

Dye-Polymer Interaction in Nylon 66

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Synopsis

Absolute orientation factors of dye and the amorphous region of the polymer nylon 66 have been determined from the dichroism of the visible band and that of the characteristic amorphous infrared band of the polymer. It has been shown that the orientations show a linear relationship with unit slope irrespective of whether the film was stretched before dyeing (prestretched) or stretched after dyeing (poststretched). The relation is the same for reactive as well as nonreactive disperse dye. The effect of thermal treatment at constant length shows that the dichroism of the dye decreases whereas that of the polymer does not and that it is reversible. It is concluded that disperse reactive as well as nonreactive dyes have specific interaction sites with the polymer.

INTRODUCTION

The dichroism of disperse dyes in relation to substrate orientation has been studied to some extent for some special cases by earlier workers.¹ Some interesting results have been reported recently by Patterson et al.,² Okajima et al.,³ and Chappel⁴ for PET and nylon. They have shown that dichroism varies linearly with birefringence or with draw ratio if the crystallinity remains unchanged in drawn samples. All these studies were done on films which were first dyed and then stretched (poststretch). Kobayashi et al.,⁵ however, compared dye dichroism and amorphous birefringence for polypropylene for both cases, namely, poststretch and prestretch. In all these studies, infrared dichroism of the amorphous band was not used to measure polymer orientation in the amorphous region. Secondly, in all previous work absolute orientation was not taken as a basis to establish the correlation. It is shown here that this is essential to get a reliable and meaningful correlation between dye and polymer orientations. In the present study, the behavior of both reactive and nonreactive disperse dyes has been examined on the same substrate in prestretch and poststretch conditions. From these results and also from the thermal disorientation effects, some important deductions regarding dye-fiber interaction in disperse dyes have been made.

EXPERIMENTAL

Materials

Nylon 66 films supplied by du Pont de Nemours were used. The polarized infrared absorption of undyed and visible dichroism of dyed unstretched

films showed that these were practically unoriented. The following disperse dyes were used: (a) Nonreactive dyes: (i) nonionic coumarene-type brightener; (ii) Leucophor PC ultraconc (Sandox) anionic brightener. (b) Reactive dyes: (i) Procynyl Blue RS (ICI); (ii) Procynyl Yellow AS (ICI).

Procedure

Films were dyed with disperse brighteners at boil for 1 hr from 0.0005% dispersion. For procynyl dyes, the films were dyed from 0.0016% and 0.012% dispersions of the yellow, and the blue dyes at 95°C in slightly acidic bath for 1 hr (M:L is 1:2500). After this, the films were removed and treated with soda ash solution (pH 10–10.5) at 95°C for 1 hr to get the dye reacted. The films were extracted with propanol and soaped to remove the unreacted dye. When a film with unreacted dye was desired, alkali treatment was omitted and films were only washed with cold water. For compound dyeing, the films were dyed from a mixed dyebath.

Stretching of the film to various draw ratios was done at room temperature in a stretching unit. In case of prestretched films, these were dimensionally stabilized by shrinking them in boiling water.

Measurement of polymer orientation by various methods including infrared dichroism has been given by Stein and Read⁶ and Padhye and Gulrajani.⁷ Polymer orientation was obtained by measuring the infrared dichroism duly corrected of the amorphous band of nylon 66 at 1140 cm⁻¹ on a Perkin-Elmer Model 21 spectrophotometer fitted with a wire grid polarizer. The visible dichroism was measured on a Beckman DK 2 spectrophotometer at the absorption maxima of the respective dyes. Absolute orientation factor was calculated according to the method of Okajima et al.³ The absolute orientation factor is given by

$$\phi = \frac{f}{f_0} = \frac{(D - 1)(D_0 + 2)}{(D_0 - 1)(D + 2)}$$

where

f = dichroic orientation factor $D - 1/D + 2$,

f_0 = dichroic orientation factor for infinite stretch, and

D = dichroic ratio = absorbance with light polarized parallel to draw direction/absorbance with light polarized perpendicular to draw direction.

The value of ϕ_v tabulated in the table are the absolute percentage orientation factors for the dye calculated from visible dichroism, and ϕ_p is the same for the polymer calculated from infrared dichroism. f_0 is the value of f extrapolated to infinite stretch and is obtained by plotting f against reciprocal of stretch and extrapolating the latter to zero. Hence, this f_0 is the orientation factor for ideal perfect molecular orientation and essentially gives the orientation factor of the transition moment direction of relevant transitions with respect to the reference polymer stretch direction.

To record the polarized spectra of films heated at constant length, the film was fixed in the two jaws of metal frame preventing it from thermal contraction. The frame was put in a glass cell which was heated by a concentric tubular wire-wound heater. The assembly was such as could be put in the sam-

ple space of the spectrophotometer. The film was allowed to attain the equilibrium temperature at each heater setting, and the film temperature was recorded by a thermometer placed in contact with the film.

RESULTS AND DISCUSSION

In an earlier work, Palekar⁹ studied the correlation between ϕ_v and ϕ_D of a reactive dye on nylon 66 both for prestretch and poststretch cases. It was observed that the graph between ϕ_v and ϕ_D is a straight line with unit slope in all cases. He concluded that this indicated that there is specific binding between the dye and the fiber. It was thought interesting to study the behavior in case of a typical nonreactive disperse dye and compare it with the correlation observed for a reactive dye. In order to make comparison more convincing, reactive and nonreactive disperse dyes were dyed from the same dye bath. The choice of the dyes was made so that (a) the two have well-separated visible absorption maxima, (b) the nonreactive dye should not be affected by alkali treatment given for fixing the reactive dyes, and (c) there should be no dye-dye interaction.

It was observed that anionic disperse brightener was suitable as the nonreactive dye since it satisfied these conditions. The study was also extended to two suitable reactive dyes.

In the present study, there are various sets of measurement. The absolute orientation factors from the visible dichroism of each of the two dyes taken up by the polymer from the compound dyebath have been measured for various degrees of stretch both for prestretch and poststretch cases. Since one of the dyes is a reactive dye, visible dichroism is measured before and after reaction stage of the dye. In each case, the absolute orientation factor of the polymer substrate is also determined from the measurement of infrared dichroism of the amorphous band. In case of the prestretch films, the percentage stretch values are those measured after shrinking treatment. The orientation factor, hence, refers to shrunk films. It is observed that polymer orientation factor is nearly the same within experimental accuracy for a given degree of stretch for both the prestretch and poststretch films. A mean value of infrared orientation factor for each percentage stretch is hence used and is given in the tables. The observations may be grouped in two categories for convenience of discussion, viz., orientation factors for (a) brightener and unreacted dye (both prestretched and poststretched films), (b) brightener and reacted dye (both prestretched and poststretched film).

The values of orientation factors calculated from visible dichroism and from infrared dichroism for different degrees of stretch are given in Tables I and II for various cases. The graph of ϕ_v against ϕ_D is shown in Figures 1 and 2.

When comparing the orientation of prestretched and poststretched film, there are two important aspects which require consideration. Firstly, the shrinkage of the prestretched film during dyeing must be taken into account when comparing the orientation with poststretched film. Secondly, when comparing the samples with two types of stretching treatment, the percentage crystallinity should not vary with the type of treatment. The second condition means that the prestretched samples should not crystallize during

TABLE I
Poststretched Films: Anionic Disperse Brightener and Procynyl Blue

Stretch, %	Visible orientation factor (ϕ_v), %				Mean infrared (i.e., polymer) orientation factor (ϕ_p), %
	Disperse brightener	Unreacted Procynyl Blue	Disperse brightener	Reacted Procynyl Blue	
120	11.8	19.0	15.7	20.6	19.5
130	17.2	25.3	20.4	25.1	24.3
140	19.7	29.6	24.5	27.4	27.5
150	22.5	32.0	27.5	29.6	29.6
160	25.3	34.1	30.4	31.8	31.7
170	28.0	36.2	33.4	33.8	33.6
180	30.4	38.1	35.6	36.0	35.4
190	33.0	40.0	37.7	38.2	37.3
200	35.4	41.9	39.6	40.2	39.1
210	37.8	43.7	41.6	42.1	41.2
220	40.0	45.5	43.5	44.2	42.8
230	42.3	47.5	45.5	46.2	44.6
240	44.3	49.3	47.4	48.0	46.4
250	46.6	51.0	49.0	50.0	48.4
260	48.5	52.8	50.7	52.0	50.1
270	50.5	54.5	52.3	54.0	51.9
280	52.5	56.0	54.0	55.8	53.7

dyeing treatment or that poststretched samples which already have dye in it should not crystallize during stretching. The importance of these conditions has been pointed out to some extent by Patterson et al.² In the present study, the prestretched films were shrunk in boiling water before the dyeing treatment, and draw ratios and orientation factors measured were those after shrinking. As for the change in crystallinity on stretching, Starkweather and Moynihan,⁸ by comparing the intensity of infrared crystalline band and poly-

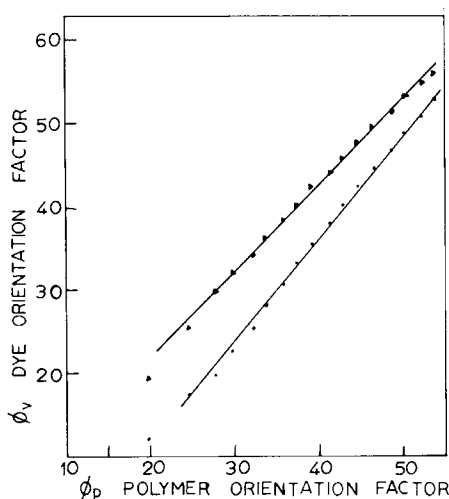


Fig. 1. Mean infrared orientation factor against visible orientation for (●) disperse brightener and (▲) unreacted Procynyl blue.

TABLE II
 Prestretched Films: Anionic Disperse Brightener and Procynyl Blue

Stretch %	Visible orientation factor (ϕ_v), %				Mean infrared orientation factor (ϕ_p), %
	Disperse brightener	Unreacted Procynyl Blue	Disperse brightener	Reacted Procynyl Blue	
120	12.4	18.3	17.2	18.2	19.5
130	17.3	21.6	22.1	21.6	24.3
140	21.7	23.3	25.9	23.3	27.5
150	25.9	27.0	28.5	27.0	29.6
160	29.6	29.2	31.0	29.2	31.7
170	31.7	31.8	33.1	31.8	33.6
180	35.0	34.2	34.8	34.2	36.4
190	36.1	36.4	37.2	36.4	37.3
200	38.4	39.6	39.0	39.6	39.1
210	40.4	40.8	41.3	40.8	41.2
220	42.3	43.0	43.2	43.0	42.8
230	44.3	45.0	45.0	45.0	44.6
240	46.5	47.1	47.0	47.1	46.4
250	48.6	49.1	49.2	49.1	48.4
260	50.6	50.9	51.1	50.9	50.9
270	52.5	52.9	52.8	52.9	51.9
280	54.5	54.4	54.6	54.4	53.7

mer density, have shown that stretching does not affect the crystallinity of nylon 66. In the present study, it is observed that the visible dichroic ratio for a sample with a given extension and dye content is the same for the prestretched as well as poststretched film. This also indicates that nylon 66 does not crystallize on stretching at room temperature. It has been shown by previous workers that change in crystallinity affects the correlation between dye and polymer orientation. Hence, the present work was done on nylon 66, and

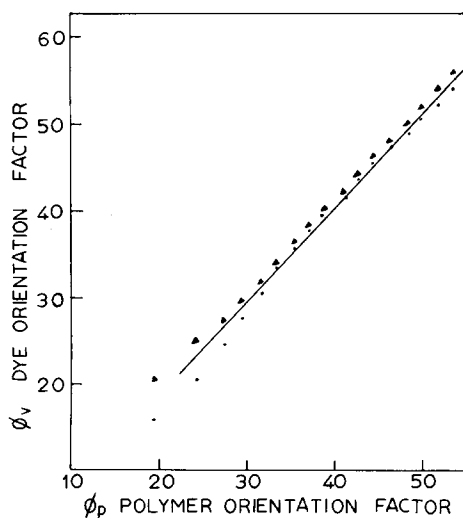


Fig. 2. Mean infrared orientation factor against visible orientation factor for (●) disperse brightener and (▲) reacted Procynyl blue.

both the factors that are known to affect the results are properly taken account of. An additional feature of the present investigations is that absolute orientation factors of the dye as well as of the amorphous region of the polymer are compared. The correlation established between the two orientations in the present case, hence, is believed to be more significant and meaningful.

From the figures it is observed that, in all cases, the graph of ϕ_v against ϕ_p is linear, with practically unit slope. This is irrespective of whether the film is prestretched or poststretched and also whether the dye is reacted, unreacted, or disperse dye. This is specially true for extensions after a small initial stretch of 130%.

The linearity of the graph of ϕ_v against ϕ_p shows that in poststretching, the dye follows the orientation of the amorphous region in the polymer. In the case of prestretch, the linearity shows that the dye distributes proportionately in the oriented and nonoriented regions within the accuracy of the experiment. These conclusions are essentially the same as those drawn by Palekar.⁹ It is reasonable to presume that the reacted dye is bound at specific sites and is molecularly dispersed. Since the disperse brightener dyed from the same dyebath shows similar correlation between ϕ_v and ϕ_p , it indicates that qualitatively the dye polymer interaction even for a nonreacted dye is the same. Quantitatively, however, the magnitude of the interaction is different since one dye is reactive while the other is not. Before the procinyl dye was reacted, the unreacted dye and the disperse brightener both essentially act as nonreactive disperse dyes, and both show the same behavior when the dye was reacted.

In a separate experiment, the behavior of nonionic brightener and the nonreacted dye was found to be similar. The data are, however, not given since the nonionic brightener was found to be unstable to alkali treatment and the dyeing of reacted dye and nonionic brightener could not be done from a compound dye bath. The study was also extended to two reactive dyes, namely, Procinyll Yellow and Procinyll Blue, dyed simultaneously from a compound dyebath. The orientations for both dyes unreacted and reacted on prestretch and poststretch films were measured. The results again give similar straight lines. When both dyes are reacted, each has a certain specific interaction site and thus the case corroborates the above deductions.

It would be pertinent to compare the present findings with the relevant findings of the earlier workers. Patterson and Ward² as well as Okajima et al. found that the total birefringence of PET and the orientation factor calculated from visible dichroism in case of prestretched polymer are not linear but depart from linearity at a certain stretch ratio. Patterson and Ward have convincingly proved that the departure is due to changes in crystallinity on stretching. However, in case of polypropylene, Koboyashi et al.⁵ found that amorphous birefringence or amorphous infrared orientation and visible orientation give a straight line in case of both prestretch and poststretch films. The slope in the two cases was observed to be different, the prestretch showing less visible orientation. According to them, this is due to dye occupying a lesser oriented portion. In the present case of nylon 66, when the dichroic orientation factor is considered instead of absolute orientation, two similar lines for prestretch and poststretch cases are observed. When absolute orientation is considered, the two lines nearly coincide and a single line

TABLE III
Change in Visible and Infrared Dichroic Ratio with Films Heated Under Constant Lengths (Film Stretched 260%)

Temperature, °C	Visible dichroic ratio			Infrared dichroic ratio
	Unreacted Procynyl Blue	Reacted Procynyl Blue	Anionic brightener	
25	1.88	1.59	2.11	1.14
40	—	1.53	—	—
43	1.81	—	2.07	—
48	1.74	—	1.99	1.16
50	—	1.49	—	—
54	1.72	—	—	—
98	—	—	—	1.19
105	1.61	1.45	1.94	—
25 on cooling	1.86	1.58	2.09	1.14

with unit slope is obtained. This shows the importance of considering the absolute orientation after finding the dichroic ratio at infinite stretch. The deductions about the dye distributing proportionately in the oriented and unoriented portions drawn by Palekar hold in the present case also.

It was thought interesting to seek further confirmation of the conclusions drawn by studying the process of relative dye and polymer disorientation by some disorienting treatment. The visible and infrared dichroic ratios of the films stretched to various draw ratios were measured at various temperatures up to 120°C. The films were held firmly at fixed length during heating. The dichroic ratios were measured again at room temperature after cooling. The dichroic ratios at various temperatures for a definite sample are given in Table III.

It is observed that (a) dye dichroism decreases with temperature for all dyes either reacted, unreacted, or dispersed; (b) infrared dichroism of the amorphous 1140 cm^{-1} band either remains constant or increases slightly at high temperature; (c) the change in both dye and polymer dichroism is practically completely reversible, i.e., films show initial dichroism at room temperature after the heating cycle.

There is very little work on the relative disorientation of the dye and the polymer with temperature. Nakayama et al.^{11,12} have shown that both in PET and polypropylene the dichroic orientation of the dye decreases at higher temperature and that it is reversible as long as some irreversible changes have not occurred in the amorphous region of the polymer. In the case of polypropylene, they measured total birefringence and concluded that there is no change in the overall amorphous orientation. It is significant to observe that they attribute the decrease in visible orientation factor to a fall in f_0 , the dichroism at infinite stretch. In both cases, they conclude that the fall in dye orientation is due to the disorientation or thermal oscillations of the dye molecules held in the polymer. It may be observed that in their study, the orientation of the amorphous region of the polymer was not specifically determined at the same temperatures as for the dye. The present study hence has a definite contribution to make.

The infrared dichroism of the amorphous band on heating at constant length shows that there is no disorientation of the polymer. In a separate study, it is observed that behavior of the infrared dichroism of the amorphous band depends on the conditions of stretching and thermal stabilization of the stretched polymer. It does not decrease at higher temperature in any case.

The dye dichroism always decreases at higher temperature. This, however, could not be due to the migration of dye to a less ordered region, firstly, because this is also observed in case of reacted dye where such migration is not possible, and secondly, on cooling, the visible dichroism again increases to the original value, which would be unlikely if the dye migrated. The fall in dichroism in all cases may be due to greater thermal motion around the site of binding which is lost when the temperature is lowered. Thus, here again, the observations support the thesis that reactive as well as disperse dyes are bound on specific sites within the polymer.

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