ELSEVIER

Polymer 44 (2003) 2313–2320

polymer

www.elsevier.com/locate/polymer

Effects of organoclay Soxhlet extraction on mechanical properties, flammability properties and organoclay dispersion of polypropylene nanocomposites

Alexander B. Morgan[a,*], Joseph D. Harris[b]

[a]Chemical Sciences, Inorganic Materials Group, The Dow Chemical Company, Midland, MI 48674, USA
[b]Analytical Sciences, Microscopy Group, The Dow Chemical Company, Midland, MI 48674, USA

Received 10 October 2002; received in revised form 21 January 2003; accepted 23 January 2003

Abstract

The organic treatment on a layered silicate used in nanocomposite synthesis is the interface between the hydrophilic layered silicate (clay) and hydrophobic polymer in the case of polypropylene. However, the typical synthesis of an organoclay can result in excess organic treatment which can hinder mechanical and flammability benefits. This excess organic treatment may result in plasticization of the polymer matrix, possibly removing some of the mechanical and flammability property benefits provided by the nanocomposite. In this paper, the effects of using Soxhlet Extraction on the Organoclays after synthesis was investigated. Soxhlet extraction times on organoclays were found to have an effect on the mechanical and flammability properties of the resulting polypropylene nanocomposite. The removal of excess organic treatment by Soxhlet extraction resulted in improvements in flex modulus, improved clay dispersion, delayed time to ignition, and lowered heat release rate during burning.

Keywords: Nanocomposites; Polypropylene; Organoclays

1. Introduction

Polymer layered-silicate nanocomposites are similar to normal polymer composites in that they use fillers to obtain properties which normally are not present for the unfilled polymer. The fillers in nanocomposites are not only nanoscale in their primary particle size, but dispersed and interact with the polymer at the nanoscale. Therefore, the dispersion of the nanoscale filler (nanofiller) is important if improved properties are to be obtained. In the case of layered silicates, the nanofiller is a clay, which in its natural state is hydrophilic, and will only disperse well into very polar polymers or water. In the case of non-polar, hydrophobic polymers such as polypropylene, and organic treatment is needed to coat the surface of the clay with a hydrophobic surface. This allows the organically treated clay (organoclay) to be dispersed in the polymer to give a nanocomposite. The quality of this clay dispersion is important, because if the nanofillers are poorly dispersed, then the mechanical [1–4], thermal [1–4], and flammability properties [4–6] obtained from nanocomposites are absent from the final product. Therefore, the organic treatment, being at the interface between the clay and the polymer, must allow the two separate polarity materials to interface, but it must also not interfere with the desired properties.

Current organoclays used are layered silicates where the organic treatment is put onto the clay by ion exchange. Due to natural defects/charge heterogeneity on the clay plates, not all of the clay plates can be fully ion exchanged. Therefore, some of the organic treatment will remain associated with the clay after ion exchange, but it will not be ionically bound to the surface, only physisorbed to the surface. This extra surfactant can be removed by solvent washes [7], but is typically not done so for commercial organoclays, which are washed only with water. Therefore, the extra surfactant associated with these organoclays will be carried along into the synthesis of a polymer nanocomposite. When the organoclay is compounded, this surfactant may serve a beneficial role, in that it helps disperse the clay plates into the polymer matrix. However, the surfactant may

---

* Corresponding author. Tel.: +1-989-638-1774; fax: +1-989-638-9716.
E-mail address: abmorgan@dow.com (A.B. Morgan).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00095-8

also affect the polymer nanocomposite properties negatively by plasticizing the polymer or inhibiting crystal growth in crystalline polymers. Further, the excess organic treatment may remove some of the flammability benefits obtained from the nanocomposite, by causing early ignition of the nanocomposite [8].

To investigate the effects of excess surfactant on the nanocomposite dispersion and mechanical properties, we used an organoclay which had its excess surfactant removed via Soxhlet extraction. The extracted clays were then used to prepare polypropylene nanocomposites by melt compounding. These nanocomposites were analyzed by several methods to determine what effects, if any, Soxhlet extracted clays would have on polypropylene nanocomposites thermal and mechanical properties. Further, the effect of Soxhlet extraction on clay dispersion would be measured.

2. Experimental

2.1. Organoclay synthesis

All layered silicates (clays) in this study were fluorinated synthetic mica (FSM) based. The FSM used in this study was Somasif ME-100, a sodium FSM from Co-op Chemical, Japan. These clays were ion exchanged in water under high shear (Cowles-type impeller blade, 1000 rpm) and high dilution (2.5 wt% FSM in water) with bis(hydrogenated tallow), dimethyl ammonium chloride (Arquad 2HT, Akzo-Nobel) in a 1 to 1 ratio (1 mol of organic treatment, or ‘quat’ molecule, per 1.0 mol exchangeable sodiums per 8 Si in the FSM unit cell formula on the FSM). The resulting organoclay was washed with water until the filtrate showed an ionic conductivity of <150 μs/cm. The resulting filter cake was dried in a forced-air oven for 24 h, and then ground and sieved to give a powder with particle size <120 μm. The resulting clay was subjected to a Soxhlet extraction with ethanol with times from 0 to 4 days. The resulting clays from these extractions were dried vigorously in a vacuum oven, ground to a fine powder, and analyzed by XRD and TGA prior to blending.

2.2. Nanocomposite melt-compounding

Polypropylene (PP, Montel PD-191) and polypropylene-graft-maleic anhydride (PPgMA, Aldrich) nanocomposites were made by melt blending in a thermoplastic mixing head (Haake Rheocord system, 250 cc mixing head). PP and PPgMA were added to the mixing head at 190 °C and 60 rpm and allowed to mix for 5 min. The clay was then added and the mixture was compounded for 10 min at 190 °C and 100 rpm. All clays and polymers were dried prior to use.

2.3. Transmission electron microscopy (TEM)

Nanocomposites were thin-sectioned at -90 °C with a Reichert Jung Ultracut E ultramicrotome equipped with a FC-4E cryo-chamber. Sections were collected on a copper grid and examined with a Philips CM-12 TEM (Serial # D769) running at an accelerating voltage of 120 kV. Images were recorded digitally with a Gatan Multiscan CCD camera, Model 749.

2.4. Thermogravimetric analysis (TGA)

All TGA data was collected on a TA instruments TGA 2950 system with autosampler at 20 °C/min, under N_2, from room temperature to 700 °C. Samples were analyzed in triplicate for error analysis.

2.5. X-Ray diffraction (XRD)

All XRD data was collected with a Bruker AXS diffractometer using Cu Kα radiation ($\lambda = 0.1505945$ nm) with a 0.02 2θ step size and a 2 s count time. All polymer nanocomposite samples were solid monolith samples, analyzed in reflectance mode, with synchronous rotation used to limit effects from surface ordering. All clay samples were ground to give a powder particle size of <40 μm and analyzed in reflectance mode.

2.6. Mechanical property testing

Samples were tested for flexural modulus following ASTM D790 Method 1 Procedure A for this type of testing. Izod impact testing followed the ASTM D256-84 procedure, and the reported results are for room temperature tests. Flexural modulus and impact values have a variation of 5% in the measurement, according to the large number of other PP samples tested on the same instrument in the same lab.

2.7. Cone calorimeter testing

Samples were analyzed on a Dark Star Research Cone Calorimeter at 35 kw/m^2 heat flux and exhaust flow of 24 l/s using the standardized cone calorimeter procedure (ASTM E-1354-92). Data collected is the average of two samples, with an error of ± 10%.

3. Results and discussion

Three areas of possible excess surfactant effect on the polymer nanocomposite were measured. These were thermal properties, mechanical properties, and clay dispersion, which were measured by TEM and XRD. XRD [1–4,9] and TEM [1–4,10–12] are the most commonly used techniques for measuring clay dispersion due to the their complimentary nature when both datum are used to interpret the nanocomposite dispersion data [13]. The organoclays to be used in this study were taken from a large batch of organoclay which had not been subjected to Soxhlet extraction with ethanol. Small batches of organoclay (50 g) were subjected to Soxhlet extraction with ethanol for times from 1 to 4 days. The unextracted clay was referred to as 0 day extraction time clay.

Soxhlet extraction did affect the nature of the clays, especially with time. Increasing extraction time did not greatly change the TGA data (Fig. 1) for these materials, with the only change in weight loss occurring between the 0 and 1 day extraction time samples. TGA data for 1, 2, 3, and 4 day extraction time samples is about the same. XRD data (Fig. 2) however, does appear different. There is a d-spacing decrease going from 0 day to 1 day extraction time, with the main peak decreasing to 2.8 nm from 3.6 nm. After the 1 day extraction time, and with increasing extraction time, the peak at approximately 2.8 nm begins to decrease in intensity as a new peak at 3.5 nm increases in height. After a 4 day extraction time, the newer peak at 3.5 nm suggests some new ordering with a different spacing. No good explanation of this spacing change currently exists.

Each of the extracted and non-extracted clays were compounded into PP + PPgMA to generate nanocomposites for study. All samples were compounded the same way, using the same base PP (Montell PD-191) and PPgMA (Aldrich PPgMA). Concentrations of clay and the ratio of PP to PPgMA were kept constant in the study. Interestingly, as Soxhlet extraction time increases, the d-spacing change between clay layers, as measured by XRD, begins to decrease (Table 1). However, overall clay dispersion (as observed by TEM, Figs. 3–7) appears to improve with increasing Soxhlet extraction times.[1] This combination of data suggests that the excess organic treatment does help the polymer intercalate in between the clay plates. Since the TEM data shows better dispersion with increasing extraction times, this suggests that the removal of excess organic treatment helps dispersion. However, when the XRD and TEM data are combined, it suggests that once the excess organic treatment is removed, the material obtained will no longer be an intercalated nanocomposite, even though the primary particle size and clay dispersion at the micro and nanoscale has been improved with the extracted clay. Another possible explanation is that the Soxhlet extraction breaks up the primary clay particles (tactoids) into smaller clay stacks, which then disperse into the polymer matrix upon melt blending as small clay stacks, rather than clay which intercalates polymer forming a nanocomposite. The resulting extracted material however, must still have some nanocomposite characteristics, as it still has improved mechanical properties with increasing Soxhlet extraction times. For the effect of clay extraction time on the mechanical properties, the flex modulus increases after 1 day extraction times, but the Izod impact values are slightly lowered. Extraction times beyond 1 day on the clay do not greatly improve the flex modulus beyond that seen for the nanocomposite made with the 1 day extracted clay. Clay extraction time did not seem to have much of an effect on thermal properties, as the TGA data (Table 2) did not suggest any interesting phenomena. For all of the nanocomposites, regardless of extraction time, the onset of decomposition is about the same. While there is less organic treatment in the extracted clays, it still has the same organic treatment which still has the same thermal decomposition temperature, and therefore, the onset of decomposition should not change much with Soxhlet extraction. This hypothesis seems to fit with the observed TGA data.

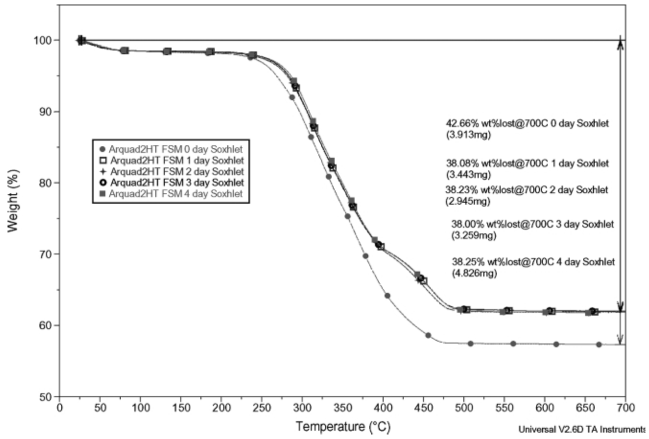

Fig. 1. TGA data Soxhlet extracted organoclays.

Soxhlet extraction time of the organoclay also had an effect on the flammability of the nanocomposite as tested by Cone Calorimeter (Table 3). In the presence of excess organic treatment, where the PP + PPgMA was compounded with Clay #1 (0 day Soxhlet extraction time), the time to ignition (T_{ig}) is shortened, even though the peak heat release rate (HRR or Peak q) is greatly reduced. As Soxhlet time is increased, the T_{ig} increases, but the peak HRR fluctuates somewhat, increasing with 1 day extraction time (Clay #2) and then slowly reducing further with increasing extraction time. The average HRR (Mean q) trends follow that observed for the peak HRR above. Given that the TGA data on the Soxhlet extracted clays shows that the excess organic treatment is removed after 1 day extraction time (Fig. 1), the Total HRR data fits well. If the excess organic treatment ignites early (as shown by the slightly reduced T_{ig}), it will also result in a slightly higher total HRR when compared to the nanocomposites where this excess organic treatment has been removed. The Total HRR values for the

---

[1] Note—TEM is a qualitative tool when used to determine overall clay dispersion. Therefore, the quality of dispersion is determined by comparing several TEM images of differing dispersion. If the number of large clay tactoids observed decreases when comparing two different clay samples, then the samples with less clay tactoids is presumed to have better dispersion. This is however, subjective to TEM interpretation experience. See Ref. [13] for more details.

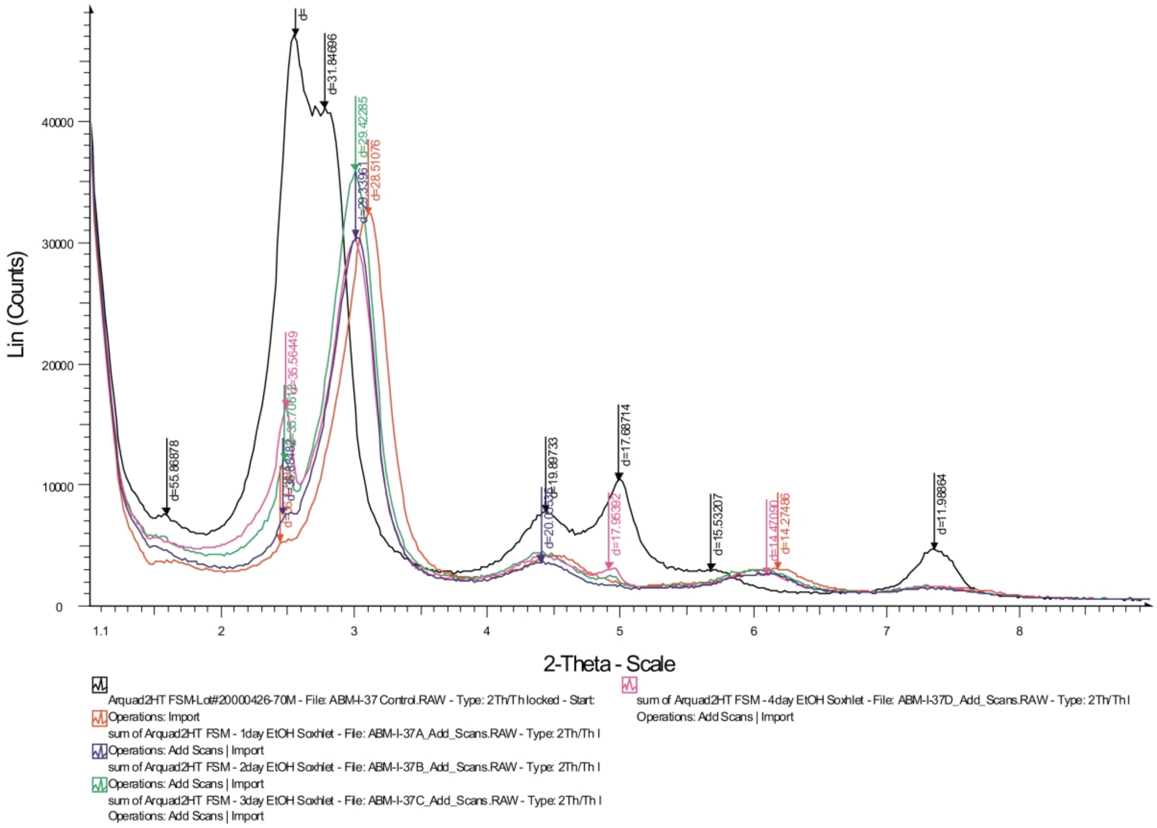

Fig. 2. XRD data for Soxhlet extracted clays. Black = 0 day, Red = 1 day, Blue = 2 day, Green = 3 day, Purple = 4 day extraction time.

Soxhlet extracted clay nanocomposites are approximately all the same, with some slight variation well within the region of error. Since the amount of organic treatment on the Soxhlet extracted clays is the same, the reason behind the lowered peak and average HRR values with increasing Soxhlet extraction times must be related to clay dispersion. TEM (Figs. 3–7) shows that as Soxhlet extraction times increase, the clay dispersion gets better. This suggests that as clay dispersion gets better, the peak and average HRR values are lowered, and T_{ig} is increased with improved clay dispersion. When this finding is combined with the mechanical properties seen in Tables 1 and 2, it suggests that the clay organic treatment and clay dispersion in the nanocomposite have different effects on nanocomposite properties. Clay organic treatment appears to have more of an effect on polymer nanocomposite mechanical properties than just clay dispersion. Conversely, clay dispersion plays a larger role in polymer nanocomposite flammability than the clay organic treatment does, although the organic treatment amount on the clay has an effect on T_{ig} and total HRR. The extractions of the clay did not appear to affect the mechanism of char formation observed with polymer nanocomposites as reported in the open literature by Gilman [5,6,8]. Since the clay plates slow down the rate of fuel release, and

Table 1
PP + PPgMA formulations—XRD and TEM data

Sample	Organoclay (wt%)	PP (wt%)	PPgMA (wt%)	XRD (100) d-spacing change (nm)	TEM	
					Microscale dispersion	Nanoscale dispersion
PP + PpgMA control	0	72	28	N/A	N/A	N/A
PP + PPgMA + Clay #1	8.5	65.9	25.6	0.2	Fair	Good
PP + PPgMA + Clay #2	7.9	66.3	25.8	0.13	Good	Good
PP + PPgMA + Clay #3	7.9	66.3	25.8	0.06	Good	Good
PP + PPgMA + Clay #4	7.9	66.3	25.8	0.01	Good	Good
PP + PPgMA + Clay #5	7.9	66.3	25.8	−0.06	Good	Good

PP/PPgMA nanocomposites + Soxhlet extracted organoclays. Clay #1: 0 day extraction time. Clay#2: 1 day extraction time. Clay #3: 2 day extraction time. Clay#4: 3 day extraction time. Clay #5: 4 day extraction time.

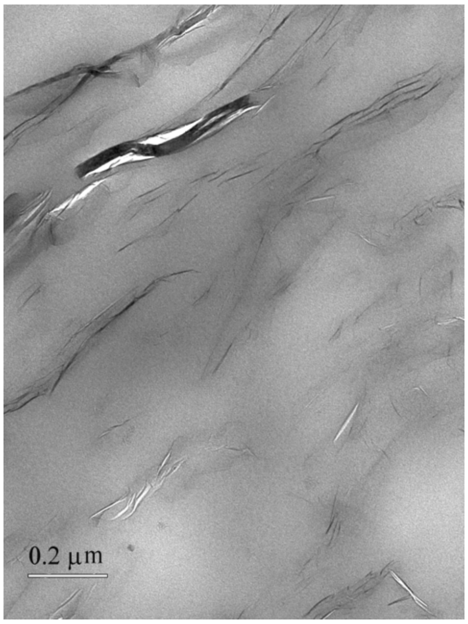

Fig. 3. Representative TEM of PP + PPgMA + Clay #1 (0 day extraction time).

this prolonged fuel release leads to char formation through longer residence times of polymer radicals, this effect can be measured by looking at the mass loss rate curves (not shown) for a polymer nanocomposite. The mass loss data for the PP extracted clay nanocomposites reported here was not very different from the HRR curve of the same nanocomposite, as has been seen in previous work [5,8]. The rate and general mechanism of char formation for these nanocomposites seem to be unchanged with the removal of excess organic treatment by Soxhlet extraction.

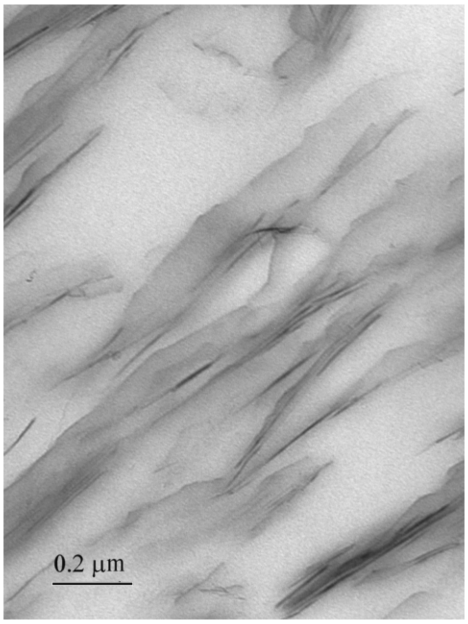

Fig. 4. Representative TEM of PP + PPgMA + Clay #2 (1 day extraction time).

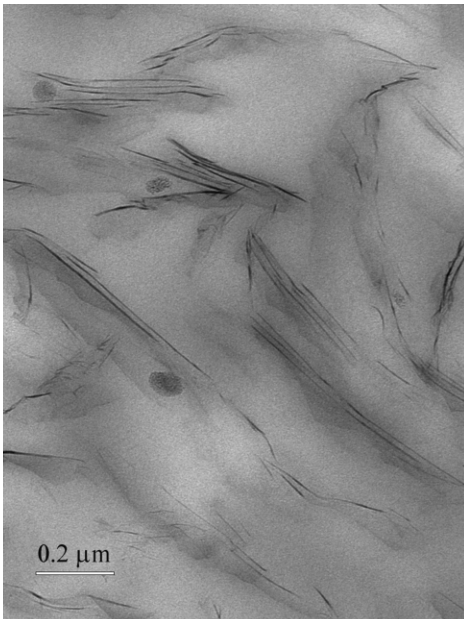

Fig. 5. Representative TEM of PP + PPgMA + Clay #3 (2 day extraction time).

4. Conclusions

Soxhlet extraction on organoclays does affect the properties of polypropylene nanocomposites when the extracted organoclays are melt-compounded. As the Soxhlet extraction removes excess organic treatment from the clay, flex modulus improves, suggesting that the excess treatment is an impediment to the mechanical property benefits gained from the formation of the nanocomposite. However, the excess organic treatment appears to be necessary for allowing the polypropylene to intercalate in between the

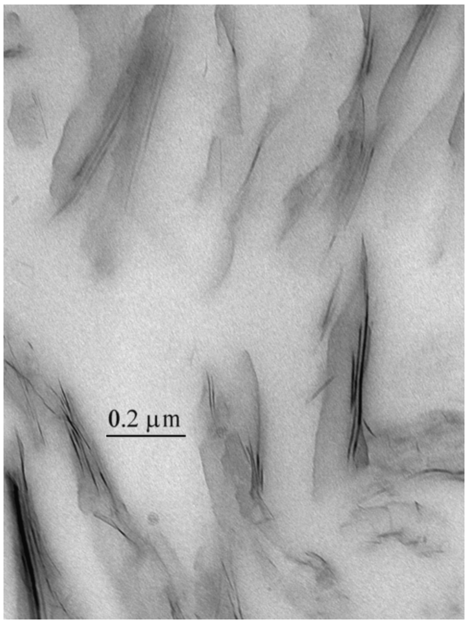

Fig. 6. Representative TEM of PP + PPgMA + Clay #4 (3 day extraction time).

Fig. 7. Representative TEM of PP + PPgMA + Clay #5 (4 day extraction time).

clay plates during melt compounding. As the treatment is removed by Soxhlet extraction, the spacing between the clay plates collapses, and during compounding, collapses further, suggesting that the polypropylene cannot enter between the clay plates during melt compounding. Interestingly, while XRD suggests that clay intercalation decreases with increased clay extraction times, TEM suggests that clay dispersion improves with increased clay extraction times. Clay extraction times, while having an effect on clay dispersion by TEM and XRD, have different effects on polymer nanocomposite mechanical and flammability properties.

As excess clay organic treatment is removed by Soxhlet extraction, mechanical properties are affected. Flex modulus increases once excess organic treatment is removed, but increased extraction times, which improves clay dispersion (as observed by TEM), does not improve flex modulus above that obtained during a 1 day extraction time. This suggests that once excess organic treatment has been removed, the detrimental effect of that excess organic treatment will also be removed. However, since clay dispersion is improved with increasing clay extraction times, this suggests that the improvement in clay dispersion does not always result in better flex modulus. As the spacing between clay plates decreases due to organic treatment removal, the flex modulus actually decreases slightly when compared to the 1 day extracted clay nanocomposite. This finding concludes that for polypropylene nanocomposite reinforcement, in regards to flex modulus, that polymer intercalation between clay layers is just as important as removing excess organic treatment, which appears to have a plasticizing effect on flex modulus. The effect of clay extraction times on impact properties is somewhat converse

Table 2
PP + PPgMA formulations—TGA, mechanical property data

Sample	Organoclay (wt%)	PP (wt%)	PPgMA (wt%)	TGA[a]				Mechanical properties		Appearance: color and transparency
				Inorganic (wt%)	dTGA Peak (C)	Onset of decomp (C)		Flex mod (MPa)	Izod (R.T.) (N-m/m)	
PP + PPgMA control	0	72	28	1.31	409	280		1296	58.7	Lt. Brown, translucent
PP + PPgMA + Clay #1	8.5	65.9	25.6	6.2 (4.81)	468	265		1992	42.7	Brown, transparent
PP + PPgMA + Clay #2	7.9	66.3	25.8	6.08 (4.77)	476	265		2151	32.1	Med. Brown, transparent
PP + PPgMA + Clay #3	7.9	66.3	25.8	6.13 (4.82)	465	265		2096	34.7	Med. Brown, transparent
PP + PPgMA + Clay #4	7.9	66.3	25.8	6.17 (4.86)	474	265		2096	34.7	Med. Brown, transparent
PP + PPgMA + Clay #5	7.9	66.3	25.8	6.35 (5.04)	474	265		2089	37.4	Med. Brown, transparent

PP/PpgMA nanocomposites + Soxhlet extracted organoclays. Clay #1: 0 day extraction time. Clay#2: 1 day extraction time. Clay #3: 2 day extraction time. Clay#4: 3 day extraction time. Clay #5: 4 day extraction time.

[a] TGA data: number in paranthesis represents inorganic residue minus residue of PP + PPgMA control.

Table 3
Cone calorimeter data for PP + PPgMA + Soxhlet extracted clays

	Units	PP + PPgMA control	PP + PPgMA + Clay #1	PP + PPgMA + Clay #2	PP + PPgMA + Clay #3	PP + PPgMA + Clay #4	PP + PPgMA + Clay #5
Heat flux	kW/m^2	35	35	35	35	35	35
T_{ig}	s	62	59	65	66	68	70
Peak q	kW/m^2	1435.4	498.4	518.6	510.3	494.1	491.0
Mean q	kW/m^2	769.9	406.4	429.3	423.8	418.4	405.1
180 s q	kW/m^2	684.3	450.1	476.3	465.2	450.5	456.4
300 s q	kW/m^2	410.6	386.1	379.3	374.4	376.6	378.1
Total q	MJ/m^2	122.9	115.8	113.7	112.3	112.9	113.4
Effective heat	MJ/kg	43.1	41.2	40.6	40.1	40.8	40.6

PP/PPgMA nanocomposites + Soxhlet extracted organoclays. Clay #1: 0 day extraction time. Clay#2: 1 day extraction time. Clay #3: 2 day extraction time. Clay#4: 3 day extraction time. Clay #5: 4 day extraction time.

to the trend observed in regards to flex modulus. Specifically, as clay is loaded into polypropylene, the flex modulus goes up but the impact strength goes down. As excess organic treatment is removed, the impact strength goes down even further. However, this decrease only extends to the 1 day extraction time clay nanocomposite. As extraction times increase, resulting in better clay dispersion and d-spacing collapse, impact strength begins to rise again, although never to the levels of the base polymer. There currently is no good explanation for the loss of impact strength in these organoclay nanocomposites. Extracted clays seem to complicate the explanation, rather than clarify it.

Clay extraction times also have an effect on the polymer nanocomposite flammability properties. The removal of the extra organic treatment by Soxhlet extraction results in delayed, rather than earlier T_{ig} for the nanocomposite when compared to the base unfilled polymer. While the T_{ig} gets further delayed by increased extraction times, the HRR value changes in a different manner. The 0 day extracted clay nanocomposite has a lower HRR than the 1 day extracted clay nanocomposite. As clay extraction time increases, the HRR begins to drop again, finally reaching a level lower than that of the 0 day extracted material. This finding, combined with the improved clay dispersion observed by TEM suggests that clay dispersion plays more of a role than just the organic treatment in polymer nanocomposite flammability once the excess organic treatment is removed.

In conclusion, the effects of clay extraction on polymer nanocomposite mechanical and flammability properties are complex. Increased clay extraction time may have no additional effect on some properties once the excess organic treatment is removed, but may have a much different effect on other properties as the extraction time is increased. Clay extraction time did not remove excess organic treatment after a 1 day extraction time, but it did change the ordering of the clay, as well as the dispersibility of the clay in the polymer matrix. Therefore, the synthesis, purification, and washing of organoclays does have an effect on the polymer nanocomposite these organoclays are compounded into.

Acknowledgements

The author wishes to thank Mike Paquette and Wanda Stringfield for organoclay synthesis. Thanks also goes to Zoran Jovanovic, Dean Millar, and Malcolm Finlayson for scientific discussions. Finally, the author wishes to thank Ralph Hale for Mechanical Property testing, Joseph Harris for TEM work, and Sylvie Boukami for Cone Calorimeter Analysis.

References

[1] Gianellis EP. Adv Mater 1996;8:29.

[2] Wang Z, Pinnavaia T. J Chem Mater 1998;10:1820.

[3] Burnside SD, Giannelis EP. Chem Mater 1995;7:1597.

[4] Alexandre M, Dubois P. Mater Sci Eng Reports 2000;28:1.

[5] Gilman JW. App Clay Sci 1999;15:31.

[6] Gilman JW, Kashiwagi T, Nyden M, Brown JET, Jackson CL, Lomakin S, Giannelis EP, Manias E. Chemistry and Technology of Polymer Additives. Cambridge: The Royal Society of Chemistry; 1999. pp. 249–265.

[7] LeBaron PC, Pinnavaia T. J Chem Mater 2001;13:3760.

[8] Gilman JW, Kashiwagi T, Morgan AB, Harris RH, Brassell LD, VanLandingham M, Jackson CL. National Institute of Standards and Technology Internal Report (NISTIR) 6531, July 2000.

[9] Giannelis EP, Burnside SD. J Polym Sci Part B 2000;38:1594.

[10] Huang X, Lewis S, Brittain WJ, Vaia RA. Macromolecules 2000;33:2000.

[11] Reichert P, Nitz H, Klinke S, Brandsch R, Thomann R, Mülhaupt R. Macromol Mater Eng 2000;275:8.

[12] Vaia RA, Jandt KA, Krammer EJ, Giannelis EP. Chem Mater 1996;8:2628.

[13] Morgan AB, Gilman JW. J App Polym Sci 2003;87:1329.