

Influence of Acid Dyes on the Thermal Behavior of Nylon 66

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ABSTRACT: To reveal the effect of acid dyes on the melt processing of recycled nylon 66, 17 acid dyes with different chemical structures were used to dye a nylon 66 yarn. The thermal stability of dyestuffs, the thermal degradation of the dyed nylon 66 during compression molding, and the melting and crystallization of the dyed nylon were investigated. During melt processing, most dyed nylon 66 changed color strength and color pattern. This is attributed to the migration and chemical reactions of dyestuffs. Acid dyes containing metal ions, such as C.I. Acid Black 60, C.I. Acid Red 186, C.I. Acid Yellow 151, and C.I. Acid Black 107, have severe impact on the thermal stability of nylon 66. The influence of metal complex acid dyes on the thermal stability of nylon 66 can be explained by a mechanism of acid-catalyzed nucleophilic acyl substitution. It was observed that the existence of acid dye in nylon 66 does not influence the melting temperature of nylon. However, some metal complex dyes reduce the crystallization temperature of molten nylon. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 371–382, 1998

Key words: nylon 66; acid dyes; color variation; thermal degradation; melting temperature; crystallization temperature

INTRODUCTION

Postconsumer carpet waste constitutes a large portion of the textile waste, which has accumulated tremendously in landfills. Reclamation of polymer materials contained in this waste product is becoming more and more important from the environmental and economic points of view. In recent years, many technologies have been developed to collect pure polymers from waste carpet.^{1–6}

Carpets made from nylon fibers, polypropylene backing, SBR latex, and CaCO₃ fillers have a large share of the carpet market and the postconsumer carpet waste pile. Recently, the authors have developed a new technology to collect nylon fibers with purity higher than 99% from postconsumer carpet waste.³ This recycled nylon can be used directly for the production of fibers and engi-

neering plastics by melt spinning and other melt processing methods.

The most important concern in melt processing of recycled nylon is the polymer thermal stability. The thermal degradation of virgin nylon polymers has been studied for many decades.^{7,8} However, reusing waste nylon is more complicated than using virgin nylons. This is because a majority of carpet nylon yarns are dyed mostly by acid dyes and finished with various chemical agents to improve their performances (e.g., antistatic, antibacteria, and flame-resistant). These dyes and additives may influence the thermal stability and processability of the recycled nylon.

Based on the authors' knowledge, no research work has been directed to reveal the effect of dyestuffs on the thermal reprocessing of recycled nylon. In this work, 17 dyestuffs representing different types of acid dyes were selected to dye nylon 66 virgin yarns. The effects of dyestuffs on the thermal degradation, melting, and crystallization of the dyed nylon were investigated.

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Table I Dyestuffs and Dyeing Conditions

Dyestuff/C.I. Number	Manufacturer/Trademark	Additives in Dye Bath
C.I. Acid Blue 25 (62055)	GAF Corp. Alizarine Supra Blue A	0.3% (v/v) formic acid
C.I. Acid Blue 45 (63010)	Ciba-Geigy Corp. Erio Fast Cyanine S Conc	0.3% (v/v) formic acid
C.I. Acid Green 41 (62560)	Telon Green 5G	0.3% (v/v) acetic acid
C.I. Acid Blue 113 (26360)	Ciba-Geigy Corporation Erionyl Navy Blue 2RN	0.3% (v/v) acetic acid and 2.5% (wt) Na ₂ SO ₄
C.I. Acid Red 114 (23635)	Ciba-Geigy Corporation Erionyl Red RS 125%	0.5% (v/v) acetic acid and 2.5% (wt) Na ₂ SO ₄
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
C.I. Acid Red 1 (18050)	Crompton & Knowles Intracid Red 2G Conc	0.5% (v/v) formic acid
C.I. Acid Blue 92 (13390)	Carolina Color & Chemical Co. Caracid Cyanine Blue R Conc PDR	0.3% (v/v) acetic acid and 2.0% (wt) Na ₂ SO ₄
C.I. Acid Yellow 23 (19140)	Cyanamid Calcocid Yellow MCG	0.3% (v/v) formic acid
C.I. Acid Yellow 40 (18950)	Du Pont Milling Yellow 5G	3.0% (wt) (NH ₄) ₂ SO ₄
C.I. Acid Green 3 (42085)	Sandoz Colors & Chemicals Acid Green 2G 100%	0.3% (v/v) sulfuric acid (30% wt)
C.I. Acid Blue 158 (14880)	Organic Dyestuffs Corporation Orcolan Fast Blue GGN 200	0.3% (v/v) formic acid
C.I. Acid Black 60 (18165)	Ciba-Geigy Corporation Irgalan Grey BRL-01 KWL 200	—
C.I. Acid Red 186 (18810)	Organic Dyestuffs Corporation Orcolan Fast Pink BN 200	0.3% (v/v) formic acid
C.I. Acid Yellow 151 (13906)	Organic Dyestuffs Corporation Orcolan Neutral Yellow WN 250	0.3% (v/v) formic acid
C.I. Acid Black 107	Ciba-Geigy Corporation Irgalan Black RBL 200	0.3% (v/v) formic acid
C.I. Acid Red 211	Ciba-Geigy Corporation Irgalan Red 2GL KWL 200	

EXPERIMENTAL

Materials

Nylon 66 yarns (1140-57-GMT) were supplied by the Monsanto Chemical Company (Greenwood, SC). The trademarks of the dyestuffs used in this work are listed in Table I. All the dyestuffs were used without purification.

Selection of Dyestuffs

Conventional dyestuffs for textiles are divided into several types according to their chemical structures and dyeing mechanisms. Although nylon fibers can be dyed by several types of dyestuffs, the most frequently used dyestuffs in the industry are acid dyes. These dyes react with the end amine groups of the polyamide forming ionic

bonds between the dye molecules and polymer chains. There is a large number of commercial acid dyes with varying chemical structures of chromophores (conjugated double bonds) and auxochromes (substituent groups) in dye molecules. It has been well documented that the difference in the chemical structure of dyes influences the color, color fastness, and even ultraviolet (UV) stability of the dyed nylon fiber.⁹ In the present study, 17 acid dyes were selected to represent different types of acid dyes. As shown in Table II, C.I. Acid Blue 25, C.I. Acid Blue 45, and C.I. Acid Green 41 represent anthraquinone type acid dyes, in which the chromophores are anthraquinone groups. C.I. Acid Blue 113, C.I. Acid Red 114, and C.I. Acid Red 151 are polyazo type acid dyes with two or three azo groups. C.I. Acid Red 1 and C.I. Acid Blue 92 are monoazo type acid dyes of small molecular size. C.I. Acid Yellow 23 and C.I. Acid

Table II Chemical Structures of the Selected Acid Dyes

Dye and C.I. Number	Chemical Structure
C.I. Acid Blue 25 (62055)	
C.I. Acid Blue 45 (63010)	
C.I. Acid Green 41 (62560)	
C.I. Acid Blue 113 (26360)	
C.I. Acid Red 114 (23635)	
C.I. Acid Red 151 (26900)	
C.I. Acid Red 1 (18050)	

Table II Continued

Dye and C.I. Number	Chemical Structure
C.I. Acid Blue 92 (13390)	
C.I. Acid Yellow 23 (19140)	
C.I. Acid Yellow 40 (18950)	
C.I. Acid Green 3 (42085)	
C.I. Acid Blue 158 (14880)	

Table II Continued

Dye and C.I. Number	Chemical Structure
C.I. Acid Black 60 (18165)	
C.I. Acid Red 186 (18810)	
C.I. Acid Yellow 151 (13906)	<p>Complex of Co^{2+}</p>
C.I. Acid Black 107	Unknown
C.I. Acid Red 211	Unknown

Yellow 40 are another type of azo dyes, in which the chromophores contain azo groups and pyrazolones. C.I. Acid Green 3 is among the diamino derivations of triphenylmethane. The 1 : 1 and 1 : 2 metal complex dyes are another subgroup of acid dyes, represented by C.I. Acid Blue 158, C.I. Acid Black 60, C.I. Acid Red 186, and C.I. Acid Yellow 151. The 1 : 1 metal complex dyes bond to fibers not only by ionic and second-order bonds, as do the regular acid dyes, but also by coordinate bonds through the metal ions.⁹ C.I. Acid Black 60, C.I. Black 107, and C.I. Red 211 are particular metallized acid dyes that have been reported to have influence on the UV stability of the dyed nylon fiber.⁹ In the current work, this group of dyes is referred to as “UV active” dyes. The chemical

structures of C.I. Acid Black 107 and C.I. Acid Red 211 are not given in the *Colour Index*.¹⁰

Dyeing of Nylon 66 Fiber

In a 250-mL three-neck flask equipped with a condenser, a thermometer, and a heating unit, about 7 g of nylon 66 yarns were immersed in 100 ml aqueous dye bath with a dye concentration of 0.5% wt (71 mg dyes per gram of fiber). Additives were also added to obtain a high dyeing level. The type and concentration of these additives were selected according to the recommendation of the dyestuff manufacturer and the *Colour Index*.¹⁰ This information is given in Table I. To ensure an optimized dye uptake, the dye bath was first heated from

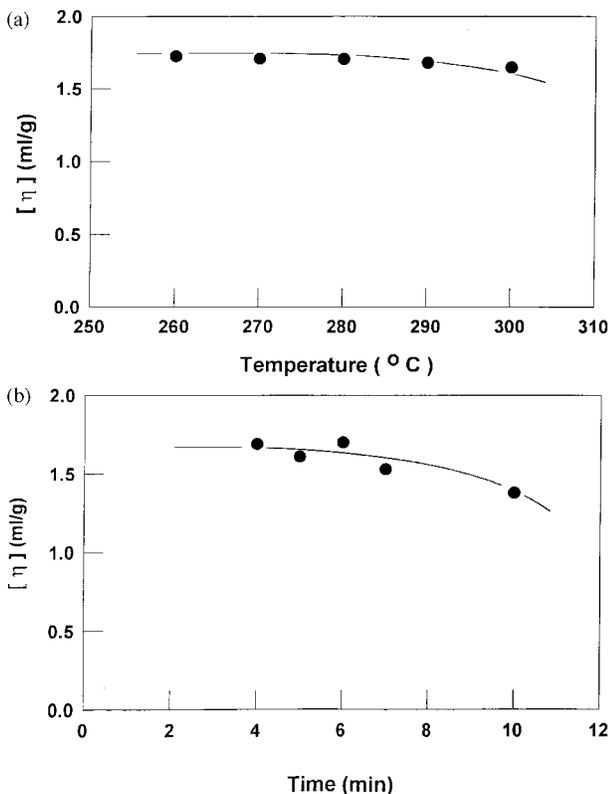


Figure 1 Effects of processing conditions on the intrinsic viscosity of compression molded nylon 66 (measured at 30 $^{\circ}\text{C}$ with 88% formic acid containing 0.1M of KCl): (a) temperature versus viscosity for a processing time of 6 min; (b) time versus viscosity for a processing temperature of 270 $^{\circ}\text{C}$.

room temperature to 100 $^{\circ}\text{C}$ with a heating rate of 1 $^{\circ}\text{C}$ min, then kept boiling (at 100 $^{\circ}\text{C}$) for 1 h. After the dyeing process, the dyed nylon 66 yarns were taken out of the dye bath and rinsed with water until no retained dyestuff could be washed out. The dyed nylon yarns were then dried at 100 $^{\circ}\text{C}$ for 2 h.

Heat Treatment of Yarns

Dyed nylon 66 yarns were cut into 1-mm-long lint with a fiber mill (Arthur Thomas Co.). The nylon lint was placed in a mold (10.16 \times 10.16 cm) and dried at 100 $^{\circ}\text{C}$ for 2 h in a vacuum oven. Nitrogen was used to release vacuum. The mold was then placed on a platen of a compression molding machine (G30H-15-B, Wabash) that was previously heated to the desired temperature. The nylon lint was compression-molded at the desired temperature in a nitrogen gas environment at a discharge rate of about 10 cc/min. The pressure applied to the mold was 862 KPa. After a specified period of

time, the mold was quenched in a water bath, and a molded nylon sheet was collected.

Colorimetric Analysis

The colorimetric analyses of the dyed nylon 66 fibers and molded sheets were performed with a CS-5 Chroma Sensor (Datacolor International). The undyed white nylon 66 fiber was used as a standard sample. The color coordinates based on CIE system were acquired by a Chroma-QC program. These parameters reflect the level of dyeing and color difference in the samples.

Thermal Analyses of Dyed Nylon Fibers and Dyestuffs

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to analyze the thermal stability of dyestuffs and the melting and crystallization of the dyed nylon fibers. The analyses were performed at 20 $^{\circ}\text{C}/\text{min}$ heating rate, 20 $^{\circ}\text{C}/\text{min}$ cooling rate (for crystallization studies), and 20 cc/min nitrogen flushing rate.

Infrared Spectrometry Analysis

Dyestuffs were dissolved in acetone. Droplets of the dye solution were placed on a KBr crystal disc. After evaporating the acetone by heating the sample at 60 $^{\circ}\text{C}$, the disc was placed in the sample window of a 2000 Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer). The IR spectrum of dyestuff was then recorded with a scan number of 20 and a resolution of 4 cm^{-1} .

Determination of Molecular Weight

The molecular weights of nylon 66 before and after processing were determined by intrinsic viscosity measurements conducted at 25 $^{\circ}\text{C}$. The solvent used was 90% formic acid with 2.3 M of KCl. The molecular weight of nylon 66 (indicated by M) was calculated from the intrinsic viscosity ($[\eta]$ in mL/g) according to the equation $[\eta] = 253 \times 10^{-3} M^{0.5}$.^{11,12}

RESULTS AND DISCUSSION

Degradation of Nylon 66 from Postconsumer Carpet

Nylon 66 recycled from waste carpet was processed with a hot compression molding machine.

Table III Color Coordinates of the Dyed Nylon 66 Fibers

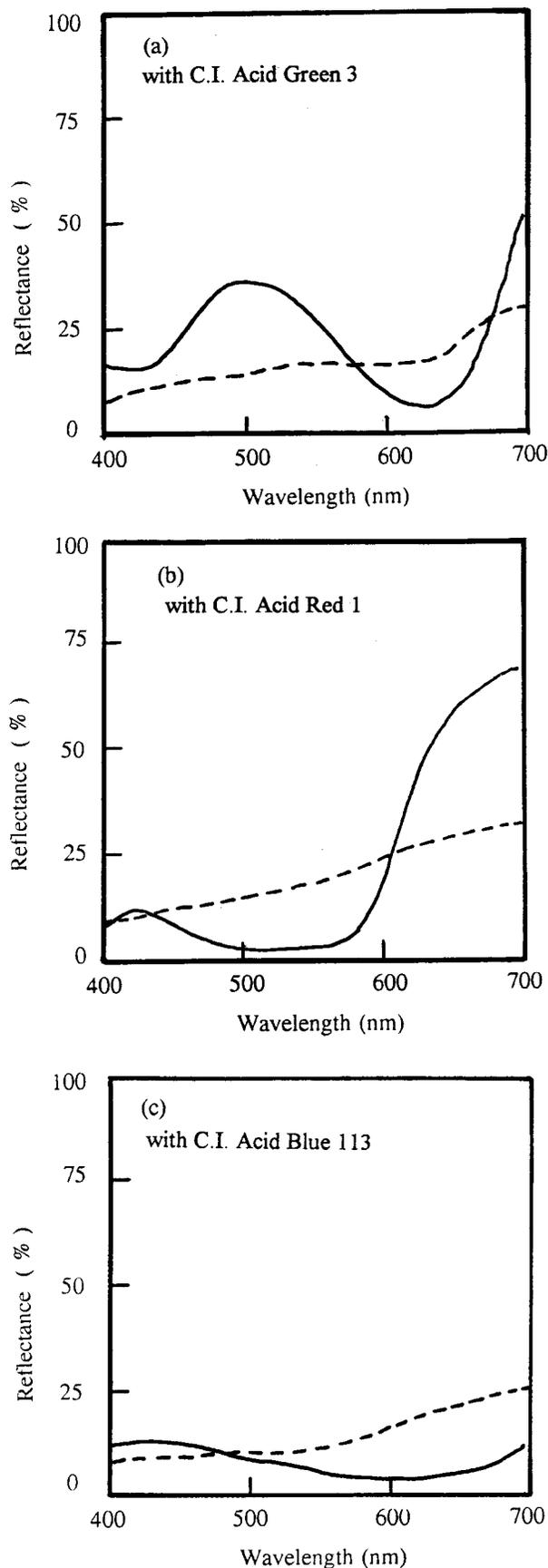
Dyestuff	L^*	C^*	a^*	b^*
None	91.53	1.21	-0.11	1.20
C.I. Acid Blue 25	18.57	39.97	8.34	-39.09
C.I. Acid Blue 45	28.69	42.54	-0.01	-42.54
C.I. Acid Green 41	28.61	25.27	-23.45	9.43
C.I. Acid Blue 113	23.12	23.82	0.52	-23.82
C.I. Acid Red 114	31.32	49.56	40.54	28.51
C.I. Acid Red 151	28.23	42.01	35.07	23.12
C.I. Acid Red 1	39.32	43.27	42.77	6.53
C.I. Acid Blue 92	16.69	24.47	4.96	-23.96
C.I. Acid Yellow 23	84.31	102.40	3.30	102.34
C.I. Acid Yellow 40	74.89	92.65	5.49	92.49
C.I. Acid Green 3	53.75	27.89	-27.88	-0.66
C.I. Acid Blue 158	15.34	9.01	-0.39	-9.00
C.I. Acid Black 60	14.21	0.87	0.24	-0.83
C.I. Acid Red 186	26.96	33.78	32.38	9.67
C.I. Acid Yellow 151	41.60	49.81	20.27	45.50
C.I. Acid Black 107	14.38	0.53	0.26	-0.47
C.I. Acid Red 211	28.69	38.53	32.02	21.44
Rose red carpet	47.58	16.92	14.41	8.88
Green carpet	61.61	19.24	-4.64	18.67

Figure 1(a) shows the effect of processing temperature on the polymer intrinsic viscosity for a processing time of 6 min. The processing temperature did not affect the intrinsic viscosity of the molded nylon until the temperature reached 280°C, whereas slight decrease in intrinsic viscosity was detected at 290 and 300°C. The effect of molding time on the intrinsic viscosity of nylon

sample molded at 270°C is indicated in Figure 1(b). Significant decrease in the intrinsic viscosity was observed when molding time exceeded 7 min. It was observed from Figure 1 that the optimum processing conditions for the recycled nylon 66 is at 270°C for 7 min. In the ensuing studies, this optimum processing condition was used.

Table IV Color Coordinates of the Molded Nylon 66

Dyestuff	L^*	C^*	a^*	b^*
None	72.90	7.92	0.40	7.92
C.I. Acid Blue 25	25.53	5.21	0.62	-5.17
C.I. Acid Blue 45	28.73	9.08	0.62	-9.06
C.I. Acid Green 41	26.77	1.63	-1.62	-0.18
C.I. Acid Blue 113	47.99	13.48	8.52	12.56
C.I. Acid Red 114	34.39	17.04	9.02	14.46
C.I. Acid Red 151	28.60	27.90	4.78	2.53
C.I. Acid Red 1	53.05	21.10	5.31	20.42
C.I. Acid Blue 92	24.46	12.31	1.07	-12.26
C.I. Acid Yellow 23	64.77	31.48	2.80	31.36
C.I. Acid Yellow 40	50.79	43.50	9.03	42.55
C.I. Acid Green 3	47.99	13.48	-0.99	13.45
C.I. Acid Blue 158	26.21	2.22	-0.26	-2.21
C.I. Acid Black 60	25.30	0.36	0.11	-0.34
C.I. Acid Red 186	24.09	7.08	7.07	0.25
C.I. Acid Yellow 151	28.20	4.25	1.63	3.92
C.I. Acid Black 107	24.92	1.11	0.24	-1.09
C.I. Acid Red 211	28.21	14.26	9.02	14.46



Stability of Dyestuff During the Melt Processing

The color of the polymer produced from the recycled nylon fiber is of prime importance. The color coordinates of the nylon fibers with the above acid dyes are given in Table III. These parameters are generally used by the industry to describe the color, color intensity, color difference, and dyeing level of fibers. In Table III, L^* is lightness; and C^* is chroma, which indicates the color saturation. The color is quantitatively described by parameters a^* and b^* . For instances, a red sample has a positive a^* , and a green sample possesses a negative a^* value. Similarly, positive b^* means yellow color, while negative b^* implies blue color. The color coordinates of two nylon yarns from sample carpets are also presented in Table III. The laboratory-dyed nylon fibers have a wide range of color coordinates, which cover those of the carpet yarns.

The color parameters of the dyed nylon after the compression molding process are shown in Table IV and are compared with those listed in Table III. After compression molding, the undyed nylon 66 exhibited decreased lightness and slightly became yellow according to the increased b^* value. All of the dyed samples showed reduced chroma values after processing. In addition, the dyed nylons that originally had high levels of lightness ($L^* > 40$) reduced their L^* values, while those that previously possessed low levels of lightness ($L^* < 40$) increased or maintained their L^* values. It is also noticeable that every molded colored sample exhibited decreased hue. For examples, the red samples ($a^* > 0$) showed decreased a^* values, and the green samples ($a^* < 0$) presented reduced absolute value of a^* levels. This pattern of color changes also applied to the yellow samples ($b^* > 0$) and blue samples ($b^* < 0$). The most obvious color changes were observed in the samples with C.I. Acid Blue 113, C.I. Acid Red 1, and C.I. Acid Green 3. These color variations also can be demonstrated by the reflectance curves, as shown in Figure 2(a-c). The melting process changed the shapes of the reflectance curves of these samples.

The reason behind the color variation is associated with the physical and chemical reactions of dyestuffs, which may occur during the melt pro-

Figure 2 Reflectance curves of nylon 66 samples dyed with (a) C.I. Acid Green 3, (b) C.I. Acid Red 1, and (c) C.I. Acid Blue 113: (—) before processing; (-----) after processing.

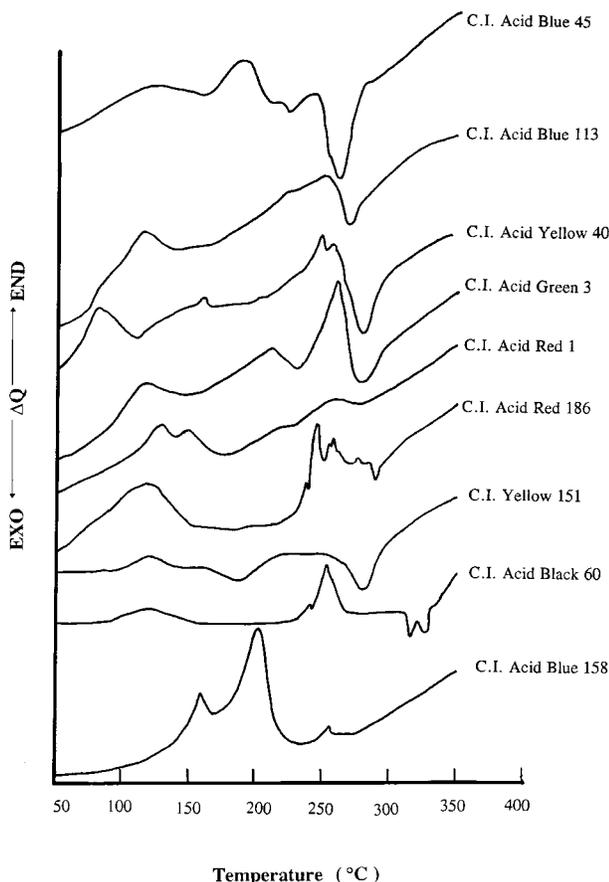


Figure 3 DSC curves for different acid dyes (20°C/min with 10 cc/min N₂).

cessing. The differential scanning calorimetry (DSC) curves of some dyestuffs, as presented in Figure 3, indicate that most dyestuffs exhibit multiple endothermic and exothermic peaks in their DSC curves. The endothermic peak around 100°C is likely associated with the removal of moisture in dyestuff. The peaks at higher temperature could be assigned to the chemical reactions of dye molecules or the possible melting (endothermic) of dye crystals. In melt processing, the motion of polymer chains and dye molecules certainly changes the location of the dyestuffs in the nylon sample. The migration of dye molecules can change the chroma and lightness of molded samples. Moreover, any chemical reaction of dyestuff upon raising temperature certainly changes the chemical characteristics of the chromophores and auxochromes in dye molecules and consequently alters the pattern of light adsorption.

The thermal stability and decomposition products of each dye rely on its original chemical structure. It would be difficult to detail the chemical reactions of every dyestuff. A typical relationship

between color change and the variation in chemical structure was studied with C.I. Acid Red 1 dye as an example. The DSC curve of C.I. Acid Red 1 exhibited three endothermic peaks, indicating the occurrences of chemical reactions. The IR spectra of this dyestuff before and after being heated at 270°C for 7 min (Fig. 4) show variations in IR adsorption peaks. For examples, the peaks at 1688 and 1650 cm⁻¹, which originally located in the IR spectrum of the unheated dyestuff, disappeared after heat treatment. These peaks are assigned to the C=O bonds of amide groups and the conjugated C=C bonds of benzene rings in C.I. Acid Red 1 molecules (Table II). Also, a shoulder peak at 1255 cm⁻¹, which is associated with the S=O bonds of -SO₃⁻ groups, was eliminated after the treatment. These variations in the IR spectrum imply structural changes in the auxochromes or chromophores of the dye molecule, being the cause for the color change, as shown in Figure 2(b).

Thermal Stability of the Dyed Nylon 66

The thermal stability of the dyed nylon is another important aspect in the reprocessing of recycled nylon. Table V presents the molecular weight of the molded nylon samples. The molecular weight of the undyed nylon 66 was 2.48×10^4 . After compression molding, the molecular weight of the undyed sample was 2.45×10^4 . The selected an-

Table V Molecular Weight of the Molded Nylon 66

Dyestuff in Fiber	$M_w (\times 10^4)$
None	2.45
C.I. Acid Blue 25	2.44
C.I. Acid Blue 45	2.43
C.I. Acid Green 41	2.41
C.I. Acid Blue 113	2.47
C.I. Acid Red 114	2.40
C.I. Acid Red 151	2.48
C.I. Acid Red 1	2.46
C.I. Acid Blue 92	2.44
C.I. Acid Yellow 23	2.41
C.I. Acid Yellow 40	2.42
C.I. Acid Green 3	2.40
C.I. Acid Blue 158	2.39
C.I. Acid Black 60	2.19
C.I. Acid Red 186	2.32
C.I. Acid Yellow 151	2.04
C.I. Acid Black 107	1.94
C.I. Acid Red 211	2.46

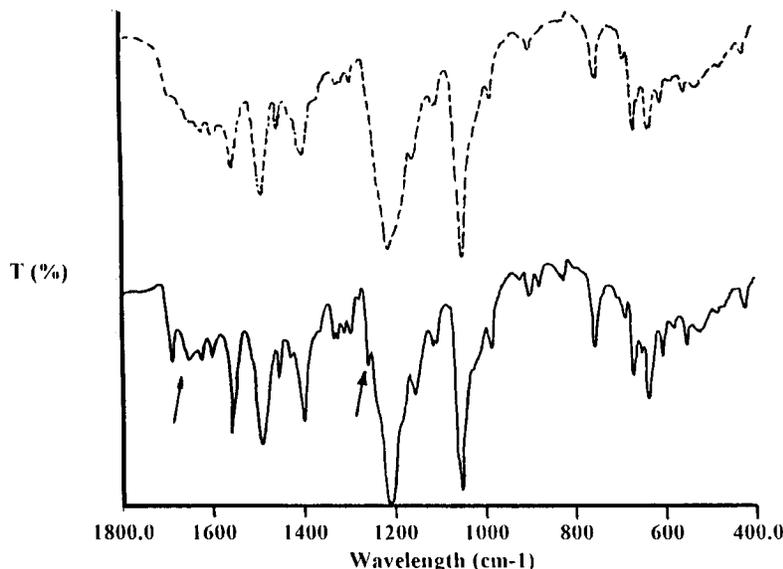


Figure 4 IR spectra of C.I. Acid Red 1: (—) original; (-----) heated at 270°C for 7 min.

thraquinone acid dyes, azo dyes, and C.I. Acid Green 3 showed no influence on the thermal degradation of nylon during melt-molding.

Among the molded nylon samples, those containing metal complex acid dyes possessed lower molecular weight than the original nylon. This suggests that selected metal complex acid dyes reduced the thermal stability of the dyed nylon.

Some of the UV-active dyes had influences on the thermal degradation of nylon 66. It was reported that C.I. Acid Black 107 and C.I. Acid Red 211 reduce the UV stability of nylon fibers, while C.I. Acid Black 60 improve the UV stability.⁹ However, Table V shows that C.I. Acid Red 211 did not affect the thermal stability of nylon, but C.I. Acid Black 60 and C.I. Acid Black 107 accelerated the thermal degradation of the nylon. Therefore, it could be concluded that the effect of acid dyes on thermal stability could not be correlated to its UV stability. This difference is due to the mechanism difference between thermal degradation and UV degradation.

Thermal Degradation Mechanism of Nylon 66

The effect of metal complex dyestuffs on nylon degradation can be explained by the mechanism of nylon thermal degradation. It has been confirmed that degradation of nylon 66 occurs at amide groups.^{8,13-16} The degradation includes an α -C—H bond transfer process, resulting in intermediate ketoamide and amine end groups in the degraded nylon 66 chains.¹⁵ These intermedi-

ate substances undergo further reactions, giving cyclopentanone, amines, and some other small compounds.¹⁶ Accordingly, the reaction between amide groups and α -C—H bonds is a key step in the degradation of nylon 66 polymer. However, the chemical mechanism behind this reaction was not detailed in the above literature.

The following mechanism, as shown in Figure 5, is proposed according to the principle of acid-catalyzed nucleophilic acyl substitution,¹⁷ and other reported information regarding the chemical reactions involved in the thermal degradation of nylon 66.^{15,16} It is well documented that the α -H in a carbonyl group-containing compound is very acidic and easy to leave from the α -C—H bond, resulting in a proton and a carbanion.¹⁷ Accordingly, the thermal degradation of the nylon 66 polymer, which has α -C—H bonds, should include the formation of protons and carbanions from α -C—H bonds. A generated proton then attacks the oxygen atom in the amide group, pulling the π -electron cloud toward the oxygen atom.¹⁷ This action results in more positive charges in the carbonyl carbon atom [Fig. 5(II)] and certainly makes the carbonyl group even more susceptible to the nucleophilic attack. A carbanion, which is nucleophilic, then attacks the positively charged carbonyl carbon atom, forming a cyclic intermediate structure [Fig. 5(III)], as reported in literature.^{8,15} This intermediate structure undergoes breakage and reactions, which produce small molecular substances.¹⁶ This acid-catalyzed nucleophilic acyl substitution mechanism can explain

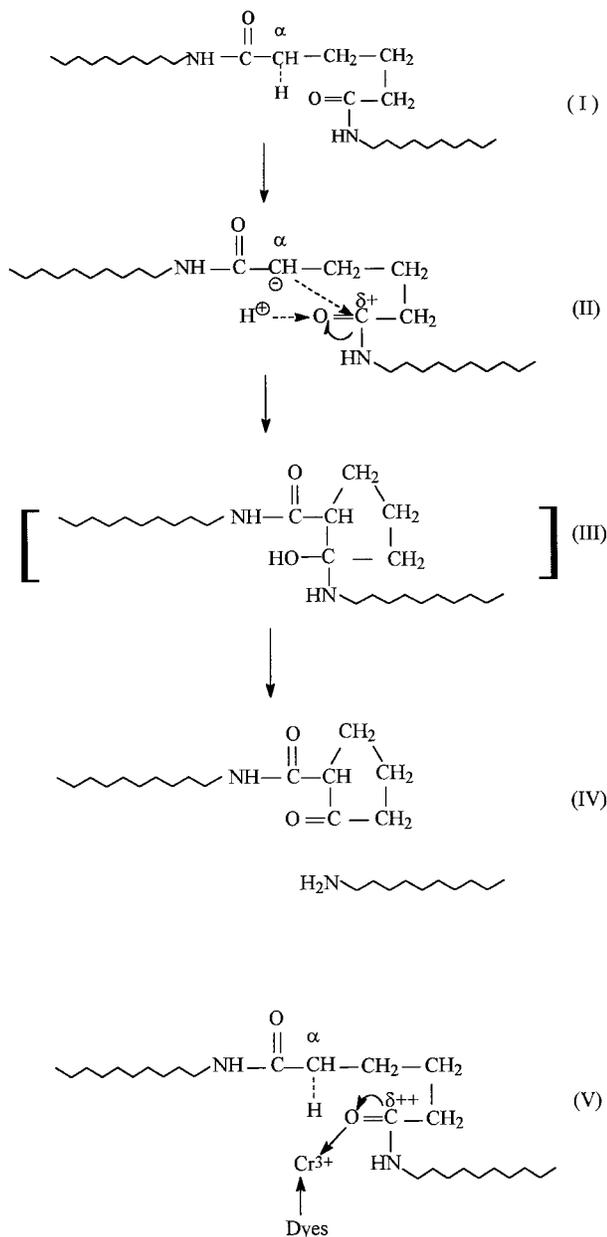


Figure 5 Suggested mechanism of the thermal degradation of nylon 66.

how the α -C-H bonds react with the amide groups during the thermal degradation of nylon 66 polymer.

When nylon 66 fiber is dyed with metal-complex acid dyes, the metal ions such as Cr^{3+} and Co^{2+} in the 1 : 1 metal-complex dyes form coordinate bonds with the amide carbonyl groups of the nylon polymer chains.⁹ The existence of coordinate bonds between metal ions and amide groups in nylon polymers has been reported by other researchers.^{18,19} Moreover, it is expected that during the melt processing of nylon, the possible decom-

position reactions of 1 : 1 or 1 : 2 metal-complex dyes should release metal ions and therefore increase the probability of the formation of coordinate bonds between metal ions and amide groups.

The coordinate bonds of amide carbonyl groups with Cr^{3+} or Co^{2+} ions will increase the electron-withdrawing abilities of oxygen atoms and result in higher positive charges at the carbonyl carbon atoms, as indicated in Fig. 5(V). This process certainly accelerates the acid-catalyzed nucleophilic acyl substitution and consequently results in more pronounced degradation in nylon chains.

Accordingly, from the viewpoint of the waste nylon fiber reclamation, metal-complex acid dyes are not recommended for the dyeing of nylon 66 carpet yarn.

Melting and Crystallization of the Dyed Nylon 66

The melting and crystallization temperatures of the dyed nylon polymers measured by DSC are listed in Table VI. The melting temperature of the undyed nylon 66 was 258.7°C. It can be seen from Table VI that the existence of dyestuffs obviously does not influence the melting temperature of dyed nylon polymers.

The anthraquinone-type acid dyes, azo-type acid dyes, and C.I. Acid Green 3 did not affect the crystallization temperature of molten nylon. The crystallization temperatures of molten nylon,

Table VI Melting Temperature and Crystallization Temperature of the Dyed Nylon 66

Dyestuff in Fiber	Melting Temperature (°C)	Crystallization Temperature (°C)
None	258.7	223.0
C.I. Acid Blue 25	256.9	222.5
C.I. Acid Blue 45	256.7	222.4
C.I. Acid Green 41	257.9	221.8
C.I. Acid Blue 113	255.0	222.0
C.I. Acid Red 114	254.5	222.0
C.I. Acid Red 151	254.9	222.5
C.I. Acid Red 1	255.0	223.3
C.I. Acid Blue 92	258.0	222.4
C.I. Acid Yellow 23	255.9	222.9
C.I. Acid Yellow 40	258.3	223.0
C.I. Acid Green 3	255.7	222.2
C.I. Acid Blue 158	255.8	215.4
C.I. Acid Black 60	258.0	220.3
C.I. Acid Red 186	255.8	220.0
C.I. Acid Black 107	257.8	215.3
C.I. Acid Red 211	257.2	222.3

which were dyed with these dyestuffs, were maintained at levels between 222.0 to 223.3°C. However, the existence of metal-complex acid dyes reduced the crystallization temperature. The most distinct effects were observed in samples dyed with C.I. Acid Blue 158 and C.I. Acid Black 107. The crystallization of molten nylon dropped from 223.0 to 215.3°C when these two dyes were used. The decrease in crystallization temperature of molten nylon is considered to be attributed to the formation of coordinate bonds between metal ions and amide groups of nylon polymer chains. These bonds may restrict the mobility of polymer chains, which is essential to the crystallization of polymer.

CONCLUSIONS

The effects of acid dyes with various structures on the thermal behavior of nylon have been revealed. After compression molding process, all samples dyed with the studied 17 acid dyes showed reduced chroma values. The processing also reduced the lightness of molded sample when the original L^* level was higher than 40; otherwise, it increased or maintained the lightness. Furthermore, every molded sample exhibited reduction in hue. The most remarkable color changes were observed when C.I. Acid Blue 113, C.I. Acid Red 1, and C.I. Acid Green 3 were used. The color changes of the molded colored nylon can be associated with migration and chemical reactions of the dyestuffs during the melt processing.

The selected anthraquinone and azo acid dyes demonstrated no influence on the thermal stability of nylon 66 during the compression molding process. The metal ion-containing acid dyes, such as C.I. Acid Black 60, C.I. Acid Red 186, C.I. Acid Yellow 151, and C.I. Acid Black 107, accelerated the degradation of nylon 66. The influence of metal-complex dyes on the thermal degradation of nylon 66 can be explained by the mechanism of acid-catalyzed nucleophilic acyl substitution.

The presence of acid dyes in nylon 66 did not influence the melting point. However, the crystallization temperature of molten nylon decreased when some metal-complex acid dyes were applied. This influence became more significant when C.I. Acid Blue 158 and C.I. Acid Black 107 were used.

It can be concluded from this research effort

that it is preferable, from a recycling point of view, not to use metal-complex acid dyes with nylon 66 fibers. Postconsumer waste carpet dyed with dyes other than metal complex acid dyes have a good chance of being economically recycled into nylon fibers or other plastic products without the need of removing the dye molecules.

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REFERENCES

1. P. C. Sharer, U.S. Pat. 5,518,188 (1996).
2. T. F. Corbin, E. A. Davis, and J. A. Dellinger, U.S. Pat. 5,169,870 (1992).
3. Y. A. Gowayed and W. Lin, U.S. patent (pending).
4. D. J. David, J. L. Dickerson, and T. F. Sincock, U.S. Pat. 5,294,384 (1994).
5. Y. Wang, *Proceedings of the First Annual Conference on the Recycling of Fibrous Textile and Carpet Waste*, Georgia Institute of Technology, Atlanta, June 12–13, 1996.
6. Y. A. Gowayed, R. Vaidyanathan, and M. El-Halwagi, *J. Elastomers Plastics*, **27**, 79 (1995).
7. M. I. Kohan, *Nylon Plastics*, Wiley, New York, 1973, Chap. 2, p. 13.
8. M. I. Kohan, *Nylon Plastics Handbook*, Hanser/Gardner, Cincinnati, 1995, Chap. 3, p. 33.
9. D. M. Nunn, *The Dyeing of Synthetic Polymer and Acetate Fibers*, H. Charlesworth & Co., Huddersfield, U.K., 1979, Chap. 4, p. 243.
10. The Society of Dyes and Colorist and The American Association of Textile Chemistry and Colorist, *Colour Index*, Vol. 1, Chorley & Pickersgill Ltd., Leeds, U.K., 1956.
11. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, p. VII–1.
12. H.-G. Wlias and R. Schumucher, *Makromol. Chem.*, **76**, 23 (1964).
13. B. G. Achhamer, F. W. Reinhart, and G. M. Kline, *J. Appl. Chem.*, **1**, 301 (1951).
14. I. Goodman, *J. Polym. Sci.*, **17**, 587 (1955).
15. A. Ballistreri, D. Garozzo, M. Giuffrida, and G. Montaudo, *Macromolecules*, **20**, 2991 (1987).
16. D. H. MacKerron and R. P. Gordon, *Polym. Degrad. Stab.*, **12**, 277 (1985).
17. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 6th ed., Prentice-Hall, Englewood Cliffs, N.J., 1992, pp. 797–799.
18. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1641 (1969).
19. A. P. More and A. M. Donald, *Polymer*, **34**, 5093 (1993).