

# THE IMPACT OF INTERFACIAL ADHESION ON THE STRAIN-TO-FAILURE OF MONTMORILLONITE/EPOXY NANOCOMPOSITES

Jaehyun Kim, Mickey Richardson, Nandika D'Souza<sup>2</sup>, and Gale A. Holmes\*

National Institute of Standards and Technology, Polymers Division  
Characterization and Methods Development Group  
100 Bureau Drive, Stop 8541  
Gaithersburg, MD 20899-8541  
E-mail: [gale.holmes@nist.gov](mailto:gale.holmes@nist.gov)

<sup>2</sup>University of North Texas  
<sup>2</sup>Department of Materials Science and Engineering  
<sup>2</sup>P. O. Box 305310,  
<sup>2</sup>Denton, TX 76203

\*Corresponding Author

## Introduction

In polymer nanocomposites, many researchers suspect that the weak interface between the host matrix and nanoparticles is responsible for the often observed reduction in the strain-to-failure relative to the pristine host matrix [1]. In 2004, a new test methodology [2] was proposed for observing the onset of clay-matrix debonding in transparent clay based nanocomposites, with the debonding process possibly indicating the onset of failure in these multiphase materials. In this initial research, the strain-to-failure of the nanocomposite with increased adhesion was lower than that of the weak interface nanocomposite. Since both nanocomposites appeared to have an intercalated morphology, these results may be associated with a change in the cure kinetics, and hence, mechanical properties, of the resin at the matrix-nanoparticle interface. To better understand these initial results, the level of matrix-nanoparticle adhesion in this research is manipulated by depositing controlled amounts of bonding and non-bonding groups on the clay surface that should promote exfoliation and adhesion without significantly altering the cure kinetics at the interface.

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## Experimental

Sodium montmorillonite (Na<sup>+</sup> Cloisite) and montmorillonite treated with dimethylbenzyltallow ammonium chloride (Cloisite 10A) were obtained from Southern Clay Products. Octadecylamine (CAS No. 124-30-1) was purchased from Aldrich, 12-aminolauric acid (CAS No. 693-57-2) was purchased from TCI America, and Jeffamine D2000 (CAS No. 9046-10-0) was purchased from Huntsman chemicals. Protonation of the octadecylamine and Jeffamine D2000 was done using reagent grade HCl acid (Mallinckrodt, CAS No. 7647-01-0).

The diglycidyl ether of 1,4-butanediol (CAS No. 2425-79-8, Common name: DGEBD), the diglycidyl ether of bisphenol-A (CAS No. 25068-38-6, common name: DGEBA) and 1,3-phenylenediamine (CAS No. 108-45-2, common name: mPDA) were obtained from Sigma-Aldrich.

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\*\*\* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the product is the best available for the purpose.

## Preparation of C12 and C18-montmorillonite

Both octadecylamine and 12-aminolauric acid were protonated with HCl acid, and then subjected to mixing with suspensions of Na-montmorillonite. The functionalized montmorillonites were recovered by filtration, washed with deionized water, and then freeze dried.

## Preparation of C18/D2000-montmorillonite

A mixture of protonated C18 and Jeffamine D2000 ( $1/3 \cdot \text{Jeffamine D2000} + 2/3 \cdot \text{C18}$ ; molar ratio) was prepared in order to see if any fractional variations of mixed interlayer species will directly affect the adhesion/exfoliation process. A single protonation and double protonation procedure was used in an attempt to ensure that either one end or both ends of the Jeffamine molecule became protonated along with the octadecylamine. These functionalized products were prepared and recovered in a similar fashion as the C12 and C18-montmorillonite samples.

## Preparation of montmorillonite nanocomposites

The clay-nanocomposites were prepared by adding approximately 263 mg of functionalized montmorillonite (5 mass %) to an epoxy mixture containing a blend of DGEBA and DGEBD. The clay/epoxy mixture was stirred and placed in the 70 °C vacuum oven for 3h, and then mixed with melted m-PDA. This clay/epoxy/m-PDA mixture was poured into the preheated silicone rubber mold, and the filled mold was immediately placed into a programmable oven preheated to 70 °C, then cured.

Table1. Description and sample identification of clays used as nanocomposites.

Clay	Organic modifier
Cloisite 10A	Dimethylbenzyltallow
C12-montmorillonite	12-aminolauric acid
C18-montmorillonite	Octadecylamine
C18/D2000-montmorillonite	Jeffamine D2000 + octadecylamine (d. and s. protonated)

## Characterizations and measurements

Tensile tests were carried out on the automated tensile testing machine reported in previous research [2]. Before testing, specimens were polished with emery papers No. 800, 1200 and 2400 to remove stress concentration sites at the edges of the sample. The specimen was loaded in tension by the sequential application of strain-steps. Strains at each step were calculated using the scanned images at each step. Each strain-step was applied to at a rate of 85  $\mu\text{m/s}$  and the delay time between the strain-steps was 10 min. The average deformation in the specimen during each strain-step was 85.7  $\mu\text{m}$ .

## Results and Discussion

Figure 1 shows representative tensile behavior of the neat epoxy and clay nanocomposites with 5 mass % of the clay. The neat epoxy specimen did not fracture until the end of the test, while Cloisite10A and C12 montmorillonite epoxy nanocomposites fractured at the earlier strain step. Compare to the neat epoxy, a little improvement of the stiffness is shown in the clay epoxy nanocomposites at the initial strain-step regions.

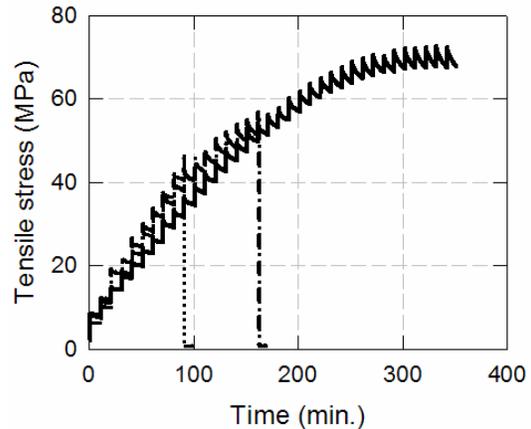


Figure 1. Tensile behavior of the neat epoxy and clay nanocomposites (—: neat epoxy, - - -: Cloisite10A, and ····: C12 montmorillonite nanocomposites).

## Conclusions

Preliminary results showed tensile strengths of Cloisite 10A/epoxy nanocomposites were not improved over that of the neat epoxy due to the

poor interfacial adhesion. Despite the improved interfacial adhesion of C12 montmorillonite epoxy nanocomposites, the tensile properties were not improved and may be associated with poor dispersion of the nanoparticles. The process that nucleates the critical flaws will be investigated in future research

## References

1. M. Alexandre and P. Dubois, *Materials Science & Engineering R-Reports*, **28**, 1 (2000).
2. Jae-Hyun Kim, Gale A. Holmes, and Chad R. Snyder, *Journal of Adhesion Science and Technology*, **20**, 1079 (2006).