

Monitoring clay exfoliation during polymer/clay compounding using fluorescence spectroscopy*

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A fluorescent probe molecule, Nile blue perchlorate, was used to monitor the compounding of nylon 11 with clay filler. Prior to compounding, Nile blue was incorporated into the gallery region between silicate layers of the clay by an ion-exchange process. While residing in the gallery, fluorescence from Nile blue was quenched because of fluorescence resorption in a high dye concentration environment. However, when clay is compounded with the nylon, clay exfoliation allowed the dye to escape the gallery region and to become dispersed in the resin matrix. During batch mixing, we observed that fluorescence increased with time indicating that dye molecules were migrating from the gallery. Experiments carried out using a twin-screw extruder to compound resin and clay showed that twin-screw compounding was much more efficient in producing clay exfoliation than was the batch mixer.

Key words: exfoliation; fluorescence spectroscopy; nanoclay composites; nylon; polymer processing; process monitoring

1. Introduction

Compounding clay with polymer resins is carried out for the purpose of producing enhanced product performance with a small amount of clay filler (Acierno *et al.*, 2004;

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Bourbigot *et al.*, 2004; Daniel *et al.*, 2003; Fong *et al.*, 2002; Fornes *et al.*, 2002; Giannelis, 1998; Krishnamoorti and Giannelis, 1997; Krishnamoorti *et al.*, 1996; McNally *et al.*, 2003; Ray and Okamoto, 2003; Yang *et al.*, 1997; Zanetti *et al.*, 2000). Performance enhancement is the result of the exfoliation of nano-sized silicate platelets from large aggregate clay particles. Dispersal of platelets throughout the resin matrix creates a large surface area interface between resin and filler producing a microstructural network that yields improved mechanical, fire retardation and barrier properties in many resin/clay mixtures (Bourbigot *et al.*, 2004; Dennis *et al.*, 2001; Fornes *et al.*, 2002; Giannelis, 1998; Gilman *et al.*, 2002; Gloaguen and Lefebvre, 2000; Liu *et al.*, 1999; Masenelli-Varlot *et al.*, 2002; Morgan *et al.*, 2002; Strawhecker and Manias, 2000; Yeh *et al.*, 2004). The key to achieving high performance nanocomposites is clay exfoliation. Examining resin/clay composites to determine microstructure and the extent of exfoliation is usually carried out through labour-intensive post processing examination using transmission electron microscopy (TEM). These observations, while yielding important information, are limited in scope because only a small micro-area of material is analysed and because the information is obtained well after processing is complete.

Using TEM in the research laboratory can help to establish compounding parameters that yield exfoliation, but, in the industrial processing environment, online measurements that yield immediate information about exfoliation in the bulk material are necessary in order to control and maintain uniform quality of the output. We have addressed the issue of real-time process monitoring by developing an instrumented slit die that is attached to the exit of a twin-screw extruder and is used to monitor dielectric and optical properties of the compounded extrudate (Bur *et al.*, 2004a). In previous work, we showed that both optical transmission and the characteristic dielectric relaxation time of the Maxwell–Wagner relaxation in the melt composite are dependent on clay exfoliation (Bur *et al.*, 2004b, 2005; Davis *et al.*, 2004; Lee *et al.*, 2005). Optical transmission through a composite having significant exfoliation was observed to increase with exfoliation because nano-sized flakes are smaller than the wavelength of light and scatter negligible light. From a dielectrics perspective, nano-sized silicate flakes act as nanocapacitors that result in a decrease in the Maxwell–Wagner relaxation frequency. Based on these measurements, we developed extent of exfoliation models that were used to compute and compare extent of exfoliation in a family of nylon/clay nanocomposites.

In this paper, we will focus on real-time observations of fluorescence spectroscopy that were carried out during batch mixing and during twin-screw extrusion compounding of nylon 11 with organo-modified clays. A fluorescent dye, Nile blue perchlorate (NB), was used as a molecular probe to detect exfoliation. The concept is based on a significant body of work regarding the impact of clays and nano-confined spaces on the fluorescence spectra of probe molecules (Ogawa and Kuroda, 1995). For example, it is known that NB will experience significant blue shift in its spectrum when placed in nano-confined regions of less than 7.5 nm (Baumann *et al.*, 2001).

At elevated concentrations, NB can form a dimer or H-structure that is non-fluorescent, and concentration quenching can occur (Bujdak *et al.*, 2002; Schoonheydt *et al.*, 1984). Iron in natural clay can also act as a fluorescence quencher (Schoonheydt *et al.*, 1984). Aggregates of NB molecules have a blue band of fluorescence that is greatly reduced upon dilution, while a red band appears. The demonstrated sensitivity of NB to its micro-environment makes it a likely candidate for a microstructure probe of polymer clay nanocomposites. This was the basis of a previous paper from this laboratory, in which we presented post-processing, room temperature results from fluorescence probe spectroscopy studies that demonstrated the sensitivity of NB to the state of intercalation and exfoliation in polystyrene and nylon 6 composites (Maupin *et al.*, 2004).

2. Experimental procedure^a

Nylon 11 (Rilsan BESNO from Atofina), a moderate viscosity extrusion grade resin with melting point at 185°C was used. The nylon 11 pellets were compounded with two montmorillonite clays from Southern Clay products designated as 15A and 30B. Also, an in-house prepared montmorillonite clay modified by cationic exchange with hexadecyl imidazolium surfactant was used (Gilman *et al.*, 2002). The 15A clay was prepared by ion exchange of natural clay with quaternary ammonium (dimethyl, dihydrogenated tallow) having a cation-exchange capacity of 1.25, and the 30B clay was produced by ion exchange with a methyl, tallow, bis-2-hydroxyethyl quaternary ammonium ion, having a cation-exchange capacity of 0.90; 30B differs from 15A by the surfactant functionality, which is polar for 30B and non-polar for 15A. Nile blue A perchlorate was obtained from Aldrich, and incorporated in the clay gallery by a second ion exchange that was designed to replace 5% mol fraction of the 15A and 30B surfactant with NB dye, and 1% mol fraction in the case of the imidazolium surfactant. Standard ion-exchange procedures using aqueous ethanol were modified for the preparation of the clays with NB. Procedures are described in a previous publication (Maupin *et al.*, 2004). The ion-exchanged clay product was washed thoroughly to remove residual NB from the surface. The clay materials containing the Nile blue dye are designated NB15A, NB30B and NBIM.

The powdered clay was compounded with the nylon resins at 4% mass fraction of clay in the resin. Prior to compounding or mixing, both resin and clay were dried overnight at 80°C. Compounding was carried out using an 18-mm Haake Rheocord model 9000 co-rotating twin-screw extruder, and batch mixing was done with the Haake batch mixer.

Fluorescence spectra were obtained using an Ocean Optics CCD spectrometer, model USB2000, with an entrance slit of 200 μm. The light source was a 30-mW, 407-nm violet laser from Power Technology. Both the batch mixer and the twin-screw extruder were instrumented with an optical fibre sensor that fitted into a standard ½ inch instrument port. For the extruder, the instrument port was located in a slit die

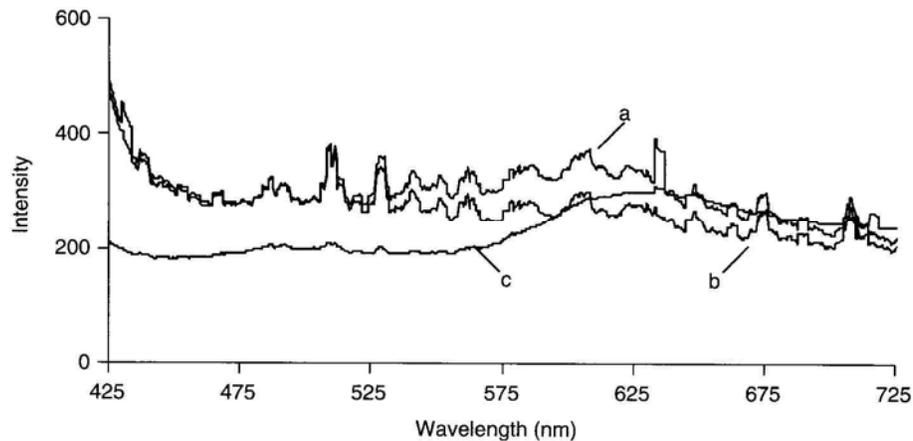


Figure 1 Fluorescence spectra from the three clays: (a) NB15A; (b) NB30B; (c) NBIM

attached to the exit. For the batch mixer, the instrument port was positioned in the front clamping plate at the mid-point between the two kneading elements. The optical fibre sensor and the instrumented slit die have been described in previous publications (Bur *et al.*, 2004a; Bur and Roth, 2004). Both compounding and mixing were carried out at 198°C.

The largest relative standard uncertainty in the measured fluorescence intensity was 2%. The standard uncertainty in the temperature measurement was 1°.

3. Results and discussion

Figure 1 shows fluorescence spectra for washed NB15A, NB30B and NBIM clays obtained at room temperature with excitation at 407 nm. Within the uncertainty of the measurement, the NB15A and NB30B clays show zero fluorescence intensity, and for NBIM, having a lower concentration of dye ion the gallery than NB15a or NB30B, a small fluorescence band is seen at 630 nm. The near zero fluorescence for all three clays indicates that the NB dye molecules undergo fluorescence concentration quenching, ie, because the concentration of dye in the gallery regions is relatively high, any fluorescence that is created is immediately resorbed by neighbouring NB molecules. It is also possible that quenching is caused by iron in the clay. Figure 1 shows that, at the outset of compounding, fluorescence from the NB clays is negligible.

Before carrying out compounding with the NB clays, free NB dye was mixed with nylon 11 neat and with nylon 11/30B and nylon/15A composites where neither the 15A or 30B clays contained NB dye. These experiments establish a baseline for the behaviour of NB dye in nylon and clay environments. The spectra of Figure 2 show

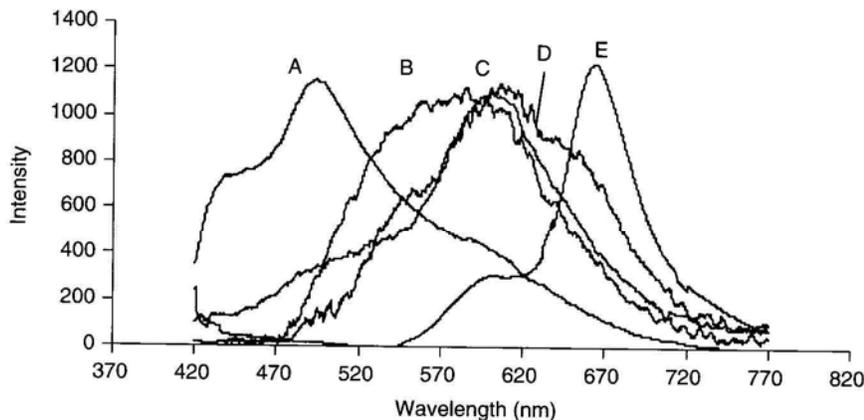


Figure 2 The spectra of NB dye in different environments: (A) free NB in nylon 11 at 195°C at the start of mixing in the batch mixer; (B) free NB in nylon 11 after twin-screw extrusion at 199°C; (C) free NB in nylon 11 after twin-screw compounding with 15A clay at 199°C; (D), free NB in nylon 11 after twin-screw compounding with 30B clay at 199°C; (E) NB in dilute ethanol solution at room temperature. All spectra obtain using 407-nm excitation

how the primary NB fluorescence band shifts with changes in mixing and the environment at the processing temperature, 195°C for the Haake batch mixer or 198°C for the twin-screw extruder. After 1 min of mixing with neat nylon 11 in the batch mixer, fluorescence intensity maximum is observed at 500 nm, which indicates that dye molecules are in an aggregate formation or molecular clusters, and are not well dispersed in the polymer matrix. Continued batch mixing did not produce significant change, but more efficient compounding of free NB with neat nylon 11 was carried out using the twin-screw extruder with a residence time of 4 min. Curve B of Figure 2 shows a shift in the fluorescence intensity maximum to 585 nm after twin-screw compounding. A larger Stokes shift was observed for the free NB dye compounded with the 15A and 30B clays that show intensity maxima in the vicinity of 610 nm. Also, we show in Figure 2 the spectra for NB in dilute ethanol solution at room temperature that has an intensity maximum at 664 nm. The primary feature of these observations is that poorly dispersed NB dye (spectra A) has an intensity maximum near 500 nm, but the maximum intensity is red shifted with dye dilution in the matrix. All of the spectra of Figure 2 were obtained using 407-nm excitation.

Fluorescence spectra from batch mixing NB15A with nylon 11 is shown in Figure 3, where we have plotted spectra and their progression with time during mixing at 198°C. Initially, a small amount of fluorescence was observed at 510 nm that is attributed to clusters of dye molecules. The fluorescence from individual, well dispersed NB molecules is seen at 616 nm. As batch mixing proceeded, we observed

that the 616-nm fluorescence band develops at the expense of the 510-nm band. The process of exfoliation allows the release of NB dye into the resin matrix, perhaps in clusters of molecules expressing fluorescence at 510 nm, and further mixing disperses it throughout the matrix permitting the 616-nm fluorescence band to appear. Exfoliation can be monitored using the ratio of intensities at 616 and 510 nm, I_{616}/I_{510} , a quantity that is plotted in Figure 4. After 10 min of mixing, I_{616}/I_{510} reached a value near unity, but the curve has a positive slope indicating that the process of exfoliation and dye dispersion was ongoing at that time.

The contrast between the results from batch mixing (Figure 3) and those from twin-screw compounding (Figure 5) of nylon 11/NB15A is striking. The spectrum from twin-screw compounding was obtained while using the optical sensor positioned at the exit of the extruder, for which measurements were made during the steady state. A fluorescence spectrum identical to that of Figure 5 was obtained repeatedly over the 10-min period for which extrusion was monitored. Comparing the spectra of Figures 3 and 5, we see that the intensity ratio that tracks exfoliation, I_{616}/I_{510} , has a value of 8.5, much higher than $I_{616}/I_{510}=1.16$ achieved from batch mixing. (The value $I_{616}/I_{510}=8.5$ was obtained by deconvoluting the spectrum of Figure 5 into fluorescence bands at 510, 616 and 710 nm.)

The evolution of fluorescence during mixing can also involve diffusion of dye from the gallery regions at processing temperature and applied stress. However, the data show that diffusion effects are small. If we assume that all of the 616-nm fluorescence that developed during batch mixing was due to diffusion, then after 10 min of diffusion, the I_{616}/I_{510} ratio is 1.16 and after 4 min the ratio is 0.7.

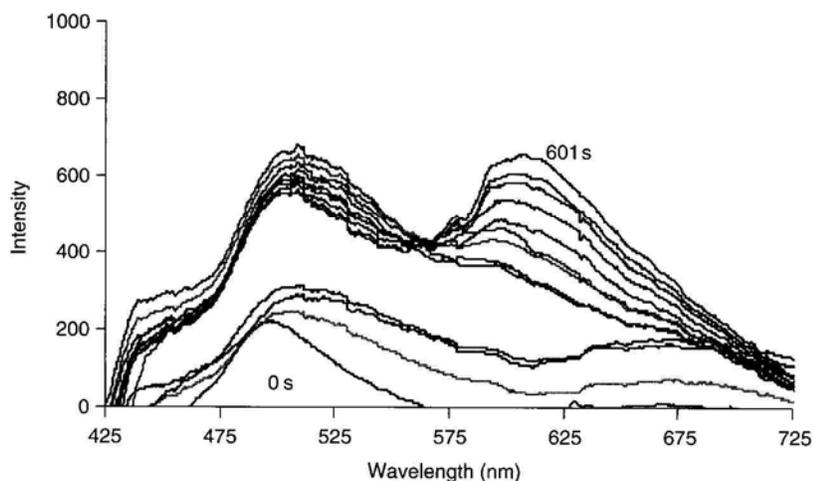


Figure 3 Fluorescence spectra of nylon 11 compounded with NB15A in the batch mixer. Spectra were obtained over a period of time from 0 to 601 s

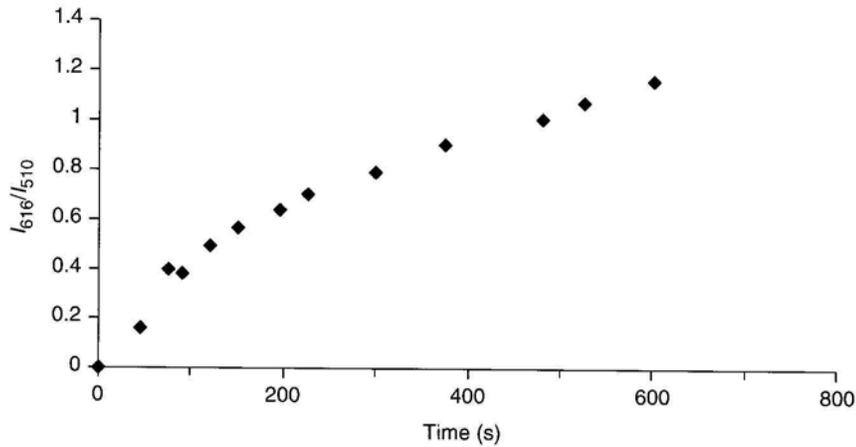


Figure 4 The intensity ratio I_{616}/I_{510} from the data of Figure 2, nylon 11 compounded with NB15A, is plotted versus time

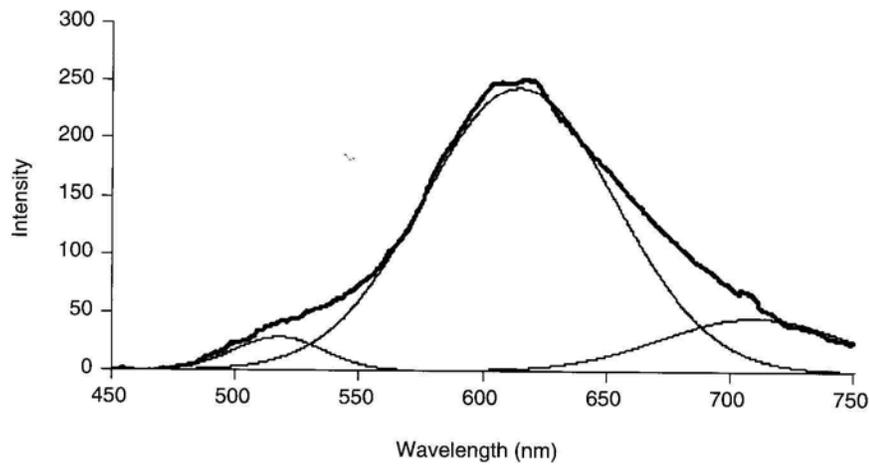


Figure 5 A fluorescence spectrum (heavy curve) obtained during the steady state twin-screw extrusion of nylon 11 compounded with NB15A. The spectrum has been deconvoluted into spectra at 510, 616 and 710 nm (light curves)

we use the 4-min ratio to compare with twin-screw extrusion for which the residence time is 4 min. Therefore, if we assume that 4 min of diffusion will yield $I_{616}/I_{510}=0.7$, then only 8% of twin-screw compounding, for which $I_{616}/I_{510}=8.5$, is due to diffusion. The argument lends support for our view that work done by shearing forces during twin-screw compounding plays a major role in producing exfoliation

in a composite that is predisposed thermodynamically to exfoliate. The major difference between batch mixing and twin-screw extrusion is the magnitude and duration of applied shear stress that the mixture experiences. In the mixer, shear forces are applied momentarily and at random intervals, whereas in the twin-screw extruder, shear force is applied uniformly over the length of travel of the screw. The superior efficiency of mixing and production of exfoliated microstructure in the twin-screw extruder is dramatically illustrated in Figure 5. In a subsequent experiment, not shown here, the nylon 11/NB15A extrudate was re-pelletized and recycled through the twin-screw extruder under the same processing conditions. The fluorescence spectra of the recycled material was identical to that of Figure 5 indicating that the extent of exfoliation achieved by compounding at π rad/s (30 rpm) and 198°C reached its maximum during the first cycle. We did not explore the impact on exfoliation due to changes in processing parameters.

The results from mixing and compounding nylon 11 with NBIM, Figures 6, 7 and 8, are similar to those for nylon 11/NB15A. In this case, it appears that exfoliation develops more quickly during batch mixing, but the results from monitoring steady state twin-screw extrusion indicate somewhat less exfoliation for nylon 11/NBIM than for nylon 11/NB15A, ie, $I_{616}/I_{510} = 6.5$. That hexadecyl imidazolium and the tallow 15A surfactants behave similarly during compounding with nylon 11 is not surprising given that both are nominally non-polar and similar in molecular dimensions.

In contrast, the fluorescence observations (Figures 9, 10 and 11) of nylon 11 with NB30B show a relatively small amount of 616-nm fluorescence, and, after 10 min of mixing, the ratio I_{616}/I_{510} was only 0.34 with a slope near zero. The data indicate that

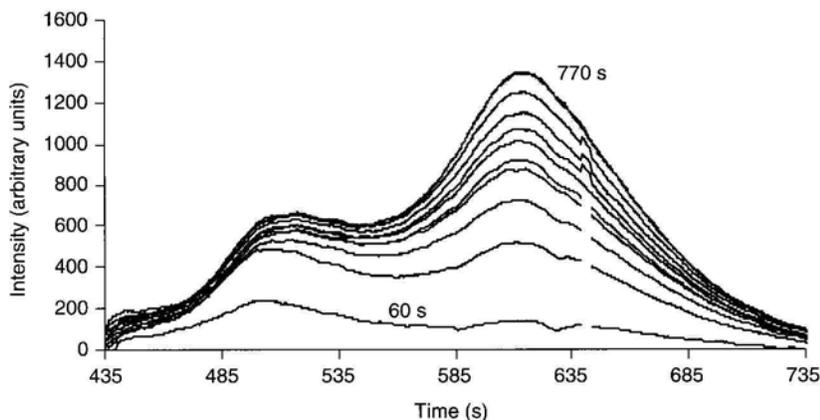


Figure 6 Fluorescence spectra of nylon 11 compounded with NBIM in the batch mixer. Spectra were obtained over a period of time from 0 to 770 s

exfoliation is limited in the nylon 11/NB30B composite and that continued batch mixing will not produce significant improvement. However, twin-screw compounding produced some improvement in the exfoliation increasing the I_{616}/I_{510} ratio to 1.8, but this value is far below that achieved for the nylon 11/NB15A and nylon 11/IMNB composites. The differences in exfoliation between the NB15A and NB30B composites

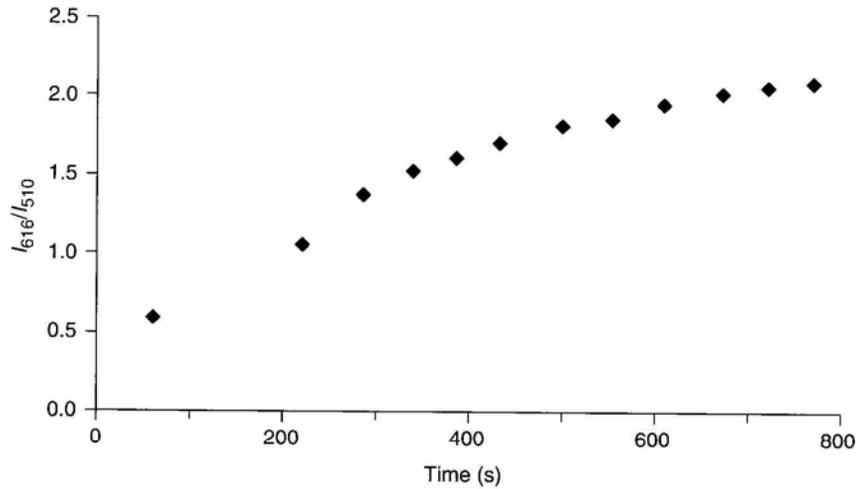


Figure 7 The intensity ratio I_{616}/I_{510} from the data of Figure 5, nylon 11 compounded with NBIM, is plotted versus time

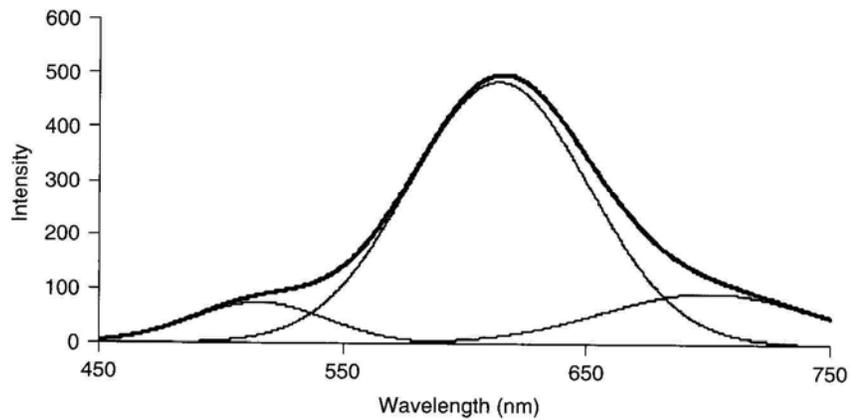


Figure 8 A fluorescence spectrum (heavy curve) obtained during the steady state twin-screw extrusion of nylon 11 compounded with NBIM. The spectrum has been deconvoluted into spectra at 510, 616 and 710 nm (light curves)

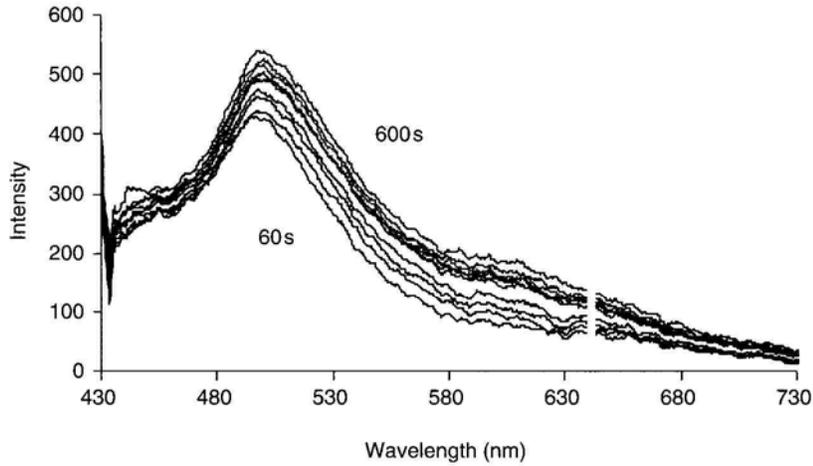


Figure 9 Fluorescence spectra of nylon 11 compounded with NB30B in the batch mixer. Spectra were obtained over a period of time from 0 to 600 s

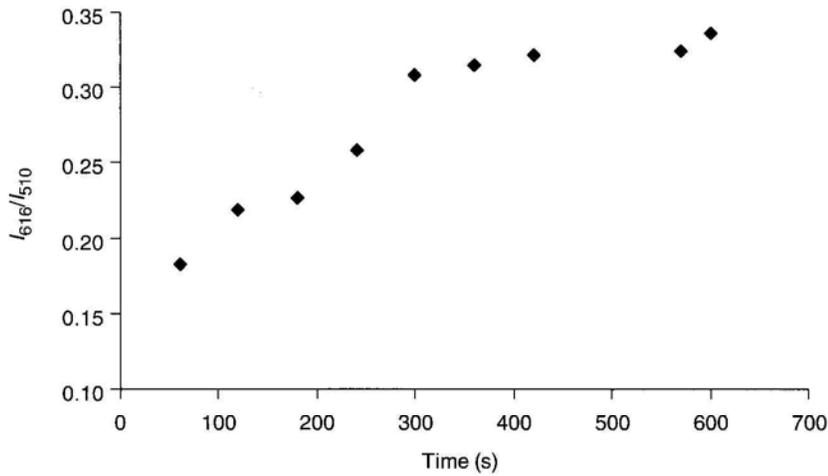


Figure 10 The intensity ratio I_{616}/I_{510} from the data of Figure 8, nylon 11 compounded with NB30B, is plotted versus time

are supported by the TEM pictures in Figures 12 and 13, which show nylon 11/NB15A nanocomposite containing a wealth of nano-sized silicate flakes and some tactoids of aggregate nanoflakes and nylon 11/NB30B composite with fewer nanoflakes along with larger tactoids and aggregates.

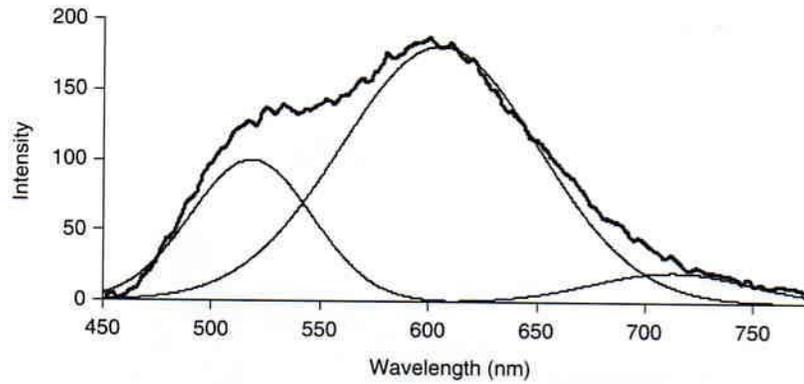


Figure 11 A fluorescence spectrum (heavy curve) obtained during the steady state twin-screw extrusion of nylon 11 compounded with NB30B. The spectrum has been deconvoluted into spectra at 510, 616 and 710 nm (light curves)

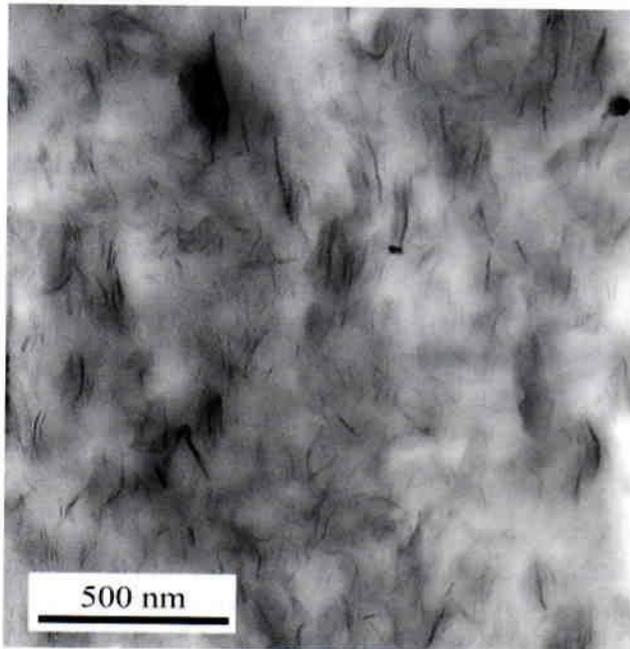


Figure 12 TEM of nylon 11 15A that was compounded in the twin-screw extruder at 198°C

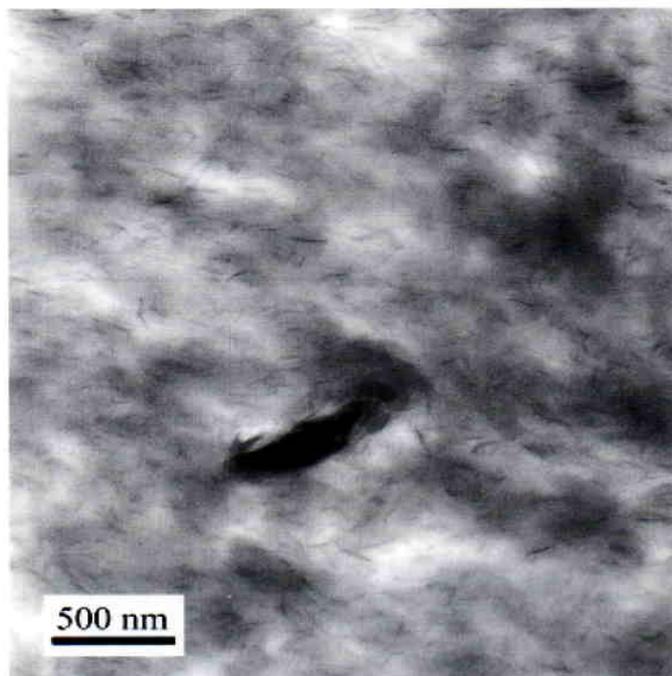


Figure 13 TEM of nylon 11 30B that was compounded in the twin-screw extruder at 198°C

An alternative way of viewing these data is to establish a scale of exfoliation that tracks the evolution of the fluorescence at 616 nm. For example, a scale from 0 to 1 is generated from the expression

$$Ex = \frac{R(t) - R(0)}{R(\infty) - R(0)} \quad (1)$$

where Ex is the extent of exfoliation, and $R(t)$, $R(0)$ and $R(\infty)$ are the fluorescence intensity ratios I_{616}/I_{510} at time t , 0 and at long times. For these data, we would set $R(0) = 0$ and $R(\infty) = 8.5$, the highest value observed. Other values of $R(\infty)$ obtained by varying processing conditions would be appropriate.

We have shown that fluorescence from NB dye is a sensitive indicator of its environment. In the gallery regions between silicate layers, fluorescence from NB is quenched either by concentration quenching or by iron in the clay. When fluorescence is observed at 616 nm, it is an indication that NB molecules have migrated from the gallery and have become dispersed in the polymer matrix. The batch mixing and

compounding experiments are distinctly different and show that twin-screw compounding is the more efficient method of producing exfoliation.

Note

- a. Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

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