

Intercalation pathways and mechanical properties of epoxy-clay nanocomposites

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Intercalation pathways between galleries impact the strain at failure of epoxy-clay hybrid nanocomposites.

Since the research of Anna Balazs and her team,¹ compatibility between organically modified clay and the host matrix has been the starting point for preparation of exfoliated clay-hybrid nanocomposites. Another important factor in nanocomposite preparation is the initial d_{001} spacing (a measure of the distance between planes of atoms) of the organically modified clay.² Recently, we investigated the mechanical properties of several epoxy-clay-hybrid (ECH) nanocomposites with primary focus on the impact of the organic modifier on the strain at failure (ε_f) of the resulting nanocomposite.³

For the ECH nanocomposites under investigation, we chose four single alkyl-chain ammonium salts. Their structure should have similar compatibility with the host epoxy matrix (see Figure 1), since it is generally accepted that the long alkyl chain dominates the compatibility of the treated clay with the host matrix.⁴ These treated clays also exhibited very different d_{001} spacings. To minimize the impact of increasing viscosity when adding the treated clays, we used an epoxy blend consisting of the diglycidyl ether of bisphenol-A (DGEBA) and a reactive diluent, the diglycidyl ether of 1,4-butanediol (DGEBD). The theoretical solubility parameters (a compatibility metric) of DGEBA and DGEBD are 9.7 and 9.9(cal/cm³)^{1/2}, respectively.

Montmorillonite (MM) clay treated with C₂₂-alkyl-chain trimethyl ammonium salt exhibited the largest d_{001} spacing (46.4Å). However, the nominal $\varepsilon_{\rm f}$ of the resulting nanocomposite is only 1.2%. Similarly, MM clay treated with the C₁₈-alkyl-chain ammonium salt (C₁₈-MM), whose dominant d_{001} spacing is 17.2Å, yielded a nanocomposite whose $\varepsilon_{\rm f}$ was only slightly better at 1.3%. For the bimodal distribution designated (C₁₈+C₆)-MM, the $\varepsilon_{\rm f}$ of the nanocomposite increases to 2.1% by replacement of one third of the molar amount of C₁₈-alkyl-chain ammonium salt with a C₆-alkyl-chain ammonium salt. Inclusion of the latter results in a decrease in the d_{001}



Figure 1. Alkyl ammonium salts used to treat montmorillonite (MM) clay with subsequent d₀₀₁ spacings. 3MeC22: Trimethyl-C₂₂. Cl⁻: Chloride ion. BTMC: Biphenyl trimethyl ammonium (85% active). 2MeBHT, DMHTB: Dimethyl benzyl hydrogenated tallow ammonium salt.

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Figure 2. 2D paraffin representation of C_{18} -MM clay, showing the ability of the iglycidyl ether of bisphenol-A (DGEBA), the diglycidyl ether of 1,4-butanediol (DGEBD), and meta-phenylene diamine (m-PDA) curing agent to interpenetrate the clay gallery.



Figure 3. 2D paraffin representation of $(C_{18}+C_6)$ -MM clay, showing the ability of DGEBA, DGEBD, and m-PDA curing agent to interpenetrate the clay gallery.

spacing to 15.0Å. The best results with respect to $\varepsilon_{\rm f}$, however, were obtained for MM clay treated with dimethyl benzyl hydrogenated tallow ammonium salt (2MeBHT). The commercial version, known as Cloisite 10A (Southern Clay), and the laboratory version, obtained by treating MM with Arquad DMHTB-80E (Akzo Nobel), yielded $\varepsilon_{\rm f}$ values of 4.1 and 2.7%, respectively.



Figure 4. 2D paraffin representation of 2MeBHT-MM clay, showing the ability of DGEBA, DGEBD, and m-PDA curing agent to interpenetrate the clay gallery.

On the basis of supporting information from differential-scanning calorimetry (DSC) studies of the organically modified clays, we hypothesize that including the C₆-alkyl-chain ammonium salt in (C₁₈+C₆)-MM creates intercalation pathways for the epoxy-resin blend. For the 2MeBHT ammonium salt, the benzyl group on the Arquad ammonium salt probably creates more systematic intercalation pathways for the epoxy blend to penetrate. DSC shows that this salt is in the molten state at the initial cure temperature of 60°C, which may also facilitate intercalation between the platelets by epoxy- and curing-agent molecules for this system.

In terms of intercalation pathways, the differences between the systems can be understood by assuming that the ammonium salts deposit on the clay surface by forming paraffin-type monolayers.⁵ Figures 2, 3, and 4 show 2D representations for C_{18} -MM, (C_{18} +C₆)-MM, and 2MeBHT-MM, respectively. With C_{18} -MM, the components of the epoxy blend cannot readily penetrate between the gallery spacings, while with (C_{18} +C₆)-MM and 2MeBHT-MM, intercalation pathways are available to facilitate penetration. In 2MeBHT-MM, they are probably more evenly distributed.

We previously reported that 2MeBHT-MM darkens uniformly above a critical strain of $\sim 1.2\%$.⁶ This darkening has been associated with debonding of the matrix from the clay platelets. Our current study indicates that some darkening is also observed in (C₁₈+C₆)-MM. However, we also found that matrix cracks, presumably resulting from organically modified clay platelets that have not been uniformly



intercalated with epoxy resin, may control the observed low values of $\varepsilon_{\rm f}$.

Although the stress-strain curves of all nanocomposites were lower than that of the neat epoxy resin, the stress-strain curve of 2MeBHT-MM is the lowest. At first glance, this suggests a potential reduction in the glass-transition temperature and crosslink density of the cured epoxy-resin blend. This would be surprising, since the 2MeBHT surfactant is a tetra-alkyl ammonium salt and should have less impact on the cure kinetics of the epoxy resin than the C_{18} and C_6 ammonium salts used in this study. We are continuing our research on these systems. During the cure cycles, the initially transparent epoxyresin blends also become less transparent, indicating some level of re-aggregation of the clay platelets. We are investigating the impact of the re-aggregation process on the morphology of the clay in the cured epoxy-resin systems.

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References

- 1. A. C. Balazs, C. Singh, and E. Zhulina, Modeling the interactions between polymers and clay surfaces through self-consistent field theory, Macromol. 31, p. 8370, 1998.
- T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites, Chem. Mater. 7, p. 2144, 1995.
- M. C. Richardson, J. H. Kim, D. Ho, C. R. Snyder, N. A. D'Souza, and G. A. Holmes, Organo-functionalized montmorillonite/epoxy nanocomposites: the effect of interlayer cation distribution on mechanical properties, Polym. Compos., 2010. doi:10.1002/pc.21019
- D. L. Ho and C. J. Glinka, Effects of solvent solubility parameters on organoclay dispersions, Chem. Mater. 15, p. 1309, 2003.
- G. Lagaly, Interaction of alkylamines with different types of layered compounds, Sol. State Ion. 22, p. 43, 1986.
- J. H. Kim, G. A. Holmes, and C. R. Snyder, A methodology for detecting interfacial debonding in clay/epoxy nanocomposites, J. Adhes. Sci. Technol. 20, p. 1079, 2006.