Available online at www.sciencedirect.com

Thermochimica Acta 429 (2005) 13–18

thermochimica acta

www.elsevier.com/locate/tca

Thermal stability analysis of organo-silicates, using solid phase microextraction techniques

G. Edwards[a], P. Halley[b], G. Kerven[c], D. Martin[a,*]

[a] *Nanomac, School of Engineering, University of Queensland, Brisbane, Qld 4072, Australia*
[b] *Centre for High Performance Polymers, School of Engineering, University of Queensland, Brisbane, Qld 4072, Australia*
[c] *Analytical Services, School of Land and Food, University of Queensland, Brisbane, Qld 4072, Australia*

Received 31 August 2004; received in revised form 16 November 2004; accepted 20 November 2004

Abstract

An analysis of thermal degradation products evolved during the melt processing of organo-layered silicates (OLS) was carried out via the use of a solid phase microextraction (SPME) technique. Two commerical OLSs and one produced in-house were prepared for comparision. The solid phase microextraction technique proved to be a very effective technique for investigating the degradation of the OLS at a specific processing temperature. The results showed that most available OLSs will degrade under typical conditions required for the melt processing of many polymers, including thermoplastic polyurethanes. It is suggested that these degradation products may lead to changes in the structure and properties of the final polymer, particularly in thermoplastic polyurethanes, which seem significantly succeptable to the presence of these products. It is also suggested that many commercially available OLSs are produced in such a way that results in an excess of unbound organic modifier, giving rise to a greater quantity of degradation products. All OLSs where compared and characterised by TGA and GC–MS.

Keywords: SPME; Organo-silicate; Nanocomposite; Cloisite^{TM}

---

1. Introduction

Recently, much attention has been paid to polymer-layered silicate nanocomposite materials, and more specifically to their production via commercially available processing methods, such as melt compounding [1–11]. Nanocomposites are attractive as they have been shown to enhance mechanical, thermal, barrier and flame retardant properties over that of the host polymer [11,12], and these effects can be observed at very low loadings of organo-layered silicate (OLS), normally between 1% and 10% by weight.

Layered silicates offer an effective form of nanofiller for nanocomposites, due to their high surface area, high aspect ratio of individual platelets, and the capacity be readily modified with a variety of organic surfactants to allow for improved compatibility between the silicate and the polymer. Most typically, the surfactants employed are alkyl ammoniums or phosphoniums, however recently imidazoliums have also been investigated [2].

Processing of these nanocomposites can be achieved by melt intercalation, in situ polymerization or solvent casting. The method used strongly depends on the host polymer system and the end application of the product. Melt intercalation has the distinct advantages of being a scalable and continuous process, and it is suitable for many thermoplastics. However, this method exposes the silicate to significant temperatures for extended periods (residence time in the extruder), and may result in the degradation of the surfactant, which may in turn affect the performance of the final product. The degradation of OLS and the production of these

---

* Corresponding author. Tel.: +61 7 3365 4176.
E-mail addresses: s353463@student.uq.edu.au (G. Edwards), p.halley@uq.edu.au (P. Halley), darrenm@cheque.uq.edu.au (D. Martin).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.11.020

degradation products are often overlooked, but must be considered in order to understand how the degradation products might affect the final nanocomposite properties and long term performance.

The analysis of thermal degradation products would traditionally require the use of solvent extraction techniques [13] or necessitate expensive combined TGA–GC–MS instrumentation. Recently, solid phase microextraction (SPME) has emerged as an effective alternative for the study of the low molecular weight compounds released by polymers whilst they undergo degradation [13,14]. This has been shown to provide better sensitivity for headspace extraction than traditional static headspace techniques. The disadvantages of the SPME approach are that it is an equilibrium-based technique, so the concentration of products adsorbed on the fibre's surface will not be a direct indicator of concentration in the headspace. If used in a static equilibrium environment, then the amount of analyte coating the surface of the fibre should be directly proportional to the concentration in the headspace [14].

In this study, the thermal degradation products of two commercially available OLS and one analogue OLS material prepared by us were investigated. This was done by exposing the OLS to a typical processing temperature (210 °C) employed for thermoplastic segmented polyurethanes (TPU), which our group have investigated. A simple novel analysis technique employing the use of solid phase microextraction fibres was used to obtain the vapour products, providing an alternative to the expensive equipment normally required to perform this type of study, such as a TGA–GC–MS [7].

2. Experimental

2.1. Materials

Montmorillonite based OLS from the Southern Clay Products Cloisite^{TM} series were examined. These were Cloisite^{TM} 15A, Cloisite^{TM} 30B. Cloisite^{TM} 15A has a modifier loading of 125 meq/100 g, and Cloisite^{TM} 30B has a loading of 90 meq/100 g. The tallow groups on the modification of both these materials have a predicted composition of ∼65% C18; ∼30% C16; ∼5% C14.

Another organoclay was prepared for comparison by modifying Cloisite^{TM} Na$^+$ (with a CEC of 92.6 meq/100 g) with Ethoquad O/12 available from Akzo Nobel. The Cloisite^{TM} Na$^+$ was modified in a 1% by weight solution, with deionised water, to which the Ethoquad O/12 was added at an amount exceeding the CEC of the Cloisite^{TM} Na$^+$ by 20%. This solution was then left stirring for 24 h, at 60 °C to allow for maximum conversion. The sample was then washed by centrifuge, where the sample was separated from solution, decanted and mixed with fresh distilled water. This was repeated until no chloride ions were detectable, which was tested by the addition of AgCl solution to the decanted water.

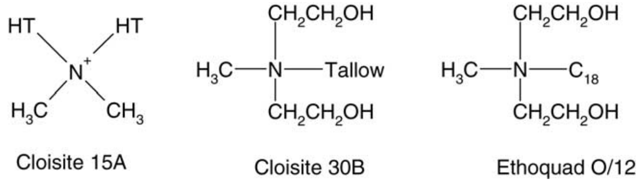

Fig. 1. Structure of the surfactants used to modify silicate surface, from left to right. Cloisite^{TM} 15A, Cloisite^{TM} 30B and Ethoquad O/12.

The commercially available OLS employ tallow based quaternary ammoniums as a surfactant. Fig. 1 shows the general structure for all of the surfactants studied in this paper. The similarity between Cloisite^{TM} 30B and Ethoquad O/12 should be noted.

2.2. TGA

A Shimadzu TGA-50 was used to analyze the thermal stability, and onset temperature of degradation for each of the clays. Approximately 15 mg of sample was placed in a platinum pan. This sample was heated over a temperature range of 30–600 °C, in an air atmosphere with a gas flow rate of 60 ml/min. The samples were heated at two separate rates, 10 °C/min and 1 °C/min. The later was used to check that the heat capacity of the clay did not affect the apparent onset temperature for degradation.

2.3. GC–MS/SPME technique

Approximately, 100 mg of sample was placed in a glass sample vial and then sealed using a Teflon septa. This vial also contained a static air environment. The sample was then raised to a temperature of 210 °C in a heated aluminum block and maintained at that temperature for 30 min. A 100 μm polydimethylsiloxane SPME fibre is exposed to the headspace [15], and allowed 15 min to adsorb material from the headspace. The fibre was then inserted into the injection port of a Shimadzu GC 17-A gas chromatograph for 1 min, with the injection port set at 265 °C and the interface set at 295 °C. The GC was operated using a SGE BPX-5 50 m × 0.25 mm × 0.25 μm column and testing was begun at 50 °C and was ramped to 280 °C at a rate of 20 °C/min. This temperature was held for the remainder of the test. The outlet gas was interfaced directly into the GC–MS–QP5050A which used a 70 eV ionization source. This system uses a quadrapole design with a 10–900 amu mass range.

3. Results and discussion

The thermal stability of OLS variants and degradation products will be discussed with reference to the processing conditions for thermoplastic polyurethane nanocomposite materials, and in comparison with pristine silicate.

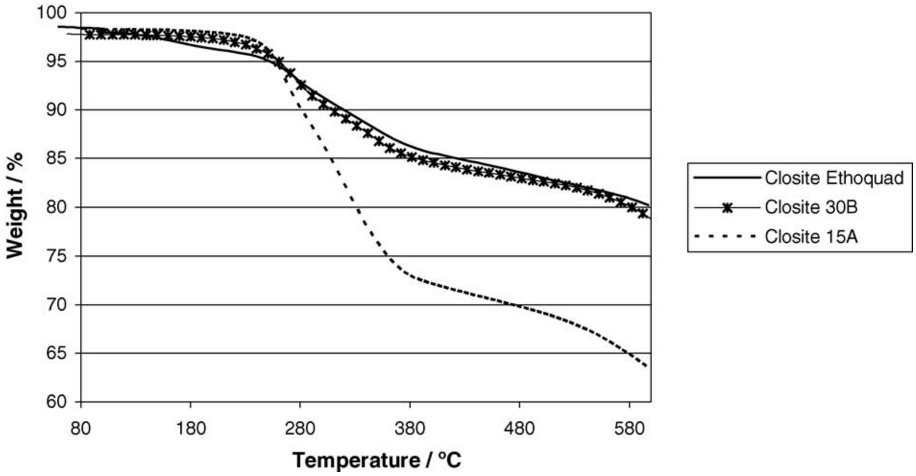

Fig. 2. Thermal degradation of MMT Ethoquad, Cloisite^{TM} 30B and Cloisite^{TM} 15A, showing % weight lost.

3.1. TGA analysis of silicate

This initial work defines the onset point for degradation of the OLS, which allows for the prediction of the OLS's behaviour under the processing conditions applicable to the system. As shown by Xie et al. [7], it is best to examine an OLS over the four separate regions shown in Fig. 2. These are (a) the free water region, (b) the region where organic substances evolve, (c) the structural water region and (d) organic carbon reactions. However, the temperature bounds listed will vary strongly with both surfactant type and heating rate, with region (b) often beginning as low as 160 °C.

In relation to polymer processing, it is unnecessary to consider temperatures above approximately 500 °C, as very few polymers are ever processed at such high temperatures. This means that for this paper, regions (c) and (d) will not be considered.

3.2. Free water loss

Free water loss can be considered to occur between 0 °C and 160 °C. However, as shown by Fig. 2 (TGA graph), most free water is lost by 120 °C if the OLS is allowed some time to equilibrate to the temperature. As shown by Xie et al. [7], and observed in Fig. 3, there are significant changes in water contained within the OLS depending on surfactant used, with more free water being associated with pure montmorillonite (MMT) than with the more hydrophobic surface modified silicates. This free water has a substantial effect on the OLS processability in a TPU system. The presence of free water within a TPU system under high temperatures will allow for the reaction of water with urethane bonds, whilst undergoing transurethanisation. This will cause the production of CO_2, which may result in a foam or a significant degree of porosity in the final product, as well as lowering the molecular weight of the final product through chain scission. Careful drying

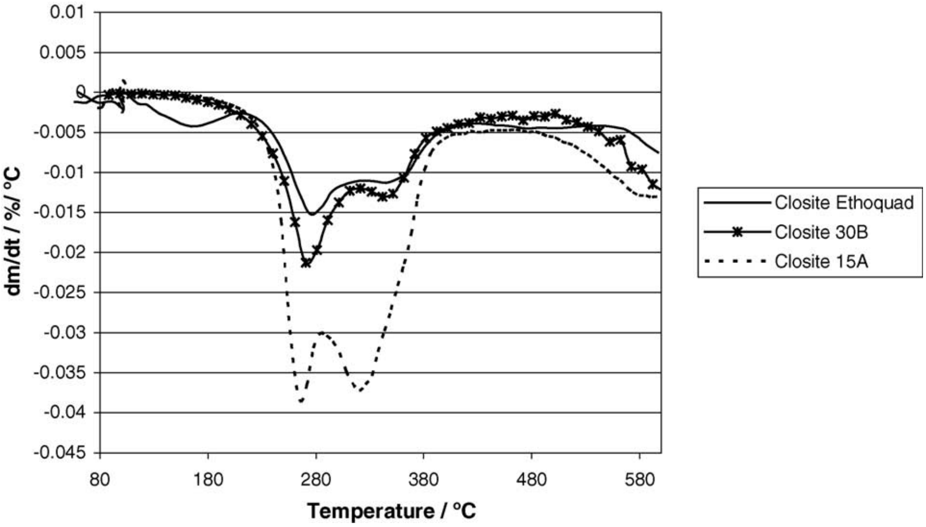

Fig. 3. Derivative plot of thermal degradation of Cloisite^{TM}, Ethoquad, Cloisite^{TM} 30B and Cloisite^{TM} 15A.

Table 1
Organic species evolved from samples at 210 °C

Sample	Cloisite^{TM} 30B	Cloisite^{TM} 15A	MMT Ethoquad
Degradation products observed	*N*,*N*-Dimethlyacetamide Linear aldehyde (C_7–C_{12}) Alkanes, linear and branched (C_9–C_{21}) Alcohol (C_8–C_{16}) Alkene alcohols (C_9–C_{16}) Chloro-alkane (C_{14}–C_{16}) Alkene (C_{13}–C_{18})	Alkanes, linear and branched (C_{13}–C_{19}) Alkene (C_{16}–C_{18}) Chloro-alkane (C_{14}–C_{16}) *N*-*N*-Dimethyloctylamine Linear aldehyde (C_{16}–C_{18})	Linear aldehyde (C_9–C_{13}) Alkene (C_{13}–C_{18}) *N*-*N*-Dimethyloctylamine

of an OLS, polymer or masterbatch (if employed) is necessary when processing any polymer which can be affected by water.

3.3. Onset of organic breakdown

A very clear difference between the thermal degradation of the pure silicate and the OLS samples is the loss of material at approximately 180 °C. This is the onset of the degradation of the organic modifier used on the silicate. The organic surfactant appears to degrade in several steps, as shown by the changes in the rate of mass loss from the surface (Figs. 1 and 2, plot of TGA and derivative plot). As the onset of degradation (180 °C) is occurring at a temperature less than the typical operating temperatures of TPU polymer processing (190–220 °C), the evolution of these degradation products must be considered, and analysised for possible impacts on the host polymer and also with respect to possible applications.

After approximately 500 °C, there is little to no sign of the surfactant on the surface, this result concurs with the results reported by Xie et al. [7].

3.4. Analysis of degradation products

Exposing the SPME fibre to the atmosphere generated within the vial, allows the fibre to adsorb the volatile organic components evolved. The SPME fibre employed here was chosen due to its previous successful application in arson investigation [15].

The degradation products from the OLS were predominately alkenes, with a similar array of products being produced in both the analogue (Ethoquad-modified MMT) and the commercially available materials, however some significant differences were seen.

The array of products seen can, when compared to the surfactant, easily be accounted for by the scission and reformation of the surfactant, however the exact mechanism is not known. A notable difference was the presence of chlorinated compounds in the degradation products of Cloisite^{TM} 30B, which mostly likely arose due to the presence of excess surfactant on the surface that has not undergone cationic exchange. The quantity of aldehydes released varies greatly between all of the samples, despite the very similar structures of Cloisite^{TM} 30B and Ethoquad. Cloisite^{TM} 15A expressed no aldehydes at all, which is consistent with the fact that the surfactant contains no oxygen in its structure.

Table 1 shows the full list of degradation products from the three samples. The presence of octadecene as a byproduct of degradation was confirmed by running a separate sample of pure octadecene prepared under the same conditions. This sample showed the same retention time, and mass spectra as those found in the samples.

Initial tests also showed that TMA was a possible product, however the inclusion of lower MW spectra showed that the product is generally hexylamine or octylamine. This was confirmed by repeating the analysis with a direct injection of TMA into the column, and finding that the elution time of TMA was significantly less than the peak recorded. This suggests, that in addition to common production of alkenes, short-chained alkyl amines are also common products.

Of concern here is both the impact of these products on the host polymer, and also how these species may influence the final long-term performance of the material. It has been shown in previous work by Finnigan et al. [17], that the melt compounding of TPUs with Cloisite^{TM} 30B produced significant decrease in properties and the melt showed signs of degradation. This is likely due to the presence of free amines and alkenes in the system, which may react with the urethane linkages within the polymer system as they undergo transurethanisation (Fig. 4, [16]). Even a small amount of this

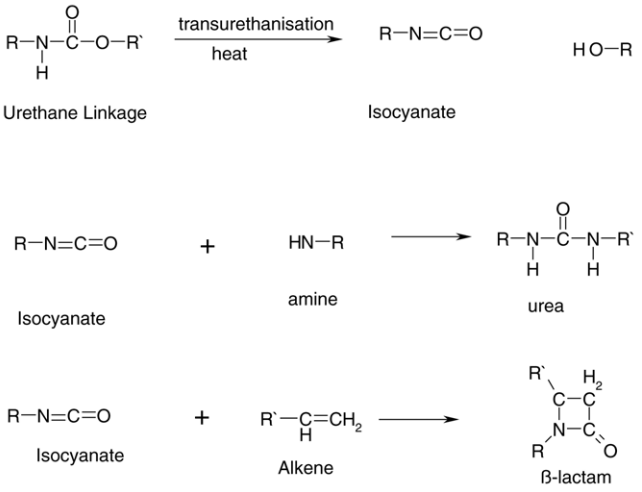

Fig. 4. Some possible reaction pathways for isocyanate produced from transurethanisation and OLS degradation products.

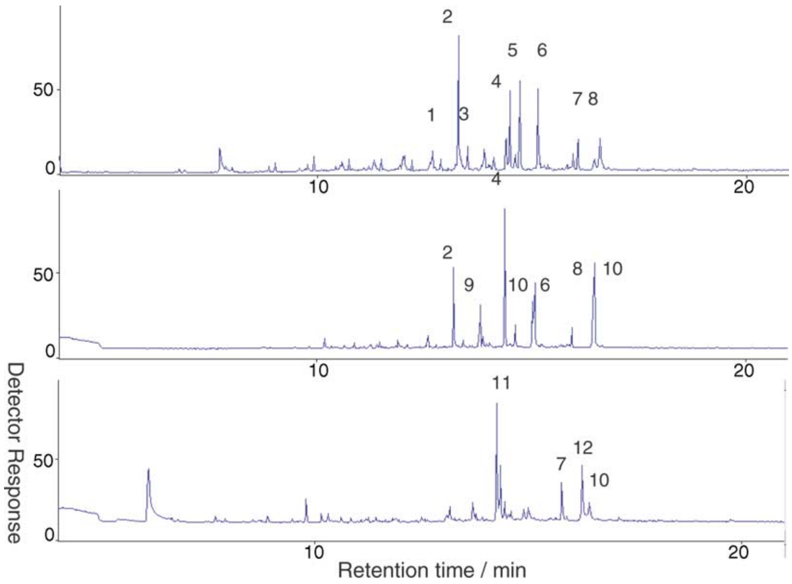

Fig. 5. Retention times for degradation products through a GC from top to bottom Cloisite^{TM} 30B, Cloisite^{TM} 15A, MMT Ethoquad (1) branched alkyl chain (trimethly dodecane, trimethly octane or ethyl undecane) (2) tetradecene (3) aldehyde (Dodecenal) (4) octadecene (5) alcohol (tridecenol) (6) chloro alkane (chloro-octadecane or chloro-tetradecane) (7) aldehyde (octadecanal) (8) chloro alkane (chloro-octadecane or chloro-tetradecane) (9) alkane (pentadecane) (10) *N*-*N*-dimethyloctylamine (11) alkenes (tridecene, hexadecene and octadecene) (12) alkene.

reaction will produce a shortened chain length, and a thus a decrease in final properties. The reaction of the isocyanate with the amine actually has a significantly higher reactivity than the reaction with the polyol produced, making this a very likely path for degradation. The effect of these degradation products may impact on other polymer systems, which need to be considered prior to using these materials.

In Fig. 3 the TGA plots show that the samples undergo three steps in the process of degradation. The origin of these steps is not fully understood, but may be related to diffusion of the surfactants, or a change in the pathway of degradation, which allows for a significantly higher rate of mass loss to occur.

Xie et al. [7] claimed that only low molecular weight material was evolved during exposure of the OLS to lower temperatures. This study shows that even long chained materials were released in significant quantities at 210 °C. This implies that the higher molecular weight material is still evolved, but rather requires more time to diffuse out of the OLS tactoids. This would not have been observed by Xie et al. [7], due to the high-temperature ramp rate used in their experiment.

In the degradation products from commercially available materials, we find the presence of chloride compounds, indicating the presence of chloride ions present in the system (Fig. 5). This however does not appear in the analogue system. The proposed source of this contaminant is from the overloading, and improper washing of the organo-silicate during its manufacture. The use of a chloride counter ion in the Cloisite^{TM} systems accounts for the presence of this species.

The final analysis of the degradation products shows a very similar pattern to the products detected by Xie et al. This demonstrates that the SPME fibre extraction process for the organo-layered silicate degradation is effective, and a valid alternative to TGA–MS systems.

4. Conclusions

The use of SPME fibres in conjunction with a GC–MS, has been shown to provide a quick and cost effective method for the analysis of the degradation of an OLS, for a given operating temperature. This technique is, therefore, useful for investigating the thermal stability of OLS candidates being considered for melt processing of nanocomposites.

The release of organic compounds during processing, as was simulated by conditions in this research, may have significant impact on the performance of the nanocomposite in terms of both physical and chemical properties. For example, the presence of low molecular weight leachable compounds may prohibit use in medical or food contact applications.

Acknowledgements

The authors wish to acknowledge Bradley Finnigan for helpful discussions, the Division of Chemical Engineering for a departmental Ph.D. scholarship, and the UQ Research Development Grants scheme for support.

References

[1] M. Alexandre, P. Dubois, Mater. Sci. Eng. 28 (2000) 1–63.
[2] E.H. Awad, et al., Thermochim. Acta 409 (2004) 3–11.

[3] R.D. Davis, J.W. Gilman, D.L. VanderHart, Polym. Degrad. Stab. 79 (2003) 111–121.

[4] C. Dohoon, et al., Plast. Eng. (January 2001) 56–60.

[5] E.A. McLaughlin, B.E. Koene, ANTEC 2002, San Francisco, CA, 2002.

[6] T.J. Pinnavaia, Z. Wang, Chem. Mater. 10 (1998) 3769–3771.

[7] W. Xie, et al., Thermochim. Acta 367–368 (2001) 339–350.

[8] C. Wan, Y. Zhang, Y. Zhang, Polym. Test. 23 (2004) 299–306.

[9] R.A. Vaia, E.P. Giannelis, Macromolecules 30 (1997) 7990–7999.

[10] Y.I. Tien, K.H. Wei, J. Polym. Res. 7 (4) (2000) 245–250.

[11] T.J. Pinnavaia, G.W. Beall, Polymer–Clay Nanocomposites, John Wiley and Sons Ltd., Chichester, 2000.

[12] K.A. Padmanabhan, Mater. Sci. Eng. 304–306 (2001) 200–205.

[13] M. Hakkarainen, M.J. Groning, Chromatogr. A. 1052 (2004) 151–159.

[14] S. Karlsson, et al., Polymer 43 (2002) 1081–1094.

[15] Sigma-Aldrich, Bulletin 922, Sigma-Aldrich, 1998.

[16] M.A. Whitehead, C.I. Williams, J. Mol. Struct. 491 (1999) 93–101.

[17] B. Finnigan, et al., Polymer 45 (2004) 2249–2260.