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IMPROVED THERMAL STABILITY OF ORGANICALLY MODIFIED LAYERED SILICATES

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Abstract—Bromide-containing impurities were found to decrease the thermal stability of quaternary alkyl ammonium-modified layered silicates. Improved purification procedures completely removed bromide and led to a 20ºC to >100ºC increase in organic modified layered silicate thermal stability. Using mass spectrometry and thermal and electrochemical analysis, N,N-dimethyl-N,N-dioctadecyl quaternary ammonium-modified montmorillonite and fluorinated synthetic mica were found to degrade primarily through elimination and nucleophilic attack by these anions. The nature of residual bromides was identified and quantified, and the efficiency of removing these anions was found to be solvent dependent; sequential extraction, first ethanol then tetrahydrofuran, gave the best results. This exhaustive extraction method represents a viable alternative to the use of expensive, more thermally stable oniumion treatments for layered silicates.

Key Words—Alkyl Ammonium, Montmorillonite, Nanocomposites, Organic Modifier Degradation, Organoclay, Synthetic Mica.

INTRODUCTION

Several researchers have recently begun to investigate the thermal degradation of the organic components in polymer-layered silicate nanocomposites and organically modified layered silicates (*e.g.* Davis *et al.*, 2003; Gilman *et al.*, 2001; VanderHart *et al.*, 2001; Xie *et al.*, 2001a, 2001b). Our own investigation of the degradation of quaternary alkyl ammonium modified clays during twin screw melt mixing (240ºC) with polyamide 6 (PA-6) (VanderHart *et al.*, 2001), generated concern that the organic modifier degradation could result in polymer degradation, decreased flame resistance, and/or poor clay dispersion and distribution. Therefore, our research focused on improved thermally stable modifiers (Gilman *et al.*, 2001) and on investigating the processing stability of organically modified montmorillonite clay/polyamide-6 nanocomposites (om-MMT/PA-6) (Davis *et al.*, 2003).

Our processing stability research revealed that *in situ* polymerized om-MMT/PA-6 nanocomposite (om-MMT is the abbreviation for organically modified montmorillonite clay, where the MMT was treated with the ammonium chloride salt of amino lauric acid) significantly degraded during injection molding at 300ºC, whereas minimal degradation of pure PA-6 was observed (Davis *et al.*, 2003). This nanocomposite degradation was attributed to hydrolytic scission of PA-6 peptide linkages. In addition, infrared (IR) spectroscopy revealed the presence of vinyl groups, presumably formed from alkyl ammonium elimination from the ammonium lauric acid, the ammonium end-group of PA-6, or both; however, we were unable to correlate organoclay degradation with the polymer degradation.

Our improved thermal stability research resulted in preparation of a family of imidazolium-based organically modified clays, which are significantly more thermally stable than the conventional quaternary ammonium-modified clays (Gilman *et al.*, 2001). For example, the onset of degradation temperature of 1,2-dimethyl-3-hexadecyl imidazolium (DMHDI)-treated MMT is >100ºC higher than N,N-dimethyl-N,N-dioctadecyl quanternary ammonium (DMDODA)-treated MMT. In addition, this novel organoclay did not degrade and formed exfoliated nanocomposites with polystyrene (PS), PA-6, and poly(ethylene terephthalate) (PET) after melt compounding at 200, 240 and 285ºC, respectively (Davis *et al.*, 2002; Davis and Mathis, 2001).

To evaluate mechanical and flammability properties of this novel family of imidazolium clays and to make comparisons with conventional organoclays, large quantities (hundreds of grams) of organoclay are needed for laboratory-scale extrusion. Inconsistencies in the thermal stability of the organoclays synthesized using current literature procedures (Gilman *et al.*, 2001), and the lack of information available on synthesizing organoclays on a large laboratory scale, prompted us to

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explore alternative organoclay synthesis and purification conditions. Discussed here are: the optimized conditions for synthesizing DMDODA clays on a large laboratory scale, the organoclay degradation products, and the quantification and identification of impurities which, when removed, increase the organoclay thermal stability by as much as 100ºC. The improved organoclay thermal stability observed in this study is important because the higher, thermally stable organic modifiers, such as imidazoliums, are more expensive relative to the quaternary ammonium organic modifiers, which are currently used in a majority of the commercial organoclays. In order to compete with other polymer property enhancing additives, the cost of organoclays must be minimized. A viable option is to improve the thermal stability of the less expensive and already commercialized organoclays through improved synthesis and purification procedures.

EXPERIMENTAL[1,2]

All reagents were used as received unless otherwise indicated. N,N-dimethyl-N,N-dioctadecyl ammonium bromide (DMDODA-Br) was purchased from Aldrich Chemical Company as a fine white solid. Prior to clay treatment, DMDODA-Br was dissolved in distilled water at 65±2ºC while gently agitating for 12 h using a magnetic stirrer.

Montmorillonite containing ionically bound Na (Na-MMT) was provided by Southern Clay Products as a 2.95% mass fraction aqueous slurry; the Na-MMT cation exchange capacity was 92 mmol of exchangeable sites per 100 g Na-MMT. Cation exchange capacity (CEC) refers to the number of cation binding sites in 100 g of clay. The cations bind ionically to negative charge sites, which reside in the clay platelets as a result of isomorphic replacement of Al or Si. Fluorinated synthetic mica, containing ionically bound Na (Na-SM), was provided by Unicoop Japan as a fine white powder; the CEC value was 120 mmol of exchangeable sites per 100 g of Na-SM.

Synthesis of organoclays: DMDODA-SM and DMDODA-MMT

Unless otherwise indicated below, the organic modification procedures of SM and MMT are identical.

A 19 L stainless steel pail was fitted with a band pail heater and a stainless steel lid that accommodated a 0.95 cm diameter mixer shaft, which was connected to a Sensodyne high-speed mixing head and a Lightnin' R-100 high-shear propeller (7.62 cm). The purpose of the high-shear propeller was to reduce Na-SM particle size to promote greater exchange. Since Na-MMT completely delaminates in water, only agitation was needed, therefore a low-shear, high-flow Lightnin' A-310 propeller (8.64 cm) was used for the DMDODA-MMT synthesis. In the reaction pail, a 1.7% mass fraction Na-SM aqueous suspension (6 kg of deionized water, 100 g Na-SM), was agitated for 24 h at 65±3ºC and at 31.4 radian/s. A preheated DMDODA-Br aqueous solution (6 L, 1.1 mmol DMDODA-Br with respect to CEC value) was added to the clay suspension and the exchange reaction proceeded for an additional 24 h (8 h for the Na-MMT exchange) under the same mixing conditions. The mixing speed was reduced to 5.2 radian/s and 1 L aliquots were removed for filtering.

Filtering organoclays: DMDODA-SM (SM-f) and DMDODA-MMT (MMT-f)

The organoclays will be denoted using the following convention: hot-water washing only while filtering, -f; hot-water washing while filtering followed by ethanol extraction, -fe; hot-water washing while filtering followed by tetrahydrofuran (THF) extraction, -ft; and hot-water washing while filtering followed by ethanol extraction, then THF extraction, -fet.

Organoclays were filtered using a 4 L Buchner funnel, Whatman #5 filter paper (24 cm, 2.5 µm pore size), and low vacuum. Aliquots from the pail reactor were poured into the Buchner funnel and washed continuously with 65±2ºC distilled water (six, 1 L portions). (A key factor to fast and efficient filtering is keeping the clay warm, wet and agitated.) A portion of the washed organoclay was dried at high vacuum (4 torr) for 14 h at 120ºC; these organoclays are labeled with -f. After cooling to 30ºC, the filtered and dried organoclay was immediately analyzed by thermogravimetric analysis (TGA) and stored in a desiccator until analyzed by chemical ionization mass spectrometry (MS), electrochemical analysis (EA), and X-ray diffraction (XRD). The remaining filtered organoclay was separated into two portions; one portion was extracted with ethanol and the other extracted with THF.

[1] Certain commercial equipment, instruments, materials, services, or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by the National Institution of Standards and Technology (NIST). In addition, NIST is not liable for the accuracy of the results from experiments not conducted at NIST.

[2] The policy of 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.

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Soxhlet extraction of filtered organoclays (ethanol, THF and ethanol-THF): DMDODA-SM (SM-fe, SM-ft, and SM-fet) and DMDODA-MMT (MMT-fe, MMT-ft, and MMT-fet)

The organoclays were soxhlet extracted continuously with refluxing solvent for 24 h in an argon atmosphere; maximum wet-clay loading was ~30 g. After cooling to room temperature, the samples were vacuum dried (0.03 Pa) for 14 h at 120ºC; these samples are labeled with -fe and -ft. A portion of the clay-fe samples was also soxhlet extracted with THF and dried as described above; these samples are labeled with -fet. All extracted and dried organoclays were analyzed using the techniques listed in the filtering procedure above.

THERMAL GRAVIMETRIC ANALYSIS (TGA)

Organic content and decomposition temperatures were measured using a TA SDT 2960. Organoclays were heated to 800ºC at 5ºC/min in breathing-quality air. Selected samples were analyzed four times resulting in a typical experimental uncertainty (1 σ) of ±0.2% mass fraction and ±1ºC. The thermograms presented in this publication are the derivatives of the TGA plots, derivative mass fraction loss (%/ºC) *vs.* temperature (ºC).

ELECTROCHEMICAL ANALYSIS (EA)

Electrochemical investigations of the trace amount of bromide, Na cation, and quaternary alkyl ammonium cation present in the organoclays were performed using an EG&G 273 Potentiostat/Galvanostat utilizing PAR CHEM software (version 4.11). The electrochemical cell was a 15 mL vial equipped with a sealed three-holed stopper. A Pt wire served as a pseudo-reference electrode, a 505 mm diameter graphite rod (Aldrich, 99.9995%, hardness 50) was the counter electrode, and a Pt electrode (surface area of 0.126 cm^2) was the working electrode. For the purpose of the analysis, the exchange value for the SM was 120 meq/100 g of SM, theoretically indicating that 5.22 mmol of DMDODA could bind ionically to 100 g of SM generating 5.22 mmol maximum concentration of bromide per 100 g of SM. For these analyses, 0.05 g of SM or MMT were stirred in 15 mL of the electrolyte system resulting in a maximum bromide concentration of 1.74×10^{-4} M (2.61×10^{-3} mmol/0.015 L). Since the supporting electrolyte should be present at much higher concentrations, the solvent/electrolyte system used was a 0.696 M solution of 1-ethyl-3-methyl-imidazolium tetrafluoroborate ($EMIBF_4$), in 99.95% dry acetonitrile.

Initial blanks were run on the pure solvent system, with pure Na-MMT, pure Na-SM, and a 1.24×10^{-3} M EMIBr solution, for comparison of the bromide oxidation peak. Intercalated DMDODA-clays were stirred, and then sonicated briefly in 15 mL of the $EMIBF_4$/MeCN solution. The resulting suspension was then filtered through a 0.2 µm Whatman PTFE filter disk to remove the particulate matter. The effluent was then placed in the electrochemical cell.

Bromide undergoes the following electrochemical reaction: $2\,Br^- \rightarrow Br_2 + 2e^-$ at ~500 mV relative to this pseudo-referenced electrochemical cell. Thus, the current measured at the peak value of this reduction is directly proportional to the amount of bromide in solution. The maximum current was observed for the main oxidation peak at ~480 mV, relative to a pseudo-reference Pt electrode. Note that a value of -266 nA/cm^2 is used to correct for the weak signal observed for both the SM and MMT effluents.

Mass spectroscopy (MS)

Thermal desorption mass spectrometry experiments were performed on a Finnigan (San Jose, CA) TSQ-70 triple quadrupole mass spectrometer. Chemical ionization (CI) was performed at a source pressure of 1.6 torr (the ratio of the ions with m/z values of 57 g/mole and 43 g/mole was adjusted to 10:1). The first two quadrupoles were operated in the RF-only mode and Q3 was generally scanned from m/z values of 60 g/mole to 700 g/mole in 0.5 s. Data were recorded for the duration of the thermal desorption experiment.

Organoclay thermal desorption was performed using a Scientific Instrument Services Model FP-15 high-temperature Direct Probe and Model PC-2F temperature controller. Samples were loaded into a glass capillary and placed in the end of the probe. The probe was inserted into the ion source of the MS. The sample probe was held at 150ºC, then the temperature was increased at 200ºC/min to 800ºC, where it was held for 1 min. At the beginning of each experiment, data acquisition was initiated at the same time the temperature ramp on the probe began. Similar experiments were conducted in which the temperature was increased at 100ºC/min, but there was no effective change in the nature of thermal desorption profiles.

X-ray diffraction (XRD)

X-ray diffraction experiments were conducted on a Bruker AXS D8 Powder diffractometer, which was equipped with Goebel Mirrors to improve the signal-to-noise ratios for weakly crystalline, anisotropic polymers. Diffraction patterns were acquired over a range of 2 to 60º2θ at a step rate of 0.0200º/20 s. The raw data were transformed into an XRD spectrum using the Bruker Evaluation Software Version 7.0. The distance between clay sheets was calculated using Bragg's Law and the 2θ peak maximum values from the XRD spectra. The 2θ values have a standard uncertainty of ±0.056º2θ.

RESULTS AND DISCUSSION

Immediately following the exchange reaction, the organically modified clays (MMT-f and SM-f) contain

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Table 1. Results from TGA analysis.

	$T_{initial}$[a]	$T_{max,1}$[a]	$T_{max,2}$[a]	DMDODA mass fraction[b,c]	Theoretical mol.% exchange[c]
MMT-f	213	299	–	0.342	100.3
MMT-fe	213	299	–	0.342	100.3
MMT-ft	240	311	414	0.339	99.4
MMT-fet	253	333	419	0.340	100.0
SM-f	215	239	317	0.418	103.5
SM-fe	215	239	317	0.418	103.5
SM-ft	240	315	425	0.393	97.3
SM-fet	255	343	–	0.392	97.0

[a] Standard uncertainty = ±1°C and (1σ)
[b] Standard uncertainty is ±0.001.
[c] If all CEC sites are exchanged with DMDODA then the theoretical mass fractions of DMDODA in DMDODA-MMT and DMDODA-SM are 0.341 and 0.404, respectively. Values >100% exchange (>0.341 and 0.404 mass fraction) indicate the presence of unbound DMDODA-Br impurity. <100% means that not all sites were exchanged

unbound DMDODA-Br, ionically bound DMDODA, and NaBr ion exchange by-product. This is important because several groups have shown that deleterious effects may result from such impurities (*e.g.* Davis *et al.*, 2003; Gilman *et al.*, 2001; Morgan and Harris, 2003; Triantafillidis *et al.*, 2002; Vaia *et al.*, 1994; Xie *et al.*, 2001a, 2001b). The results presented below indicate that the efficiency of removing the DMDODA-Br and NaBr impurities is solvent dependent. This is important because both sources of the residual bromide impurities were found to decrease the thermal stability of the organoclay (Table 1, Figures 1–3).

Before continuing, it is imperative to understand what Figures 4–7 represent and how to interpret them. Figures 4–7 are chemical ionization MS spectra as a function of time and temperature, both shown on the *x* axis. Each figure contains five spectra and each spectrum is scaled on the *y* axis from 0% to 100%, referred to as 'relative abundance'. Spectra A–D represent degradation products where the relative abundance values reflect the amount of a degradation product measured at any point in the experiment relative to the maximum amount of that degradation product measured during the experiment. There is no correlation between the *y* axis values of the different spectra.

Spectrum E is the total ion thermogram, which is a composite of spectrum A–D. At time *t* during the experiment there is *a* amount of degradation product A, *b* amount of B, *c* amount of C, and *d* amount of D. Therefore, we know at time *t* the fraction of a degradation product relative to the total amount of degradation products formed at time *t*. We also know these fractions at every time during the experiment, *e.g.* at *t*, t_1, t_2, and we know how these fractions relate to each. These fractions translate into time-dependent and degradation product-dependent scaling factors that are used to adjust the intensity of spectra A–D prior to combining to form spectrum E. Therefore, for example, a strong similarity between spectrum E and spectrum B from time *t* to t_1 is an indication that B is a dominant degradation product during this time period. Keep in mind that all spectra represent amounts of degradation

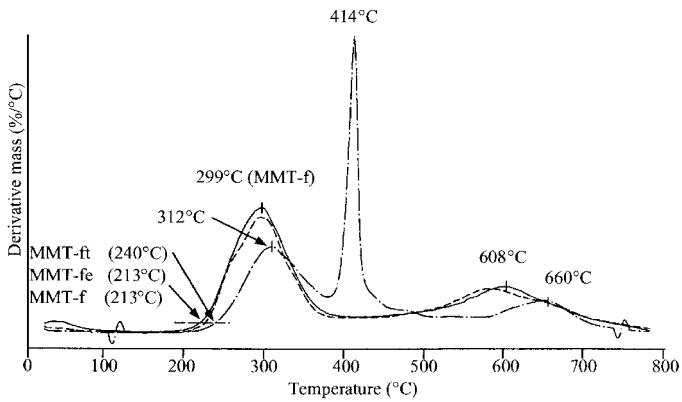


Figure 1. Thermograms of DMDODA-MMT samples MMT-f, MMT-fe and MMT-ft. Peaks above 500ºC represent the decomposition of aromatized pre-char formed from degradation of the DMDODA and dehydroxylation of MMT. Note the initial degradation temperature is ~27ºC higher in the THF extracted organoclay.

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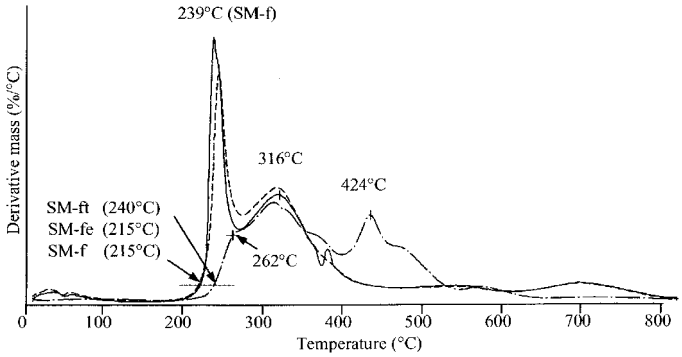


Figure 2. Thermograms of DMDODA-SM samples SM-f, SM-fe and SM-ft. Peaks above 500ºC represent the decomposition of aromatized pre-char formed from degradation of the DMDODA. Note the initial degradation temperature is ~25ºC higher in the THF-extracted organoclay.

products formed during the experiment. A value of 0% means that none of that degradation product or products was generated at that time in the experiment.

The proposed degradation pathways that lead to the primary degradation products are illustrated in Figure 8; these products are based on chemical ionization MS analysis (Figures 4–7). The strong similarities between the total ion spectrum (E) and spectra B (octadecene) and C (N,N-dimethyl-N-octadecyl tertiary amine) indicate that the octadecene and N,N-dimethyl-N-octadecyl tertiary amine represent the primary degradation products of the organic modifier. On the other hand, few similarities between the total ion spectrum (E) and spectra A (trimethyl amine) and D (N-methyl-N,N-dioctadecyl amine) suggest that trimethyl amine and N-methyl-N,N-dioctadecyl amine are minor products of the degradation process.

After 24 h of ethanol extraction, these DMDODA-treated organoclays (MMT-fe and SM-fe) still contained residual unexchanged DMDODA-bromide (Table 2) and exhibited the lowest thermal stability (Table 1 and Figures 1–3). Similarly, Xie *et al.* (2001b) and coworkers have shown that the thermal stability of om-clay is increased with more complete removal of the unbound organic modifier salt. Using THF as the extraction solvent increased the initial degradation temperature ($T_{initial}$, defined as the temperature at 5% mass fraction loss in the TGA curve) and the peak maximum temperature (T_{max}) of the first degradation event of these organoclays (MMT-ft and SM-ft). The THF-extracted organoclays only contained sodium bromide, as detected by electrochemical analysis. The greatest thermal stability was achieved after a sequential extraction of first, ethanol and then, THF (MMT-fet and SM-fet samples, see Table 1). For example, $T_{initial}$ increased by 40ºC and $T_{1,max}$ increased by 104ºC for DMDODA-SM when the sequential dual extraction was used rather than the single ethanol solvent extraction (Table 1 and Figure 3). This increased thermal stability is a result of removing both sources of bromide from the organoclays. In fact, decreased thermal stability of a cation in the presence of a halide is quite common behavior, *e.g.* Ngo *et al.* (2000) observed a 100ºC decrease of imidazolium cation thermal stability when a halide counter ion was used. Measurements by EA (Table 2) and TGA (Table 1) suggested quantities of organobromide in the organoclays which are identical, within standard experimental uncertainty.

The proposed degradation pathways are illustrated in Figure 8. Analysis by EA and TGA indicates that the

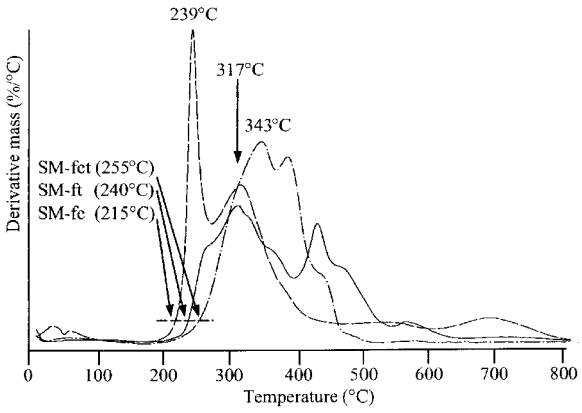


Figure 3. Thermograms of DMDODA-SM samples SM-fe, SM-ft and SM-fet. Exothermic peaks above 500ºC represent the decomposition of aromatized pre-char formed from degradation of the DMDODA. Note that the two-solvent-extraction approach increases the thermal stability of the ionically bound organic modifier by ~40ºC.

Table 2. Mol.% residual bromides in organoclays relative to CEC value, as determined by EA.

	DMDODA-Br	NaBr
MMT-fe	<1.0%	nd
MMT-ft	nd	4.5%
MMT-fet	nd	nd
SM-fe	3.7%	nd
SM-ft	nd	2.0%
SM-fet	nd	nd

nd: not detected within the sensitivity of the technique

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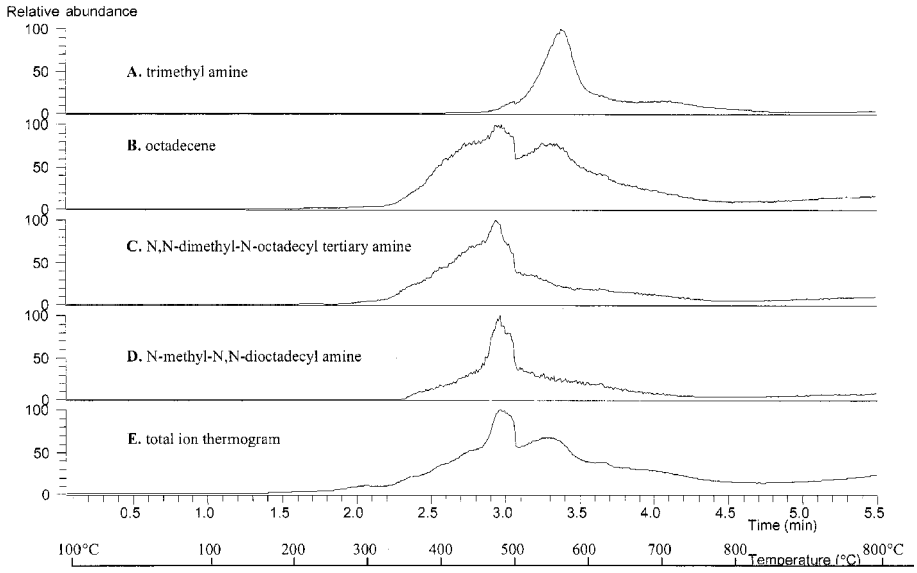


Figure 4. Chemical ionization MS analysis of MMT-fe. The largest peak in each spectrum is set at 100%, therefore, there is no correlation between the relative amounts of degradation products and the relative abundance values presented in spectra A–D.

decreased thermal stability of the single solvent extraction organoclays may result from the presence of bromide. The degradation products are those resulting from bromide-involved elimination and nucleophilic attack; the formation of these degradation products is supported by chemical ionization MS analysis (Figures 4–7). Degradation initially proceeds through elimination of octadecene and generates N,N-dimethyl-N-octadecyl amine (spectra B and C of Figures 4–7). This degradation event is delayed using THF, rather than ethanol, as the single extraction solvent; however, the elimination degradation always begins before nucleophilic attack (D spectra), which formed N-methyl-N,N-dioctadecyl amine. It is unclear how trimethyl amine (spectrum A) is produced and it is unlikely that the hydrogen bromide and methyl bromide primary degradation by-products are involved due to their high volatility. A possibility is that the trimethyl amine may result from the degradation of the elimination or nucleophilic degradation products since the appearance of trimethyl amine is nearly synonymous with the onset of their degradation.

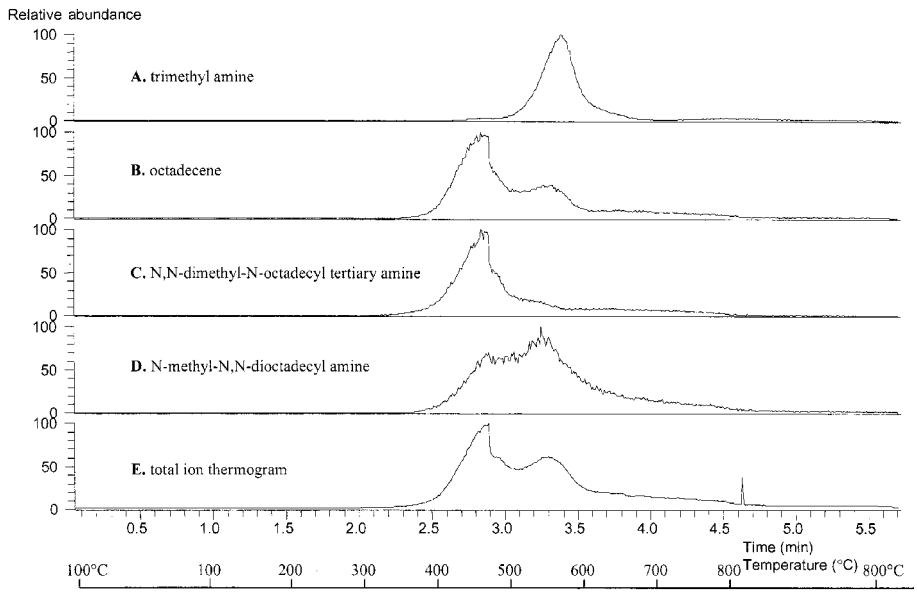


Figure 5. Chemical ionization MS analysis of MMT-ft.

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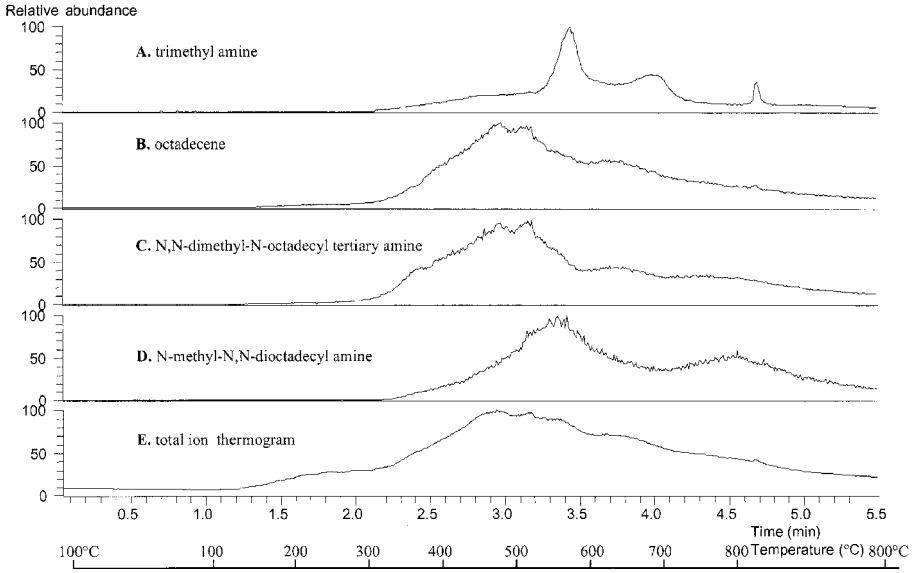


Figure 6. Chemical ionization MS analysis of SM-fe.

As described above, the total ion spectrum (spectrum E of Figures 4–7) is a composite of spectra A–D, and reflects the amount of each degradation product relative to the total amount of degradation products detected at each temperature. Strong similarities between the total ion spectrum and the elimination spectra (B and C) and few similarities to the nucleophilic spectra (D) and trimethyl amine spectra (A) indicate that elimination is the primary degradation pathway throughout the entire degradation process for all the DMDODA-clays. Based on the amount of degradation products measured by MS analysis, approximately 90% degradation occurs via elimination and 9% via nucleophilic attack; trimethyl amine is <1% of the total degradation products. The total ion thermograms also show that the initial degradation temperature of the ethanol single-extraction organoclays (Figures 4 and 6) was lower than the THF single-extraction organoclays (Figures 5 and 7). This observation correlates with the TGA results discussed above.

Degradation proceeding primarily via elimination is reasonable because in the presence of a weak base nucleophile (bromide), sterically hindered sites primar-

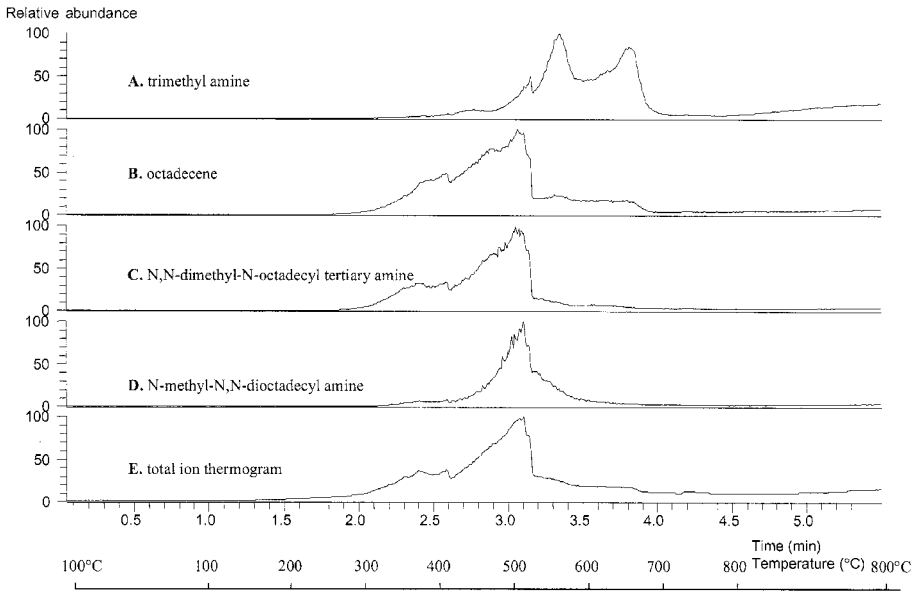


Figure 7. Chemical ionization MS analysis of SM-ft.

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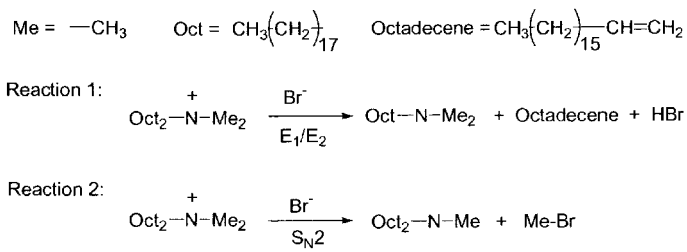


Figure 8. Proposed DMDODA-clay thermal degradation routes based on the chemical ionization MS analysis.

ily degrade through E_2 elimination rather than S_N2. For example, neo pentyl carbon ammonium sites, similar to DMDODA, are not susceptible to nucleophilic attack, rather E_2 pathways only. In addition, E_1 pathways are also possible if the environment is a highly dielectric ionizing solvent, which may be the case in a molten organoclay. Therefore, we propose that the primary degradation route of the DMDODA-clay is via E_1 or E_2 elimination. In addition to this research, we detected only elimination degradation products in our study of PA-6 nanocomposite degradation during high-temperature processing (Davis *et al.*, 2003). However, contrary to our findings provided here, we previously found that nucleophilic degradation was the primary pathway in our NMR study of organoclay dispersion in polyamide 6 (VanderHart *et al.*, 2001). Perhaps this difference results from the presence of PA-6 which may alter the dielectric environment and/or DMDODA conformation. Xie *et al.* (2001a, 2001b) have shown that the degradation products of quaternary alkyl ammonium-treated clays are both alkane and alkenes, implying, though not mentioned in these manuscripts, that the degradation proceeds through both elimination and nucleophilic attack.

The distance between organoclay platelets, referred to as the gallery spacing, is dependent on several factors; one of which is the presence of excess unbound organic modifier. X-ray diffraction shows that the all DMDODA-MMT samples have a gallery spacing of ~2.42 nm. The gallery spacing of the SM-fe sample was 3.80 nm and 3.51 nm for the SM-fet sample. The difference in the om-SM gallery spacings is attributed to excess unbound DMDODA-Br dissolved between the clay platelets and forcing the platelets further apart. The difference between the om-SM and om-MMT gallery spacing is attributed to a greater concentration of surface bound DMDODA in the SM samples, due to a higher CEC value. Higher CEC-value layered silicates have larger gallery spacing because the increased crowding of organic modifiers on the surface forces the modifiers away from the layered silicate surface (Vaia *et al.*, 1994).

It is important to note that this synthesis and purification procedure was designed for large laboratory-scale organoclay treatment experiments, *e.g.* in an academic or industrial research laboratory. Smaller scales, *e.g.* 100 mg, can be purified efficiently using stir-centrifuge washing with a single organic solvent. However, this is a time-consuming approach when purifying hundreds of grams of organoclay. At the industrial scale, organoclays are generally minimally washed using water to reduce manufacturing cost. This study indicates more extensive purification improves the organoclay thermal stability, which could result in more commercial applications for organoclays.

CONCLUSIONS

The thermal stability of DMDODA-treated MMT and SM is strongly dependent on the presence of bromide-containing impurities. Hot water-washed organoclays and ethanol-extracted organoclays contain unbound DMDODA-Br and are the least stable organoclays. The THF-extracted organoclays are more stable, presumably due to the removal of all DMDODA-Br; however, these organoclays contain another bromide source, NaBr. Extraction, first with ethanol, then with THF, removes both bromide impurities and results in the highest organoclay thermal stability. It is proposed that the organic modifier degrades primarily via elimination and secondarily by nucleophilic attack by bromide. This exhaustive extraction method represents a viable alternative to the use of expensive, more thermally stable onium ion treatments for layered silicates. This is significant as most of the commercial applications of layered silicate nanocomposites will only be commercialized if they are cost competitive with conventional additive approaches to modify polymer properties.

REFERENCES

Davis, C.H. and Mathias, L.J. (2001) Self reinforcing polymeric materials. School of Polymers and High Performance Materials, University of Southern Mississippi, USA, dissertation.

Davis, C.H., Mathias, L.J., Gilman, J.W., Schiraldi, D.A., Shields, R., Trulove, P., Sutto, T. and DeLong, H. (2002) Effects of melt processing conditions on the quality of poly(ethylene terephthalate) montmorillonite clay nanocomposites. *Journal of Polymer Science: Part B: Polymer Physics*, **40**, 2661–2666.

Davis, R.D., Gilman, J.W. and VanderHart, D.L. (2003)

https://doi.org/10.1346/CCMN.2004.0520203 Published online by Cambridge University Press

Processing Degradation of Polyamide-6 Montmorillonite and Clay Organic Modifier. *Polymer Degradation and Stability*, **79**, 111–121.

Gilman, J.W., Awad, W.H., Davis, R.D., Shields, J.R., Kashiwagi, T., VanderHart, D.L., Harris, R.H., Davis, C.H., Morgan, A.B., Sutto, T., Callahan, J., Trulove, P. and Delong, H. (2001) Polymer layered silicate nanocomposites from thermally stable trialkyl-imidazolium treated montmorillonite. *Chemistry of Materials*, **14**, 3776–3785.

Morgan, A.B. and Harris, J.D. (2003) Effects of organoclay soxhlet extraction on mechanical properties, flammability properties and organoclay dispersion of polypropylene nanocomposites. *Polymer*, **44**, 2313–2320.

Ngo, H.L., LeCompte, K., Hargens, L. and McEwn, A.B. (2000) Thermal stability of imidazolium ionic liquids. *Thermochimica Acta*, **357**, 97–102.

Triantafillidis, C.S., LeBaron, P.C. and Pinnavaia, T.J. (2002) Homostructured mixed inorganic-organic ion clays: A new approach to epoxy polymer-exfoliated clay nanocomposites with a reduced organic modifier content. *Chemistry of Materials*, **14**, 4088–4095.

Vaia, R.A., Teukolsky, R.K. and Giannelis, E.P. (1994) Interlayer structure and molecular environment of alkylammonium layered silicates. *Chemistry of Materials*, **6**, 1017–1022.

VanderHart, D.L., Asano, A. and Gilman, J.W. (2001) Solid state NMR investigation of paramagnetic nylon-6 clay nanocomposites. *Macromolecules*, **34**, 3819–3822.

Xie, W., Gao, Z., Pan, W., Vaia, R., Hunter, D. and Singh, A. (2001a) Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chemistry of Materials*, **13**, 2979–2990.

Xie, W., Gao, Z., Liu, K., Pan, W., Vaia, R., Hunter, D. and Singh, A. (2001b) Thermal characterization of organically modified montmorillonite. *Thermochimica Acta*, **367**, 339–350.

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https://doi.org/10.1346/CCMN.2004.0520203 Published online by Cambridge University Press