

# INTERFACIAL BONDING AND MECHANISM IN NANOCLAY/EPOXY COMPOSITE

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## Introduction

Numerous researches have been done on the development of organomodified montmorillonite (MMT) (commonly called “Nanoclay”) reinforced polymer nanocomposites recently. It was found that only a small amount of nanoclay being added into polymer matrices can provide certain degree of their strength enhancement. However, most of the works done previously have neglected to comprehensively study the basic reinforcing mechanism of the composites, particular the interaction between nanoclay and surrounding matrix even though high tensile strength and modulus were obtained. In this paper, images obtained from Transmission Electron Microscope (TEM) proved that interlocking and bridging effects did exist in the composites. Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis revealed that a chemical bonding at an interface between the matrix and nanoclay of the composites did exist.

## Experimental

### Materials and Sample Fabrication

Araldite GY251 resin (Diglycidylether of bisphenol A, DGEBA) and hardener HY956 (Triethylenetetramine) were used to produce nanoclay/epoxy composites. Organomodified nanoclay (DK4 series, modified with dioctadecyl dimethyl ammonium chloride) was obtained from the Zhejiang FengHong Clay Chemical Co., Ltd China. The mean diameter, density and moisture content of the nanoclay were less than 25nm, 0.25-0.35g/cm<sup>3</sup> and 96-98% respectively.

By using the previous experimental set-up [1], the nanoclay was added into the resin with pre-determined weight content. The nanoclay/resin mixture was placed

on the rotating platform and then put into a bell jar under vacuum for spinning and vacuuming. The hardener was then added into the mixture followed by appropriate spinning procedure for an hour to allow the formation of semi-cured uniformly-dispersed nanoclay/epoxy samples. Finally, all cured samples were taken out from the mold for XPS and TEM analysis.

## Experimental Results and Discussions

### Transmission Electron Microscope (TEM)

TEM can provide direct visualization of the fracture structure morphology. A pristine epoxy and an epoxy with 4%wt. nanoclay samples are shown in Figures 1 and 2 respectively, the pattern of the cracks along the loading direction of the samples is easily observed. The mode I crack opening was created inside the pristine and 4%.wt of nanoclay samples. By comparing with these two samples, the pristine sample had more voids that subsequently may form crack easily once it is subject to a tensile load.

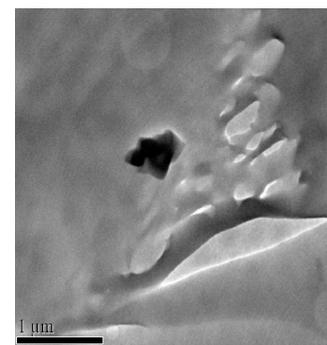
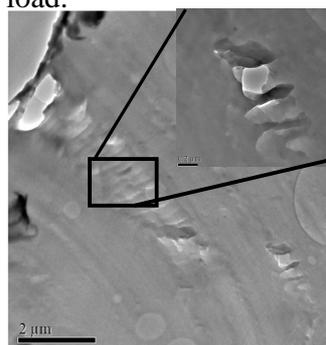


Figure 1 TEM photograph of pristine epoxy      Figure 2 TEM photograph of 4% wt. of nanoclay

For the nanoclay sample, due to the interlocking effect, the addition of the nanoclay can alter the

crack formation mechanism. Meanwhile, a bridging effect due to the good bonding between a nanoclay cluster and surrounding matrix could resist the crack, located near the cluster, opening in the sample. The nanoclay clusters can interlock the polymer chains and eventually form strong barriers to stop crack propagation. High residual stress due to the existence of nanoclay clusters inside the micrometer sized polymer matrix grains would be created at the surface of the nanoclay clusters and polymer matrix interface. According to the Hall-Petch equation, the formation of the boundaries between the nanoclay clusters and polymer matrix can fine the matrix grains and further improve the flexural strength of nanocomposites. At the same time, this effect causes the nanoclay clusters work as dislocations. Therefore, it results in increasing the fracture energy of the nanocomposites and thus to improve its fracture toughness.

#### *X-ray photoelectron spectroscopy (XPS)*

In order to determine whether any chemical bonding existed between the nanoclay and its surrounding matrix, XPS analysis was performed to investigate the peak shift of binding energy in the epoxy, nanoclay and nanoclay/epoxy composites. Table 1 show the binding energy and atomic concentrations of the element identified. The results were retrieved from high energy resolution narrow-scan spectra that were obtained by measuring the strongest signals found in the wide-scan survey spectrum. According to the results, Carbon, Oxygen, Aluminum and Silicon were the significant elements with high energy resolution.

In general, epoxy is mainly composed of Carbon, Nitrogen and Oxygen while MMT contains Oxygen and metallic elements, such as Aluminum and Silicon. The peaks centre of C1s spectrum is at 283.375eV, 284eV and 284.88eV for epoxy, nanoclay/epoxy composite and nanoclay respectively. The binding energy of 283.375eV corresponds to the energy of C1s core level for aromatic ring, whereas the binding energy with peak at 284.88eV was attributed to C-C bonds and identified as originating from amorphous carbon phase or adventitious carbon [2]. At the same time, the binding energy with peak at 284eV was attributed to C-O bonds and identified as amorphous/graphic carbon [3]. As expected, Oxygen in nanoclay was reacted with carbon in epoxy and thus the percentage of concentration in nanoclay was dramatically reduced while the percentage of concentration in nanoclay/epoxy greatly increased. Therefore, it reveals that the Carbon and Oxygen peak shifts are principally due to the chemical bonding between the interfacial of matrix and nanoclay.

	Element	Peak position (eV)	At. Concentration (%)
Epoxy	C 1s	283.375	79.03
	O 1s	532	14.96
	Al 2p	—	0.06
	Si 2p	101	0.61
Nanoclay/epoxy composites	C 1s	284	65.8
	O 1s	530.625	23.56
	Al 2p	73	2
	Si 2p	101.25	5.42
Nanoclay	C 1s	284.88	5.52
	O 1s	531.5	62.71
	Al 2p	74.5	7.23
	Si 2p	102.75	19.52

Table 1 Quantitative XPS analysis of the Epoxy, Nanoclay/epoxy composites and Nanoclay

### Conclusion

The fracture surface of the sample after the test was then investigated morphologically using by TEM. It was found that the addition of nanoclay can bridge up the voids to avoid the formation of crack due to the interlocking effect. Nanoclay clusters with the diameter of 10 nm enhanced the mechanical interlocking inside the composites and thus, breaking up the crack propagation. The formation of boundaries between the nanoclay clusters and epoxy can fine the matrix grains and further improve the flexural strength of the composites. On the other hand, XPS analysis revealed that some carbon atoms were substituted with oxygen atoms by forming C-O bonds, which to some extent explained the lowered carbon content in epoxy and also lower oxygen content in nanoclay/epoxy composite. Meanwhile, the peak shifts of Carbon, Oxygen, Aluminum and Silicon were proved that the chemical bonding at the interface between the matrix and nanoclay did exist.

### Acknowledgement

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### References

1. Chan M.L., Lau K.T., Ho M.P., Cheng A. and Wong T.T, New Equipment and Approaches for Fabrication of Uniformly-Dispersed Nanoclay Cluster/Epoxy Composites. *Polymers and Polymer Composites* .2008; vol 16, 8:471-476
2. Liu Y., Jing X. Pyrolysis and structure of hyperbranched polyborate modified phenolic resin. *Carbon* 2007; 45:1965-1971.
3. Gates C. Bruce, Knözinger H. 1975, *Advances in Catalysis*, New York. p.155.

