

Effects of Acid Dyes on Crystallization and Mechanical Properties of Melt-Reprocessed Nylon 66

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ABSTRACT: Nylon fibers dyed with different types of acid dyes were melt reprocessed using a compression-molding machine. The crystalline structure and mechanical properties of the melt-reprocessed nylon were experimentally evaluated. It was found that metal complex acid dyes showed much more distinct effects on the structure and mechanical properties of melt-reprocessed nylon than nonmetallized acid dyes. They decreased the crystallization rate of the molten nylon and reduced its crystallinity. They also reduced the imperfect form I structure in the crystalline region. Compression-molded nylon samples showed inferior mechanical properties in the presence of metal complex acid dyes. The coordinate bonds between the Cr^{3+} ions and amide groups are possibly formed in melt-reprocessed nylon, which could be the reason for the changes in the structure and properties of melt-reprocessed nylon. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2386–2396, 1999

Key words: nylon 66; acid dyes; crystallization; crystalline structure; mechanical property; coordinate bond

INTRODUCTION

In the United States alone, over 3 billion pounds of postconsumer carpet waste are sent to landfills every year. These carpets typically contain (by weight) 40–60% nylon fibers and 8–15% polypropylene fibers and slit film. The rest of the carpet weight is latex adhesives and fillers. Because of the obvious economic and environmental merits of recycling polymers from postconsumer carpets, increased efforts have been directed to reclaim these polymers^{1–8} and to develop value-added products.^{9–12}

Our previously developed novel technique can be used to economically collect nylon polymer and fibers with purity up to 99% from postconsumer

carpet waste without the removal of dyes and finishes.⁸ This recycled nylon can be used as a material for the production of engineered plastics and extrusion of fibers without using compatibilizers, which are often used in melt processing of recycled comingle polymers. A major concern with the utilization of this recycled nylon is whether and how dyes influence the thermal stability and morphology of the recycled nylon during melt reprocessing.

Although the structure and performance of nylon have been well documented,¹³ the above-mentioned concern has not yet been addressed. In a previous investigation we studied the effect of acid dyes on the thermal behavior of nylon 66.¹⁴ Seventeen dyestuffs representing different groups of acid dyes were selected to dye virgin nylon 66 yarns. Dyed samples were melt reprocessed using a compression-molding machine. We found that although the existence of acid dyes did not influence the melting temperature of nylon, metal complex acid dyes had severe impact on its ther-

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Table I Dyestuffs and Dyeing Conditions

Dyestuff (C.I. Number)	Manufacturer and Trademark	Additives in Dye Bath	Code
C.I. acid blue 45 (63010)	Ciba-Geigy Corporation, Erio Fast Cyanine S Conc	0.3% (v/v) formic acid	A
C.I. acid red 151 (26900)	Sandoz Chemicals, Nylosan Red F/C-2R	0.5% (v/v) acetic acid and 2.5% (wt) Na ₂ SO ₄	B
C.I. acid yellow 23 (19140)	Cyanamid, Calcocid Yellow MCG	0.3% (v/v) formic acid	C
C.I. acid blue 158 (14880)	Organic Dyestuffs Corp., Orcolan Fast Blue GGN 200	0.3% (v/v) formic acid	D
C.I. acid black 60 (18165)	Ciba-Geigy Corp., Irgalan Grey BRL-01 KWL 200	—	E
C.I. acid red 186 (18810)	Organic Dyestuffs Corp., Orcolan Fast Pink BN 200	0.3% (v/v) formic acid	F

mal stability. In the present work, the effect of acid dyes on the crystallization, crystalline structure, and mechanical properties of reprocessed nylon are investigated. Special attention is given to metal complex acid dyes.

EXPERIMENTAL

Nylon Fibers and Dyestuffs

Nylon 66 yarns (1140-57-GMT) were supplied by Monsanto Chemical Company (Greenwood, SC). The molecular weight of the nylon as measured was 2.45×10^4 .¹⁴ The most frequently used dyestuffs for nylon fiber in the industry are acid dyes. There are a large number of commercial acid dyes with various types of chromophores. In the present study, anthraquinone dyes, polyazo dyes, and pyrazolone dyes were selected that were represented by C.I. Acid Blue 45, C.I. Acid Red 151, and C.I. Acid Yellow 23, respectively. The metal complex acid dyes chosen were C.I. Acid Blue 158, C.I. Acid Black 60, and C.I. Acid Red 186. The trademarks and dyeing conditions of the selected dyestuffs are listed in Table I. The chemical structures of the applied dyes are given in Table II. All dyestuffs were used without purification.

Dyeing of Nylon 66 Fibers

About 7 g of predried nylon 66 yarns were immersed in a 100-mL aqueous dye bath with a dye concentration of 0.5 wt % (71 mg dyes/g fiber). Additives were selected according to the recommendation of the dyestuff manufacturers and the Colour Index¹⁵ to improve dyeing uniformity. The

dye bath was first heated to 100°C with a heating rate of 1°C/min, then it was kept boiling for 1 h. After the dyeing process, the dyed nylon 66 yarns were taken out of the dye bath and thoroughly rinsed with water until no physically retained dyestuff could be washed out. The dyed nylon yarns were then dried at 100°C for 2 h in a vacuum oven. The weight gain of the nylon fibers, which reflects the amount of dyes in the fibers, was measured. The dye contents in the dyed fibers were kept at levels of 14 ± 2 mg dyes/g fibers. The color shades of these samples were evaluated using color coordinates based on a CIE system.¹⁴

Compression Molding of Nylon

Dyed nylon 66 yarns were cut into 1-mm length lint with a fiber mill manufactured by Arthur Thomas Company. The nylon lint was placed in a mold (10.16×10.16 cm) and dried at 100°C for 2 h in a vacuum oven. Nitrogen was used to release vacuum. The mold was then placed between the platens of a compression-molding machine (G30H-15-B, Wabash) that had been heated to 250°C. The nylon lint was compression molded at 860 kPa for 7 min. The temperature of the platens was then raised to 268°C and the pressure was reduced to 30 kPa. The mold was left between the platens under these conditions for 5 min. The mold was then removed from the compression-molding machine and air cooled to room temperature. Throughout the process, nitrogen gas was discharged around the mold at 10 mL/min to eliminate the possibility of sample degradation due to contact with air. This process produced nylon plates with dimensions of $10.16 \times 10.16 \times 0.1$ cm.

Table II Chemical Structures of Selected Acid Dyes

Dye Code	Chemical Structure
A	
B	
C	
D	

Differential Scanning Colorimetry (DSC)

A Perkin–Elmer DSC-2 differential scanning calorimeter was used to analyze the melting and crystallization behavior of the dyed nylons. Indium was utilized to calibrate the instrument. Six grams of nylon samples were used in each analysis. Nitrogen was used at a flushing rate of 10 mL/min. The temperature profile for the DSC run varied, depending on the analysis purpose. For

example, to investigate the crystallization of molten nylon, nylon samples were heated from room temperature to 280°C at 20°C/min, and the temperature was held at 280°C for 2 min to remove the effect of previous processing history. Sample temperature was then reduced at a rate of –20°C/min. To reveal the melting behavior of the crystalline region, the sample temperature was program raised to 280°C at 20°C/min.

Table II Continued

Dry Code	Chemical Structure
E	
F	

IR Spectrometry Analysis

A 2000 FTIR spectrometer (Perkin–Elmer) equipped with an IR microscope (Spectra-Tech Inc.) was used to analyze the samples. Samples for FTIR analysis were prepared in a DSC furnace by heating nylon fibers containing acid dyes to 280°C at 20°C/min followed by cooling to 25°C at –20°C/min. IR spectra were recorded with a scan number of 64 and a resolution of 2 cm⁻¹.

Mechanical Properties of Molded Nylon

Test specimens were cut from the compression-molded nylon plates. All the surfaces of the specimen were free of visible flaws, scratches, or imperfections. The length, width, and height of each specimen was 100, 10, and 1 mm, respectively.

Tension tests were performed with an Instron 4505 instrument. The gauge length and speed of the crosshead for the test were 50 mm and 1.5 mm/min, respectively, in accordance with ASTM D638.

RESULTS AND DISCUSSION

Crystallization Behavior of Dyed Molten Nylon

The crystallization behavior of dyed and undyed nylon samples was investigated using DSC. From the results shown in Figure 1, undyed nylon showed a crystallization peak at 224°C. The presence of C.I. Acid Blue 45, C.I. Acid Red 151, and C.I. Acid Yellow 23 dyes in the nylon did not

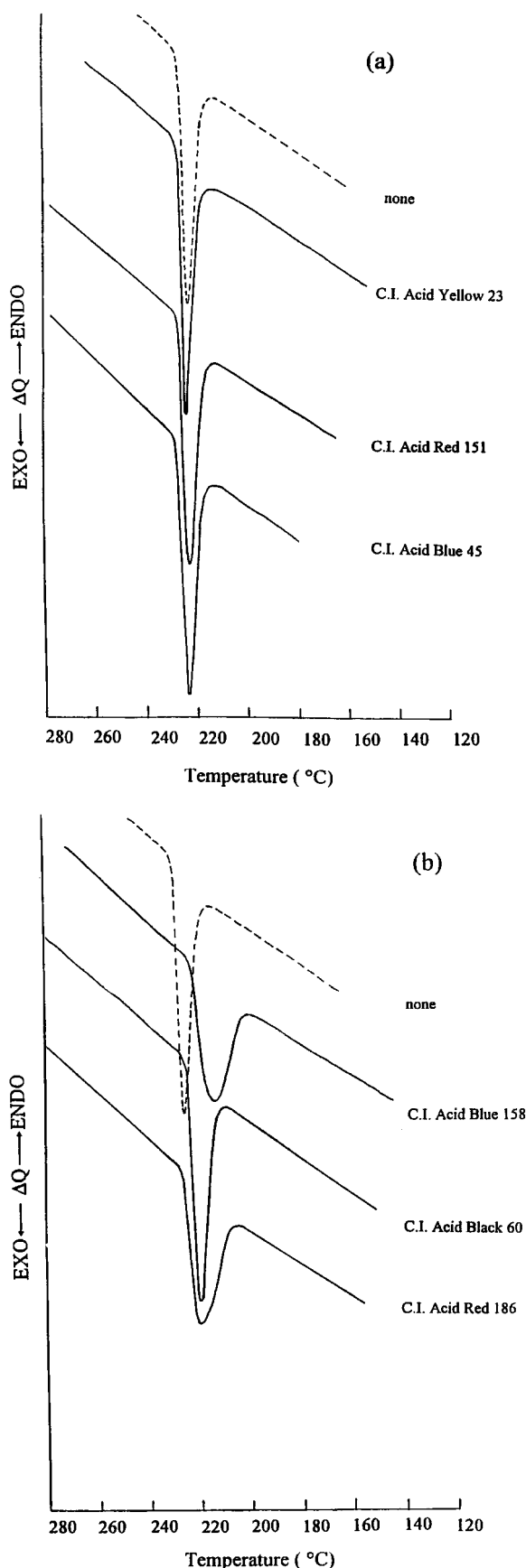


Table III Effect of Acid Dyes on Crystallization Heat (H_c) and Crystallization Temperature (T_c) of Molten Dyed Nylon 66

Dye in Nylon	H_c (cal/g)	T_c ($^{\circ}$ C)
None	12.1	224.0
A	12.5	223.0
B	12.7	222.0
C	12.4	223.0
D	12.3	215.4
E	12.1	219.8
F	12.5	218.8

The cooling rate for the DSC measurement was -20° C/min.

influence the position and shape of the crystallization peak [Fig. 1(a)]. However, from Figure 1(b), it can be observed that all metal complex acid dyes reduced the crystallization temperature, as well as broadened the crystallization peak of the dyed samples. Crystallization temperature and heat of crystallization are summarized in Table III. All samples had basically the same level of crystallization heat. However, the nylon samples with enclosed metal complex dyes had crystallization temperatures about 5 – 9° C lower than that of undyed nylon samples.

The influence of dyes on the crystallization of nylon was further investigated by an isothermal crystallization test using DSC. Two dyes were tested: C.I. Acid Blue 158 as an example of a 1 : 1 metal complex dyes and C.I. Acid Blue 45 as a nonmetal containing acid dye. Figure 2 shows the crystallization curves of undyed nylon and the two types of dyed nylon samples at 210 , 220 , and 230° C. A distinct difference among the crystallization curves can be observed. In the presence of dyes, the time associated with the appearance of the crystallization peak increased and the crystallization peak appeared to be much broader. This result implies that the applied acid dyes reduced the crystallization rate of the nylon. The width at half-peak height of the crystallization curve ($t_{1/2 \max}$) was used to describe the effect of acid dyes at different temperatures. A higher value of ($t_{1/2 \max}$) means a lower crystallization

Figure 1 DSC Cooling curves of nylon 66 samples containing different types of acid dyes. The cooling rate was -20° C/min. (a) Acid dyes; (b) metal complex acid dyes.

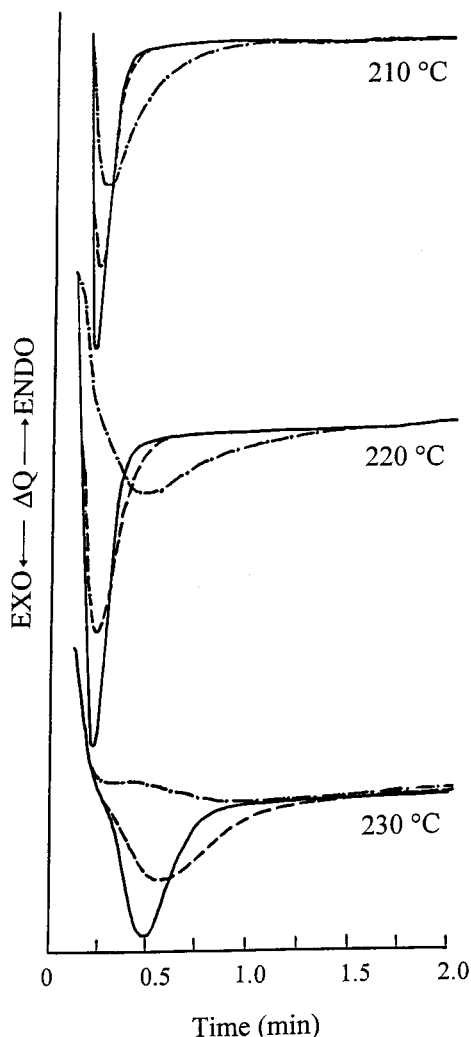


Figure 2 Isothermal crystallization curves of nylon samples at 210, 220, and 230°C: (—) without dye; (---) with C.I. Acid Blue 45; (- - -) with C.I. Acid Blue 158.

rate. The effect of acid dyes on the crystallization of nylon became more significant at higher crystallization temperatures (Fig. 3). The metal complex dye C.I. Acid Blue 158 had a more pronounced effect on the crystallization rate than the nonmetal complex dye C.I. Acid Blue 45.

The crystallization of the nylon melt upon cooling is governed by nucleation and crystal growth.¹⁶ Hydrogen bonds between the nylon chains play a role as nucleation sites during cooling.¹⁷ The above-described crystallization behavior of the dyed nylon samples can be understood by taking into account the possible interactions between the nylon chains and the dye molecules. For instance, the association of amine groups at the ends of polyamide chains with bulky acid dyes

should reduce chain mobility. Also, hydrogen bonding between amide groups may be altered by the possible formation of coordinate bonds between the Cr^{3+} of the metal complex dyes and the amide groups of the nylon after the melting process.

Effect of Acid Dyes on Formation of Crystalline Structure of Nylon

The formation of crystalline structures in nylon upon cooling of molten nylon was investigated by DSC, and the applied temperature profile was selected according to literature data.¹⁶⁻²¹ Figure 4 shows the melting peaks of three nylon samples, which were crystallized from their melts at different cooling rates.

In Figure 4(a) the undyed nylon shows twin melting peaks at 258°C (peak I) and 251°C (peak II) at a cooling rate of $-5^\circ\text{C}/\text{min}$. As the cooling rate increased, peak II shifted toward low temperature values and showed reduced peak height; meanwhile, peak I increased in height without a significant change of peak position. Similar phenomena were observed with a nylon sample containing C.I. Acid Blue 45 [Fig. 4(b)]. However, the nylon sample containing 1 : 1 metal complex dye C.I. Acid Blue 158 showed a different effect of the cooling rate on the melting behavior [Fig. 4(c)]. Unlike undyed nylon, this sample exhibited a single peak at 251°C, even when crystallized at $-5^\circ\text{C}/\text{min}$. The melting peak at 258°C (peak I) disappeared.

The multiple endothermic behavior in connection with polymer morphology has been studied

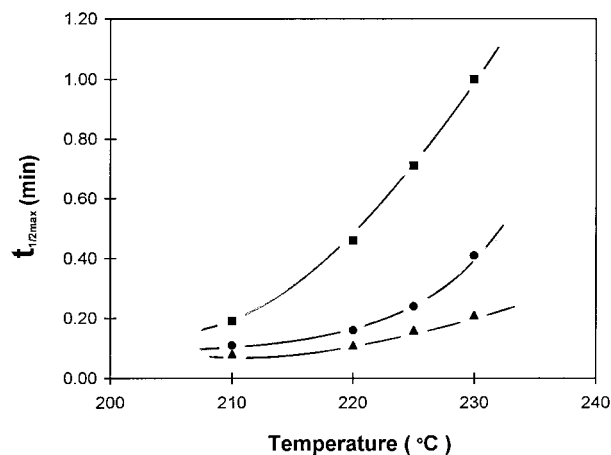
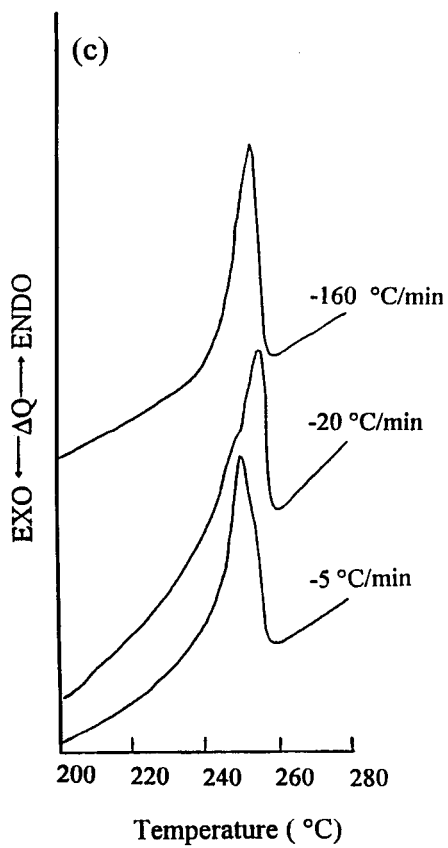
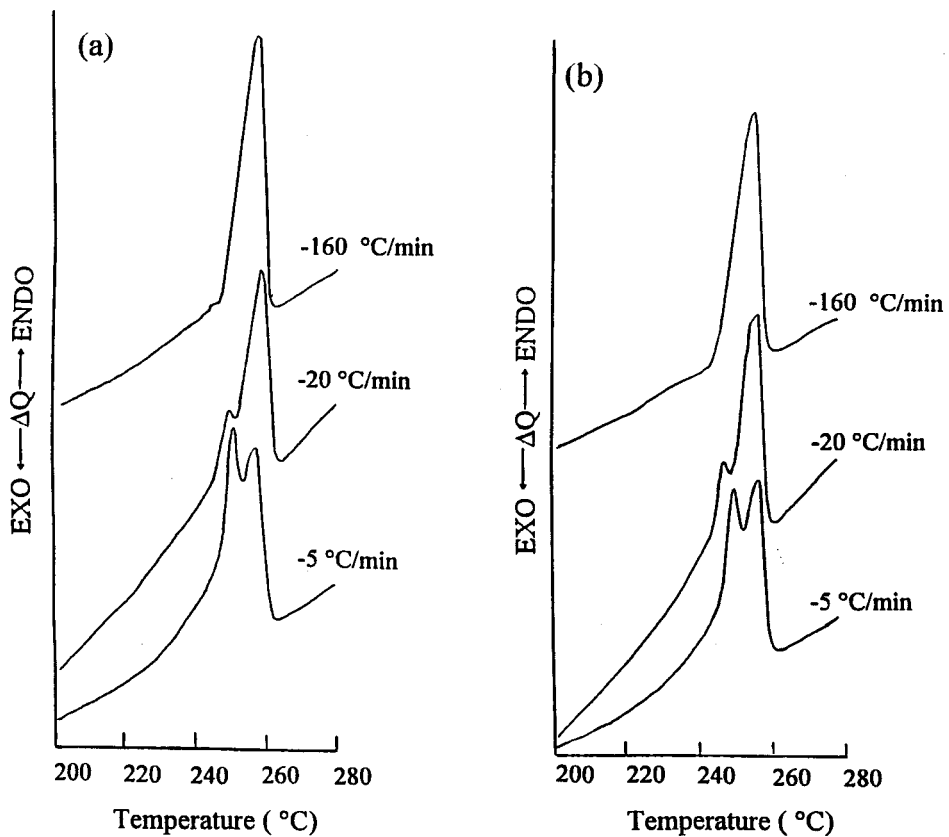


Figure 3 Effect of temperature on the $t_{1/2 \text{ max}}$ of molten nylon samples: (▲) without dye; (●) with C.I. Acid Blue 45; (■) with C.I. Acid Blue 158.



by many researchers.^{18–21} Sweet and Bell²¹ concluded that twin melting peaks of nylon polymers implies the existence of two crystalline structures: a structure (form I) that is less perfect and is recrystallizable upon heating, and another structure (form II) that does not recrystallize during melting. In the DSC experiment form I melted at a relatively low temperature and then recrystallized, resulting in a new crystalline structure that melted at about 258°C (peak I). The form II crystalline structure melted at about 251°C and exhibited an endothermic peak II.

Using this argument, the crystalline behavior as shown in Figure 4(a) can be explained. As the cooling rate for the nylon melt is increased, the crystal size and perfection of the obtained crystalline structure decreases. This is indicated by the decrease in the peak temperature and peak height of the form II endotherm, as well as the rise in peak I. By comparing Figure 4(a)–(c), it was observed that at low cooling rates the metal complex dye depressed the formation of recrystallizable form I structure. This observation can be explained by the fact that the presence of metal complex dyes in nylon slowed down the crystallization rate as was concluded from the information shown in Figures 1–3. Generally, slow crystallization can allow the formation of a perfect crystalline structure.

Another similar investigation was conducted with nylon samples that were compression molded and cooled by air flow (at about $-2^{\circ}\text{C}/\text{min}$) or quenched in water. DSC curves of most air-cooled samples showed twin melting peaks with peak I as a shoulder or a small peak [Fig. 5(a)]. This implies that the obtained crystalline structure contained less form I structure. However, when the melt samples were quenched in water, most samples showed a single peak at 259°C, which corresponds to a form I structure [Fig. 5(b)]. These results are in agreement with those shown in Figure 4. The melting heat and peak temperature of these water-quenched nylon samples are summarized in Table IV. Those containing metallized acid dyes showed clearly reduced melting heat at peak I. This result supports the conclusion that the existence of metal complex dyes in nylon caused the reduction of a recrystallizable structure.

Kohan reported that the crystallinity of nylon 66 can be determined by the IR absorbency ratio (A_{1199}/A_{1180}) that increases with the percent crystallinity determined by X-ray diffraction.²² In Figure 6 the A_{1199}/A_{1180} ratios are given for nylon samples that were heated to 280°C at 20°C/min and then cooled to 25°C at $-20^{\circ}\text{C}/\text{min}$. Samples containing metal complex dyes presented lower levels of IR absorbency ratio compared to those having nonmetal acid dyes. This implies that the presence of metallized acid dyes in nylon reduced the crystallinity of the nylon. This result is consistent with the above conclusions.

Tensile Behavior of Compression-Molded Nylon

The tensile test data for the compression-molded and air-cooled nylon samples are listed in Table V. The reproducibility of the measurement was demonstrated by at least five samples per data point. Three typical stress–strain curves for undyed nylon and nylons with nonmetal acid dyes and metal complex acid dyes are shown in Figure 7. It can be observed that nylon samples with acid dyes showed a reduction in strength, initial modulus, and elongation to break. Metal complex acid dyes had a more significant reduction than nonmetallized acid dyes. The cause of the observed mechanical property deterioration is complicated by the fact that several structural factors of melt-reprocessed dyed nylon were affected by acid dyes. For instance, in melt-reprocessed dyed nylon samples, metal complex acid dyes accelerated the thermal degradation of nylon 66,¹⁴ reduced the amount of form I structure in the crystalline region, and decreased the percent crystallinity. In addition, the possible formation of metal-amide coordinate bonds upon melting process can cause an effect that is similar to transition metal salt-induced stress cracking of nylon polymers.^{23,24}

Interaction between Nylon and Dyestuffs

From the above investigations, metallized acid dyes have more significant influences on the structure and properties of melt-processed nylon than nonmetallized acid dyes. This observation can be explained by the possible interactions between polyamide and metallized acid dyes. Sev-

Figure 4 DSC curves of nylon 66 samples crystallized from melts at -5 , -20 , and $-160^{\circ}\text{C}/\text{min}$: (a) without dye; (b) with C.I. Acid Blue 45; (c) with C.I. Acid Blue 158 (measurement was performed at $20^{\circ}\text{C}/\text{min}$).

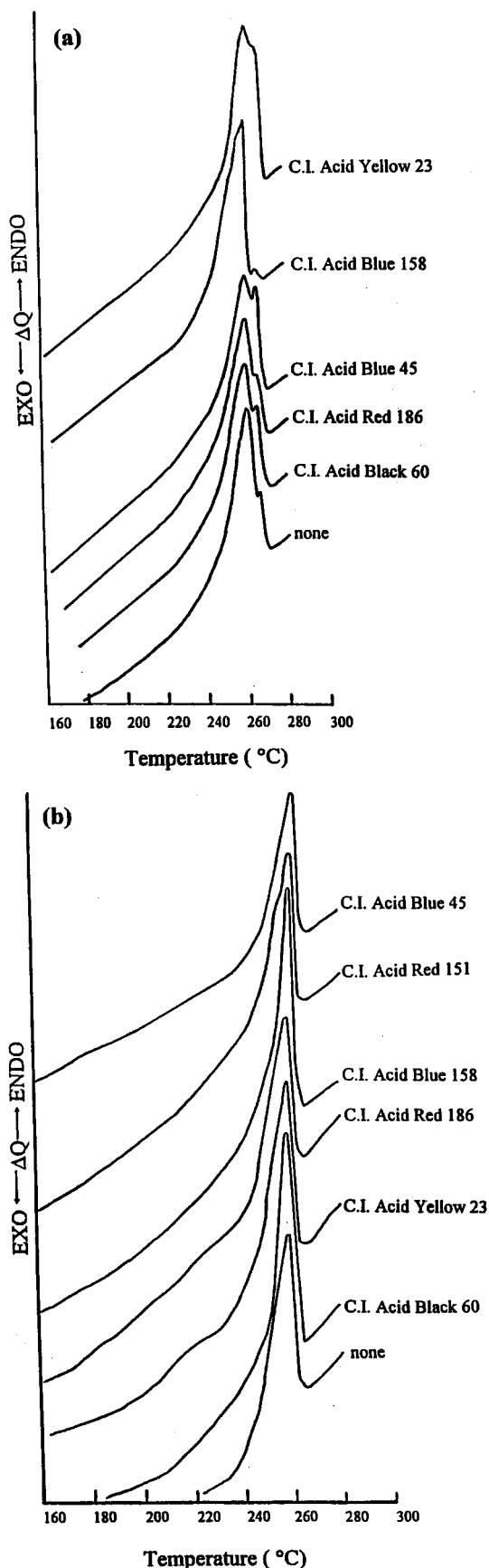


Table IV Melting Heat (H_m) and Melting Temperature (T_m) of Compression-Molded Nylons

Dye in Nylon	H_m (cal/g)	T_m (°C)
None	16.4	260.0
A	15.6	259.5
B	16.4	259.4
C	16.2	259.6
D	15.0	259.3
E	14.4	260.1
F	13.5	258.4

The nylon samples were quenched in water after the molding process. The DSC measurement was performed at 20°C/min.

eral groups reported that the amide groups of nylon polymer can form coordinate bonds with several types of transition metal ions.²³⁻²⁶ When 1 : 1 metal complex acid dyes are used, the dye molecules bond to the polyamide not only by ionic and second-order bonds as do regular acid dyes, but also by coordinate bonds through the metal ions.²⁷ Moreover, in the melt processing of nylon many 1 : 1 and 1 : 2 acid dyes undergo decomposition.¹⁴ It is expected that the probability of the formation of coordinate bonds between amide groups and Cr^{3+} ions increased upon melting process.

In the present study the possibility of coordination between amide groups and Cr^{3+} ions in the melt-reprocessed nylon samples was examined by FTIR analysis. Distinguishable changes in the C=O stretching band were observed. As indicated in Figure 8, amide I bands of all samples showed split peaks at 1639 and 1643 cm^{-1} , as well as shoulders between 1650 and 1700 cm^{-1} . For the undyed nylon sample and nylon with C.I. Acid Blue 45, the peak at 1639 cm^{-1} was higher than that at 1643 cm^{-1} . For samples with metal complex acid dyes, such as C.I. Acid Black 60, C.I. Acid Blue 158, and C.I. Acid Red 186, the peaks at 1639 cm^{-1} became equal or lower than those at 1642 cm^{-1} . In the presence of metallized acid dyes the peak at 1639 cm^{-1} decreased.

These variations in the C=O stretching band reflect differences in the C=O bonds of nylon

Figure 5 DSC curves of compression-molded nylon 66 samples containing various acid dyes: (a) cooled by air flow; (b) quenched in water (measurement was performed at 20°C/min).

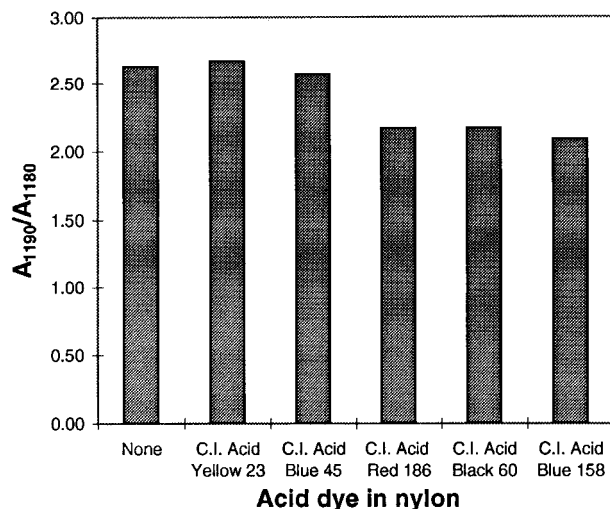


Figure 6 IR absorbency ratio (A_{1190}/A_{1180}) of nylon 66 samples crystallized from melts at $-20^{\circ}\text{C}/\text{min}$.

samples. It has been reported that the low frequency peak at 1639 cm^{-1} within the $\text{C}=\text{O}$ stretching band is associated with the hydrogen-bonded $\text{C}=\text{O}$ bonds, and the peak at 1643 cm^{-1} is assigned to "free" carbonyl bonds.^{28,29} The appearance of shoulders between 1650 and 1700 cm^{-1} were also interpreted as the formation of different types of carbonyl compounds during the thermal degradation/oxidation of nylon.²⁹ Accordingly, the observed decrease in the height of the peak at 1639 cm^{-1} in the metallized acid dye containing nylon samples indicates the decrease in hydrogen bonding between the amide groups of the nylon chains.

Dunn and Sansom²⁴ used IR to investigate the presence of coordinate bonds between amide carbonyl groups and transition metal salts. They concluded that the formation of coordinate bonds between carbonyl oxygen atoms and transition

Table V Mechanical Property of Compression-Molded Nylon 66

Dyes in Nylon	Strength (MPa)	Initial Modulus (GPa)	Elongation to Break (%)
None	72.30 ± 3.18	2.38 ± 0.25	11.72 ± 3.53
A	68.00 ± 2.16	2.06 ± 0.12	4.83 ± 1.41
C	67.90 ± 2.01	2.27 ± 0.16	2.88 ± 0.16
D	66.00 ± 2.00	1.73 ± 0.08	6.67 ± 1.34
E	67.00 ± 3.49	2.17 ± 0.04	6.10 ± 0.71
F	56.18 ± 2.00	2.08 ± 0.10	4.14 ± 0.64

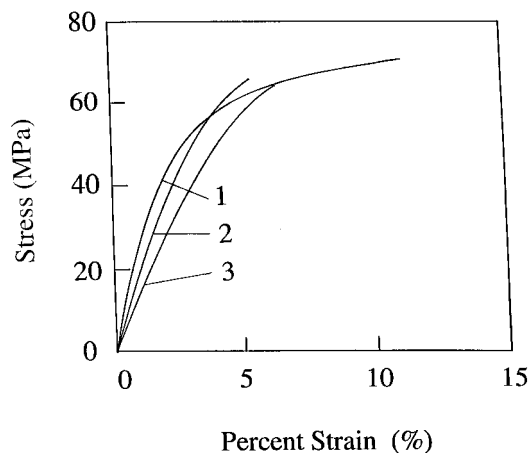


Figure 7 Stress-strain curves of melt-reprocessed nylon samples: (1) without dye; (2) with C.I. Acid Blue 45; (3) with C.I. Acid Blue 158.

metal ions is the cause of the hydrogen-bond reduction. Accordingly, in the melt-processed nylon samples containing metallized acid dyes, the observed decrease in hydrogen bonding can be considered as evidence of possible coordinate bonds between amide groups and Cr^{3+} ions. We suggest that such an interaction between the amide groups and Cr^{3+} ions is probably the reason why metallized acid dyes exhibit much more significant effects on the structure and properties of the melt-processed nylon than regular nonmetallized acid dyes.

CONCLUSIONS

The effects of acid dyes on the crystalline structure and mechanical properties of melt-reprocessed nylon 66 were investigated. Nonmetallized acid dyes (such as anthraquinone, polyazo, and pyrazolone dyes) had less significant influence on the structures and properties of the reprocessed nylon. Metal complex acid dyes showed distinct effects on the structure and mechanical properties of the melt-processed nylon. DSC and IR analyses indicated that metal complex acid dyes in nylon 66 significantly reduced the crystallization rate of the molten nylon and decreased the percent crystallinity of the melt-processed nylon. They also changed the crystalline structure of the nylon by reducing the amount of form I crystalline structure, which is less perfect and is usually formed as a result of fast cooling. Furthermore, metal complex acid dyes considerably affected the mechanical properties of the melt-reprocessed nylon.

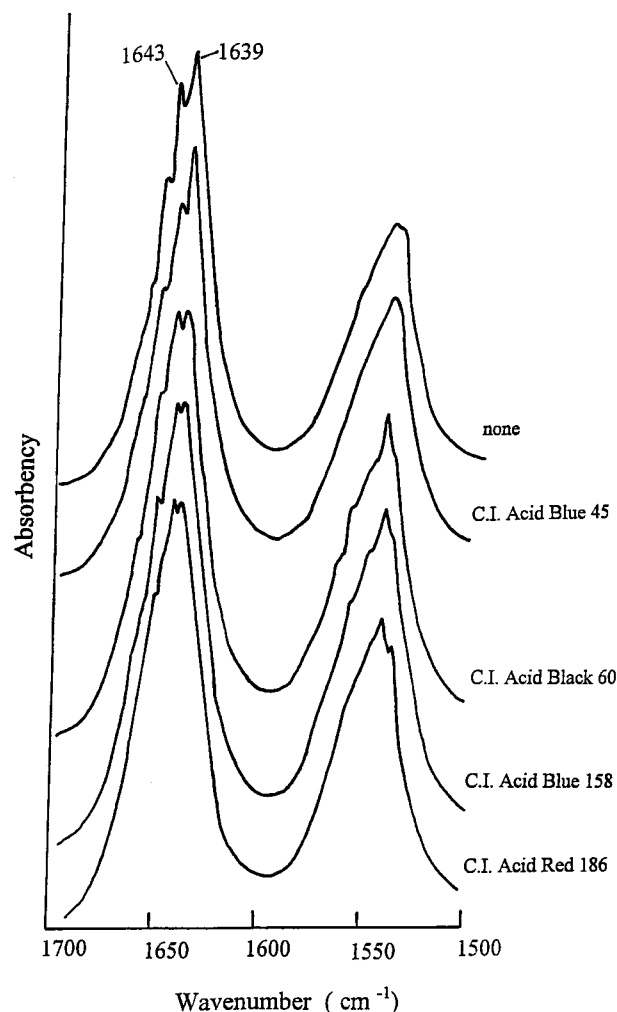


Figure 8 IR spectra of melt-reprocessed nylon 66 samples containing different acid dyes.

The observed influence of metal complex dyes on melt-reprocessed nylon can be explained by the possible interaction between Cr^{3+} ions and polyamide chains. We speculated that in melt-reprocessed dyed nylon the Cr^{3+} ions freed from decomposed dye molecules form coordinate bonds with amide groups.

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