

# The sorption of a syntan on nylon and its resist effectiveness towards reactive dyes

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## Abstract

The sorption behavior of a commercial syntan on nylon and its resist effectiveness towards the uptake of reactive dyes on both nylon and nylon/cotton blend fabrics were investigated. The sorption isotherms of the syntan on nylon at pH 4 fitted a dual sorption mechanism consisting of partition and Langmuir type models. Whereas Langmuir sorption saturation was little influenced by temperature in the range of 50–80 °C, partition coefficients and Langmuir affinity constants increased with increasing temperature, indicating that syntan sorption was endothermic. The ability of the syntan to resist the uptake of reactive dyes was greatly influenced by the nature of the dye and the temperature of syntan application; the observed increase in resist effectiveness that accompanied an increase in the temperature of syntan application can be attributed to a corresponding larger uptake of syntan and greater extent of diffusion of the syntan within the nylon substrate, together with a lower extent of syntan desorption during reactive dyeing.

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**Keywords:** Dye-resist agent; Syntan; Nylon; Sorption; Dyeing; Resist effectiveness

## 1. Introduction

In the field of the wet processing of textiles, syntans are mainly used as the fixing agents to improve the wet fastness properties of acid dyes on nylon fibers [1–3]. In addition, syntans are also used as dye-resist agents to protect the nylon fiber component from cross-staining during the dyeing of wool/nylon and cellulosic/nylon fiber blends [2,4,5] as well as stain-blockers to impart stain-resistance to nylon carpets [6–8]. Syntans intended for use as fixing agents and dye-resist agents are, typically, water-soluble anionic condensates of formaldehyde with sulfonated phenols, thiophenol, hydroxyaryl sulfone or naphthylamine-sulphonic acids [2,5].

Syntans are usually applied to nylon under weakly acidic (e.g. pH 4–5) conditions [9,10]; the isothermal adsorption of syntans is of significance with regard to the mechanism of syntan–fiber interaction. Several researchers have examined

the equilibrium isotherms of syntan sorption on nylon. Guthrie and Cook found that the sorption of the commercial syntan *Ci-batex PA* (Ciba–Geigy) on nylon 6 followed a Freundlich mechanism in the concentration range of 0.05–0.25 g dm<sup>−3</sup> [11], whereas Burkinshaw and Maseka found that the sorption of the commercial syntan *Matexil FA-SNX* (ICI) on conventional and microfiber nylon 6,6 followed a BET mechanism in the concentration range of 1–16 g dm<sup>−3</sup> [1,9]. The disagreement in the results obtained by the different researchers may be attributed to differences in the concentration ranges employed [1,9]. According to the BET sorption mechanism, the formation of multilayers of adsorbed syntan molecules at the periphery of nylon fibers occurs. In view of the above disagreement in terms of the mechanism of syntan adsorption on polyamide fibers, it was deemed necessary to attempt to elucidate the mechanism of syntan sorption on nylon.

Nylon/cellulosic fiber blends are widely used in lightweight suiting, dresswear, leisure shirts, sportswear, uniforms and upholstery fabrics [5]. In order to obtain reserve and contrast effects, syntans are commonly employed to prevent direct dyes

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and reactive dyes from staining the nylon component [5]. Although the use of syntans as dye-resist agents for nylon/cellulosic fiber blends has been reported, no detailed information concerning the resist effectiveness of syntans to the uptake of reactive dyes by nylon is available.

In this work, the sorption of a commercial syntan on nylon and cotton was compared and the sorption isotherms on nylon in the concentration range of 0.5–30% omf were carried out at different temperatures. A dual sorption mechanism comprising Langmuir and Nernst-type partitioning was proposed to describe the observed syntan sorption on nylon. In addition, the syntan was used as a dye-resist agent for the uptake of reactive dyes by nylon and its resist effectiveness towards the uptake of reactive dyes by nylon fabrics and the nylon component of nylon/cotton blends was evaluated. In particular, the investigation on the influence of temperature of syntan application on syntan sorption and desorption as well as resist effectiveness was emphasized.

## 2. Experimental

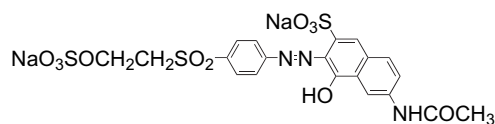
### 2.1. Materials

The nylon 6,6 staple fiber (1.67 dtex; 38 mm), kindly provided by Changshu Cotton Textile Mill, China, was scoured prior to use by treating in a scouring bath containing 0.5 g dm<sup>-3</sup> non-ionic surfactant (polyoxyethylene ether) and 1 g dm<sup>-3</sup> sodium carbonate at 80 °C for 60 min using a 50:1 liquor ratio. The scoured fiber was then rinsed thoroughly in tap water, allowed to dry in the open air and kept in a desiccator with silica gel. The scoured, woven nylon 6,6 fabric (*Tactel*, 44.44 dtex/34F, 1.31 dtex) and knitted nylon 6,6 fabric (77.78 dtex/2) were supplied by Du Pont and Wuxi Mingliya Knitting Fashion Apparel Co. Ltd, China, respectively. The defatted staple cotton for medical purposes was purchased from Hexian Medicinal Cotton Mill, China, and used as received. The scoured and bleached, knitted cotton fabric (13.88 tex) was purchased from Wuxi Changfeng Bleaching and Dyeing Co. Ltd, China.

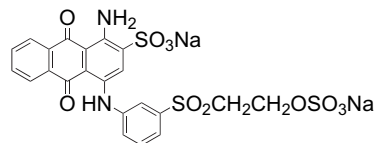
A commercial syntan of *Mesitol NBS* used as an anionic dye-resist agent was generously supplied by LanXess Co. It is a methylene-bonded condensation product of arylsulfonic acids and hydroxyaryl sulfone. *Remazol Brilliant Red F3B* (C.I. Reactive Red 180) was supplied by DyStar. *Everzol Brilliant Orange 3R* (C.I. Reactive Orange 16), *Brilliant Blue R* (C.I. Reactive Blue 19) and *Black B* (C.I. Reactive Black 5) were from Everlight Chemical Industrial Co. The dye structures are given in Scheme 1. Citric acid, glacial acetic acid, disodium hydrogen phosphate, sodium acetate, sodium carbonate and sodium sulfate were of analytical reagent grade. The leveling agent *Cibacel DBC* and the soaping agent *Cibapon R* for reactive dyeing were kindly provided by Huntsman International.

### 2.2. Sorption of the syntan

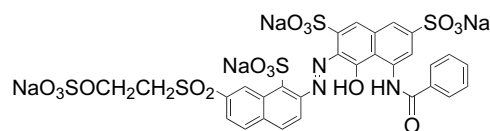
All experiments of syntan sorption were carried out in sealed glass tubes immersed in an universal dyeing machine.



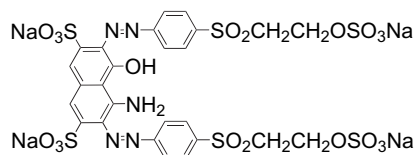
C.I. Reactive Orange 16 (MW = 617 Da)



C.I. Reactive Blue 19 (MW = 626 Da)



C.I. Reactive Red 180 (MW = 933 Da)



C.I. Reactive Black 5 (MW = 991 Da)

Scheme 1.

#### 2.2.1. Effect of pH on sorption

The nylon and cotton staple fibers were treated with 2% omf *Mesitol NBS* at pH values of 2.2, 3, 4, 5, 6 and 7 at 70 °C for 60 min using a 100:1 liquor ratio. The McIlvaine buffers (citric acid and disodium hydrogen phosphate mixture) were added to adjust pH.

#### 2.2.2. Sorption rates

The nylon and cotton staple fibers were treated with 2% omf *Mesitol NBS* at pH 4 and 70 °C for different times using a 100:1 liquor ratio. The pH was adjusted with acetic acid and sodium acetate.

#### 2.2.3. Equilibrium sorption isotherms

The sorption isotherms for *Mesitol NBS* on the nylon staple fibers were measured in a series of *Mesitol NBS* solutions of various concentrations (0.5–30% omf) at pH 4 (acetic acid/sodium acetate) at 50, 70, 80 and 90 °C for 5 h using a 100:1 liquor ratio. In the similar conditions, the sorption isotherms for the syntan on knitted and woven nylon fabrics were also obtained at the syntan concentrations ranging from 0.5 to 20% omf using liquor ratios of 100:1 and 50:1.

#### 2.2.4. Determination of syntan concentration

At the end of each treatment, the concentration of syntan remained in the treatment solution was determined by reference to the extinction coefficient of a calibration plot of syntan

at the maximum adsorption wavelength of 265 nm. The absorbance of the treatment solution was measured using a *Shimadzu* 2550 UV/vis spectrophotometer. The quantity of syntan on the fibers was calculated by taking into account the initial and final concentration of syntan in solution, the concentration of syntan on the fibers and the weight of the dried fibers.

### 2.3. Application of the syntan as a dye-resist agent

All dye-resist treatments and dyeing experiments were carried out in partially sealed and conical flasks immersed in an universal dyeing machine.

#### 2.3.1. Dye-resist treatment and reactive dyeing for knitted nylon fabrics

The knitted nylon fabrics (2 g) were pretreated in a series of *Mesitol NBS* solutions of various concentrations (0, 0.5, 1, 1.5, 2, 3, 4, 5% omf) at pH 4 (acetic acid/sodium acetate) at 60 and 80 °C for 30 min using a 30:1 liquor ratio. Afterwards, they were dyed with *Everzol Brilliant Orange 3R* using a 30:1 liquor ratio according to the profile shown in Fig. 1. The dye-bath was composed as follows: 2.5% omf dye, 1 g dm<sup>-3</sup> *Cibacel DBC*, 50 g dm<sup>-3</sup> sodium sulfate and 10 g dm<sup>-3</sup> sodium carbonate. The final soaping was carried out in a solution of 3 g dm<sup>-3</sup> *Cibapon R* at 90 °C for 15 min.

#### 2.3.2. Desorption of the syntan from knitted nylon fabrics during imitated reactive dyeing

Two samples of knitted nylon fabrics (2 g) were pretreated with 3.62% omf *Mesitol NBS* at 60 °C and 1.50% omf *Mesitol NBS* at 80 °C, respectively. The pretreatment was done at pH 4 for 30 min using a 30:1 liquor ratio. Afterwards, the samples were rinsed and dried in the open air. Under the two conditions, the same quantity of syntan sorption on nylon was nearly achieved. In order to explore the desorption of the syntan from nylon during imitated reactive dyeing, the syntanned samples were treated in sodium sulfate solution (50 g dm<sup>-3</sup>) in the absence and presence of sodium carbonate (10 g dm<sup>-3</sup>) at 60 °C for different times without the addition of reactive dyes. The percent of syntan desorption from syntanned nylon was calculated by taking into account the original quantity of

syntan sorption on nylon and the concentration of syntan in the desorption solution after appropriate time intervals.

#### 2.3.3. Dye-resist treatment and reactive dyeing for nylon/cotton blends

In order to imitate the one-bath reactive dyeing of nylon/cotton blends, nylon fabrics (4 g) and cotton fabrics (4 g), which had been not pretreated or pretreated together with 2% omf *Mesitol NBS* at 50, 60, 70 and 80 °C for 30 min using a pH of 4 (acetic acid/sodium acetate) and a 20:1 liquor ratio, were immersed together into the dyebath. The dyeing was carried out using a 20:1 liquor ratio according to the profile shown in Fig. 1. The dyebath was composed as follows: 2.5% omf dye, 1 g dm<sup>-3</sup> *Cibacel DBC*, 80 g dm<sup>-3</sup> sodium sulfate and 20 g dm<sup>-3</sup> sodium carbonate, where the quantity of dyes was calculated for the total weight of the blend. The final soaping was carried out as described above.

#### 2.3.4. Evaluation of apparent color depth and dye-resist effectiveness

The apparent color depth (*K/S* value) of each dyed sample was measured using a *HunterLab UltraScan XE* reflectance spectrophotometer (illuminant D65; 10° standard observer) at the wavelength of maximum absorption. Each sample was fold twice, giving a thickness of four layers of fabric. The resist effectiveness towards reactive dyes was calculated using Eq. (1).

$$\%RE = 100 \times [(K/S)_u - (K/S)_t] / (K/S)_u \quad (1)$$

where  $(K/S)_t$  and  $(K/S)_u$  are the *K/S* values of the dyed nylon fabrics treated with and without *Mesitol NBS*, respectively.

## 3. Results and discussion

### 3.1. Sorption of syntan on nylon and cotton staple fibers

#### 3.1.1. Effect of pH on sorption

The effect of pH on the sorption of syntan on nylon and cotton staple fibers is shown in Fig. 2, where  $C_f$  denotes the concentration of syntan on the fibers. For nylon, the extent of syntan sorption increased with decreasing pH in the range of pH 2.2–7. This observation is in consistent with those for the sorption of several commercial syntans on nylon 6,6 and

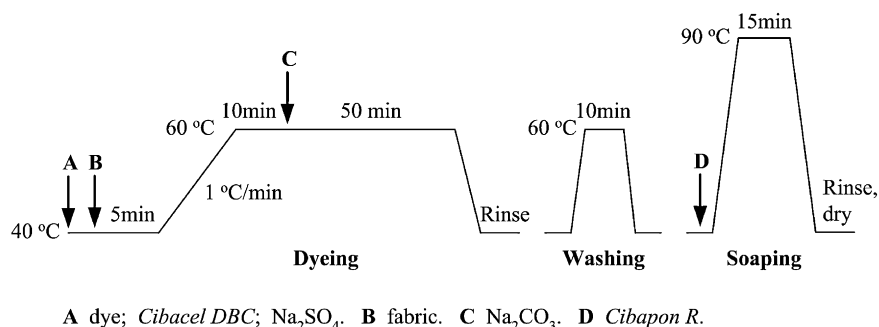


Fig. 1. Dyeing profile for knitted nylon fabrics and nylon/cotton blends.

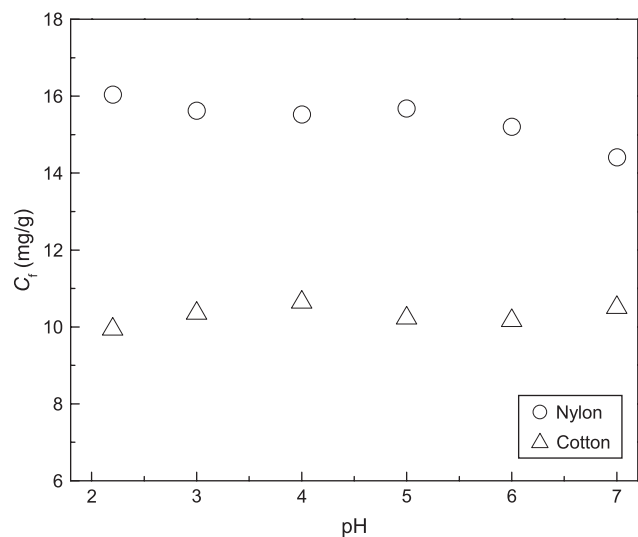


Fig. 2. Effect of pH on the sorption of syntan on nylon and cotton staple fibers at 70 °C for 60 min using a 100:1 liquor ratio.

wool fabric [1,2,4]. This indicates that the electrostatic interactions between the positively charged amino groups in nylon and the anionic sulfonate groups in syntan have an important role in the sorption of syntan on nylon. The higher extent of sorption at pH 2.2 is due to the correspondingly greater protonated amino end groups which give rise to ion–ion interaction. Though the quantity of the protonated amino end groups in nylon was greatly reduced at pH 7, the quantity of syntan absorbed by nylon still reached to a relatively high extent. This implies that there are non-electrostatic interactions between syntan and nylon.

Fig. 2 shows that the quantity of syntan absorbed by cotton was not obviously influenced by pH though the more negatively charged surface potential at higher pH could exert a repulsion effect on the anionic syntan. The extent of syntan sorption on nylon was higher than that on cotton at each pH. This indicates that the affinity of syntan to nylon is greater than that to cotton which can be attributed to the particular interaction of syntan with nylon, this being different from that with cotton in nature.

### 3.1.2. Sorption rates

As shown in Fig. 3, the initial rates of syntan sorption on both nylon and cotton were faster, and the quantity of sorption reached to a very high value in short times. Furthermore, the extent of syntan sorption on nylon increased with increasing time, and reached to a constant in 2 h whereas the extent of syntan sorption on cotton slowly changed with increasing time and the increment in the sorption quantity was very small. Therefore it may be postulated that when nylon/cotton blends are treated in syntan solution, a competition of syntan sorption on nylon and cotton will occur and the syntan will be primarily absorbed by nylon. In addition, the rapid sorption of syntan on both nylon and cotton implies that only a short period is needed for the dye-resist treatment of nylon/cotton blends in order to obtain normal dye-resist effectiveness.

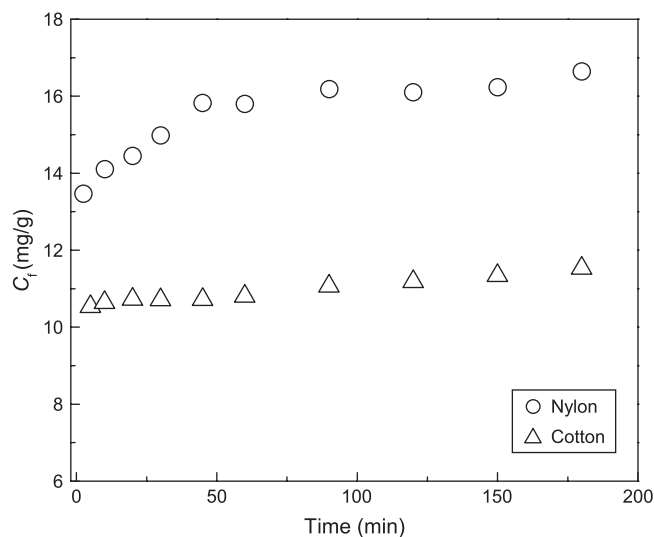


Fig. 3. Sorption rates of syntan on nylon and cotton staple fibers at pH 4 and 70 °C using a 100:1 liquor ratio.

### 3.2. Sorption isotherms of syntan on nylon

In general, equilibrium sorption will be reached in longer times when the syntan concentrations are high. Therefore the isotherms were determined on the basis of the sorption for 5 h. The sorption isotherms of the syntan on nylon staple fibers at various temperatures are given in Fig. 4. Here  $C_s$  is the concentration of syntan in the solution at equilibrium.

In order to analyze these isotherms well, the dual sorption mechanism of Langmuir plus Nernst-type partitioning expressed by Eq. (2) was proposed:

$$C_f = C_P + C_L = K_P C_s + \frac{SK_L C_s}{1 + K_L C_s} \quad (2)$$

where  $C_P$  and  $C_L$  are the concentration of syntan on nylon by Nernst-type partitioning and Langmuir sorption, respectively;  $S$  is the saturation concentration of syntan on nylon by Langmuir sorption;  $K_P$  and  $K_L$  are the partition coefficient and the Langmuir affinity constant, respectively.

In order to explore whether the proposed sorption mechanism is applicable to other nylon fibers in different physical states or having different physical and chemical properties, the isotherms of the syntan on the woven (microfiber) and knitted (conventional) nylon fabrics were also measured.

The sorption parameters,  $K_P$ ,  $K_L$  and  $S$ , were obtained using non-linear least squares fitting procedure to minimize the deviation between calculated and measured data, and summarized in Table 1. Figs. 5–7 show the sorption isotherms of syntan on the nylon staple fiber at 70 °C and a 100:1 liquor ratio, the woven nylon fabric at 60 °C and a 100:1 liquor ratio and the knitted nylon fabric at 60 °C and a 50:1 liquor ratio, respectively which were calculated using the parameters (Table 1) based on the dual sorption model. All of the experimental points exactly superposed with the fitted curves, suggesting the validity of the proposed sorption mechanism.

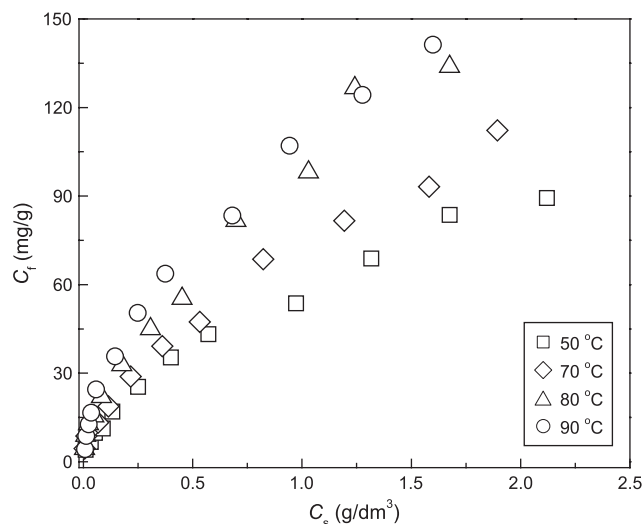


Fig. 4. Sorption isotherms of syntan on nylon staple fibers at pH 4 using a 100:1 liquor ratio.

Similar results were obtained for the sorption isotherms under other conditions. Therefore it is concluded that the proposed sorption mechanism is applicable to all of the nylon fibers used in this study.

From Figs. 5–7, it is evident that the contribution of Langmuir sorption to total sorption varied according to nylon fiber categories and syntan concentrations. In particular, the contribution was quite great for the sorption of syntan on knitted nylon fabrics. According to the  $C_s$  or  $C_t$  values at the intersection points of the Nernst lines and the Langmuir curves together with the sorption data and the initial syntan concentrations used in these experiments, the initial syntan concentrations were obtained, below which the quantities of syntan on nylon absorbed by Langmuir sorption were larger than those by partitioning sorption. They were approximately 10% omf at four temperatures using a 100:1 liquor ratio for nylon staple fibers, 5% omf at 60 °C and 4% omf at 80 °C using a 100:1 liquor ratio for woven nylon fabrics, and 0.6% omf at 60 °C using two liquor ratios of 50:1 and 100:1 for knitted nylon fabrics. Though the concentrations of syntan used as a dye-resist agent depend on the concentrations of dyes, the sulfonate group numbers of dyes, the characteristics of the nylon and other

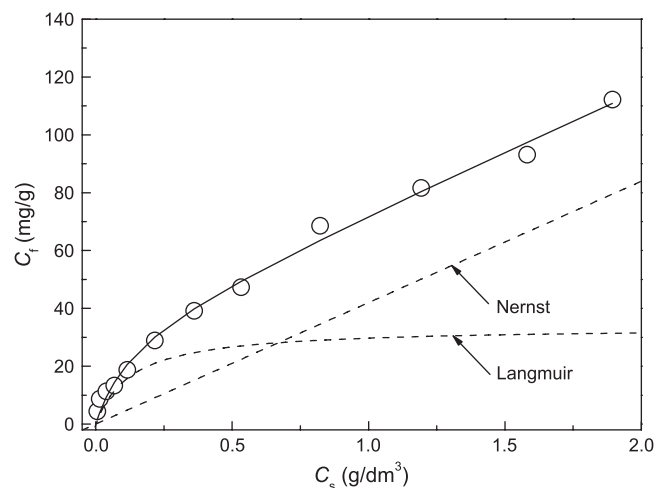


Fig. 5. Sorption isotherm of syntan on the nylon staple fiber calculated using the parameters based on the dual sorption mechanism at pH 4 and 70 °C using a 100:1 liquor ratio.

fibers of blends, liquor ratios, and application pH, etc., it may be concluded from the above results that under acidic conditions, the sorption of syntan occurs primarily on the protonated amino groups in nylon by Langmuir mechanism at low concentrations whereas it occurs primarily by virtue of hydrogen bonding between the uncharged polar groups in syntan and nylon and the hydrophobic interaction between the non-polar moieties in syntan and nylon by partitioning mechanism at higher concentrations.

As shown in Table 1, the different nylon fibers exhibited much variation in the sorption parameters. The  $S$  values should be greatly dependent on the content and accessibility of amino end groups in nylon, the specific surface area and swelling of nylon fibers, application temperature, etc. The syntan sorption on knitted nylon fabrics showed a small Langmuir saturation value ( $S$ ) with a remarkably high Langmuir affinity constant ( $K_L$ ), which could be caused by the low content of amino

Table 1  
Thermodynamic parameters of syntan sorption on nylon at pH 4

Samples	Temperature (°C)	Liquor ratio	$K_L$ ( $10^{-3}$ L/mg)	$S$ (mg/g)	$K_P$ ( $10^{-3}$ L/g)
Nylon staple fibers	50	100:1	4.24	37.74	27.42
	70	100:1	7.73	33.54	41.98
	80	100:1	10.84	36.51	64.27
	90	100:1	11.04	49.79	60.39
Knitted nylon fabrics	60	50:1	188.61	4.47	20.23
	60	100:1	130.09	3.56	19.79
Woven nylon fabrics	60	100:1	4.28	18.85	12.89
	80	100:1	9.31	17.41	15.84

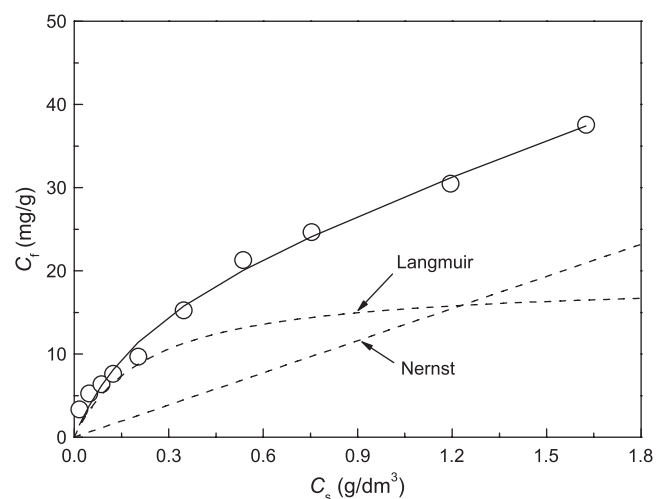


Fig. 6. Sorption isotherm of syntan on the woven nylon fabric calculated using the parameters based on the dual sorption mechanism at pH 4 and 60 °C using a 100:1 liquor ratio.



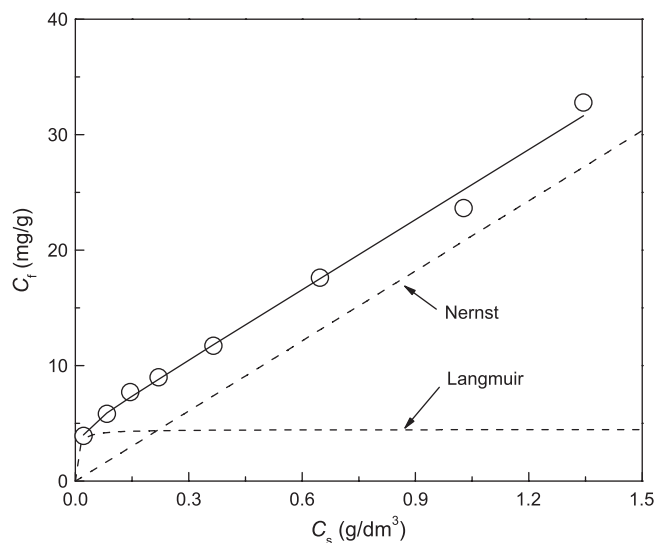


Fig. 7. Sorption isotherm of syntan on the knitted nylon fabric calculated using the parameters based on the dual sorption mechanism at pH 4 and 60 °C using a 50:1 liquor ratio.

groups in nylon fibers. Table 1 clearly shows that the  $S$  value was little affected by temperature in the range of 50–80 °C, but became larger at 90 °C, this being attributed to the higher fiber swelling and the consequent greater accessibility of amino groups in nylon when the treatment had been carried out at 90 °C.

The  $K_P$  and  $K_L$  values exhibited a tendency to increase with increasing temperature, indicating that the heat effect of syntan sorption towards nylon is endothermic. This could be a consequence of heat consumption for the disassociation of syntan aggregates and the swelling of nylon fibers that accompanied an increase in temperature.

From Table 1, it can be noted that liquor ratio had a remarkable influence on the  $K_L$  values. As  $K_L$  implies the electrostatic binding constant of the anionic sulfonate groups in syntan with the positively charged amino end groups in nylon fibers, the charge density of the sulfonate anions affects the  $K_L$  values. The  $K_L$  values increased with decreasing liquor ratio, which may be attributed to a corresponding increase in the effective concentration of syntan in the treatment bath.

### 3.3. Application of the syntan as a dye-resist agent

#### 3.3.1. Resisting the uptake of reactive dyes by knitted nylon fabrics

In order to discuss some important factors influencing the ability of syntan to resist the uptake of reactive dyes by nylon fibers and give better explanations for the fact that the dye-resist treatment at high temperatures can exhibit greater resist effectiveness, the knitted nylon fabrics were treated in the syntan solutions and subsequently dyed with *Everzol Brilliant Orange 3R*.

Fig. 8 shows that the quantity of syntan absorbed by nylon linearly increased and the apparent color depth of the corresponding syntanned and dyed nylon decreased with an

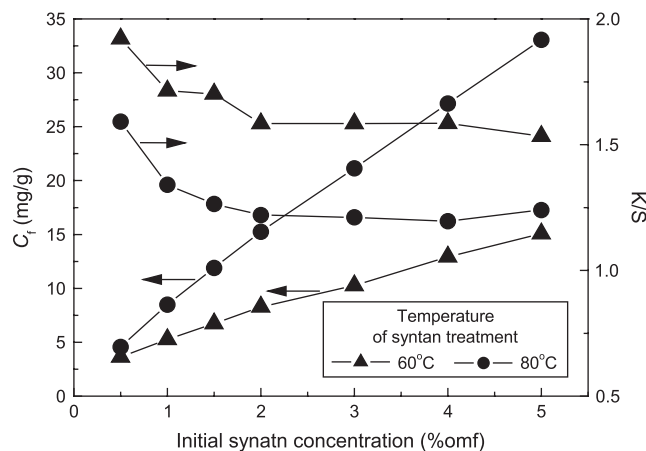


Fig. 8. Influence of the initial concentration of syntan in solution on the quantity of syntan absorbed by knitted nylon fabrics at 60 and 80 °C and the apparent color depth of the syntanned fabrics dyed with C.I. Reactive Orange 16.

increase in the initial concentration of syntan in solution at two temperatures. On the other hand, in the case of the same initial syntan concentration, the pretreatment at 80 °C showed the higher extent of syntan sorption and the better dye-resist effect than that at 60 °C.

The ability of syntan to resist the uptake of acid dyes by nylon fibers under acidic dyeing conditions has been discussed by several workers [2,12,13]. This ability can be attributed to ion–ion repulsion effects operating between the anionic syntan and the anionic dye molecules, occupation of protonated amino end group dye sites in nylon by the syntan and a decrease in the coefficient of dye diffusion within the fiber caused by the presence of the large molecular size syntan. In the same way, the syntan absorbed by nylon fibers exerted the resist effect on the uptake of reactive dyes. According to the results shown in Fig. 8, the decreased color depth of syntanned and dyed nylon fabrics with an increase in the initial syntan concentration and the temperature of syntan application can be preliminarily explained by the higher extent of syntan sorption and the consequent stronger ion–ion repulsion forces operating between the anionic syntan in nylon and the anionic dyes in solution.

Fig. 9 is a further plot of Fig. 8 from which it is clear that in the case of the same extent of syntan sorption, the pretreatment at 80 °C displayed the greater resist effectiveness than that at 60 °C. It is evident that the greater syntan diffusion into the microvoids of nylon fibers during the pretreatment at the higher temperature exerted the stronger steric hindrance and blocking effect on the diffusion of reactive dyes into the fiber interior during the subsequent dyeing.

From Figs. 8 and 9, it is found that a constant resist effectiveness was reached after the quantity of syntan absorbed by nylon exceeded 10 mg/g for the pretreatment at 60 °C and 15 mg/g at 80 °C, respectively. This observation implies that the dye-resist effect is restricted by the number of the anionic sulfonate groups in reactive dyes, the size of dye molecules and the affinity or reactivity of reactive dyes to nylon fibers. Therefore it is of much importance to select the appropriate reactive dyes for the coloration of nylon/cellulosic fiber blends.

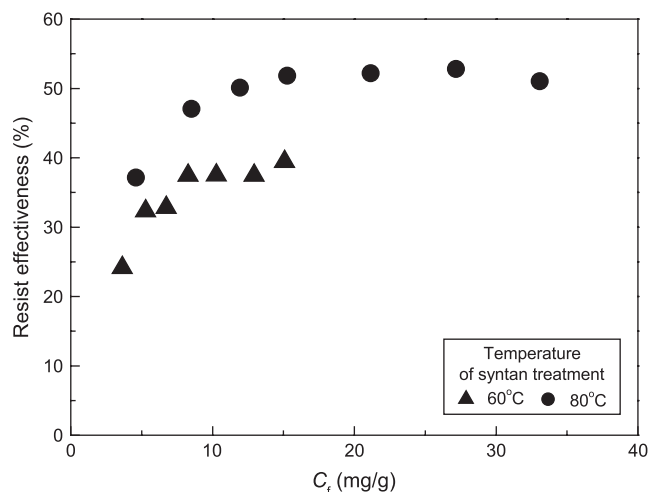


Fig. 9. Influence of the temperature of syntan application and the quantity of syntan absorbed by knitted nylon fabrics on the resist effectiveness against C.I. Reactive Orange 16.

### 3.3.2. Desorption of the syntan from nylon fibers during imitated reactive dyeing

Earlier work showed that the syntan desorbed more or less from the syntanned nylon and wool under acidic dyeing conditions [2,13] and the extent of syntan desorption depended greatly on the temperature of syntan application during wool dyeing [2]. Once the syntan desorption takes place, the ability of syntan to resist the uptake of dyes would be reduced, and the interaction of the desorbed syntan with the dyes in solution might occur. Owing to lack of the information concerning syntan desorption during the dyeing of reactive dyes, the study on syntan desorption was performed under the imitated reactive dyeing conditions. For this study, knitted nylon fabrics were pretreated with 3.62% omf *Mesitol* NBS at 60 °C and 1.50% omf *Mesitol* NBS at 80 °C, respectively so that the same quantity of syntan absorbed by nylon was nearly achieved. Subsequently, the syntanned fabrics were immersed in sodium sulfate solution in the absence and presence of sodium carbonate at 60 °C.

Fig. 10 shows that the percent of syntan desorption was very low and less than 5% in the presence of sodium sulfate irrespective of pretreatment temperature, implying that the syntan absorbed by nylon fibers can impart the good resist effect to the uptake of reactive dyes prior to the alkali addition. However it should be noted that the syntan desorbed quickly at the initial stage in sodium sulfate solution in the presence of sodium carbonate, and a majority of desorption occurred within 15–20 min. In particular, the percent of syntan desorption that occurred when pretreatment had been performed at 60 °C was considerably higher than that obtained at 80 °C, and furthermore, the loss of syntan approached 50% from the pretreated fabric at 60 °C after this desorption treatment for 15 min whereas the corresponding value was 18% from the pretreated fabric at 80 °C. It is evident that the pretreatment at high temperatures can greatly enhance syntan diffusion within the fiber and decrease the extent of syntan desorption in alkaline solution. This implies that the dye-resist

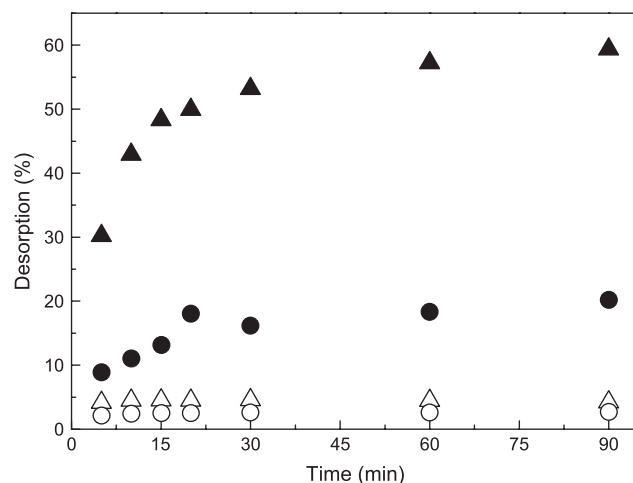


Fig. 10. Desorption rates of syntan from knitted nylon fabrics in sodium sulfate solution in the absence and presence of sodium carbonate at 60 °C (Temperature of syntan treatment: ( $\Delta$ ,  $\blacktriangle$ ) 60 °C, ( $\circ$ ,  $\bullet$ ) 80 °C; desorption solution: ( $\Delta$ ,  $\circ$ )  $\text{Na}_2\text{SO}_4$ , ( $\blacktriangle$ ,  $\bullet$ )  $\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$ ).

treatment at higher temperatures can exhibit the greater ability of syntan to resist the uptake of reactive dyes at the sorption and fixation stages.

### 3.3.3. Resisting the uptake of reactive dyes by the nylon component of nylon/cotton blends

Four reactive dyes having the different number of anionic groups and the different molecular weight were selected to dye the imitated nylon/cotton blends. The apparent color depth of each dyed sample and the resist effectiveness of syntan were evaluated. As shown in Fig. 11, the apparent color depth of cotton was hardly influenced by the application of syntan whereas the apparent color depth of nylon decreased with an increase in the temperature of syntan application. Furthermore, Fig. 12 clearly shows that the resist effectiveness increased with increasing temperature of syntan application. The phenomenon can be explained by the fact that the quantity of syntan sorption on nylon increased and the diffusion of syntan into nylon interior was enhanced with increasing temperature of syntan application, and the extent of syntan desorption was reduced during reactive dyeing.

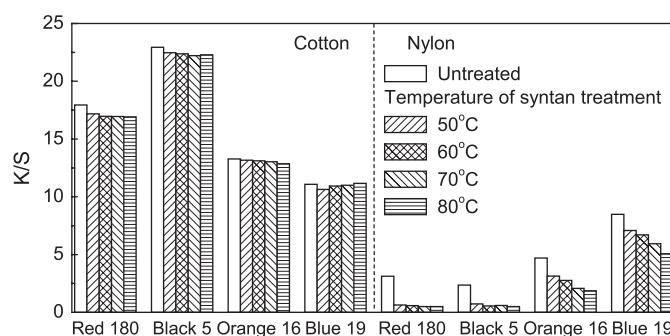


Fig. 11. Apparent color depth of nylon/cotton blends pretreated in syntan solutions at different temperatures and subsequently dyed with four reactive dyes.

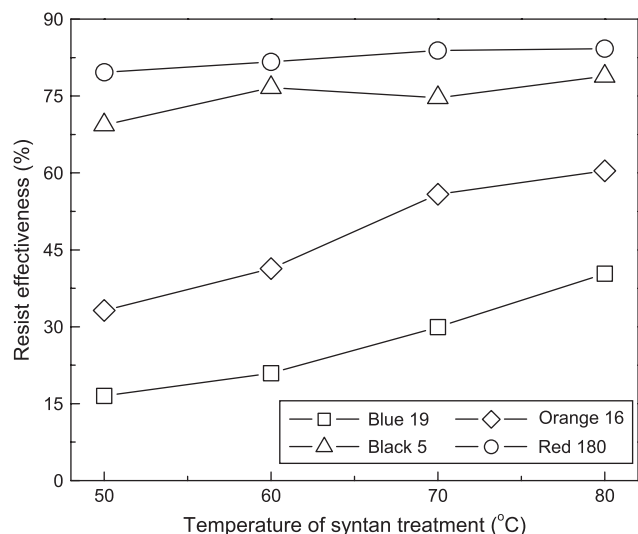


Fig. 12. Resist effectiveness of the nylon component of resist-treated nylon/cotton blends to four reactive dyes.

The resist effectiveness of syntan to four reactive dyes varied greatly. The higher the number of anionic groups in reactive dyes, the greater the resist effectiveness (Red 180  $\approx$  Black 5 > Orange 16 > Blue 19). Both Blue 19 and Orange 16 with one sulfonate group and one sulphatoethylsulphone group are poorly resisted since the ion–ion repulsion between the anionic syntan absorbed by nylon and the anionic dyes approaching the nylon surface is weak. Another important reason may be that the syntan absorbed by nylon exerts a weak hindrance effect on the diffusion of the two dyes into nylon interior as they have the high diffusion power resulting from their small molecular size and comparatively more hydrophobic character. Conversely, Black 5 and Red 180 with four anionic groups and the large molecular size are strongly resisted due to the stronger ion–ion repulsion between the dye anions of higher charges and the anionic syntan absorbed by nylon as well as their low diffusion power into nylon interior.

#### 4. Conclusions

The sorption isotherms of a commercial syntan on different nylon fibers at pH 4 were analyzed well by means of the dual sorption mechanism consisting of partition and Langmuir type

sorption. The electrostatic interactions operating between the anionic syntan molecules and the protonated amino groups in nylon contribute to Langmuir sorption, whereas the non-electrostatic interactions between syntan and nylon contribute to partition sorption. The partition coefficients and Langmuir affinity constants increased with increasing temperature, implying that the sorption of syntan towards nylon is an endothermic reaction process.

The syntan exhibited faster sorption rates and higher sorption quantity on nylon than on cotton. When applied to nylon/cotton blends, the syntan imparted the resist effect to the uptake of reactive dyes by nylon component. The resist effectiveness towards reactive dyes was significantly improved by increasing the number of sulfonate groups in dyes and the size of dye molecules. The reactive dyes with more sulfonated groups and larger molecule size have to be selected in order to achieve good dye-resist effects. In addition, the resist effectiveness increased with increasing temperature of syntan pre-treatment which can be attributed to the corresponding larger quantity of syntan sorption, the greater degree of syntan diffusion into nylon interior and the lower extent of syntan desorption during reactive dyeing. The explanation is well supported by the investigations on the influence of temperature of syntan application on the syntan sorption and corresponding dye-resist effect as well as the syntan desorption under imitated reactive dyeing conditions.

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