POLYMER LAYERED SILICATE NANOCOMPOSITES: THERMAL STABILITY OF ORGANIC CATIONIC TREATMENTS

by

Jeffrey W. Gilman, Alexander B. Morgan, Richard H. Harris, Jr.
Fire Science Division, Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899

Paul C. Trulove
Air Force Office of Scientific Research
Arlington, VA 22203

Hugh C. De Long
Chemistry Department, U.S. Naval Academy
Annapolis, MD 21402

Thomas E. Sutto
Naval Research Laboratory, Chemistry Division
Washington, DC 20603

Reprinted from Polymeric Materials Science & Engineering (ACS), Vol. 83, 59 2000.

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

POLYMER LAYERED SILICATE NANOCOMPOSITES: THERMAL STABILITY OF ORGANIC CATIONIC TREATMENTS

Jeffrey W. Gilman[1], Alexander B. Morgan[1], Richard H. Harris Jr.[1], Paul C. Trulove[2], Hugh C. De Long[3] and Thomas E. Sutto[4]

[1] Fire Science Division, Building and Fire Research Laboratory
National Institute of Standards and Technology[1], Gaithersburg, MD 20899
[2]Air Force Office of Scientific Research, Arlington, VA, 22203
[3]Chemistry Department, U.S. Naval Academy, Annapolis, MD, 21402
[4]Naval Research Laboratory, Chemistry Division, Washington, DC, 20603

Introduction

Nanocomposites result from the combination of materials with vastly different properties at the nanometer scale. Some examples of these include: polymers combined with layered-silicate[1], polymers combined with nano-silica[2,3], hybrid materials prepared by sol-gel methods[4], and POSS nanocomposites[5]. All these materials exhibit many unique properties, such as improved thermal stability, reduced flammability, improved mechanical properties, etc. However, for successful preparation of nanocomposites, and for their subsequent incorporation into end-products, nanocomposites must maintain their unique chemical and physical properties during processing. We report here on our recent results, which show improved thermal stability (140 °C higher) for new organic cationic treatments used to compatibilize layered-silicates with polymers and monomers. This work was motivated by concern about processing degradation, which we observed in polymer/montmorillonite (MMT) nanocomposites.

Experimental

The polystyrene used here was Dow Styron 663[4] (M_w 290,000)[6]. The preparation of polystyrene /montmorillonite (MMT) samples was done via extrusion in a twin-screw extruder (25 mm) at 205 °C. Polyamide-6/MMT nanocomposites were obtained from Ube America, New York, NY; and Southern Clay Products Inc., Gonzales, TX. Ethyl methyl imidazolium BF_4 salt (EMIM$^+$ BF_4^-) was prepared according to a literature procedure[7]. EMIM-MMT was prepared using standard ion exchange methods[8]. EMIM$^+$ BF_4^- (1.7 ml, 1.1 mmol, 1.2 equivalent was added to a suspension of sodium MMT (NaMMT,10 g, cation exchange capacity(CEC) 0.90 mmol/g, Cloisite Na^+, Southern Clay Products) in water (100 mL) at room temperature. The resulting precipitate was collected and washed in a Soxhlett extractor, using ethanol, overnight to remove excess EMIM salts. EMIM-MMT was dried at 90 °C for 1 h and at 150 °C for 2 h. X-ray diffraction (XRD) data were collected on a Phillips diffractometer using Cu Kα radiation, (λ=0.1505945 nm) at ambient temperatures with a 0.02 2q step size and a 2 s count time. Thermal gravimetric analysis (TGA) data were collected from 30 °C to 700 °C at 10 °C/min under N_2 using a TA Instruments SDT 2960. Each sample was run in triplicate. M_w data from gel permeation chromatography (GPC) was calibrated with PS M_w standards.

Results and Discussion

The onset of thermal decomposition (T_{dec}) of the organic modification associated with a layered-silicate sets the upper limit on the processing temperature for preparing polymer layered-silicate nanocomposites, and for additional processing (injection or compression molding, etc.) of the nanocomposite. We have observed degradation during processing of both PS/MMT[9] and PA-6/MMT nanocomposites[10].

The extrusion of PS with a quaternary ammonium modified MMT (AMMT), in a twin-screw extruder at 205 °C, results in a nanocomposite with both exfoliated individual MMT layers and intercalated MMT tactoids[11]. However, as the GPC data in Figure 1 shows, the molecular weight (M_w) of the PS is degraded under these processing conditions. Furthermore, as the amount of AMMT is increased from 2 % to 5 % the extent of M_w degradation increases. The effect levels off between 5 % and 10 % loading of AMMT. A previous TGA-FTIR study also shows evidence for aliphatic decomposition products, in addition to styrene, from the PS/AMMT samples[12].

Finally, since the M_w degradation does not occur when pure polymer is extruded, or if the PS is extruded with NaMMT, it appears that the presence of the quaternary ammonium in the MMT is responsible for this phenomenon. This degradation is of particular concern in our efforts to reduce the flammability of PS, since this effect must work in opposition to the flame retardant effect of nano-dispersed MMT[12]. In addition, this could also limit the improvements in other physical properties observed for PS/MMT nanocomposites.

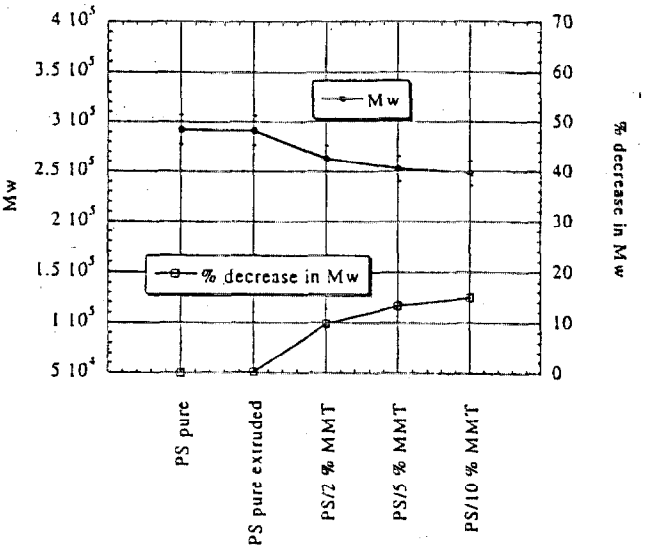

Figure 1. GPC data for PS/AMMT nanocomposites. Significant loss of M_w is evident at all concentrations of AMMT. Standard uncertainty in the M_w data is shown as an error bar in the plot.

Although, it has been suggested that processing stabilizers might be used here to minimize the processing degradation, Krishnamoorti and co-workers have found that this is not very effective[13]. Processing at lower temperature can avoid this problem, but may not be feasible for rapid manufacturing.

We have also observed processing degradation in PA-6/MMT nanocomposites[10]. In a PA-6/MMT nanocomposite prepared by *in situ* polymerization of caprolactam in the presence of alkyl-ammonium modified MMT, we found (by NMR) the stability of the γ-crystal phase of PA-6 in the nanocomposite is severely lowered when the PA-6/MMT was injection molded at 295 °C. In a PA-6/MMT nanocomposite, prepared by melt blending PA-6 with quaternary alkyl-ammonium modified MMT (AMMT) at 225 °C in a twin screw extruder, we found evidence (by NMR) of the thermal degradation products from quaternary alkyl-ammonium. To facilitate rapid manufacturing, industrial processing temperatures of PA-6 are in excess of 300 °C[14]. Therefore, processing stability at these temperatures is imperative if PA-6/MMT nanocomposites are going to find real world use.

The elimination of α-olefins, following the Hofmann rule, is the primary mechanism of thermal degradation of alkyl ammonium compounds[15]. A typical T_{dec} reported for alkyl ammonium treated MMT is 200 °C[16]. The processing conditions discussed above are over 200 °C, and so it is reasonable to expect that degradation of the AMMT will occur while processing the nanocomposites as described above.

To improve the thermal stability of cationic treatments used to compatibilize layered-silicates (and other anionic nano-materials) we have prepared and evaluated alkyl imidazolium exchanged MMT. Ethyl methyl imidazolium BF_4 salt (1 in Figure 2, (EMIM$^+$ BF_4^-) contains a

delocalized cation; it is a room temperature liquid, and is soluble in water and polar organic solvents[17].

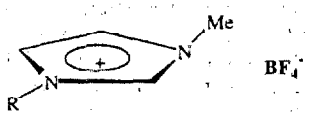

Figure 2. Ethyl methyl imidazolium tetrafluoro borate, 1, R= ethyl.

Ion exchange of the $EMIM^+$ for Na^+ in MMT yielded EMIM-MMT. XRD analysis of EMIM-MMT (Figure 3) shows a d-spacing of 1.24 nm. This is a 0.14 nm increase in layer spacing, and corresponds to the thickness of the plainer EMIM cation intercalated in the gallery in the horizontal geometry. Figure 4 shows the comparison of the thermal stabilities (in N_2) of AMMT and EMIM-MMT. The T_{dec} of EMIM-MMT is 140 °C *higher* than the T_{dec} for AMMT, and the peak T_{dec} (dTGA) is 175 °C *higher* for EMIM-MMT than that for AMMT. This significantly improves the processing window for polymer/layered-silicate nanocomposites.

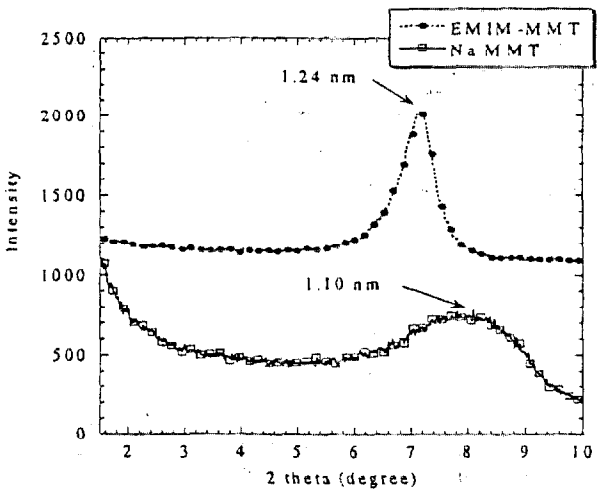

Figure 3. XRD plots for Na-MMT and EMIM-MMT.

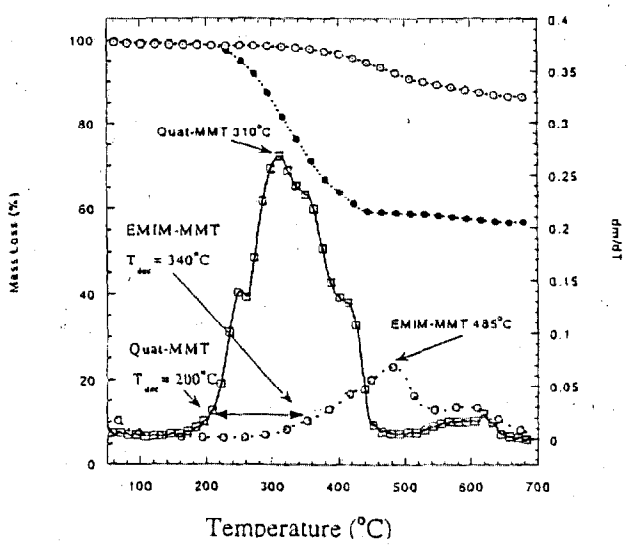

Figure 4. TGA (in N_2) and derivative TGA (dTGA) of AMMT and EMIM-MMT. Standard deviation for AMMT peak dm/dt is 0.45 °C, and for EMIM MMT peak dm/dt is 0.98 °C

Conclusions

The EMIM modified MMT is stable at high temperat should allow standard processing of PS (>200 °C), PA-6 (> 30 other polymers with high T_{melt} with organic-modified MMT nanocomposites without processing degradation. Standard N- synthetic methods can be used to readily prepare long-ch substituted imidazolium salts, and this will allow tunin imidazolium treatment to compatibize it with monomers and pol the preparation of polymer layered-silicates with improved p stability and potentially better properties[18].

Acknowledgement

We would like to thank the Flammability of Polyr Nanocomposites Consortium and the Air Force Office of Research for funding.

References

(†) This work was carried out by the National Institute of Stan Technology (NIST), an agency of the U. S. government statute is not subject to copyright in the United States.

(1) Giannelis, E., *Advanced Materials* **1996**, *8*, 29.

(2) Barthet, C., Hickey, A. J., Cairns, D. B., and Armes, S. *Mater.* **1999**, *11*, 408.

(3) Tsagaropoulos, G. and Eisenberg, A., *Macromolecules* 1 396.

(4) Novak, B.M., *Adv. Mater.* **1993**, *5*, 422.

(5) Lichtenhan, J., Schawb, J. *Polymer Preprints*, 2000, *41 (1)*,

(‡) Certain commercial equipment, instruments, materials, ser companies are identified in this paper in order to specify ad the experimental procedure. This in no way implies endors recommendation by NIST.

(6) According to ISO 31-8, the term "Molecular Weight" replaced by "Relative Molecular Mass", symbol M_r. Thu nomenclature and notation were used here, $M_{r,n}$ insteac historically conventional M_n for the average molecular weig similar notation for M_w, M_z, M_v) would be used. It would the "Number Average Relative Molecular Mass". The con notation, rather than the ISO notation, has been employed he

(7) Wilkes, J.S. Levisky, J.A. Wilson, R.A. Hussey, C.L. *Inorg* **1982**, 21, 1263.

(8) Vaia, R.A.; Teukolsky, R. K.; Giannelis, E. P. *Chem. Mate* 6, 1017.

(9) Gilman, J. "Flammability of Polymer Clay Nanocor Consortium: Year One Report" April, 2000, NISTIR in pres

(10) VanderHart, D. L. Gilman, J. W. Hunter, D. L. Ats manuscript in preparation.

(11) Gilman J. W., Jackson, C. L. Morgan, A. B. Harris, R. Jr., E. Giannelis, E. P. Wuthenow, M. Hilton, D. Phillips, S. S *Chem. Mater.*

(12) Gilman, J.W., *Applied Clay Sci.* **1999**, *15*, 31.

(13) R. Krishnamorti, personal communication.

(14) Hughes, K., Bohan, J., Jay, T., and Prins, A. *Proceeding o Retardants Chemical Assoc. Meeting, March*, 2000, *85-89*.

(15) Saunders, W. H., Jr. in Ionic Aliphatic Reactions, Prent Englewood Cliffs, N. J.,1965, pp. 67-68.

(16) Xie, W., Gao, Z., Pan, W-P, Vaia, R., Hunter, D. and Si *PMSE Polymer Preprint*, 2000, 284.

(17) Carlin, R. T. and Wilkes, J. S. in Chemistry of Non Solvents, A. Popov and G. Mamantov, Editors, Chapter Publishers, New York (1994).

(18) A similar approach using N-alkyl pyridinium modified silicates appears in: Takekoshi, T., Khouri, F., Campbell, J. T. and Dai, K. US Patent 5,707,439 (to General Electric) 199