

# Some Physical Properties of Various Amine-Pretreated Nomex Aramid Yarns

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**ABSTRACT:** In this study we pretreated Aramid yarns with ethylenediamine (EDA), diethylene triamine (DETA), and triethylene tetraamine (TETA) under different conditions to study some of their physical properties. The tensile strength retention, dye absorption (basic dye), and wicking height changed increasing pretreatment temperature, time period, and amines concentration. The glass-transition temperature and the density of the crystals were ranked as follows: EDA > DETA > TETA; however, the degrees of the surface void were inverse. We concluded that the polymer chains of the Aramid fibers were rearranged through shrink-

age of the pretreated Aramid fibers during pretreatment, and the hydrolysis of the Nomex polymer chains occurred under higher amine concentrations. The former phenomena were confirmed with differential scanning calorimetry, dynamic mechanical analysis, and X-ray diffraction analyses, and the latter were confirmed with Fourier transform infrared spectroscopy and basic dye adsorption analysis. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 70–76, 2005

**Key words:** adsorption; amorphous; differential scanning calorimetry (DSC); FT-IR; glass transition

## INTRODUCTION

It is well known that commercially available Nomex is difficult to dye because of its extremely high glass-transition temperature ( $T_g$ ).<sup>1</sup> Generally, the recommended method for dyeing Nomex involves high concentrations of a dye carrier in the dye bath and a high dyeing temperature for a long dyeing time.<sup>2</sup> Several researchers in previous studies<sup>3–9</sup> have investigated the dyeing ability of Aramid fibers. Nechwatal and Rossbach<sup>10</sup> showed that the pretreatment of Aramid fibers with benzyl alcohol could change the fine structure to increase the degree of crystallization. The author of another study<sup>7</sup> pointed out that heat treatment could improve the dyeing ability of the cationic dye on the Aramid fibers. From the pretreatment of organic solvents such as dimethylformamide, dimethyl acetamide, and dimethyl sulfoxide, Moore et al.<sup>2</sup> found that those solvents could create the voids in the treated fibers to increase the dyeing ability of Aramid fibers. However, information about the physical properties of pretreated Aramid fibers with amines is lacking.

Three amines [ethylenediamine (EDA), diethylene triamine (DETA), and triethylene tetraamine (TETA)] were used to pretreat Aramid yarns under different conditions to study some of their physical properties,

including wicking height (WH; fabrics), shrinkage, strength retention,  $T_g$  [differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA)], X-ray diffraction (XRD) patterns, Fourier transform infrared (FTIR) patterns, and morphology [scanning electron microscopy (SEM) photographs]. Additionally, the cationic dye adsorptions of the pretreated fibers were also examined in this study to confirm the surface states.

## EXPERIMENTAL

### Materials

Continuous filament yarns and fabrics of Nomex type 430 (200D/100f) that was desized, scoured, and bleached [20 s × 20 s ends (68) and picks (44)] were supplied by E. I. DuPont. The EDA, DETA, and TETA (Sigma Chemical Co., St. Louis, MO) used were reagent grade. The C. I. Basic Yellow 13 (Hodogaya Chemical Ltd., Kawasaki, Japan) used in this study was in the form of a commercial dye formulation.

### Methods

Skeins or fabrics of Aramid yarn (ca. 2.5 g) were pretreated at different temperatures, for different time periods, and at different concentrations of the three amines at a liquid ratio of 15. After pretreatment, the skeins were washed in water at 100°C for 30 min,

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TABLE I  
Dyeing and Physical Properties of the Three Amine-Pretreated Nomex Yarns and Fabrics

Amine	Pretreatment conditions			Dyeing and physical properties				
	Temperature (°C)	Time (min)	Amine concentration (%)	[D] <sub>f</sub> (g of dye/kg of fiber)	WH (mm)	ΔTSR (%)	Shrinkage (%)	T <sub>g</sub> (DMA)/T <sub>g</sub> (DSC)
Control	—	—	—	2.41	9.5	—	—	278.89/140.25
	30	60	100	12.65	13.9	-7.3	—	—
	60	60	100	14.82	14.2	-8.6	—	—
	80	60	100	15.90	14.5	-10.5	—	—
	100	60	100	16.42	14.7	-18.7	—	—
EDA	80	30	100	13.22	14.1	-6.1	—	—
	80	60	100	15.90	14.5	-10.5	—	—
	80	90	100	16.17	14.7	-12.1	—	—
	80	120	100	16.19	15.0	-14.0	—	—
	80	60	30	3.12	12.0	6.1	6.3	—
	80	60	50	3.54	12.6	5.7	6.8	—
	80	60	70	9.61	13.9	4.6	6.8	—
	80	60	100	15.90	14.5	-10.5	7.0	312.82/215.47
	30	60	100	14.76	14.1	-5.5	—	—
	60	60	100	16.40	14.5	-7.8	—	—
	80	60	100	17.42	14.8	-8.2	—	—
	100	60	100	17.86	15.1	-11.8	—	—
	DETA	80	30	100	14.02	14.3	-2.0	—
80		60	100	17.42	14.8	-8.2	—	—
80		90	100	17.65	15.1	-11.4	—	—
80		120	100	18.05	15.3	-12.2	—	—
80		60	30	3.52	12.3	6.9	6.2	—
80		60	50	4.56	13.0	6.4	6.5	—
80		60	70	11.23	14.3	5.5	6.8	—
80		60	100	17.42	14.8	-8.2	6.9	308.94/209.34
30		60	100	14.82	14.2	-3.6	—	—
60		60	100	16.28	14.7	-4.5	—	—
80		60	100	17.95	15.1	-4.8	—	—
100		60	100	18.25	15.5	-5.6	—	—
TETA		80	30	100	14.56	14.4	0.9	—
	80	60	100	17.95	15.1	-4.5	—	—
	80	90	100	18.02	15.3	-5.1	—	—
	80	120	100	18.35	15.4	-5.8	—	—
	80	60	30	3.86	12.5	7.3	6.0	—
	80	60	50	4.95	13.3	6.8	6.2	—
	80	60	70	12.92	14.8	6.0	6.5	—
	80	60	100	17.95	15.1	-4.8	6.7	303.10/157.98

dried in an oven at 80°C for 30 min, and conditioned for other examinations.

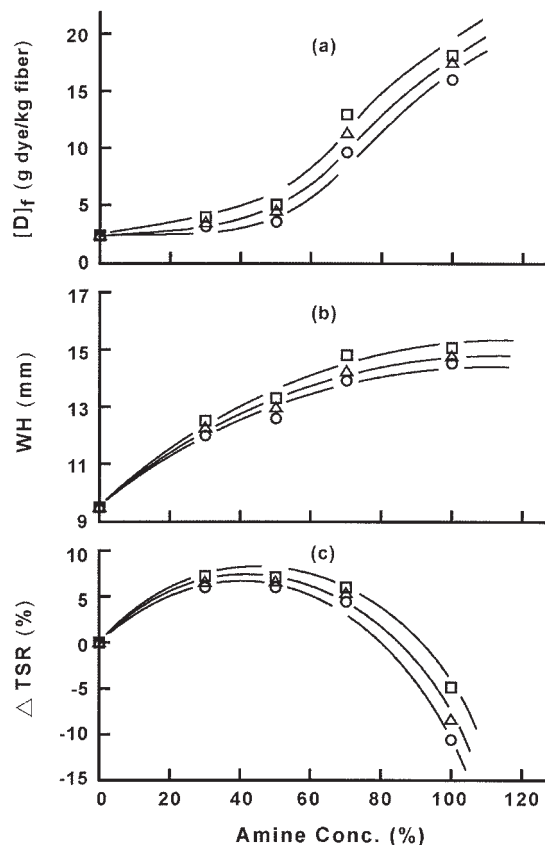
The samples were dyed in a finite aqueous bath (liquor ratio = 30) containing 4% (on the weight of fiber) commercial C. I. Basic Yellow 13 and 5 g/L sodium sulfate at 120°C for 60 min. The dye adsorption values were measured by the removal of aliquots of dye liquor and, after suitable dilution, the spectrophotometric determination of dye concentration.

The WHs of the pretreated Aramid fabric samples were measured with the method of JIS L 190. The tensile strengths of the pretreated Aramid filaments were measured on an Instron tensile tester (Machinery Industrial Co. Ltd., Taichung, Taiwan). T<sub>g</sub> values were determined with DSC (DSC Q1000, TA Instruments Inc., New Jersey; all scans were carried out at a heating rate of 15°C/min under flowing nitrogen at a flow rate of 25 mL/min) and

DMA (DMA-2980, PerkinElmer Co. Ltd., Connecticut; all scans were carried out at a heating rate of 5°C/min and a frequency of 1 Hz). The morphologies of the pretreated Aramid fibers were examined with SEM (JSM-5200) (Jeol Ltd., Tachigawa, Japan). In addition, the wide-angle X-ray diffraction (WAXD) patterns of the pretreated Aramid filaments were evaluated with an X-ray powder diffractometer (MAC Science, Yokohama, Japan MXP18). IR spectroscopic measurements of the various pretreated fabric samples were recorded directly on a FTIR spectrometer (FTIR Spectrum One, PerkinElmer) with attenuated total reflectance equipment.

## RESULTS AND DISCUSSION

The changes in tensile strength retention (ΔTSR), WH, shrinkage, and basic dye uptake ([D]<sub>f</sub>, g of dye/kg of

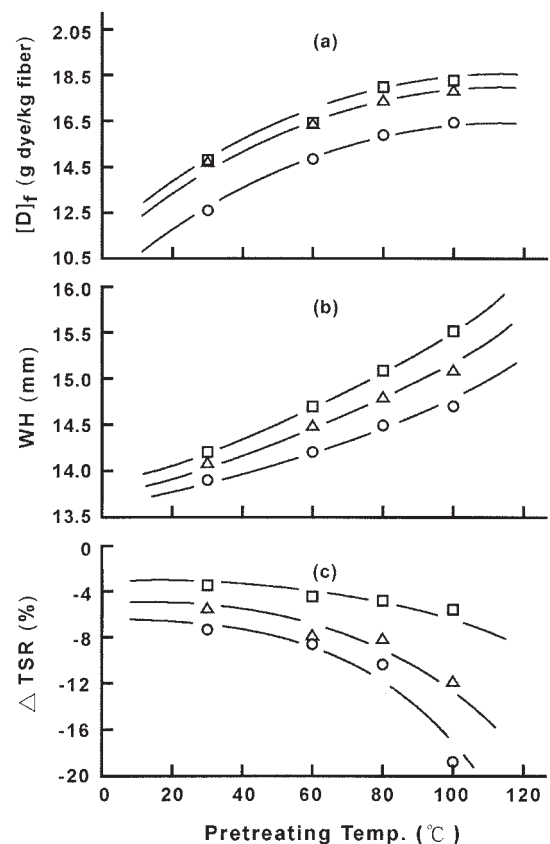


**Figure 1** Values of (a)  $[D]_f$ , (b) WH, and (c)  $\Delta$ TSR of the pretreated fibers/fabrics at 80°C for 60 min at different amine concentrations: ( $\square$ ) TETA, ( $\Delta$ ) DETA, and ( $\circ$ ) EDA.

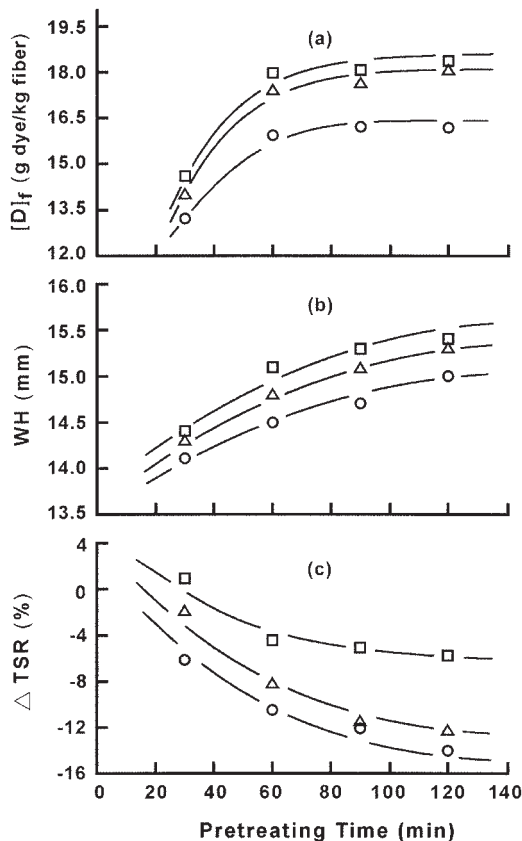
fiber) values of the EDA-, DETA-, and TETA-pretreated Aramid yarns (fabrics for WH) under different conditions are listed in Table I.  $[D]_f$ , WH, and  $\Delta$ TSR data for the three amines were plotted with the concentration of amines in the pretreatment bath, the pretreatment temperature, and the pretreatment time period and are shown in Figures 1–3, respectively. Figures 1–3 and Table I show that  $\Delta$ TSR increased and then decreased with increasing amine concentration in the bath; however,  $[D]_f$ , WH, and shrinkage increased with increasing amine concentration in the bath.  $\Delta$ TSR decreased with increasing pretreatment temperature and time period; however,  $[D]_f$  and WH showed inverse tendencies. These results may have been caused by the interactions between the Aramid fibers and the amines. In these conditions, we suggest that the amines could have attacked the polymer chains of the Aramid fibers in the alkaline solution to swell and/or degrade the polymer chains, and thus, the surface, inner structures, and physical properties (e.g., strength, WH, and dye adsorption) of the pretreated fibers were changed. Moore and Weigmann<sup>1</sup> found that the pretreatment of organic solvents could change the dyeing ability and fine structure of Aramid fiber.

Figures 1–3 and Table I also show that the values of  $[D]_f$  and WH of the pretreated fibers/fabrics were all

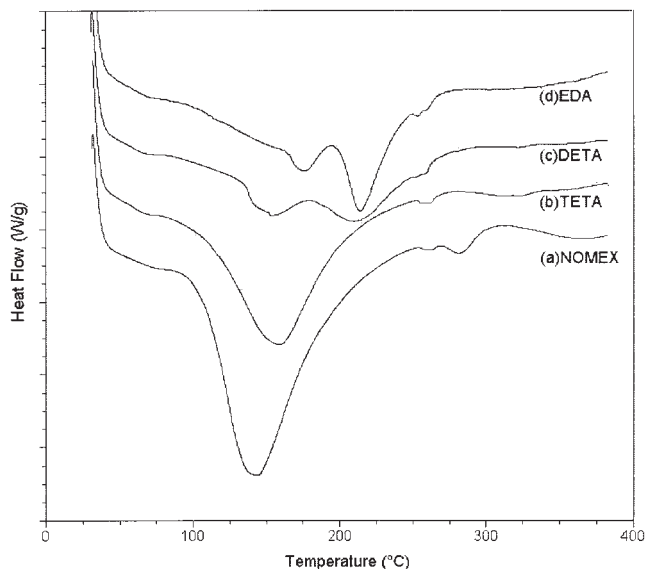
higher than those of the untreated fibers/fabrics. At a given pretreatment temperature, time period, or amine concentration, the plus values of  $\Delta$ TSR,  $[D]_f$ , and WH were ranked in the following order: TETA > DETA > EDA; however, the minus values of  $\Delta$ TSR and the values of shrinkage were ranked in the order EDA > DETA > TETA. Generally, the dye diffusion depends on the segmental mobility of the polymer chains, which in turn, depends on  $T_g$ .<sup>11,12</sup> Amines may decrease the  $T_g$  of pretreated Aramid fibers. To confirm the fine structure of the pretreated fibers, the  $T_g$  values were determined with DSC [Fig. 4(a–d) for no pretreatment and TETA, DETA, and EDA pretreatment] and DMA [Fig. 5(a–d) for no pretreatment and TETA, DETA, and EDA pretreatment], and the data are listed in Table I. The  $T_g$  values of the various amine-pretreated fibers were in the rank EDA > DETA > TETA > No pretreatment for both DSC and DMA. The tendency was inverse to the tendencies  $[D]_f$  and WH in Table I, which show the series TETA > DETA > EDA > No pretreatment. These results were interesting for us, and we further studied the other fine structure indices of the pretreated Aramid fibers. Additionally, the patterns of DSC obtained



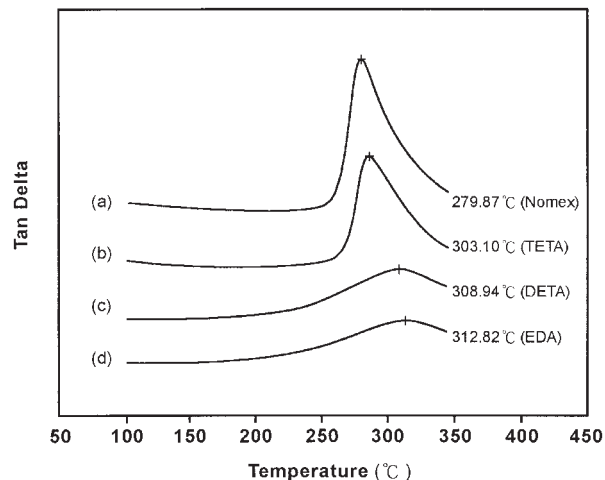
**Figure 2** Values of (a)  $[D]_f$ , (b) WH, and (c)  $\Delta$ TSR of the pretreated fibers/fabrics at 100% amine concentration for 60 min at different pretreatment temperatures: ( $\square$ ) TETA, ( $\Delta$ ) DETA, and ( $\circ$ ) EDA.



**Figure 3** Values of (a)  $[D]_f$ , (b) WH, and (c)  $\Delta$ TSR of the pretreated fibers/fabrics at 80°C and 100% amine concentration for different pretreatment times: (□) TETA, (△) DETA, and (○) EDA.

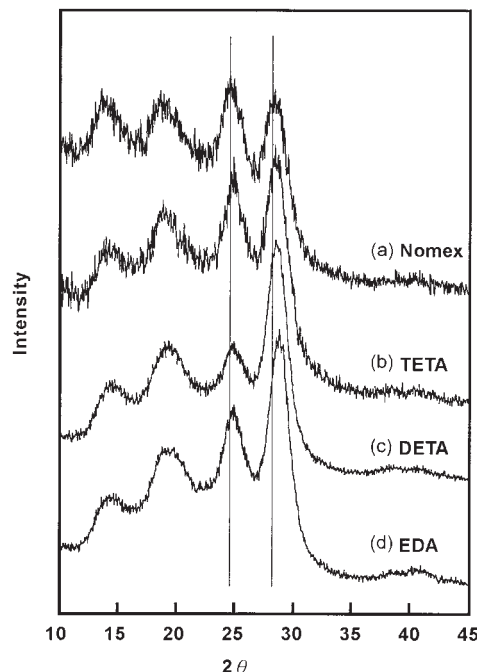


**Figure 4** DSC patterns of the (a) untreated and (b) TETA-, (c) DETA-, and (d) EDA-pretreated fibers at 100% amine concentration and 100°C for 60 min.

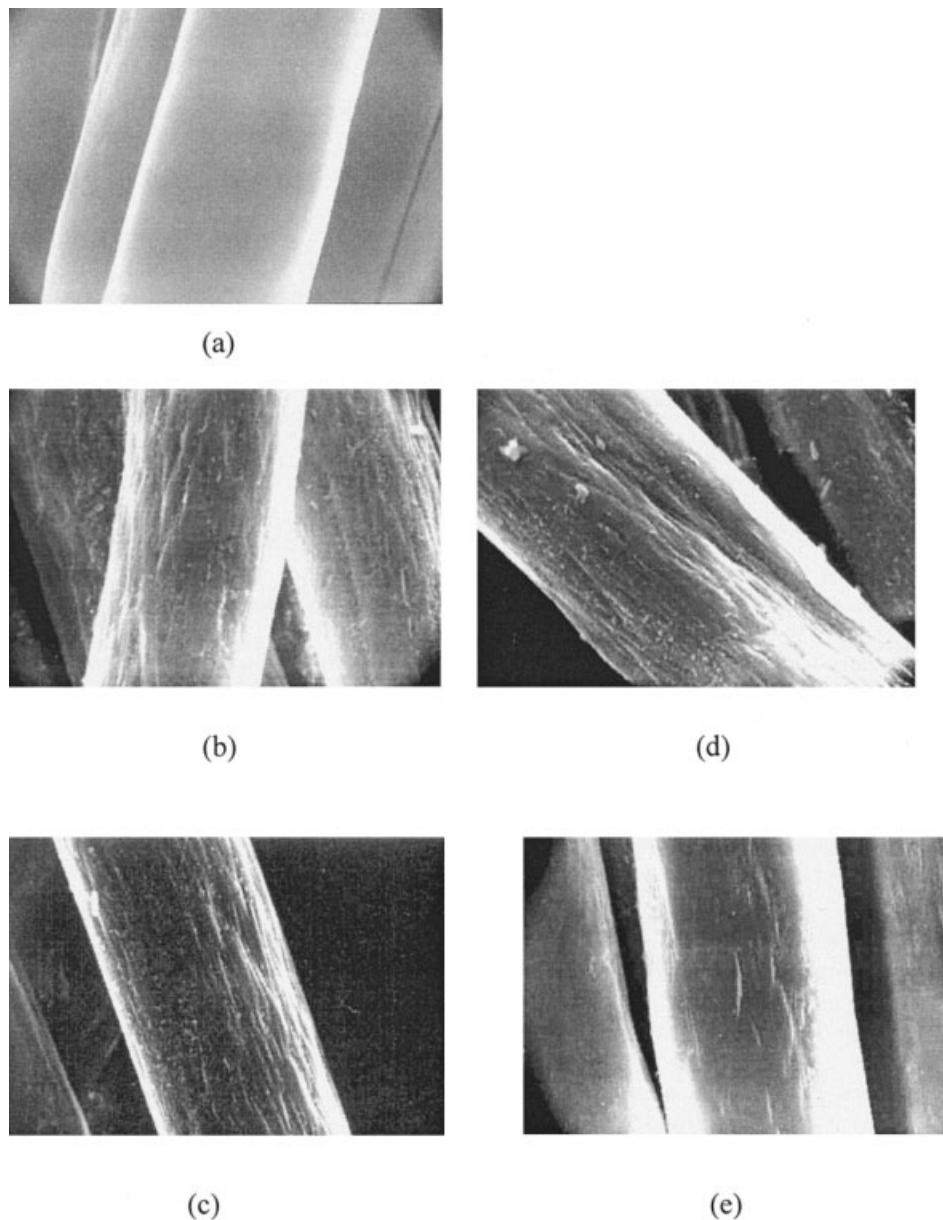


**Figure 5** DMA results of the (a) untreated and (b) TETA-, (c) DETA-, and (d) EDA-pretreated fibers at 100% amine concentration and 100°C for 60 min. Tan  $\delta$  is loss tangent.

from DETA- and EDA-pretreated fabrics showed two endothermic peaks around 150–210 and 175–215°C. These results strongly support the presence of two different conditions of rearrangement of polymer chains in the amorphous region for the two pretreated Aramid fabrics. The lower values of  $T_g$  of the amine-pretreated fibers were believed to be caused by the swelling of the polymer chains in the amorphous region of the Aramid fiber under the amine solutions.



**Figure 6** XRD patterns of the (a) untreated and (b) TETA-, (c) DETA-, and (d) EDA-pretreated fibers at 100% amine concentration and 100°C for 60 min.



**Figure 7** SEM pictures of the (a) untreated fibers, (b) EDA-pretreated fibers, (c) DETA-pretreated fibers, (d) TETA-pretreated fibers at 100% amine concentration and 100°C for 60 min, and (e) TETA-pretreated fibers at 70% amine concentration and 100°C for 60 min.

The WAXD patterns of the untreated and TETA-, DETA-, and EDA-pretreated Aramid filaments are shown in Figure 6(a–d), and the values of  $2\theta$  (scattering angle) (ca. 28 and 25°) for those samples were in the rank EDA > DETA > TETA > No pretreatment. The four peaks of the untreated Aramid fiber were similar to those in a report by Lewin and Preston.<sup>13</sup> From Bragg's equation,<sup>14</sup> these results reveal that the values of the density of crystals for the three amine-pretreated fibers were ranked in the order EDA > DETA > TETA > No pretreatment. We believe that the amine molecules could penetrate into the crystalline regions of the Aramid

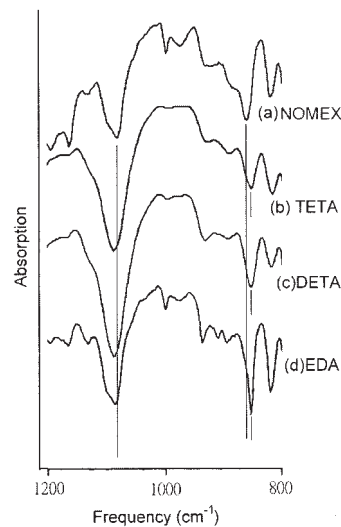
fiber to change and rearrange the array of polymer chains in the crystalline region. We also found that the molecular size of the amines agreed with this ranking. These phenomena may have been caused by the interaction between the polymer chains of the Aramid fibers and the amine solvents and agreed with results reported by Nechwatal and Rossbach.<sup>10</sup> Moore et al.<sup>1</sup> pointed out that a molecule of smaller molecular weight occupies a significantly smaller volume than a molecule of larger molecular weight and would, thus, be expected to diffuse into the polymer at a faster rate and interact more strongly with Nomex.



From the  $T_g$  and WAXD pattern results of the amine-pretreated Aramid fibers, we believe that the polymer chains were rearranged by pretreatment with the amines to increase the density of molecular chains in the Aramid fibers through shrinkage of the pretreated Aramid fibers. The higher values of  $T_g$  of the amine-pretreated fibers than those of the unpretreated fibers also attributed to the rearrangement of the molecular chains.

There were also some other possible reasons for the higher  $[D]_f$  and WH values for the amine-pretreated fibers (listed in Table I). One reason was the surface and/or inner void of the pretreated fibers. Some studies<sup>15-17</sup> have shown that the dyeing ability of alkaline-hydrolyzed Polyester (PET) fibers was significantly affected by the void on the fibers. Several authors<sup>2,16,18,19</sup> have pointed out that the alkaline-hydrolyzed PET fibers would increase moisture sorption properties and softness. Another study<sup>2</sup> revealed that the changes in dyeing ability of solvent-treated Aramid fibers may have been due to microvoid formation occurring in the fiber structure during treatment. The heat treatment of Aramid fibers could also improve the dyeing ability of the cationic dye.<sup>7</sup> To confirm the existence of a void in/on the amine-pretreated Aramid fibers, the morphologies of the various pretreated Aramid fibers were examined with SEM [Fig. 7(a-d) separately for no pretreatment and TETA, DETA, and EDA pretreatment]. Figure 7 reveals that the degrees of the surface void of the pretreated fibers were ranked in the order TETA > DETA > EDA > No pretreatment. This ranking agreed with the rank of  $[D]_f$  and WH for the three amine-pretreated Aramid fibers, as listed in Table I.

Although no pretreated Aramid fiber had a lower  $T_g$ , surface voids may have strongly improved the dyeing properties of the basic dye. Disperse dye is adsorbed in the free volume of the Aramid fibers, and the basic dye may only be adsorbed on the surface of the void or pore in/on the fiber. The basic dye may be adsorbed on the amide or amine end groups on Aramid. Saoaya<sup>7</sup> dyed heat-treated Aramid fibers with cationic dye. The authors of previous studies<sup>20,21</sup> have pointed out that the basic dye adsorption of crosslinked cotton was caused by the affinity between the basic dye and the  $-\text{NH}-$  of the crosslinking agent on the treated fabrics. Therefore, the basic dye may only be adsorbed on the functional group  $-\text{NH}-$  on the surface of the void or pore (thus, the adsorption of basic dye would not be affected by  $T_g$  values), and the higher the degree of void is, the more basic dye adsorbed would be. The FTIR patterns of the unpretreated and the three pretreated fabrics are shown in Figure 8(a-d). The interesting and important absorption band was the primary amine group ( $862\text{ cm}^{-1}$ ). This absorption band shifted to  $856$ ,  $855$ , and  $854\text{ cm}^{-1}$  for the TETA-, DETA-, and EDA-pretreated



**Figure 8** FTIR patterns of the (a) unpretreated and (b) TETA-, (c) DETA-, and (d) EDA-pretreated fabrics at 100% amine concentration and 100°C for 60 min.

fabrics, respectively. Those phenomena indicated changes around the primary amine end group in the Aramid fibers and strongly supported the interaction between Aramid fibers and the amines under higher concentrations, which would have caused the degradation (hydrolysis) of the Aramid polymer molecules to form the void.

However, there were sharper and deeper voids (pores), shown in Figure 7(b,c), in the 100% EDA- and DETA-pretreated Aramid fibers. This phenomenon may have caused the higher degree of stress concentration and agreed with the lower strength for the 100% DETA- and EDA-pretreated fibers than that for the 100% TETA-pretreated fibers (Table I and Figs. 1-3).

Additionally, the higher value of the change in  $\Delta\text{TSR}$  for the lower concentration of amine-pretreated fibers [Table I and Fig. 1(c), the plus values of  $\Delta\text{TSR}$ ] may have been due to a higher degree of density in the polymer chains (through shrinkage) and a lower degree of voids [Fig. 6(e) for 70% TETA-pretreated fiber cf. with Fig. 6(d) for 100% TETA-pretreated fiber] for the pretreated Aramid fibers.

## CONCLUSIONS

$\Delta\text{TSR}$  increased and then decreased;  $[D]_f$ , WH, and shrinkage increased with increasing pretreatment temperature, time period, and amine concentration for all three amines. At a given pretreatment temperature, time period, and amine concentration, the minus values of  $\Delta\text{TSR}$  were ranked in the order EDA > DETA > TETA; however, the plus values of  $\Delta\text{TSR}$  and  $[D]_f$  and WH were ranked inversely. The values of the  $T_g$  obtained from DMA and DSC and the density of the

crystals obtained from XRD of the pretreated fibers were in the rank EDA > DETA > TETA > No pretreatment. The degree of the surface voids (pores directly observed from the patterns of SEM) of the pretreated fibers were TETA > DETA > EDA > No pretreatment. From the FTIR surface reflectance of those pretreated fabrics, we concluded that pretreatment with amines of higher concentrations may have caused the degradation (hydrolysis) of the Nomex polymer chains. In this study, we suggest that amines could have attacked the polymers of the Aramid fibers in the alkaline solution to swell or degrade the polymer chain, and so the surface, inner structures, and physical properties (e.g., strength, WH, and dye adsorption) of the pretreated fibers were changed and could also swell the polymers in the amorphous region of the Aramid fibers to decrease  $T_g$  and penetrate into the crystalline regions in the Aramid fibers to change and rearrange the polymer array of crystalline structure.

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