

The Use of 1,2-Dimethyl-3-(benzyl ethyl iso-butyl POSS)imidazolium Chloride as an Organic Modifier in Polymer – Layered Silicate Nanocomposites

D. M. Fox¹, P. H. Maupin², S. Bellayer³, M. Murariu³, J. W. Gilman³, P. C. Trulove⁴, and H. C. De Long⁴

¹Naval Research Laboratory
Chemistry Division, Washington DC, 20375

²U. S. Department of Energy
Office of Sciences, Division of Chemical Science, Washington
DC, 20585

³National Institute of Standards and Technology
Fire Sciences Division, Gaithersburg MD, 20899

⁴Air Force Office of Scientific Research
Directorate of Chemistry and Life Sciences,
Arlington, VA, 22203

INTRODUCTION

Polymer – layered silicate nanocomposites (PLSNs) are attractive due to their enhanced thermal stability, and improved flame retardant, mechanical, and barrier properties.¹ The use of imidazolium based room-temperature ionic liquids (RTILs) as organic modifiers for polymer – layered silicate nanocomposites (PLSNs) has gained significant attention, because they exhibit superior processing characteristics over the conventional surfactants, quaternary ammonium and phosphonium salts.² In this work, we investigated the use and impact of 1,2-dimethyl-3-(benzyl ethyl iso-butyl POSS)imidazolium chloride (DMIPOSS) as the organic modifier on the preparation of PLSNs. We also evaluated the use of Nile Blue as a fluorescing agent to monitor the extent of intercalation and exfoliation in the PLSNs. The improved thermal stability of the PLSNs was measured using thermal gravimetric analysis (TGA).

EXPERIMENTAL

The DMIPOSS was prepared by reacting 1,2-dimethylimidazole and chlorobenzylethylisobutyl-POSS in THF. The organically modified silicates were prepared by cation exchange between DMIPOSS and sodium montmorillonite (NaMMT) in an ethanol-water solution. For the fluorescent clays, the appropriate ratios of Nile Blue A Perchlorate and DMIPOSS were completely dissolved in the ethanol-water solution prior to adding the NaMMT. PLSNs were prepared using a D.A.C.A. twin-screw extruder at 10-20°C above the polymer melting points.

The extent of intercalation and/or exfoliation was determined using powder x-ray diffraction (XRD), transmission electron microscopy (TEM), laser-induced confocal microscopy (LICM), and laser-induced fluorescence spectroscopy (LIFS). PLSNs prepared using montmorillonite (MMT) modified with DMIPOSS and blended with polystyrene (PS), polyamide-6 (PA-6), and the co-polymer poly(ethylene vinyl acetate) (EVA). Finally, the effects of partial loading of DMIPOSS into the clay galleries on the PA-6 nanocomposites properties were examined.

RESULTS AND DISCUSSION

The organically modified clays using DMIPOSS exhibit higher thermal stabilities than the clays using conventional surfactants and simple alkyl chain imidazolium salts. Although the use of DMIPOSS increases the clay gallery spacing and improves the thermal stability of the modified clay, the clay fails to exfoliate when melt blended with PS, EVA, or PA-6. This leads to a lesser improvement in polymer thermal stability when compared to PLSNs prepared using 1-hexadecyl-2,3-dimethylimidazolium modified clay (DMHdI-MMT) or N,N-dimethyl-N,N-diocetadecylammonium modified clay (DMDOdAmm-MMT). There is evidence that the POSS-MMT or POSS-POSS

interactions are strong enough to prevent complete exfoliation. (cf Figure 1) To further investigate, we prepared several partially exchanged clays by adding 5%, 20%, and 40% DMIPOSS of the total cation exchange capacity (CEC). To more readily measure the extent of intercalation or exfoliation once the PLSNs were prepared, 5% (CEC basis) Nile Blue was added to the DMIPOSS-MMT mixtures.³ Preliminary studies have suggested that a lower loading of DMIPOSS does improve the exfoliation of the clays in the prepared PLSNs. The thermal stability data of the clays and PLSNs will be presented and the extent of intercalation and exfoliation will be discussed.

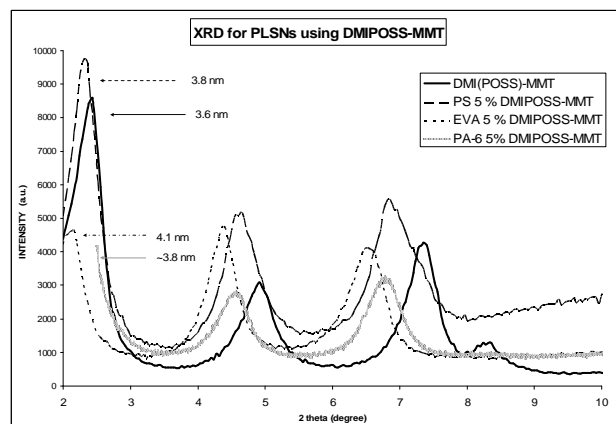


Fig 1. XRD for PLSNs using 5% DMIPOSS-MMT indicating intercalation rather than exfoliation

ACKNOWLEDGEMENTS

The policy of the National Institute of Standards and Technology (NIST) is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements. The identification of any commercial product or trade name does not imply endorsement or recommendation by NIST or the United States Air Force (USAF). Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the USAF or NIST.

REFERENCES

1. Alexandre, M; Dubois, P. *Mater. Sci. Eng. R: Rep.*, **28**, 1, (2000).
2. W. H. Awad, J. W. Gilman, M. Nyden, R. H. Harris, Jr., T. E. Sutto, J. H. Callahan, P. C. Trulove, H. C. De Long, and D. M. Fox, *Thermochim. Acta*, **409**, 3 (2004).
3. P. H. Maupin, J. W. Gilman, R. H. Harris, Jr., S. Bellayer, A. J. Bur, S. C. Roth, M. Murariu, A. B. Morgan, J. D. Harris, *Macromol. Rapid Comm.*, **25**, 788, (2004).