Correlation between K/S values of PET dyeings and oligomer content

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ABSTRACT

The study examines the effect of stabilization of polyester (PET) fabric under various conditions (temperature, time and tension) on the migration of oligomers, and on K/S values of PET dyeings. The oligomer content of PET fibers is determined gravimetrically using dichloromethane and petroleum ether as a solvent. Dyeings of PET fabrics are performed on a Mathis jet JFL dyeing machine. The various stabilized samples are dyed with Terasil Red CA – FR disperse dye under infinite dye bath conditions and K/S values of dyeings are determined on Spectraflash 600 plus CT (Datacolor). Based on the results it was established that oligomer migration was affected by temperature, time, and the stabilization tension. The content of oligomers was reduced the most in polyester fabric that was stabilized in a restricted state at higher temperatures and longer times. K/S values of PET dyeings decreased with increased tension and time of stabilization.

Introduction

The preparation of polyester fibers (PET) is usually carried out by polycondensation of dimethyl ester of terephthalic acids and diols. In addition to the polymer, linear and cyclic oligomers are formed. The production of cyclic oligomers during the formation of poly(ethylene terephthalate) by melt polycondensation is inherent [1].

Heat setting is essential phase during polyester processing to improve dimensional stability [2]. Industrial setting of polyester fabrics is usually done in the presence of some tension. The range of setting temperature used is quite wide, 140 °C in a steam and 190 to 220 °C in dry air. The time of heat setting varies from less than a second to over 60 min [3].

It is known that oligomers present in polyester fibers cause problems during polyester processing [4, 5]. Structural changes in the polyester fiber during heat setting are responsible for the migration of oligomers [6]. Structural changes of polyester fibers during stabilization in restricted and unrestricted state are briefly described by Gupta [3].

The influencee of structure and morphology of polyester on its dye diffusion behavior has been well described by several researches [7, 8]. Over a range of annealing temperatures, the disperse dye uptake of annealed PET fibers initially decrease as the annealing temperature increase, and then it increase over the value of the untreated control at higher annealing temperatures. An increase in dye uptake with increasing annealing temperature was interpreted as an increase in the accesibility of the dye molecule [9, 10].

Experimental

Polyester (PET) fabric, manufactured by Velana d. d., was used throughout this research. The fabric was washed at 95 °C using the following ingredients: 2 g/l of washing agent Felosan JET (Bezema), 0.5 g/l Na_2CO_3, and 0.5 g/l of dispersing agent Sequion MC 200 (Giovanni Bozzetto S.p.A.). To investigate the influence of stabilization under various conditions (time, temperature, and tension) on the quantity of oligomers, the fabric was stabilized in Ernst BENZ dryer, type TFK 15 – M500.
Dyeings of PET fabrics were performed on a Mathis jet JFL dyeing machine. The various stabilized samples were dyed with Terasil Red CA – FR disperse dye under infinite dye bath conditions for 30 min at 130 °C and liquor ratio 1000:1. The pH was adjusted to 4.5 – 5 using acetic acid. Dyed samples were washed at 70 °C for 15 min in a solution containing 2 g/l of sodium dithionite and 3 ml/l of sodium hydroxide 38 °Bé. The K/S values were measured using a Datacolor SF 600 plus CT colorimeter using a mesuring aperture of 9 mm. The K/S value of each sample was measured five times and the average K/S value was recorded.
The quantity of the oligomers on the treated fabric was determined gravimetrically according to the following procedure: 5 g of PET fabric was conditioned in a standard state (20 °C, 65 % relative moisture) for 24 hours. The conditioned PET sample was then wrapped in filter paper and inserted into the Soxhlet apparatus. Petroleum ether (Riedel-de Haen) and dichloromethane (Merck) were used for the extraction. The spin finish plus approximately 5 % oligomers (cont. spin finish) was extracted with petroleum ether [4], while both the spin finish and oligomers were extracted with dichloromethane. Each extraction was repeated. Each extraction took 10 to 12 minutes; the total extraction time was 4 hours. Extracts and PET samples were dried at 60 °C until a constant mass was reached. The quantity of spin finish on the PET sample, extracted with petroleum ether was calculated using equation 1:

$$p_{PE} = \frac{m_{pPE}}{m_{ac}} \cdot 100\,\% \quad , \qquad (1)$$

where p_{PE} is the quantity of spin finish on the PET fabric (%)
m_{pPE} is the mass of spin finish on PET the fabric (g)
m_{ac} is the mass of dry PET fabric without spin finish (g).

The quantity of oligomers and spin finish on the PET fabric, extracted with dichloromethane, was determined using the equation 2:

$$p_{MK} = \frac{m_{pMK}}{m_{ac}} \cdot 100\,\% \quad , \qquad (2)$$

where p_{MK} is the quantity of oligomers and spin finish on the PET fabric (%)
m_{pMK} is the mass of oligomers and spin finish on the PET fabric (g)
m_{ac} is the mass of dry PET fabric without oligomers and spin finish (g).

The percent of oligomers on the PET fabric (p) was calculated using equation 3:

$$p(\%) = p_{MK} - p_{PE} \qquad (3)$$

Results and Discussion

Quantity of oligomers

Untreated polyester fabric (reference - washed and dryed at 130 °C) contains 1.42 % of oligomers. Table 1 and 2 summarise the average values of the quantity of oligomers in PET fabric stabilized at different conditions. Oligomer migration is affected by temperature and time of stabilization, and by stabilization tension. The content of oligomers decreases with increasing time of stabilization in unrestricted state at a given temperature (Table 1). The sample stabilized for 60 min (U6) contains 22 % less oligomers than sample stabilized for 0.5 min (U1).

Table1: Average values of the quantities of oligomers p (%) for polyester fabric stabilized in unrestricted state (samples UX, X = 1, 2, 3, …)

Experiment/ Sample	**Stabilization (unrestricted state)**		**p (%)**
	Time (min)	**Temperature (°C)**	
U	/	/	1.42
U1	0.5	190	1.16
U2	1	190	1.13
U3	5	190	1.10
U4	10	190	0.95
U5	30	190	0.94
U6	60	190	0.90
U7	0.5	210	1.18
U8	1	210	1.05
U9	5	210	0.96
U10	10	210	0.87
U11	30	210	0.82
U12	60	210	0.82

The oligomer content decreases with increased time of stabilization in restricted state (Table 2); the sample which was stabilized for 60 min at 210 °C (R12) contains 33 % less oligomers than the sample stabilized for 0.5 min (R7).

Table2: Average values of the quantities of oligomers p (%) for polyester fabric stabilized in restricted state (samples RX, = 1, 2, 3, …).

Experiment/ Sample	**Stabilization (restricted state)**		**p (%)**
	Time (min)	**Temperature (°C)**	
U	/	/	1.42
R1	0.5	190	1.14
R2	1	190	1.04
R3	5	190	0.98
R4	10	190	0.89
R5	30	190	0.79
R6	60	190	0.74
R7	0.5	210	1.00
R8	1	210	0.91
R9	5	210	0.82
R10	10	210	0.81
R11	30	210	0.73
R12	60	210	0.67

The influence of stabilization tension on oligomer content is negligible at lower stabilization temperatures (190 °C). With increasing stabilization temperature and time the influence of tension on oligomer migration increases (Figure 1). Sample that was stabilized 60 min at 210 °C in restricted state (R12) shows almost 19 % lower oligomer content compared with sample which was stabilized in unrestricted state (U12).

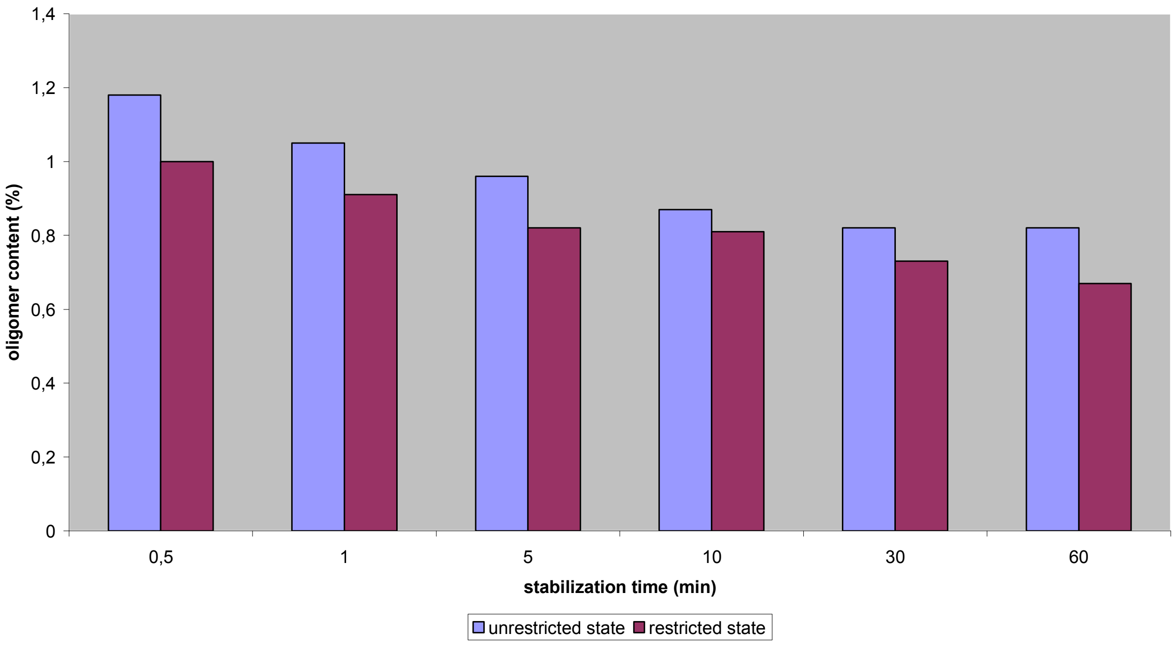

Figure 1: The influence of stabilization tension and time on oligomer content. Stabilization temperature is 210 °C.

K/S values of PET dyeings

K/S value at λ_{max} (λ_{max} = 520 nm) of reference PET sample is 26.63. In Table 3 and 4 K/S values of dyed PET samples, stabilized at different conditions are presented. K/S values of stabilized samples in unrestricted and restricted state decrease in comparison with untreated PET sample (U).

Table 3: K/S values at λ_{max} of dyed PET samples, stabilized in unrestricted state.

Experiment/ Sample	**Stabilization (unrestricted state)**		**K/S value at λ_{max}**
	Time (min)	**Temperature (°C)**	
U	/	/	26.63
U1	0.5	190	18.23
U6	60	190	17.14
U7	0.5	210	18.61
U12	60	210	18.05

It can be seen from Table 3 and 4 that samples stabilized in restricted state possess lower K/S values compared with samples stabilized in unrestricted state.

Table 4: K/S values at λ_{max} of dyed PET samples, stabilized in restricted state.

Experiment/ Sample	Stabilization (restricted state)		K/S value at λ_{max}
	Time (min)	Temperature (°C)	
U	/	/	26.63
R1	0.5	190	17.16
R6	60	190	16.58
R7	0.5	210	17.25
R12	60	210	16.78

Conclusions

- The content of oligomers is the lowest in polyester fabric that was stabilized in a restricted state at higher temperatures and longer times (210 °C, 60 min).
- In comparison with untreated sample (U) with the highest oligomer content and the highest K/S value the use of higher stabilization temperatures decreases the oligomer content and dye uptake (K/S value).
- The increased temperature of stabilization at given time (0.5 or 60 min) results in higher K/S value (in accordance with results in literature 9 and 10), although the lower oligomer content is observed.
- Lower K/S values of PET dyeings were observed on samples, stabilized in restricted state. This finding correlates with lower oligomer content of samples that were stabilized in restricted state.

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