Effect of Comonomer on Structure and Properties of Textured Cationic Dyeable Polyester

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SYNOPSIS

Cationic dyeable polyester (CDPET) yarns were produced through melt blending of cationic dyeable chips having 2 mol % of sodium salt of dimethyl ester of 5-sulfoisophthalic acid (DMS salt) and normal polyester chips in different proportions to obtain yarns having varying amount of comonomer in the fiber. These different partially oriented CDPET yarns were texturized under identical conditions on a draw-texturing machine. It has been observed that with increase in the amount of salt content in the CDPET, the dye uptake increases, but the tensile and crimp properties are adversely affected. The crystalline content, crystal size, overall orientation, and heat of fusion decrease with increase in salt content in CDPET yarns. The dyeability of CDPET yarns with both disperse dyes and cationic dyes improves with increase in DMS salt content. The changes in the mechanical and dyeing properties of textured CDPET have been explained on the basis of structural studies. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The single most important aesthetic property of a fabric, while a potential user makes his or her decision to purchase it, is the brightness and depth of its color. Though polyester fiber has an edge over other synthetic fibers used in the apparel industry, it is not possible to get bright and lively shades on polyester due to inherent structural deficiencies. Polyester fiber is difficult to dye because of its high crystallinity, marked hydrophobicity, and lack of chemically active groups. Development of cationic dyeable polyester yarn has overcome this problem of dullness of shades in regular polyester fiber. In our earlier article,[1] we compared the texturing behavior of normal regular polyester and cationic dyeable polyester having a comparatively lower amount of salt content. The cationic dyeable polyester (CDPET) fiber is now being produced using varying amount of sodium salt of dimethyl ester of 5-sulfoisophthalic acid as a comonomer. Ichihashi[2] reported the effect of salt content on the dyeing prop-

erties of drawn CDPET. Datye[3] discussed the effect of salt content on viscosity, molecular weight, and melt flow properties of CDPET polymer. Timm and Hsieh[4] compared the microstructure and macrostructure of sulfonated polyester with normal polyester. The texturing behavior of CDPET fiber is influenced to a great extent by the composition and fine structure of the fiber. This article is intended to discuss the effect of comonomer content on the structural and mechanical properties of texturized CDPET yarn. In this study we concentrate on the characterization of the structure and mechanical and dyeing properties of cationic dyeable polyester with varying DMS salt content.

EXPERIMENTAL

Normal polyester chips and cationic dyeable polyester chips (having 2.0 mol % DMS salt content) were blended mechanically in the proportions of 100/0, 75/25, 50/50, 25/75, and 0/100 in the melt extruder. These blended chips were extruded in the pilot spinning machine under identical conditions, with spinning temperature of 285°C and spinning

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speed of 2800 m/min to get partially oriented polyester yarns with 0, 0.5, 1.0, 1.5, and 2.0 mol % of dimethyl ester of 5-sulfo isophthalic acid sodium salt. The tensile properties of these POY yarns are given in Table I.

All the five POY polyester yarns were textured on a Scragg SDS 600 texturing machine with a positorque friction twisting assembly and a first heater length of 1.5 m at a texturing speed of 319 m/min. The following parameters were kept constant during texturing:

Draw ratio: 1.649
D/Y ratio: 1.830
First heater temperature: 175°C
Heating contact time: 0.282 s
Second heater temperature: 100°C

Crystallinity

Fifty milligrams of fine powder of textured filaments were compressed under constant pressure in an aluminium holder having a small rectangular cavity. The equatorial scans were then recorded with the help of a Phillips wide-angle X-ray diffractometer using the reflection technique. The crystallinity was then calculated by fitting the amorphous scan into the intensity scan of the sample. The technique has been used by Farrow and Preston[5] to compute the degree of crystallinity of polyester fiber. The degree of crystallinity is given by the expression

$$\text{Degree of crystallinity} = \frac{C}{C + A} \quad (1)$$

where C is the area under the crystalline curve and A is the area under the amorphous curve.

The density crystallinity was calculated from the density value, which was measured on a density gradient column using a mixture of n-heptane and carbon tetrachloride. The crystallinity (volume fraction) was calculated from the following equation:

$$\text{Crystallinity (\%)} = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100 \quad (2)$$

where ρ_c is the crystalline density and ρ_a is the amorphous density; 1.455 and 1.335 g/cm^3 were used as their values, respectively.

Crystal Size

A 010 reflection was used for the measurement of lateral dimensions of crystallites. The crystal size

Table I   Properties of POY Polyester Yarn with Different Amount of DMS Salt

DMS Salt Content (mol %)	Tenacity [(kN m)/kg]	Breaking Elongation (%)
0.0	185.1	130.1
0.5	172.3	130.6
1.0	165.9	129.2
1.5	163.3	126.2
2.0	162.0	126.6

was calculated using the Scherrer equation, which gives the crystal dimension t normal to a plane as

$$t = \frac{\lambda K}{\beta \cos \theta} \quad (3)$$

where $K = 0.89$, λ = wavelength of the X-ray beam, β = half breadth (i.e., the width in radians at half the maximum intensity for that plane), and θ = Bragg angle.

Birefringence

Birefringence of textured samples was measured using a Leitz polarizing microscope. This involves measurement of the two refractive indexes of the filament using liquids of matching refractive index. The birefringence is given by

$$\Delta n = n_{\parallel} - n_{\perp} \quad (4)$$

where $n_{\parallel}$ is the refractive index along the molecular axis and $n_{\perp}$ is the refractive index perpendicular to this axis.

Crystallite Orientation

A thin, flat bundle of well-parallelized filaments was prepared using approximately 200 filaments. The intensity distributions of the (010), ($\bar{1}$10), and (100) planes were measured using a Geiger counter diffractometer. From the intensity scans, an average value of $\cos^2\alpha$, (viz., $\overline{\cos^2\alpha}$, where α is the angle between the plane and the fiber axis) was obtained using the following relationship:

$$\overline{\cos^2\alpha} = \frac{\int_0^{\pi/2} I(\alpha) \sin \alpha \cos^2\alpha \, d\alpha}{\int_0^{\pi/2} I(\alpha) \sin \alpha \, d\alpha} \quad (5)$$

The average distribution of the c axis (i.e., the molecules in the crystalline regions) can be represented by the Herman's orientation factor f_c for the crystals, which is given by

$$f_c = 1 - \frac{3}{2}\overline{\sin^2\theta} = \frac{3\overline{\cos^2\theta} - 1}{2} \qquad (6)$$

where $\overline{\cos^2\theta}$ is the average value of $\cos^2\theta$, and θ is the angle between the c axis of the crystalline and the fiber axis. The value of f_c varies from zero for randomly oriented fiber to unity for a perfectly oriented fiber. The value of $\cos^2\theta$ is determined from the following equation derived from an application of Wilchinsky's method:

$$\cos^2\theta = 1 - 0.8786 \cos^2\alpha_1 - 0.7733 \cos^2\alpha_2$$
$$- 0.3484 \cos^2\alpha_3 \qquad (7)$$

where the suffixes 1, 2, and 3 stand for the (010), ($\bar{1}$10), and (100) plane.

Amorphous Orientation

The amorphous orientation of the textured yarns was calculated from the following relationship[6]:

$$f_a = (\Delta n - \Delta n_{c_0}\beta f_c)/(1 - \beta)\Delta n_{a_0} \qquad (8)$$

where β is the volume fraction of the crystalline phase, f_c and f_a are the Herman's orientation factors for the crystalline and amorphous phase, respectively, $\Delta n_{a_0} = .275$ and $\Delta n_{c_0} = 0.212$, and Δn is the birefringence of the sample.

Heat of Fusion

A Mettler TA 4000 DSC system was used for measuring the heat of fusion. The thermograms were obtained using the following parameters:

Scanning range: 25 mW
Heating rate: 10°C/min
Weight of sample: 5 mg

Tensile Properties

The tensile properties of textured yarn samples were measured on an Instron tensile tester (Model 6021). Pretension on the yarn was kept at 0.882 (kN m)/ kg. Tenacity and breaking elongation were obtained based on 20 readings.

Crimp Properties

Crimp contraction and crimp stability were measured on a Texturmat-M. A yarn hank of 2500 dtex was dry heated at 120°C for 10 min for crimp development and then conditioned in a standard atmosphere before the length measurements under different loads on the instrument. Crimp contraction and crimp stability were calculated from the following equations:

$$\text{Crimp contraction } (\%) = \frac{l_g - l_z}{l_g} \times 100 \qquad (9)$$

$$\text{Crimp stability } (\%) = \frac{l_g - l_b}{l_g - l_z} \times 100 \qquad (10)$$

where l_g is the length with loading at 500 cN, l_z is the length with loading at 2.5 cN, and l_b is the length with loading first at 2500 cN for 10 s followed by unloading to 2.5 cN.

Dyeing Properties

The textured yarns were dyed with both disperse and cationic dyes in the presence of carrier. Foron blue SE-2R and Sandocryl yellow BLE were used as disperse and cationic dyes, respectively. The reflectance of dyed material was measured at a wavelength of minimum reflectance. Kubelka-Munk values were used to indicate the depth of the color and were calculated from the following equation:

$$K/S = \frac{(1 - R)^2}{2R} \qquad (11)$$

RESULTS AND DISCUSSION

Structural Properties

The crystalline fraction in the textured yarn was determined using X-ray diffraction and density and differential scanning calorimetry. It is observed in Table II that the crystallinity decreases with increase in DMS salt content in the polyester fiber. It is found that the crystalline peak of normal PET is sharper as compared to CDPET. The crystallinity measured from an X-ray diffractometer is always lower as compared to density crystallinity. Hong and co-workers[7] have also observed a drop in X-ray crystallinity of the drawn cationic dyeable polyester with an increase in cationic salt residue in the polymer. Teli et al.[8] have found that the crystallinity

Table II   Effect of DMS Salt on Structural Properties

DMS Salt (mol %)	X-ray Cryst. (%)	Density Cryst. (%)	Heat of Fusion (J/g)	Crystal Size (Å)	Amorph. Orient. f_d	Crystal. Orient. f_c	Birefringence Δn
0	41.39	48.91	64.96	24.23	.5461	.8224	.162
0.5	37.14	47.98	62.34	21.68	.5183	.8104	.156
1.0	35.96	46.75	61.06	20.60	.4796	.8082	.148
1.5	34.05	44.59	60.40	18.72	.4290	.8001	.141
2.0	31.61	43.36	57.55	16.17	.3745	.7974	.136

measured from X-ray, infrared (IR), and density of cationic dyeable polyester was less as compared to regular polyester. In the DSC method, the heat of fusion is used to indicate the crystalline fraction in the fibers. Higher crystallinity is expected from higher values of heat of fusion. With an increase in salt content in the CDPET fiber, the heat of fusion decreases, as shown in Table II. The shapes of the melting endotherms are different. A double melting endotherm is obtained from the cationic dyeable polyester, where as a single melting peak is observed for the regular polyester. The high melting temperature peak of the cationic dyeable polyester is also lower than that of normal PET. The different melting temperature and heat of fusion with increased salt content indicates different size, fraction, and distribution of crystalline structure.

The effect of salt content on crystal size is shown in Table II. The size of crystal decreases with increase in DMS salt content. The presence of a large side group may prevent the chain molecules from coming close to each other and obstructing the formation of bigger crystals, as indicated by the sharpness of crystalline peak of the X-ray graph. The sulfonated side groups are thought to cause formation of smaller crystals in CDPET with higher DMS salt content. The difference between the refractive index along the axis and the radial direction of fibers gives the overall degree of molecular orientation of the fiber. It is observed in Table II that birefringence decreases with increase in salt content of textured cationic dyeable polyester yarn, which indicates the decrease in the overall chain orientation in the crystalline and noncrystalline domains. The presence of a large —SO₃Na side group in the molecular chain of the CDPET fiber causes an increase in chain rigidity, resulting in a decrease in orientation of chain molecules. Obviously, the frequency of presence of the —SO₃Na group will increase with the increase in salt content.

Herman's orientation factor for crystalline and amorphous region decreases with increase in DMS

salt content in the cationic dyeable polyester fiber, as shown in Table II. The lower overall orientation with increased DMS salt can be attributed to the lower orientation of chains in the noncrystalline domains as well as to less aligned crystals. The sulfonated side groups are not only excluded from the crystals, but their presence could limit the size and orientation of crystallites formed.

Tensile Properties

It is observed that with increase in DMS salt content in CDPET fiber, the tensile properties of textured yarn become inferior. Figure 1 shows that the drop in tenacity and breaking elongation is high in the textured samples with higher amount of DMS salt in the CDPET fiber. The drop in tenacity from regular polyester to CDPET having 1.5 mol % is about 12%. But from 1.5 to 2.0 mol %, the drop in tenacity is about 33% in the textured CDPET yarn. From
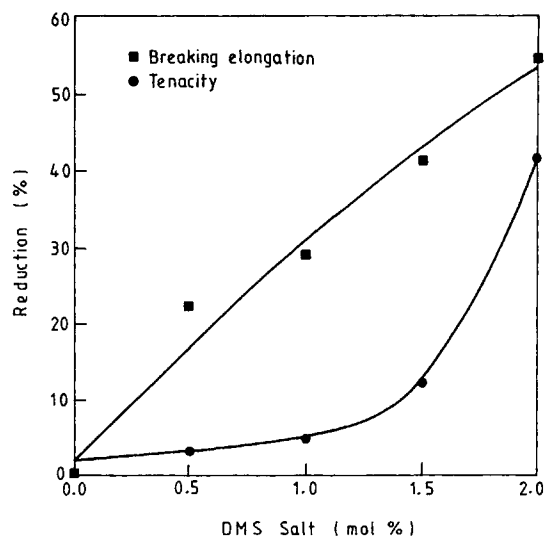

Figure 1   Effect of DMS salt (mol %) on the reduction in tenacity and breaking elongation of polyester textured yarn.
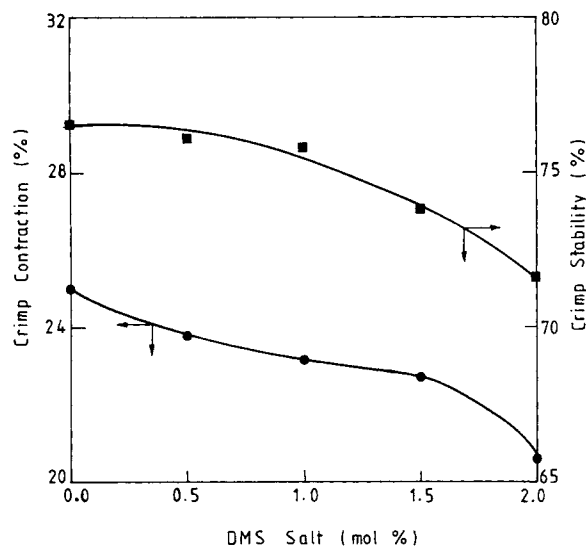
Figure 2 Effect of DMS salt (mol %) on crimp contraction and crimp stability of polyester textured yarn.

the structural studies, we have seen that crystallinity as well as orientation decreases with increase in DMS salt content. Degradation in CDPET yarns having higher DMS salt content may take place during texturing at a temperature of 175°C, resulting in a rapid reduction in tensile properties. Hong et al.[7] have found that with increasing DMS salt content, intrinsic viscosity decreases gradually, indicating a decrease in molecular weight. Addition of a compound containing an anionic group disturbs the regularity of the polyester polymer chain molecules which make the structure of cationic dyeable polyester less compact than that of normal polyester. This is reflected in the lower tensile properties of CDPET having higher DMS salt content.

Crimp Properties

The crimp properties in textured yarn have been characterized by crimp contraction and crimp stability. It can be observed from Figure 2 that both crimp contraction and crimp stability decrease with increase in DMS salt content in the CDPET fiber. Structural studies have already revealed that the crystalline content in CDPET fibers decreases with the increase in DMS salt percent. Incorporation of the bulky sulfonate group increases chain rigidity, which, in turn, restricts the twisting effect in texturing. Crimp contraction decreases with decrease in actual twist during texturing. The changes in the value of both crimp contraction and crimp stability is greater in CDPET, with 1.5 mol % to 2.0 mol %. It is also evident from X-ray and differential scan-

ning calorimetry studies that CDPET with 2.0 mol % DMS salt has a large amount of amorphous content. The crystal size of this CDPET is also small, indicating less stable crystal structure as compared to CDPET with less amount of DMS salt content. The lower crystalline content and smaller size of crystal in CDPET with a large amount of DMS salt results in a lower value of crimp contraction and crimp stability.

Dyeing Properties

Cationic dyeable polyester can be dyed with both disperse and cationic dyes. It is shown in Figure 3 that the dye uptake in terms of K/S of disperse dyed textured CDPET increase with increase in DMS salt content in the fiber. Up to 1.5 mol %, the rate of increase is slow and then the dye uptake rises sharply. Results in Table II indicate that the birefringence values, and hence the overall orientation in the molecular chain, decrease as the DMS salt increases in CDPET. Hong et al.[7] have also found the same trend with DMS salt in drawn CDPET. In addition, the crystalline fraction decreases with an increase in DMS salt in CDPET. These changes in fine structure contribute to the ease of dyeing, resulting in an increase in dye uptake in CDPET with higher amount of DMS salt. The higher rate of increase in dye uptake with higher DMS salt content is reflected in a rapid decrease in crystalline fraction in CDPET.

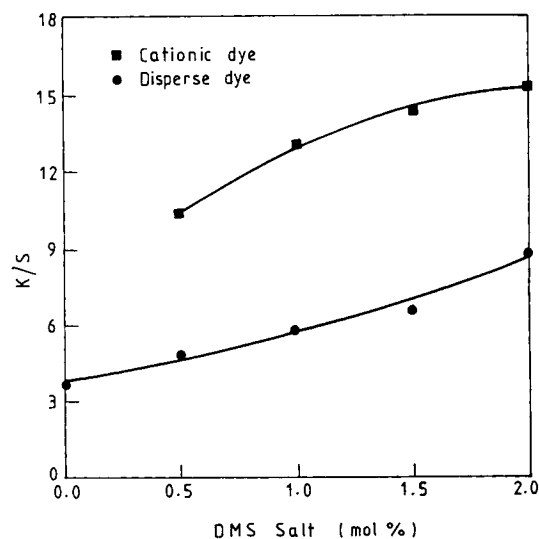Figure 3 shows the gradual increase in dye uptake with increase in DMS salt content in cationic dyed

Figure 3 Effect of DMS salt (mol %) on dye uptake of disperse and cationic dyes by polyester textured yarn.

CDPET. The mechanism of dyeing of CDPET with cationic dyes is different from that of dyeing with disperse dyes. In the former case, the affinity values play a more important role than diffusion. The dyeability of CDPET with cationic dyes is based on the presence of specific anionic bonding sites in these fibers. The bonds of the ionic type play an essential role in dye–fiber interaction. The anionic bonding sites in CDPET fiber will increase with increase in DMS salt content; nonetheless, diffusion of cationic dyes into CDPET is less as compared to dye diffusion in acrylic fibers and gives ring dyeing (most of the dye present on the fiber is confined within a surface layer which has a thickness less than one third of the fiber diameter), as reported by Rao et al.[9] However, the decreased crystalline fraction and orientation may play an important role in enhancing the diffusion of dye. Increased anionic bonding sites, higher amorphous fraction, and more disorientation in the fiber with increased DMS salt content contribute to the improved dyeability of cationic dyes on CDPET.

CONCLUSIONS

Cationic dyeable polyester yarns having different amounts of DMS salt have been produced through melt blending of normal polyester and cationic dyeable polyester chips. The presence of DMS salt disturbs the structure of CDPET fiber. With increasing DMS salt in CDPET, the crystalline fraction, orientation, and crystal size decrease, which, in turn,

results in lower mechanical properties. Tenacity, crimp contraction, and crimp stability reduce with increase in DMS salt content in CDPET. The dyeability of both disperse dyes and cationic dyes on CDPET improves with increase in DMS salt content. The proper amount of DMS salt in CDPET is important to get a fiber with good dyeability as well as satisfactory mechanical properties. The mechanical properties of textured CDPET with more than 1.5 mol % DMS salt decrease rapidly, indicating the limit of increase in DMS salt in CDPET fiber.

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