Microstructure, Barrier Properties and Mechanical Properties of Nylon-12 Nanocomposite Films

Cecilia Stevens, Ph.D.[a]*
Marek Gnatowski, Ph.D.[a]
Scott Duncan, Ph.D.[b]

a. Polymer Engineering Company Ltd., #110-3070 Norland Ave., Burnaby, BC, Canada, V5B3A6 pecltd@telus.net.
b. DRDC Suffield, Scott.Duncan@drdc-rddc.gc.ca

Thin films of nylon-12 with 10% nanoclay content were prepared by various mixing and extrusion methods. The films were than assessed for chemical permeability and tensile strength and also by FTIR. TEM images were taken of film cross-sections. Materials mixed by batch blending and single-screw extrusion prior to extrusion as a film showed incomplete exfoliation of the nanoclay particles and poor dispersion. Materials mixed by twin-screw extrusion showed better exfoliation and dispersion, but also showed significant breakdown in nanoclay platelet size. FTIR spectra showed a correlation between dispersion and peak height for the 1030 cm^{-1} clay peak. Exfoliation and dispersion appear more important than platelet size to both the strength and barrier properties of the thin films.

Introduction

Undispersed nanoclays exist as lamellar structures; these structures must be exfoliated in order to disperse individual nanoclay platelets in a polymer medium and exploit the increased barrier properties that nanoclays add to the material. Several recent studies have examined the effect of shear on exfoliation during the mixing of materials.[1-4] Relatively little attention, however, has been given to the question of platelet size reduction during mixing. Moreover, studies of the microstructure of nanoclay-containing polymers have generally focused on the effect on mechanical properties, although increased barrier properties are frequently a desirable attribute of the composite materials.

In the work presented here, samples of nylon 12 with 10% nanoclay have been prepared by various mixing methods prior to extrusion as a thin film. These films were then assessed in terms of platelet size, exfoliation, dispersion, FTIR spectroscopy, permeability to corrosives, and mechanical properties.

Experimental

Table 1—Blending Methods

Sample	Blending method
A	None (100% nylon reference)
B	Single-screw extruder (25mm)
C	R.E.E. prep mixer (3 min.)
D	*Twin-screw Brabender D6/2 extruder
E	*Twin-screw Brabender TSE 20mm extruder

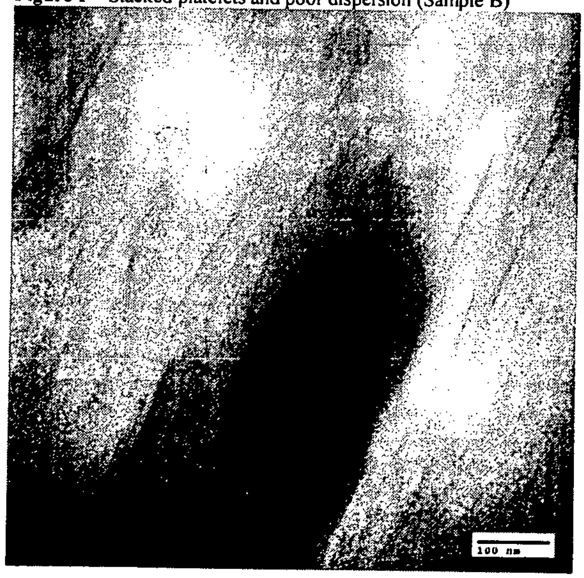
*Thanks to Andrew Yacykewych of W.C. Brabender for his assistance in this project.

The polymer used was nylon 12 L25 from EMS-Grivory and the nanoclay was I30E from Nanocor. Blending methods are summarised above. The blends were extruded into thin films using a 25mm single-screw extruder with ribbon die. Platelet measurements and goodness of dispersion were assessed from representative TEM images. FTIR spectra were normalised using the 3293 cm^{-1} nylon peak. Barrier properties were measured in terms of breakthrough time upon exposure to a corrosive compound.

Results and Discussion

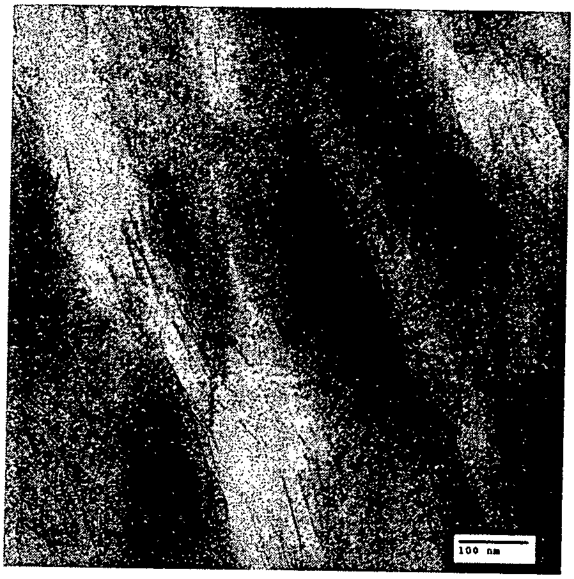
Micro-structure

Figure 1—Stacked platelets and poor dispersion (Sample B)



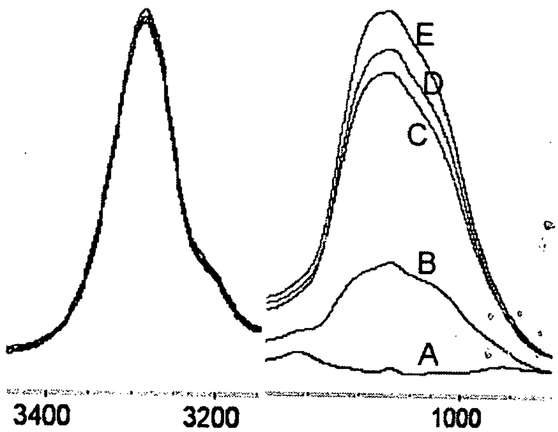
In all films, the nanoclay platelets showed orientation in the direction of film extrusion. The batch-blended and single-screw pre-extruded films also showed stacks of platelets that were left undispersed by blending (Figure 1). TEM inspection of Samples D and E, both blended by twin-screw extrusion, did not reveal any platelet stacks, but did show somewhat smaller platelets as well as better dispersion (Figure 2). Platelet measurements show a decrease in platelet size with increased blending efficiency and dispersion (Table 2).

Figure 2—Improved exfoliation and dispersion (Sample E)



FTIR Spectroscopy

Figure 3—3290 cm^{-1} nylon peak and 1030 cm^{-1} clay peak for samples A-E



Normalised FTIR spectra of the films show an unexpected variation in intensity for the clay peaks; all films have 10% clay content, and should therefore have similar peak heights. In fact, the clay contributions to the spectra vary significantly when compared to the nylon peaks (Figure 3). A comparison of normalised peak height for the 1030 cm^{-1} clay peak shows that the peak height appears to be inversely correlated to platelet size (Table 2). The peak height is also directly correlated to dispersion, for which there is no convenient numerical index. This finding suggests that transmission FTIR may permit the quantification of dispersion for the samples examined here.

Barrier properties

All nanoclay-containing films showed better barrier performance than pure nylon-12, although the film with the best dispersion (and smallest platelet size) gave the best performance (Table 2). This result is interesting given the platelet-size dependence of the commonly-accepted 'tortuous path' theory of nanoclay barrier enhancement.

Table 2—Platelet size, FTIR peak height, and breakthrough time.

Sample	Average platelet width (nm)	Normalised peak height, 1030 cm^{-1}	Break-through time (h)
A	-	0.00	5.4
B	171	0.32	
C	158	0.73	
D	144	0.87	8.8
E	111	1.05	15.4

Mechanical properties

As has been previously observed,[5] the addition of nanoclay to nylon-12 generally decreases the strength of the nylon in both stress and strain. In the current work, it was found that both yield and failure stress and failure strain improved with better dispersion, although not to the level of pure resin. For example, failure stress for sample A (pure nylon) was 80.6 MPa, decreasing to 32.9 MPa for sample B, and gradually increasing to 74.7 MPa for sample E.

Conclusions

Several methods of nanoclay dispersion in nylon-12 thin films were assessed. It was found that average platelet size begins to decrease before the nanoclay is completely dispersed.

FTIR studies of 10% nanoclay/nylon-12 thin films prepared by various blending methods showed a direct correlation between goodness of dispersion and intensity of the clay peak at 1030 cm^{-1}.

An evaluation of the barrier properties of the thin films showed that the barrier properties are best for the sample with the most intense mixing history and smallest platelet size. This sample also shows excellent dispersion, suggesting that dispersion may be an over-riding factor in barrier enhancement for nanoclay-containing thin films.

A comparison of mechanical properties of the thin films shows that dispersion was also the over-riding factor in material performance.

References

1. Dolgovskij, M.K., P.D. Fasulo, F. Lortie, C.W. Macosko, R.A. Ottaviani, and W.R. Rodgers. in *Antec 2003*. 2003. Nashville, TN, USA.
2. Huang, H.-X., C.-Y. Wang, Y.-F. Huang, G. Jiang, and Y.-H. Zhang. in *Antec 2003*. 2003. Nashville, TN, USA.
3. Wang, K., S. Liang, R. Du, Q. Zhang, and Q. Fu, *Polymer*, 2004. *45*: p. 7953-7960.
4. Zhang, Q., Y. Wang, and Q. Fu, *J. Poly. Sci., B*, 2002. *41*: p. 1-10.
5. Masenelli-Varlot, K., E. Reynaud, G. Vigier, and J. Varlet, *J. Poly. Sci., B*, 2001. *40*: p. 272-283.

#527027
CA028847