

# Interaction of Anhydrous Ferric Chloride with Nylon 6

LI-CHUNG CHAO and ENG-PI CHANG, *Hooker Chemical & Plastics Corp. Research Center, Niagara Falls, New York 14302*

## Synopsis

The interaction of anhydrous ferric chloride with nylon 6 has been inferred from Fourier transform infrared spectroscopy (FTIR), wide-angle x-ray diffraction (WAXD), thermal (DSC and TGA), and rheological (Rheometrics) measurements. At very low additive concentration of  $\sim 0.25$  wt %, an about 50-fold melt viscosity increase of nylon 6 was observed. However, progressive decrease in melt viscosity was also observed with increasing additive concentrations indicative of degradation as confirmed by the enhancement of weight loss with TGA at a lower temperature. Decrease in crystallinity content of the filled nylon samples is inferred from the reduction of the melting endotherms with DSC, pronounced reduction in diffraction intensity with WAXD, an increase in amorphous  $\text{CH}_2$  bending band ( $1400\text{ cm}^{-1}$ ) with FTIR. The above results can be attributed to the strong complex formation between the  $\text{FeCl}_3$  and the N—H groups as suggested by the subtraction spectra of FTIR where decreased intensities of the 690, 1200, and  $1265\text{ cm}^{-1}$  bands were observed.

## INTRODUCTION

The interaction of some metal halides with nylon 6 has been studied fairly extensively.<sup>1-5</sup> Valenti et al.,<sup>1</sup> in their studies of melting point depression, crystallization kinetics, and melt viscosity, have suggested the occurrence of a strong binding between the amide group and the LiCl or LiBr salt. Dunn and Sansom,<sup>2,3</sup> using IR and NMR techniques, have studied the stress cracking effect of some metal halides such as  $\text{ZnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{MnCl}_2$  on nylon 6 and proposed the complexation of the metal atom with the carbonyl oxygen of the amide group which causes stress cracking by interference with the hydrogen bonding in the polyamide. Barmisky and King<sup>4</sup> have also observed the solvent nature of  $\text{SbCl}_3$  for nylon. More recently, Szafner and Kocsis,<sup>5</sup> based on the melt viscosity enhancement observation of nylon 6 by Cr(III) ion, have attributed the phenomenon to the formation of a mixed complex. The purpose of this article is to report similar viscosity enhancement effect in nylon 6 with a Friedel-Crafts catalyst,  $\text{FeCl}_3$ . Possible catalytic effect of this metal halide on degradation and impeding effect on the crystallization of nylon 6 are attributed to the complex formation between the  $\text{FeCl}_3$  and the N—H groups as inferred from the thermal rheological and spectroscopic data.

## EXPERIMENTAL

### Materials

The commercial nylon 6 sample used was Plaskon 8200 from Allied Chemical Corp. The anhydrous ferric chloride was purchased from Matheson, Coleman and Bell and used without further purification.

### Sample Preparation

A nitrogen atmosphere glove bag to remove moisture and oxygen was used during the preparation of all samples. Nylon 6 pellets were first ground with a microblender (Janke & Kunkel KG) and then sifted through a 60-mesh screen to obtain the desired particle size. The polymer was then dried for 4 hr at 80°C in a vacuum oven prior to use. Nylon 6 and ferric chloride were premixed and then transferred onto a small two-roller mill and blended under a blanket of nitrogen at 240°C. The blend was removed from the roll mill and pressed into films ~20 mil thick on a Carver Press at 240°C under a force of ~10,000 pounds. Such films were used for the WAXD, DSC, TGA, and rheological measurements. Melt-pressed films of ~0.5 to 1.0 mil were used for the FTIR measurements which were carried out by Professor Jack Koenig at the Case Western Reserve University using a Digilab FTS-14 Fourier transform spectrometer which has been described in detail previously.<sup>6</sup>

### Differential Scanning Calorimetry

Thermal analyses were pursued on a Perkin-Elmer DSC-2 calorimeter. Samples, 25 mg each, were placed in an aluminum pan with a lid. The heating rate was 10°C/min under a N<sub>2</sub> flow of 40 cm<sup>3</sup>/min.

The percentage of crystallinity can also be derived using

$$\% \text{ of crystallinity} = \frac{\Delta H_f \text{ (or } \Delta H_c)}{\Delta H_u} \times 100\% \quad (1)$$

where  $\Delta H_f$  (or  $\Delta H_c$ ) and  $\Delta H_u$  are the heats of fusion (or crystallization) of the actual nylon 6 sample and the theoretical 100% crystalline nylon 6 sample, respectively.  $\Delta H_f$  is usually derived from the area under the melting peak in differential scanning calorimetry. The published value for the heat of fusion of 100% crystalline nylon 6 is 5500 cal/mole, or 48.5 cal/g.<sup>7</sup>

### Thermogravimetric Analysis

The TGA measurements were carried out on a Mettler Thermoanalyzer. About 10-mg samples were weighed with an analytical balance in a platinum crucible. The sample was heated at a heating rate of 10°C/min up to 500°C under N<sub>2</sub> atmosphere, after which it was held isothermally. Temperatures at which different percentages of weight loss were observed were determined from the TGA thermograms.

### Wide-Angle X-Ray Diffraction

WAXD was carried out with a Phillips Norelco diffractometer in the reflectance mode. This is equipped with an Advanced Metal Research focusing monochromator fitted with a graphite crystal and a proportional detector. Bragg angle  $2\theta$  scans from 4° to 40° were obtained by stacking up layers of the 5-mil samples and scanned at a speed of 1°C/min. The scattering pattern was recorded directly on a strip chart with a speed of 1/2 in./min.

## Melt Viscosity Measurement

The shear dependence of the melt viscosity was carried out with the 2.5-cm-diam cone and plate on a Rheometrics dynamic mechanical spectrometer. The environmental chamber was blanketed with nitrogen to prevent oxidative degradation. Melt viscosity was measured at 250°C.

## RESULTS AND DISCUSSION

### Rheological Measurements

Figure 1 shows the shear rate dependence of melt viscosity of nylon 6 samples filled with different weight percent of  $\text{FeCl}_3$ . The data indicate that all the filled samples, irrespective of their concentration, show about a 10- to 50-fold increase in melt viscosity at 0.1–1.0  $\text{sec}^{-1}$  shear rate. As the shear rate increases, the filled samples also show significant shear thinning effect as compared with the more Newtonian nature of the control sample. Such tremendous increase in melt viscosity (especially the 0.25 wt % filled sample) suggests complexation between the additive and the polymer matrix, an effect similarly observed by previous workers on other metal halides.<sup>2-5</sup> At higher loading of  $\text{FeCl}_3$ , progressive decrease in melt viscosity was observed, suggesting the possible degradation of the polymer by the additive which is confirmed by the TGA measurements as discussed in a later section.

### Thermal Analyses

Table I compares the TGA and DSC results, while Figure 2 shows the TGA thermograms of the samples. It is apparent from the TGA data that addition of  $\text{FeCl}_3$  in nylon 6 hastens substantially the degradation processes, as indicated

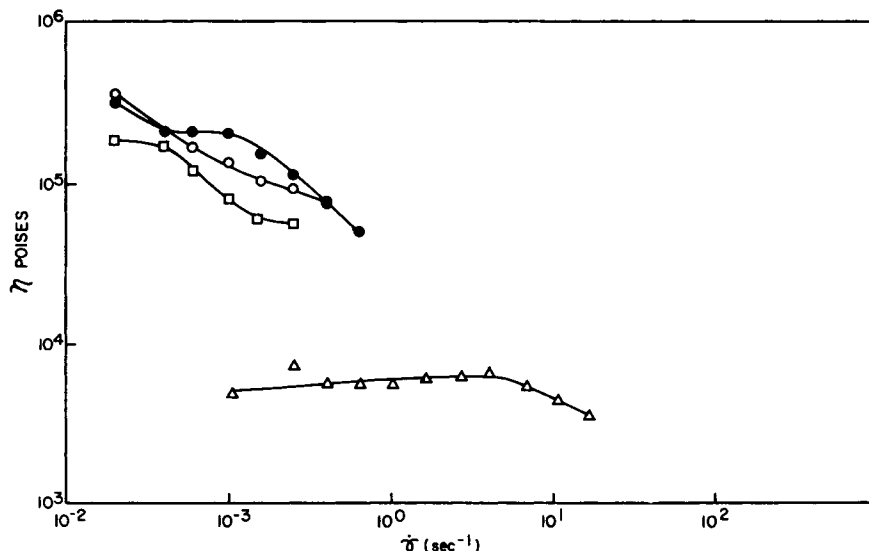


Fig. 1. Shear rate dependence of melt viscosity for nylon 6 samples filled with different concentration of  $\text{FeCl}_3$ : (— $\Delta$ —) 0 wt %; (— $\bullet$ —) 0.25 wt %; (— $\circ$ —) 5 wt %; (— $\square$ —) 12.5 wt %.

TABLE I  
DSC and TGA Results of FeCl<sub>3</sub>-Filled Nylon 6 Samples

Sample	mp, °C	$H_f$ , cal/gm	DSC $X_c$ , % (normalized)	Initial	Rapid	TGA temp., °C		
						1% wt. loss	5% wt. loss	20% wt. loss
Nylon 6	225	15.2	31.4	347	482	384	405	425
Nylon 6/FeCl <sub>3</sub> 95 ÷ 5 wt %	210	12.2	25.0	325	462	325	352	389
Nylon 6/FeCl <sub>3</sub> 87.5 ÷ 12.5 wt %	191	7.6	15.7	303	462	300	325	347

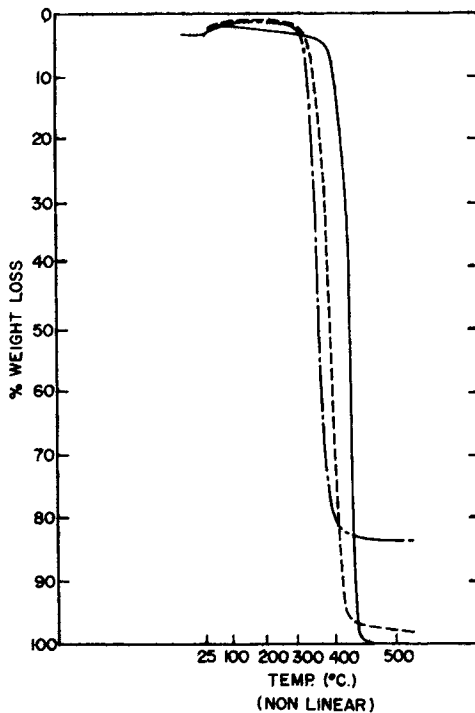


Fig. 2. TGA thermograms of nylon 6 samples filled with different concentration of  $\text{FeCl}_3$ : (—) 0 wt %; (---) 5 wt %; (- - -) 12.5 wt %.

by the much lower temperatures at which different percentages of weight loss were observed. The actual catalytic mechanism on the degradation of nylon 6 by  $\text{FeCl}_3$  is presently not known, but it is believed the strong Lewis acid nature of  $\text{FeCl}_3$  could affect the depolymerization,<sup>8,9</sup> crosslinking,<sup>10,11</sup> and thermal cleavage<sup>10,12</sup> kinetics and mechanism of nylon 6.

The impeding effect of the additive on the crystallization of the nylon 6 is also evident from the DSC data. For the unfilled sample based on the heat of fusion measurement, about 31% crystallinity was observed. With the addition of 5 wt %  $\text{FeCl}_3$ , a depression in melting point approximately  $20^\circ\text{C}$  was observed, together with decreased crystallinity content of  $\sim 25\%$ . Further decrease in crystallinity content ( $\sim 16\%$ ), together with broadening of a lower-temperature melting endotherm, was observed with the 12.5 wt % filled sample. The progressive decrease in melting point and broadening of the melting transition can be attributed to the strong interaction between the additive and the polymer matrix.

Figure 3 shows the x-ray diffraction pattern of the samples, and it can be observed that with increasing concentration of  $\text{FeCl}_3$  additive, there is a continuous decrease in intensity of the diffraction peaks at  $2\theta = 21^\circ$  and  $24^\circ$ . The x-ray diffraction data are in agreement with the DSC results which indicate that the crystallization process of nylon 6 is progressively hindered with increasing amount of  $\text{FeCl}_3$ . It is surmised that a strong complexation of  $\text{FeCl}_3$  with the amide group would perturb the hydrogen bonding which is the chain stabilizing force for the crystalline chain conformation,<sup>13,14</sup> and this would result in a decrease in the crystallinity content. The increase in melt viscosity can also be

TABLE II  
Major Infrared Bands of Nylon 6 and Nylon 6/(12.5 wt %) FeCl<sub>3</sub> (450–1500 cm<sup>-1</sup>)

Absorption, cm <sup>-1</sup>		Assignment (ref.)	Subtracted spectrum nylon 6/FeCl <sub>3</sub> -nylon 6
nylon 6	nylon 6/FeCl <sub>3</sub>		
580	588	amide VI out-of-plane bending <sup>15,16</sup>	decreased
690	695	amide V <sup>15,17,18</sup>	decreased pronouncedly
730	730	CH <sub>2</sub> rocking <sup>15</sup>	internal ref. assumed no effect
975	982	$\begin{array}{c} \text{O} \\    \\ \text{C} \end{array}$ NH in plane <sup>18</sup>	decreased
1075	1075	most probably C—C stretching <sup>17</sup>	no effect
1120	1118	C—C stretching <sup>18</sup>	no effect
1170	1172	skeletal motion involving $\begin{array}{c} \text{O} \\    \\ \text{C} \end{array}$ NH <sup>15</sup>	decreased pronouncedly
1202	1202	amide III <sup>19</sup>	decreased pronouncedly
1262	1262	amide III <sup>19</sup>	decreased pronouncedly
1280 (shoulder)	1282	CH <sub>2</sub> wagging <sup>17</sup>	increased
1374	1372	CH <sub>2</sub> twisting <sup>17</sup>	increased
1420	—	CH <sub>2</sub> deformation adj. to amide group <sup>20</sup>	decreased
1420	1438	CH <sub>2</sub> deformation (amorphous) <sup>15</sup>	increased pronouncedly
1464	1460	CH <sub>2</sub> deformation <sup>15</sup>	increased pronouncedly

attributed to such complex formation which acts like intra- and interchain crosslinks, thus immobilizing the diffusion and crystallization of the polymer chains.

### FTIR Spectroscopy

Figure 4(a) compares the FTIR spectra of nylon 6 with that filled with 12.5 wt % FeCl<sub>3</sub>, while Figure 4(b) shows the subtracted spectrum of the two samples. Owing to the thickness of the samples, direct observation of the N—H stretching and C=O stretching mode was not possible, and so other amide modes in the region of 450 to 1500 cm<sup>-1</sup> were examined in the subtracted spectrum with scaling based on the 728 cm<sup>-1</sup> band.

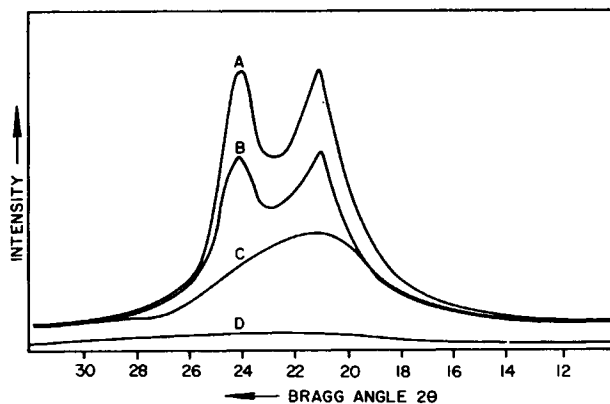


Fig. 3. Wide-angle x-ray diffraction pattern of nylon 6 samples filled with different concentration of FeCl<sub>3</sub>: A, 0 wt %; B, 5 wt %; C, 12.5 wt %; D, 25 wt %.

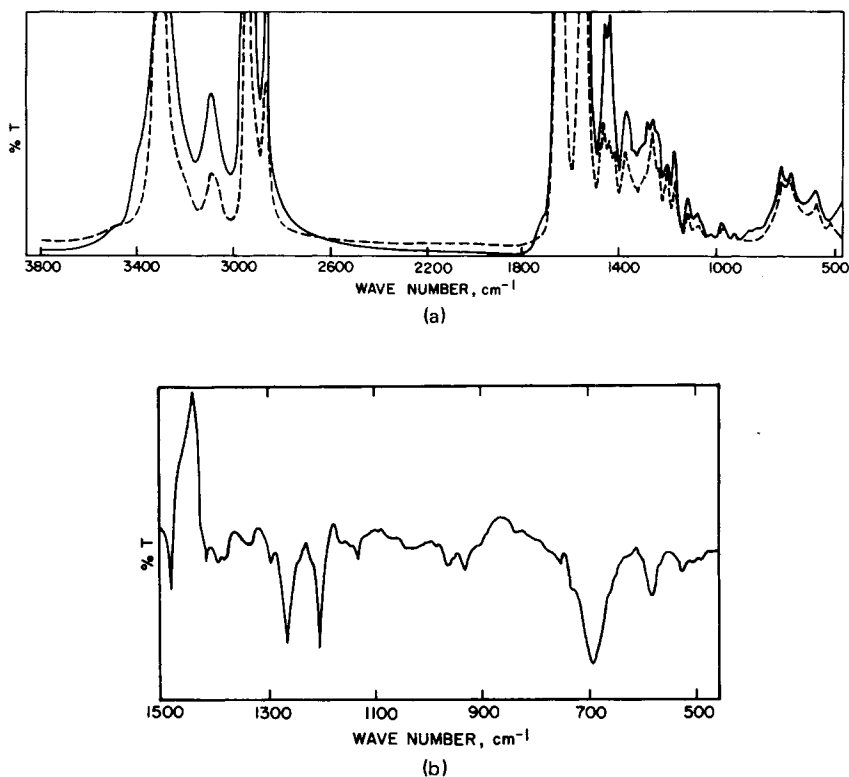


Fig. 4 (a) FTIR spectra of nylon 6 (---) and nylon 6/FeCl<sub>3</sub> (—) (87.5:12.5 wt %). (b) Subtracted FTIR spectrum of Fig. 4(a).

Table II summarizes the results together with assignment of the major bands. The results can be interpreted in terms of a complex formation between the FeCl<sub>3</sub> and N—H group which is evident from the pronounced decrease in intensities of the 690, 1200, and 1265 cm<sup>-1</sup> bands. These three bands have been assigned respectively to the amide V,<sup>15,17,18</sup> amide III, and amide III<sup>19</sup> associated with N—H bending mode; and interaction of these modes with FeCl<sub>3</sub> should result in a decrease in these modes. Additionally, one observes that the amorphous methylene modes at the 1438 and 1464 cm<sup>-1</sup> bands have increased precipitously in intensity, which is in agreement with the reduced crystallinity observed in x-ray diffraction and DSC analyses. This increase in intensity of the amorphous methylene modes suggests some sort of disordering process along the polymer backbone which is caused presumably by the interaction of the FeCl<sub>3</sub> with the N—H groups. It is believed that such complexation would reduce the number of interchain hydrogen bonding which stabilizes the crystalline chain conformation as discussed previously.

## CONCLUSIONS

Based on the FTIR spectroscopy results, it is inferred that a complex formation between the FeCl<sub>3</sub> and N—H groups of nylon 6 occurs. Such complex formation results in a sharp increase in melt viscosity and a significant decrease in the

crystallinity content. Progressive decrease in melt viscosity was observed with increasing concentration of the additive suggestive of the polymer degradation as indicated by the enhancement of weight loss at lower temperatures.

The authors would like to thank Messrs. R. Bonk, C. E. Benson, J. Forcucci, R. O. Kirsten, and I. Zsolnay for their technical assistance; Drs. R. D. Carlson and E. L. Slagowski of Hooker Research Center for their valuable discussion; and Professor J. L. Koenig at the Case Western Reserve University for the FTIR analyses and his interpretation.

### References

1. B. Valenti, E. Bianchi, G. Greppi, A. Tealdi, and A. Cifeori, *J. Phys. Chem.*, **77** (3), 389 (1973).
2. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1641 (1969).
3. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1657 (1969).
4. D. S. Barmky and G. King, in *Proc. Int. Wool Text., Res. Conf. Australia*, 1955, B-139.
5. A. Szafner and J. K. Kocsis, *Polymer*, **16**, 879 (1975).
6. J. L. Koenig and D. L. Tabb, *J. Macromol. Sci-Phys.*, **9**(1), 141 (1974).
7. I. Kirshenbaum, *J. Polym. Sci.*, **A3**, 1869 (1965).
8. N. D. Katovzhaov and A. S. Strapikheev, *Zh. Pkl. Khim.*, **36**, 625, 1363 (1959).
9. S. Smith, *J. Polym. Sci.*, **30**, 459 (1958).
10. M. B. Nieman, *Aging and Stabilization of Polymers*, Consultant Bureau, New York, 1965, Chap. VIII.
11. Y. Yoshizawa, H. Saito, and K. Nukada, *J. Polym. Sci. Polym. Let. Ed.*, **10**, 145 (1972).
12. T. J. Reardon, M.S. thesis, Dept. of Textiles, Clemson University, Clemson, S.C.
13. H. Arimoto, *J. Polym. Sci. Part A*, **2**, 2283 (1964).
14. D. R. Holmes, C. W. Bunn, and D. J. Smith, *J. Polym. Sci.*, **17**, 159 (1955).
15. H. Arimoto, *J. Polym. Sci. Part A*, **2**, 2283 (1964).
16. I. Matsubara and J. H. Magill, *Polymer*, **7**, 199 (1966).
17. M. C. Tobin and M. J. Carrans, *J. Chem. Phys.*, **25**, 1044 (1956).
18. I. Sandeman and A. Keller, *J. Polym. Sci.*, **19**, 401 (1956).
19. C. G. Cannon, *Spectrochim. Acta*, **16**, 302 (1960).
20. A. Miyake, *J. Polym. Sci.*, **44**, 223 (1960).

Received June 19, 1980

Accepted July 21, 1980