens of each composition were tested.



Fig. 2. Specimen dimensions of Single Edge Notch Bending (SEBN) test (mm)

- Scanning electron microscope (SEM): SEM images were obtained on a JSM 6100 scanning electron microscope at 10KV voltage and different magnifications (x100, x500, x2000 and x6000). SEM was performed on the fractured surfaces.

# Results



#### **1-** X-ray diffraction (XRD) analysis:

# Fig.3. X-ray diffraction curves of nanocomposites fabricated by 4 methods and post cured at $140^{\circ}C$ (1hr).

In Figure 3, the clay C20A has two distinct peaks at around  $3.44-3.77^{\circ}$  and at around  $7.1-7.3^{\circ}$ . In the mixtures of VE and C20A, there is one peak at around  $1.4-1.9^{\circ}$  (for samples made from

methods 1 and 3) and another peak around  $5-6^{\circ}$  (for samples made from method 4). These results show that the intercalation/exfoliation of C20A in vinyl ester nanocomposites, fabricated from methods 1, 3, 4, is very good.



#### 2- Glass Transition Temperature by DSC Dynamic Scan:

Fig.4. Glass transition temperature of vinyl ester and nanocomposites

Figure 4 shows the glass transition temperature for different materials. Upon addition of the clay and on post curing, the glass transition temperatures increase for all systems except for those mixed by the high pressure method (method 4) and for Derakane prepared by method 3. Mixing by methods 1 and 2 seem to give higher glass transition temperatures.



# **3-** Flexural properties:

Fig.5. Flexural strength of vinyl ester and nanocomposites

The flexural strength of the nanocomposites fabricated from synthesized VE or Derakane decreases as compared to the samples made of pure synthesized VE and Derakane (Figure 5). This happens in spite of the good intercalation/exfoliation of the clays in the resin. This may be due to the poor interaction between the clays and the resin.

#### 4- Fracture test results:

Table 1 and Figure 6 show the fracture test results. The stress intensity factor and the strain energy release rate increase upon the addition of clays for different mixing methods. The increase in strain energy release rate varies from 14% to 47% as compared to the value for pure resin (for synthesized vinyl ester). Interestingly the strain energy release rate for pure Derakane is higher than that for synthesized vinyl ester. On top of that, addition of clays can either decrease or increase the strain energy release rate for Derakane. One possible reason for the higher value of strain energy release rate for Derakane as compared to that of synthesized vinyl ester may be due to the presence of wax additive in Derakane. Also the decrease in strain energy release rate for sample number 8 (last sample in Table 1) may be due to the extraction of wax and styrene from Derakane before the addition of clays.

Nanocomposites	Average		Increase (%, compared to VE m-45-0-RT)		Increase (%, compared to D m-45-0-RT)	
	$\frac{K_{1C}}{(MPam^{1/2})}$	G <sub>1C</sub> (Kj.m <sup>2</sup> )	K <sub>1C</sub>	G <sub>1C</sub>	K <sub>1C</sub>	G <sub>1C</sub>
VE m 45 0 T60 (1)	1.024	0.299	0	0		
D m 45 0 T60 (2)	0.994	0.397			0	0
VE 1R 40 3 T60 (3)	1.192	0.411	16	37		
VE 1R 45 3 T60 (4)	1.229	0.43	20	44		
VE2H 45 3 T60	1.083	0.341	6	14		
D2H 45 3 T60	1.126	0.395			13	-1
VE3H 45 3 T60 (5)	1.234	0.438	21	47		
D3H 45 3 T60 (6)	1.229	0.422			24	6
VE4HP 45 3 T60 (7)	1.209	0.408	18	36		
D4HP 45 2 T60 (8)	1.2	0.356			21	-10

 Table 1: Critical-stress-intensity factor and Critical strain energy release rate of vinyl ester and nanocomposites



Fig.6. Stress intensity factor and strain energy release rate of vinyl ester and nanocomposites

#### 5- SEM observation



**Fig.7. SEM photos of vinylester and nanocomposites:** (1) VE m 45 0 T60, (2) D m 45 0 T60, (3) VE 1R 40 3 T60, (4) VE 1R 45 3 T60, (5) VE 3H 45 3 T60, (6) D 3H 45 3 T60, (7) VE 4HP 45 3 T60, (8) D 4HP 45 2 T60,

Figure 7 shows the Scanning Electron Microscope photos of vinyl ester and nanocomposites. The top two photos represent the pure samples of syn. VE and Derakane. Adding the clays provides rougher surface appearance and this corresponds to increase in fracture toughness. However, comparing the appearance of samples 2 and 8 and correlating this with values shown in Table 1 and Figure 6 indicates that even though the appearance of sample 2 is smoother than that of sample 6, sample 2 has higher toughness value. This may be due to the presence of wax in sample 2 and the lack of wax in sample 8, even though clay is added in the case of sample 8.

# Conclusion

- X-Ray diffraction curves show that the intercalation/exfoliation of nanoclays fabricated using method 1, 3 and 4 are good.
- Nanoclay 20A addition to synthesized vinyl ester helps increase nanocomposites  $K_{1C}$  and  $G_{1C}$  (compared to VE m-45-0-RT). This augmentation is maximized for VE3H 45 3 T60 (21%; 47 %), followed by VE 1R 45 3 T60 (20%; 44 %) and VE4H 45 3 T60 (18 %; 37%). It is minimum for VE2H 45 3 T60. This phenomenon also applies to glass transition temperature of nanocomposites.
- Commercial vinyl ester such as Derakane contains many fillers, among them wax plays an important role in the mechanical properties of the resin and that with clay added. The benefits of adding clay into the commercial resin are not as much as compared to the case of synthesized vinyl ester resin. Since it is difficult to know the exact type and amount of fillers in the commercial resin, it is not possible to provide an explanation on this effect.

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