Alkyl-Imidazolium Salts and Their Applications in Polymer Clay Nanocomposites

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Polymer melt intercalation is a promising approach to synthesize polymer-layered silicate nanocomposites using conventional polymer processing techniques.[1] In this process the layered silicate is mixed with a molten polymer matrix. If the silicate surfaces are sufficiently compatible with the chosen polymer, then the polymer can enter the interlayer space and form either an intercalated or an exfoliated nanocomposite. Crucial to the exfoliation process is the pre-intercalation of the sheet-silicate before melt-blending with the molten polymer. This pre-intercalation can be viewed as a surfactant type of modification of the clay surfaces, allowing them to be funtionalized to enhance their compatibility with the chosen polymer, and thus exfoliated throughout the polymer. Exfoliation, or a high level of intercalation is important in producing the enhanced physical and mechanical properties of polymer/clay nanocomposites, as it is only with such separation of individual clay sheets that high aspect ratios are obtained with the inorganic reinforcing materials.[2]

One of the important properties of the intercalant-surfacant is its thermal stability, since melt blending of polymers often requires temperatures in excess of 250 ^{o}C. If the intercalant-surfactant decomposes during the melt blending process, then exfoliation of the clay nano-composite does not occur, and there is no enhancement of the physical and mechanical properties of the polymer. Most commonly, substituted ammonium cations are used in exchange reactions with the Na sites of the various types of sheet silicates studied.[3] Unfortunately, these substituted ammonium cations are not sufficiently thermally stable to allow for melt blending with the many types of engineering polymers.[4] Therefore, our research has shifted to the use of the more thermally stable substituted imidazolium cations, which are similar to those used for various types of ionic liquids.[4]

These imidazolium cations are substituted with various types of alkyl chains, ranging in length from propyl to eicosyl, as well as branched alkyl substituents, benzyl-type substituents and ether-like substituents. Also important to the overall thermal stability of the intercalant is the type of counter anion chosen. Halogens have proven to be extremely detrimental to the thermal stability of the intercalate, while flouorinated anions, such as BF_4^- and PF_6^- have resulted in intercalates with high thermal stability.[5] Presented here will be a review of the synthetic aspects of this work, as well as the thermal stability and structural characteristics of the intercalates, and their effects on several different types of polymer/clay nanocomposites. Figures 1 and 2 show the structural aspects of a melt-blended poly(ethylene terephthalate) PET and montmorillonite (MMT) intercalated with 1,2-dimethyl-3-n-hexadecylimidazolium, which is thermally stable at PET processing conditions.

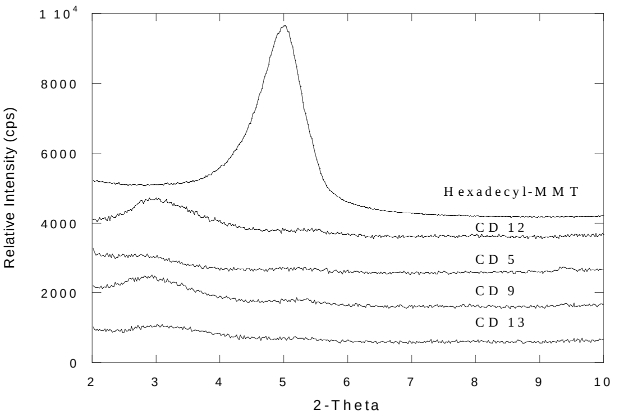

Figure 1. XRD spectra of the nanocomposites shows a shift in the major peak of hexadecyl-MMT from 4.8° 2θ to a weaker, broader peak ranging from 2.8° to 3.2 ° 2θ. Note that XRD spectra of PET-nanocomposites CD 5 and CD 13 contained no major peaks due to complete exfoliation of the clay.[6]

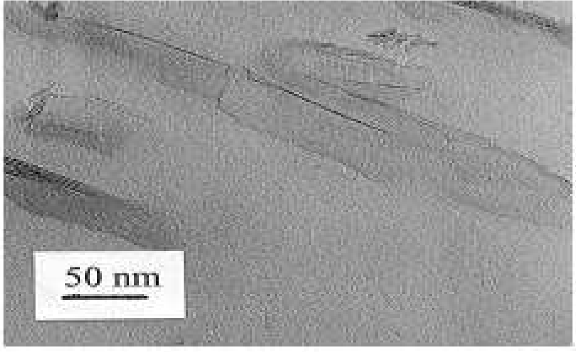

Figure 2. TEM images of CD 12 showing high levels of dispersion and exfoliation, average tactoids of 4 sheets, and no micron sized particles.[6]

References

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