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Influence of texturing conditions on characteristics and dyeing behaviour of polyamide 66 yarn

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The influence of texturing parameters, such as draw ratio and heater temperature, on characteristics and dyeing behaviour of polyamide 66 yarn has been studied. It is observed that the draw ratio and heater temperature have negligible influence on dye exhaustion, but they both markedly influence the dyeing kinetics. This has been measured by apparent diffusion coefficients and discussed on the basis of crystallinity and degree of orientation data.

Keywords: Degree of crystallinity, Degree of orientation, Diffusion coefficient, Draw ratio, Polyamide 66 yarn, Texturing
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1 Introduction

Polyamide fibres and their blends with other fibres are generally used for the production of versatile garment items, household furnishing and fabrics for technical purposes. These products differ w.r.t. dye fastness and other properties for specified end use. The important areas where polyamide fibres can be applied are the manufacturing of socks and different kinds of knitted fabric for sports and leisure. Particular problem may occur in dyeing of textile products made of flat and textured polyamide 66 filament considering the uniformity of dyeing (streakiness). Streakiness appears mainly as a consequence of non-uniformity of single filament, depending on thermal history of fibres[1,2].

Man-made fibres have skin/core structure. There are certain differences regarding the orientation of polymer molecules, i.e. there is a crystallinity gradient from fibre surface to core. The skin is the region of higher orientation and greater density as compared to core. There is still controversy with regard to precise difference between core and skin but the bulk of evidence is in the favour of difference both in crystallinity and orientation. This kind of fibre structure influences dyeing and finishing behaviour of polyamide fibres. Considering the skin as an outer zone of increased orientation and density, it is clear that the skin acts as a retarding membrane which decreases the rate of dye diffusion. During dyeing, the molecules of dye from the water dispersion or solution are absorbed on the surface of fibre and then they penetrate into the core. The diffusion of relatively large dye molecules (mol. wt., 200-1100; mol length, 1-5 nm) is very slow and it depends on the available space between the molecules of fibres, i.e. on the density of molecules. The mechanism of diffusion can be explained according to the pore theory and free volume theory. The fibre surface is generally at a higher energy level and is inherently less uniform than the fibre core, i.e. the surface has higher and more variable dyeing transition temperature than the core. Hence, the surface (the outer 3-5% of the fibre radius) is a variable energy barrier which must be overcome or made more uniform to achieve acceptable fabric dye rate uniformity[1]. In general, the thermal history of fibres,

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starting with their formation to manufacturing of end product, influences significantly their accessibility to dye molecules or other chemical agents. If less heated filaments from the core come to the surface of multifilament yarns, there will be a difference in the dye shade of the filament originating from the core of the yarn and the one positioned on the yarn surface.

The difference in polyamide 66 fibre dye affinity is the consequence of non-uniformity in the forming, drawing and texturing processes. General requirements regarding the dyeing quality of polyamide 66 fibres are high light fastness, high wash fastness and dye uniformity within one yarn package and between different dyeing lots. Among the various dyes that can be applied on polyamide 66 yarns, acid dyes play significant role as they fulfil most of the demands regarding dyeing quality. Hence, the selection of dyes should be made carefully and they should be mutually compatible w.r.t. dyeing speed, dye migration and light and wash fastness, especially if the three-chromatic combinations of dyes are dealt with[3].

Texturing is a multi-parameter process. The texturing parameters of polyamide filament influence considerably its behaviour in the processes that follow especially dyeing when all the defects which appeared during texturing become easily noticeable on dyed fabric. This paper reports the influence of texturing parameters, such as draw ratio and heater temperature, on the structure and dyeing kinetics of partially oriented polyamide 66 yarn.

2 Materials and Methods

Polyamide 66 partially oriented and draw textured yarn [56(44)F13×2 dtex: yarn count (POY), 56; yarn count (DTY), 44; F13, no. of monofilaments; and 2, two-ply] was used for the study. The yarn was textured on Industrie et Commerce Bernard Terrat (ICBT), France machine for friction texturing with long heater. Texturing speed (700 m/min), the relation between surface speed of frictional disc and linear fibre speed [D/Y (2.5)], take-up (0.960) and configuration of discs (1-5-1) were kept constant and the draw ratio was changed (1.265, 1.275, 1.285, 1.295 and 1.310). With draw ratio of 1.295 (standard for this yarn count), the texturing temperature was varied (205°C, 215°C and 225°C).

For the purpose of yarn characterization, the degree of whiteness, degree of crystallinity, degree of orientation, elasticity characteristics, shrinkage, yarn count, breaking strength and breaking elongation of the textured polyamide yarn were determined before dyeing. Whiteness was assessed on reflectance spectrophotometer Spectraflash 300 (Datacolor, USA). The light source D_{65} and observer 10° and equations CIE-Ganz 82 and Berger 76 were used[4].

Degree of crystallinity of the yarn was determined by measuring the specific weight on the apparatus for specific weight determination[5].

Degree of orientation of single filaments was determined by measuring the birefringence using polarised microscope[6].

Yarn elasticity characteristics, such as crimp contraction (CC), crimp module (CM) and crimp stability (CS), were determined in accordance with the standard DIN 53840.

Shrinkage of samples was determined according to the standard DIN 53866. Yarn count (expressed in dtex) was determined in accordance with the standard JUS ISO 2060 (Yugoslav Standard) by measuring weight of 100 m long yarn on analytical scale.

Breaking strength and breaking elongation were determined on mechanical dynamometer (Calderara Bosi, Italy) using two different ranges of breaking strength (0-500 g and 0-3000 g) and the breaking elongation range of 0-300 mm (0-60% at yarn length of 0.5 m) according to the standard DIN 53834 T1.

The polyamide yarn (weight 2g ±5%) textured at different draw ratios and different heater temperatures was dyed with acid dye in the dyebath containing the following ingredients:

0.95% Erionyl BlueA-R (Ciba, Switzerland)
1 g/L Sarabid NS (Ciba, Switzerland)
0.7 g/L CH_3COOH
Liquor ratio – 1:100

The dyeing kinetics is shown in Fig.1.

Polyamide yarn was heated in distilled water at 60°C for 10 min and dyed in John Jeffreys (UK)

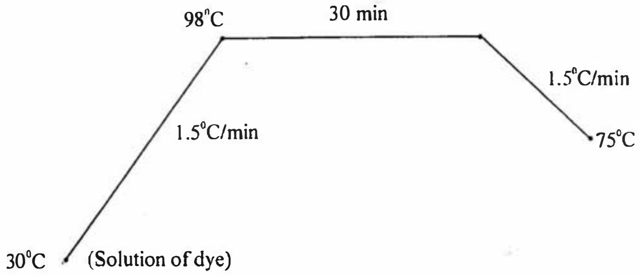

Fig. 1—Dyeing diagram

dyeing apparatus. The rate of dyeing was observed by sampling the dyebath at start and after different time intervals (10, 15, 30, 45, 60, 75 and 95 min), and absorbance was measured using the colorimeter at the wavelength of maximum absorbance (λ_{max}) and room temperature. The exhaustion (E) was expressed as the percentage decrease in dyebath concentration. The calibration diagram of the absorbance *vs.* dye concentration was obtained by measuring the absorbance of the solutions of known dye concentration for the same wavelength. The concentration of dye remaining in the dyebath (C_t) at various dyeing times was calculated and the amount of dye on the fibre at time t (C_f) was obtained by taking the difference. Diffusion coefficient was measured using the relationship between C_f/C_∞ (relative amount of dye sorbed) and $t^{1/2}$. According to the second Fick's law, at initial stage the dyeing process is controlled by diffusion and the C_f is neither too small nor too large. C_∞ is the concentration of dye in the fibre at equilibrium, which is 90 min of dyeing in this study. The diffusion coefficient (D) could be estimated as linear fit slope by using the following equation:

$$\frac{C_f}{C_\infty}=2\sqrt{\frac{D\cdot t}{\pi}}$$

3 Results and Discussion

Table 1 shows the characteristics of partially oriented draw textured polyamide 66 filament yarn produced under different draw ratios. Table 2 shows the same characteristics at different texturing temperatures.

It is known that the mechanical stress and heat may result in the disorientation of structural elements at all levels of supermolecular structure during the texturing process. The micro-voids are formed and the disorientation and micro-void dimensions increase within the cross-section of single filament with increased texturing intensity. Therefore, the fibre morphology is significantly modified after texturing process. The orientation of textured yarn is layered, with the greatest orientation within the layers close to the outer surface of filament, depending on the molecular orientation of flat filament[7]. Degree of orientation results (Tables 1 and 2) show that the orientation of single filament increases insignificantly in the axial directions by increasing draw ratio, keeping the other texturing parameters constant. On the other hand, it can be observed that the orientation increases insignificantly at draw ratio of 1.295, which is also a standard draw ratio for the yarn count 56(44)f13×2 dtex at 205°C. This can be explained by the lower mobility of same macromolecule segments, while at 225°C the fall of orientation may appear probably due to the higher segmental mobility and

Table 1—Characteristics of partially oriented polyamide 66 [56(44)f13×2 dtex] yarn draw textured at 215°C with different draw ratios

Draw ratio	Yarn count dtex	Breaking strength cN/tex	Breaking elongation %	Crimp conctraction %	Crimp module %	Crimp stability %	Shrinkage %	Degree of crystallinity %	Degree of orientation (n_e-n_o)	Whiteness degree	
										CIE-Ganz 82	Berger 76
1.265	89.39	41.8	27.8	52.9	36.03	85.2	3.8	42	0.05415	73.5	73.1
1.275	89.08	40.7	28.4	52.6	36.5	87.7	4.2	44	0.05455	75.0	74.7
1.285	87.65	42.6	27.3	51.7	35.9	85.3	4.8	52	0.05526	75.2	74.8
1.295	87.29	42.5	27.8	51.5	35.9	86.4	4.6	57	0.05593	69.7	69.2
1.310	85.53	43.3	26.4	56.3	36.3	85.9	4.4	68	0.05965	74.2	74.1

n_e–Index of refraction (extraordinary ray) and n_0–Index of refraction (ordinary ray)

Table 2—Characteristics of partially oriented polyamide 66 [56(44)f13×2 dtex] yarn draw textured with 1.295 draw ratio at different temperatures

Texturing temp. °C	Yarn count dtex	Breaking strength cN/tex	Breaking elongation %	Crimp contraction %	Crimp module %	Crimp stability %	Shrinkage %	Degree of crystallinity %	Degree of orientation (n_e-n_o)	Whiteness degree	
										CIE-Ganz 82	Berger 76
205	87.32	41.9	28.2	51.2	34.6	87.3	4.8	38	0.05591	84.8	84.4
215	87.29	42.5	27.8	51.5	35.9	86.4	4.6	57	0.05593	69.7	69.2
225	86.92	40.9	28.6	52.3	35.7	87.5	5.1	47	0.05586	83.7	83.3

insufficient time for structure relaxation. Texturing process decreases the filament density, probably due to the intensive void creation, and in certain cases, the crystallinity gradient may also decrease as well. At the same time, the crystalline orientation degree decreases. This shows the strong disorientation in both amorphous and crystalline regions in the fibre. It is assumed that the crystal size is a bit smaller, but the melting interval spreads in textured filament which shows increase in filament microdefect. The results (Table 1) concerning the crystallinity gradient of the polyamide yarn textured at 215°C with different draw ratios show that with the increase in draw ratio the crystallinity gradient increases. However, the increase in texturing temperature (Table 2) results in decrease in crystallinity gradient, probably due to the increase in low molecular weight fraction, decrease in fraction with longer molecules and increase in disorientation of molecules. The draw ratio increase influences directly the yarn strength. High draw ratio results in high yarn tensions which may cause the filament breakage, and even the yarn breakage. It often happens with partially oriented filaments[7]. It is well known that the strength of all kinds of filament decreases by texturing, depending on the intensity of tensions, temperature and texturing time. The strength decrease in texturing is due to the formation of hidden microdefects and disorientation of structural elements. The decrease in breaking strength in texturing depends on the orientation degree or on the draw ratio of the filament. The study shows that the change in draw ratio may cause insignificant changes in yarn strength. At the same time, the increase in temperature results in the decrease yarn strength with all values being higher than 30 cN/tex (DIN 53834 T1). This is acceptable for the yarn count studied. The textured filament shrinkage is important characteristics as it determines the behaviour in subsequent heat treatments as thermosetting, dyeing and finishing. It is the measure of structure stability and the relaxation of inner tensions within the filament. It can be observed that when the texturing temperature rises the shrinkage of the polyamide yarn increases, which can be explained by the increase in yarn instability.

Kinetics of dyeing represents the dye transportation from dyebath to fabric and it can be graphically presented by the dye exhaustion curve, showing the relationship between the dye concentration on the fibre and the dyeing time. Diffusion is a process of dye penetration into fibre and it is determined by the diffusion coefficient using the application of Fick's law[8]. The diffusion coefficient determined with indirect methods, such as the change in dye concentration in dyebath with the time, represents the so called apparent diffusion coefficient. The dye diffusion into the fibre is determined by the relationship between C_f/C_∞ and $t^{1/2}$, that is the apparent diffusion coefficient representing the slope of the linear part of the diagram. Figs 2-5 show the relationship between C_f/C_∞ and $t^{1/2}$ as well as the linear approximation for the polyamide yarn textured

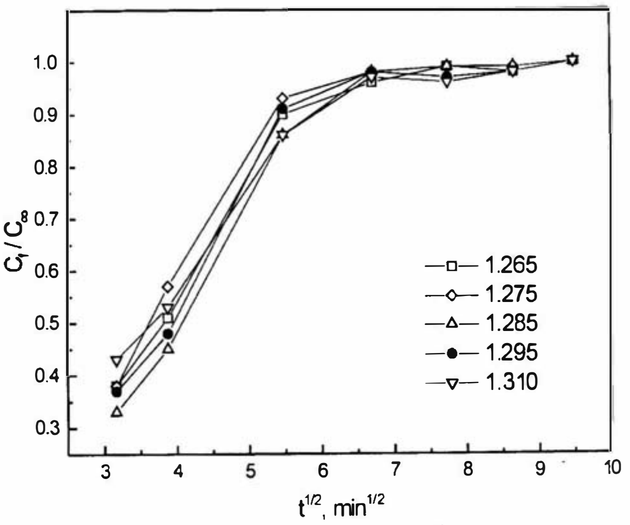

Fig. 2—Relationship between C_f/C_∞ and $t^{1/2}$ of dyed polyamide 66 (44f13×2 dtex) yarn draw textured at 215°C with different draw ratios

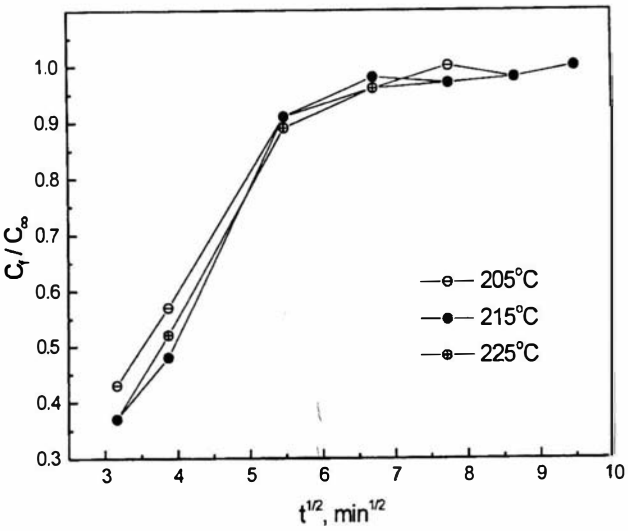

Fig. 3—Relationship between C_f/C_∞ and $t^{1/2}$ of dyed polyamide 66 (44f13×2 dtex) yarn draw textured with 1.295 draw ratio at different texturing temperatures

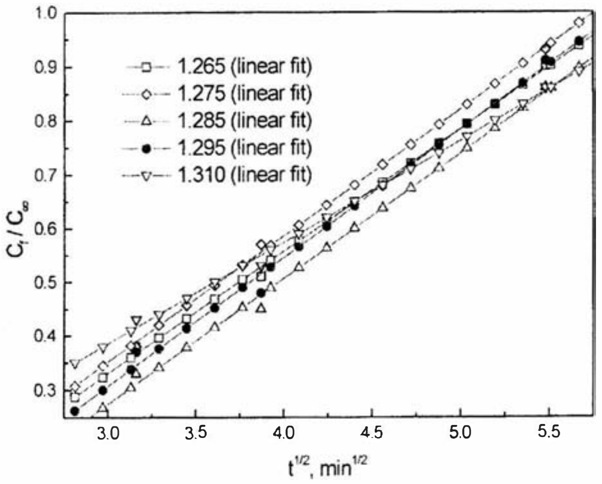

Fig. 4—Linear approximation of the C_f/C_∞ *vs.* $t^{1/2}$ of dyed polyamide 66 (44f13x2 dtex) yarn draw textured at 215°C with different draw ratios

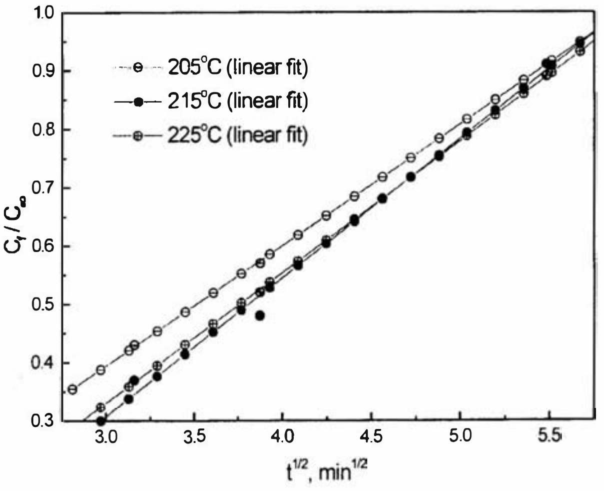

Fig. 5—Linear approximation of the C_f/C_∞ *vs.* $t^{1/2}$ of dyed polyamide 66 (44f13x2 dtex) yarn draw textured with 1.295 draw ratio at different texturing temperatures

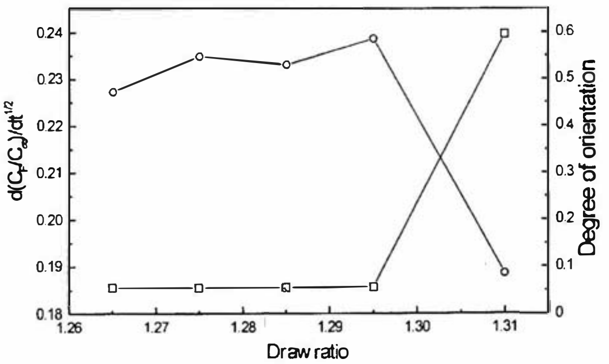

Fig. 6—Dependence of $d(C_f/C_\infty)/t^{1/2}$ (-o-) and the degree of orientation (-□-) on the draw ratio of polyamide 66 (44f13x2 dtex) yarn draw textured at 215°C

Table 3—Slopes corresponding to the apparent diffusion coefficient for Erionyl Blue A-R dyed polyamide 66 (44f13x2 dtex) yarn draw textured at 215°C with different draw ratios

Draw ratio	Linear part on diagram min	Coefficient of correlation	Part on ordinate	$d(C_f/C_\infty)/dt^{1/2}$ $\min^{-1/2}$
1.265	10–30	0.99816	−0.35089	0.22723
1.275	10–30	0.99904	−0.35231	0.23477
1.285	10–30	0.99633	−0.42464	0.23293
1.295	10–30	0.99403	−0.40840	0.23862
1.310	10–30	0.99687	−0.18021	0.18870

Table 4—Slopes corresponding to the apparent diffusion coefficient for Erionyl Blue A-R dyed polyamide 66 (44f13x2 dtex) yarn draw textured with 1.295 draw ratio at different texturing temperature

Texturing temp. °C	Linear part on diagram min	Coefficient of correlation	Part on ordinate	$d(C_f/C_\infty)/dt^{1/2}$ $\min^{-1/2}$
205	10-30	0.99988	-0.22914	0.20763
215	10-30	0.99403	-0.40840	0.23862
225	10-30	0.99981	-0.34537	0.22511

at 215°C with different draw ratios and for the yarn textured with 1.295 draw ratio at different temperatures respectively.

Linear part exists in the diagram for first 30 min of dyeing of polyamide yarn textured at 215°C with different draw ratios as well as of the yarn textured with 1.295 draw ratio at 205, 215 and 225°C. The values of apparent diffusion coefficient shown in Tables 3 and 4 are obtained from the linear approximation diagrams of the relationship between C_f/C_∞ and $t^{1/2}$ (Figs 4 and 5). Extrapolation of the linear part of the diagram at time t=0 shows the negative value on ordinate which shows the existence of potential barrier in dyeing, probably resulting from the preparation agents added while texturing.

Tables 3 and 4 show that the dye diffusion coefficient changes insignificantly for polyamide yarn textured at 215°C and draw ratios changing from 1.265 to 1.295. The diffusion coefficient decreases significantly at 1.310 draw ratio as a consequence of higher orientation and crystallinity. Also, the equilibrium exhaustion is approximately the same at different draw ratios. However, the difference in dyeing rate due to different diffusion coefficients is also observed.

Figure 6 shows the correlation between the diffusion coefficient and the degree of orientation as a function of draw ratio for the yarn textured at 215°C. It is observed that with the increase in draw ratio from 1.265 to 1.295, both the diffusion coefficient and the degree of orientation change slightly. As already stated, when the draw ratio is increased to 1.310, there is a sudden fall in diffusion coefficient as a consequence of growth in orientation of fibre.

By increasing the texturing temperature at 1.295 draw ratio, the increase in diffusion coefficient can be observed which is in accordance with the higher disorientation of molecules and raise in voids in the fibre for dye. Also, the equilibrium exhaustion of dye is approximately the same when the texturing temperature is changed. The potential barrier is lowest at standard texturing conditions (texturing temperature, 215°C and draw ratio, 1.295) for the studied yarn count.

4 Conclusions

The draw ratio and the heater temperature during texturing process affect the characteristics of polyamide 66 filament yarns and their behaviour during dyeing. When texturing parameters are changed, the exhaustion of dye remains almost the same, and the difference in dyeing behaviour is confined to the diffusion coefficient changes. The most obvious changes in the diffusion rate appear when the draw ratio is increased to 1.310 due to the high crystallinity and orientation of fibre. The smallest potential barrier is observed under the standard conditions of texturing process (draw ratio, 1.295 and texturing temperature, 215°C) for the given yarn.

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