

Alkylammonium Functionalized Montmorillonite-Epoxy Composites: Improvements in Mechanical Properties

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ABSTRACT

Organofunctionalized montmorillonite clays (MM) have been prepared with ammonium cations having a distribution of alkyl chain lengths. Relative to clays treated with alkylammonium cations having no distribution of chain lengths, the ultimate tensile stress of the epoxy-based composites increased. Also, depending on the preparation of the functionalized clays, an increase in the strain-to-failure is also noticed. The tensile stress and strain-to-failure of the organofunctionalized clays are compared to neat epoxy. The epoxy matrix chosen consists of diglycidyl ether of bisphenol A (DGEBA), 1,4-butanediol diglycidyl ether (1,4-BDE) and cured with meta-phenylenediamine (m-PDA). All MM composites were prepared using 5 mass % loading of the organomodified clay. The goal of this research was to compare the impact of surface treatment on MM clays that were used in the preparation of epoxy-based composites.

Keywords: montmorillonite clays, organofunctionalized, epoxy, composites, ultimate tensile stress

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INTRODUCTION

Organofunctionalized MM clays have been extensively used as fillers in polymer composites [1,2]. Known for their cation-exchanging abilities, alkylammonium ions have been used for functionalizing MM clays, mainly by the replacement of sodium ions. Alkylammonium ions having long chain alkyl groups can effectively push apart the adjacent aluminosilicate layers to distances that should allow easy access for incoming monomers and curing agents. It has been shown that eventual polymerizing/curing that takes place between separated MM layers results in composites that have well-dispersed clay layers [3,4]. Improvements in the mechanical properties of well dispersed clay composites can thus be expected to occur.

In this report, we demonstrate that one of the main factors for clay dispersion and mechanical property enhancement comes not by using long chain alkylammonium ions, but by using a mixed alkylammonium ion system consisting of long alkyl chains and short alkyl chains. We also report on the influence of a processing step used during the functionalization of the MM. Alkylammonium treated MM washed with water and with an ethanol/water mixture results in differences in dispersion and in the mechanical properties for a few of the samples to be discussed.

EXPERIMENTAL

MM Functionalization/ Epoxy Blending

The starting material was Na^+ Cloisite (Southern Clay Products; 92 mequiv/100 g), which was used with no pre-treatment before organofunctionalization. Cloisite 10A (Southern Clay Products) was used as a reference organomodified MM. The alkylammonium ions of interest are octadecylammonium (C18), hexylammonium (C6), propylammonium (C3), and two vendor-supplied alkylammonium salts; Maquat (BTMC-85; Mason Chemical Company) and Arquad (DMHTB-80E; Azko Nobel) [5].

Organomodified MM containing mixtures of protonated alkylamines were prepared by mixing a 2/3 : 1/3 molar ratio of C18/C6 and C18/C3 (0.024 mmol, total alkylammonium), to aqueous dispersions containing 10 g Na^+ Cloisite. C18 modified MM was prepared by mixing 0.024 mmol of protonated C18 to a 10 g dispersion of Na^+ Cloisite. Arquad and Maquat modified MM were prepared by mixing aqueous solutions of each salt (0.024 mmol) with 10 g dispersions of Na^+ Cloisite.

The exchanged MM were then subjected to Büchner filtration, and washed with either warm deionized water (18 MΩ-cm), or with a 50:50 (v/v) ethanol : warm deionized water mixture. Due to the ability of the alkylammoniums to behave as surfactants, more foaming was observed during the ethanol-water wash than in water alone. Knowing that a large excess amount of alkylammonium was used for sodium exchange, the increased solubility of the alkylammoniums in the ethanol-water mixture results in a significant reduction of excess alkylammoniums in the treated clays.

Epoxy Blending/Mechanical Testing

The organomodified MM clays were mechanically stirred into a mixture of epoxies containing DGEBA and 1,4-BDE for 1 h, at room temperature. The blended mixtures were then subjected to degassing at 70 °C for 2 h. After degassing, melted m-PDA (70 °C) was blended into the mixture and dog bone shaped specimens were prepared using silicone rubber molds. Per dog bone sample, the mass percentage of the two epoxies and curing agent are: DGEBA, 67 %; 1,4-BDE, 20 %; m-PDA, 13 % The curing profile used was 60 °C for 3 h and 121 °C for 2 h.

Each dog bone sample was polished using #1200 and #2400 emery paper. We attempted to achieve an average thickness and average width of each dog bone section to be approximately (1.55 ± 0.04) mm by (4.05 ± 0.04) mm. To aid in the strain-to-failure calculations, two transverse fiducial marks were placed with a green permanent marker, 10 mm apart.

Each specimen was then loaded in tension by the sequential application of step-strains. Each step-strain was applied at a rate of 85 μm/s and the average deformation in the specimen during each step-strain was 85.7 μm. The delay time between the applications of successive step-strains was 10 min. Images were scanned using a movable camera, and automatically saved after every step-strain.

RESULTS

All but two of the organomodified MM easily blended into the DGEBA/1,4-BDE mixture. These two samples were the MM-Maquat and the ethanol-water washed MM-C18. Successful blending, by our standards, is described by the absence of settled material at the bottom of the epoxy blend after the 2 h degassing step.

After curing, most of the dog bone samples did not have any noticeable aggregates in them, except for the two materials described above, plus the water washed MM-C18. The water washed MM-C18 blended well during the mixing and degassing steps, but had noticeable aggregates in the dog bone samples, which occurred during the curing cycle.

Figure 1 shows the stress-strain curves for several of the composite samples, with respect to neat epoxy. According to this figure, the composite having the largest tensile stress was the MM-(C18+C3), and the composite having the longest strain was Cloisite 10A. The composites having the lowest stress and strain values were the ones having only one type of alkylammonium ion, independent of alkyl chain length.

Figure 2 shows the stress-strain curves for several of the water and ethanol-water washed samples, with respect to neat epoxy. This figure shows a significant improvement in strain for the MM-(C18+C6) samples, based on washing with ethanol-water. In contrast to this improvement, the MM-(C18) samples decreased in strain (and tensile stress) when washed with the alcoholic mixture. There are no significant differences in the MM-(C18+C3) samples (shown) and in the Cloisite 10A samples (not shown). The expected standard uncertainty has been calculated to be 1 % of the values reported for the tensile strength measurements.

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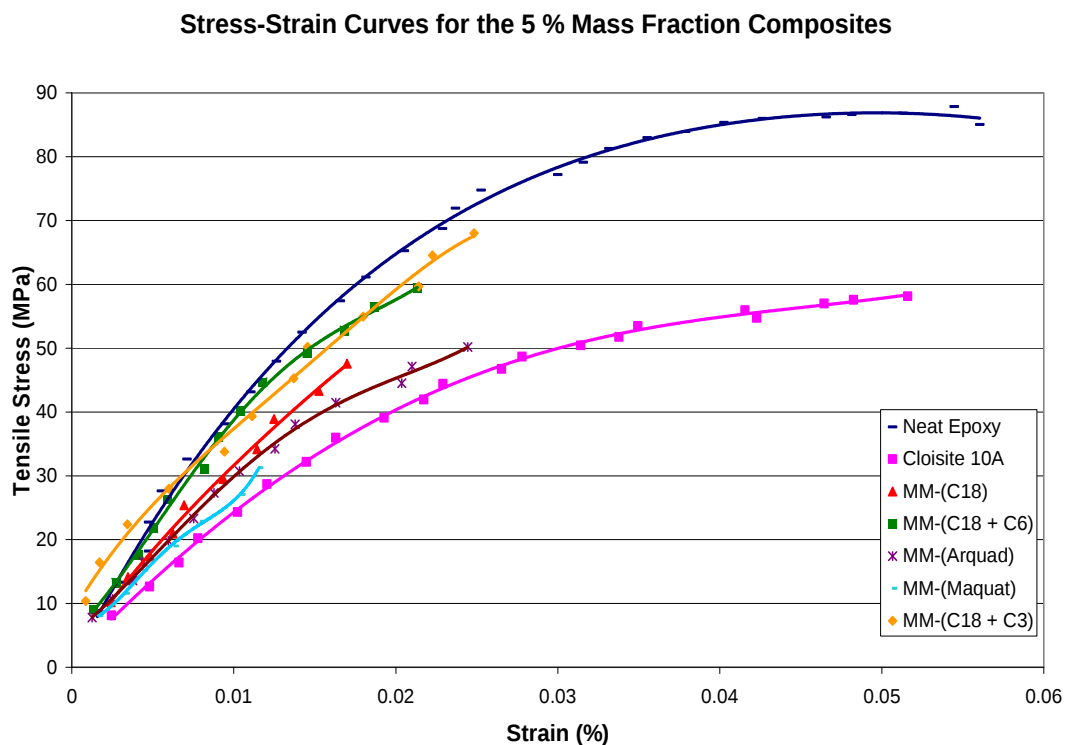


Figure 1. Stress-strain Curves for the Water Washed Organomodified MM/epoxy Samples (standard uncertainty ± 1 %).

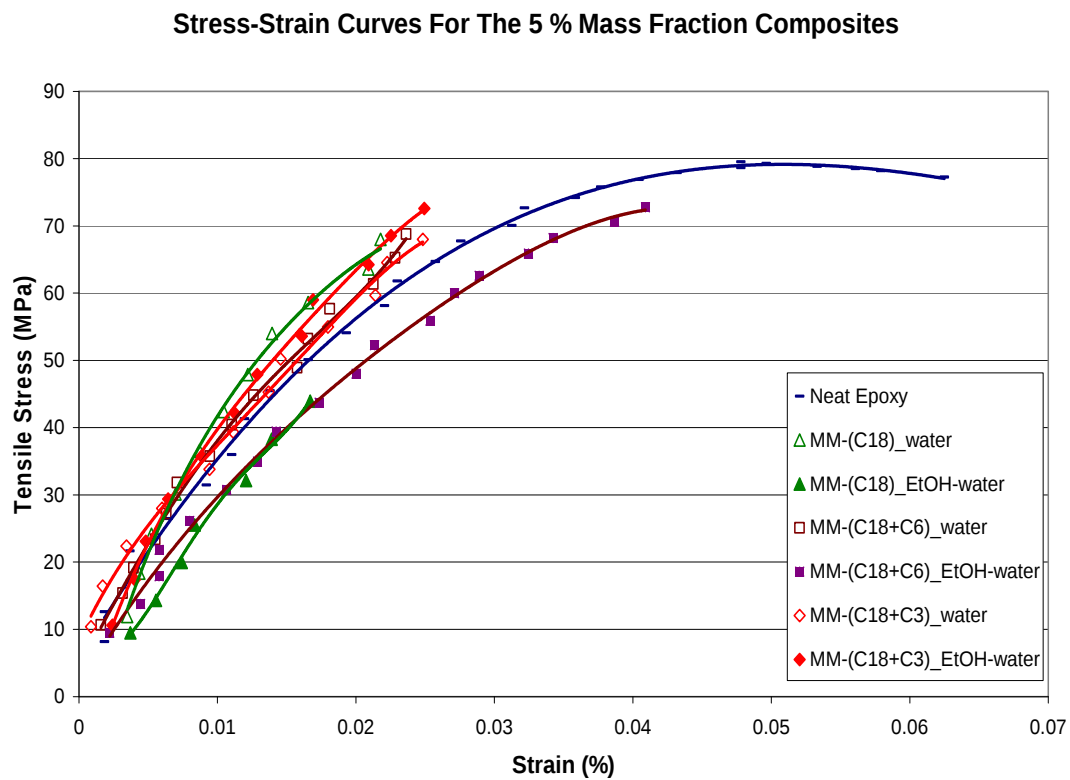


Figure 2. Stress-strain Curves for Selected Water and Ethanol-water washed Organomodified MM/epoxy Samples (standard uncertainty $\pm 1\%$).

REFERENCES

- [1]. Y. H. Lee; C. B. Park; M. Sain; M. Kontopoulou; W. Zheng, *Journal of Applied Polymer Science*, 105, 1993 (2007).
- [2]. S. Xue; T. J. Pinnavaia, *Microporous and Mesoporous Materials*, 107, 134 (2008).
- [3]. T. Lan; P. D. Kaviratna; T. J. Pinnavaia, *Chemistry of Materials*, 7, 2144 (1995).
- [4]. P. B. Messersmith; E. P. Giannelis, *Chemistry of Materials*, 6, 1719 (1994).
- [5]. Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.