

Over-Dyeing Phenomenon and Dichroism of Dyed Polymer

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Synopsis

Visible dichroism reflects the orientation of the amorphous region of a polymer. Thus the dichroism of a polymer must be constant irrespective of the amount of dye on the polymer. It is generally believed, however, that a fiber specimen must not be over-dyed if the dichroism is to be measured quantitatively. The dichroism of cellulose and poly(vinyl alcohol) dyed with Congo Red was measured carefully, and the causes of this phenomenon were investigated. The "over-dyeing" phenomenon is apparent. When the correct absorbance is measured, Lambert-Beer's law holds good over the range of the possible dye content. The orientation of the dye molecules in polymer is independent of the dye content up to saturation.

INTRODUCTION

Visible dichroism reflects the orientation of the amorphous region of polymer, and thus dichroism of a polymer must be constant irrespective of the amount of dye on the polymer when the dichroic dye molecules are absorbed parallel to the amorphous chain of polymer.

It is generally believed, however, that the fiber specimen must not be over-dyed if the dichroism is to be measured quantitatively, because the parallel absorbance D_{\parallel} increases in proportion to perpendicular absorbance D_{\perp} in the early stage of dyeing, but there is deviation from this linearity when the specimen is dyed too deeply and consequently dichroism decreases as shown in Figure 1.¹⁻⁴

Various causes have been suggested for this phenomenon as follows.

(1) Skin-core effect. When dyeing is carried out heterogeneously through the fiber, dichroism decreases with increasing thickness of the dyed layer, provided that the degree of orientation of the skin is higher than that of the core.

(2) Preferential absorption of the dye molecules to a well-oriented crystalline surface. At progressively deeper dyeing the greater part of the dye molecules is absorbed by the less oriented amorphous region and dichroism becomes smaller.

(3) Multilayer absorption. A disturbance in orientation of the dye

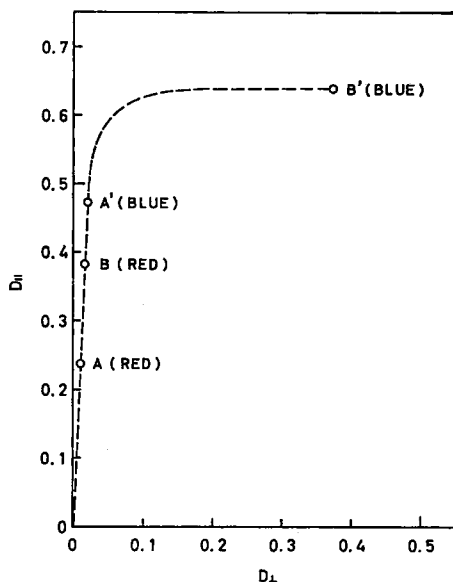


Fig. 1. Relation between parallel and perpendicular absorbance of fiber.

molecules loosely absorbed in the secondary or higher-ordered layer causes a decrease in dichroism.

(4) Deviation from the Lambert-Beer's law at deeper dyeing.

In the present study, the dichroism of cellulose and poly(vinyl alcohol) dyed with Congo Red was measured carefully, and the causes of this phenomenon were investigated.

DICHROISM OF FILM

Experimental

A spectrophotometer especially equipped with a polarizer in front of the cell was used.

Measurements were carried out as follows. A sample was placed in a cell containing dichlorobenzene, the refractive index of which ($n = 1.54$) is equal to the refractive index of regenerated cellulose or poly(vinyl alcohol). An undyed specimen was placed in a reference cell containing the same solution. On dipping the sample in such a solution measurements could be carried out without reflection or scattering of light on the surface of specimen, even when it is a pack of the stacked strips.

The absence of stray light in the transmitted light was verified by replacing a sample with a very dark dyed strip in the cell and repeated measurements.

Results

Cellophane Film. As commercial cellophane was anisotropic in the machine direction, 1×4 cm. strips fitting the cell were cut from cellophane

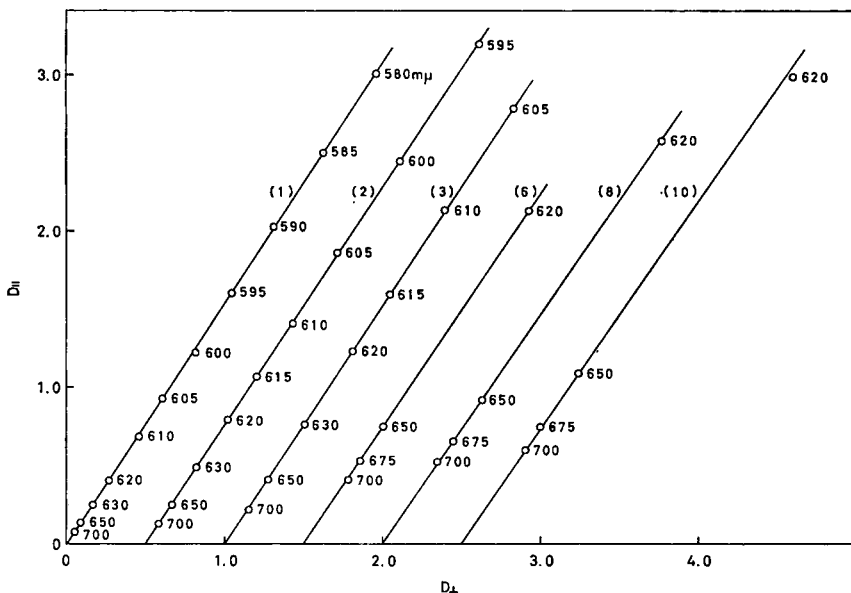


Fig. 2. Relation between parallel and perpendicular absorbance of cellophane.

with longer side parallel to the optical axis. The strips were then washed in boiling water till free from glycerol and were dyed with Congo Red.

Parallel and perpendicular absorbances, D_{\parallel} and D_{\perp} of a pack of the stacked strips were measured at various wavelengths and D_{\parallel} versus D_{\perp} plotted on rectangular coordinates (Fig. 2). The dye content of the strips was about 9%. The measured points fall on a straight line passing through the origin. The number beside each point in the figure represents the wavelength of measurement, and the number N of stacks in the pack is shown in parentheses near each straight line. In Figure 2 the origin of each line is shifted to avoid over-crowding. The relation between the absorbance and the numbers N at each wavelength agree with Lambert's law.

Another cellophane was dyed with saturated Congo Red solution at the boiling temperature until the dye content in the cellophane reached 22%. After the dichroism of this specimen was measured, the absorbed dye was stripped to 8.6% or 2.8% by dipping in 50% ethanol solution at room temperature, and the change in dichroism was measured (Table I).

TABLE I
Change in Dichroism with Varying Dye Content

Dye content, %	Dichroism	Wavelength range, $m\mu$
22.0	0.22 ₀	600-700
8.6	0.23 ₄	590-700
2.8	0.23 ₉	575-660

As the dye content of the specimen decreased the measured dichroism was somewhat higher. But the change in dichroism with varying dye contents is very small compared with that of the over-dyeing phenomenon; for example, in Figure 1 the dichroism of point *B* is 0.88 and this value is lowered to 0.19 at point *B'*.

Poly(vinyl Alcohol) Film. As mentioned above, no over-dyeing phenomenon is observed with the cellophane film, which may be due to the insufficient dye content because of its low accessibility. Therefore poly(vinyl alcohol) film was used in the expectation that the more intense dyeing may bring about the over-dyeing phenomenon.

Poly(vinyl alcohol) and Congo Red were dissolved together in water at 80°C. and the hot solution was cast into a film on a glass plate. After being dried to optimum moisture content, the film was stretched to three times its original length. The dye content was varied from 0.1 to 120%. Results are listed in Table II.

TABLE II
Change in Dichroism with Dye Content

Dye content, %	Dichroism	Wavelength range, m μ
120	0.67 ₉	625-650
50	0.66 ₀	610-650
10	0.68 ₈	595-650
3	0.75 ₆	590-650
0.3	0.74 ₂	560-600
0.1	0.73 ₈	545-600

Results are very similar to those obtained with cellophane (Table I). The six poly(vinyl alcohol) specimens were stretched to the same degree at the same time, but these specimens may show some differences in the deformation mechanism because of the high contents of dyestuff. Dichroism, nevertheless, is nearly equal over the unexpectedly wide range of dye contents.

The "over-dyeing" phenomenon is not likely to appear on film of the highest dye concentration, and the Lambert-Beer's law holds good.

DICHROISM OF FIBER AND OVER-DYEING PHENOMENON

Experimental

The principle of the apparatus used is the same as the Leitz Mikroskop-Photometer. A sodium lamp was used as the light source unless otherwise noted.

The samples used were model filaments of regenerated cellulose and poly(vinyl alcohol). The poly(vinyl alcohol) filament was made by melt spinning and was not acetalized, so its dyeing behavior was similar to that

of cellulose. The dyeing with Congo Red was carried out at room temperature as the filament was soluble in boiling water. All the model filaments were homogeneous and transparent, having no skin-core structure and containing no voids.

Results

Unlike film, reports on the dichroism of filaments always indicate the presence of an over-dyeing phenomenon, as do also our present data, even when equilibrium and homogeneous dyeing is attained by careful operation. Therefore, the possibility mentioned in the introduction of this paper, of a skin-core effect must be denied.

When a filament dyed with Congo Red is placed in hydrochloric acid vapor, it turns blue and the D_{\parallel} and D_{\perp} absorbances increase, as the blue filament absorbs yellow light more intensely than the red filament does. Therefore in Figure 1 the points A and B of the red filaments shift to A' and B' , respectively. When the filaments turn blue, the point A' still falls on the line connecting A and B , but the absorbance of B' is too high and deviates so much from the line, that the dichroism is smaller than that of A , B , and A' . The change is reversible; when the blue filaments come in contact with ammonium vapor they turn red again and the blue points A' and B' revert to the red points A and B , respectively.

TABLE III
Position on a Film and Absorbance^a

Position (distance from edge of film), mm.	Absorbance	
	D_{\parallel}	D_{\perp}
0.1	1.71	0.131
0.3	1.98	0.131
0.5	2.04	0.131
0.7	2.06	0.131
0.9	2.14	0.131
1.1	2.14	0.131
1.3	2.14	0.131

^a Film width was 4 mm.; the area examined was a circle of 0.02 mm. diameter.

A similar change can be observed when the absorbance of the same red filament is measured by using yellow and green light ($546 m\mu$). In this case the absorbance of the filament changes according to the wavelength of the light source used, the state of dye in the filament being unchanged.

These fundamental observations lead to a conclusion that the over-dyeing phenomenon is not necessarily caused by the change in orientation of the absorbed dye molecules.

A specimen of uniform film was shifted stepwise on the microscope stage and absorbance readings were repeated after each shift in position across the film. It was found that parallel absorbance increases as the observed position shifts inward from the edge and levels off at about 1 mm. from the edges, and perpendicular absorbance remains constant, as shown in Table III.

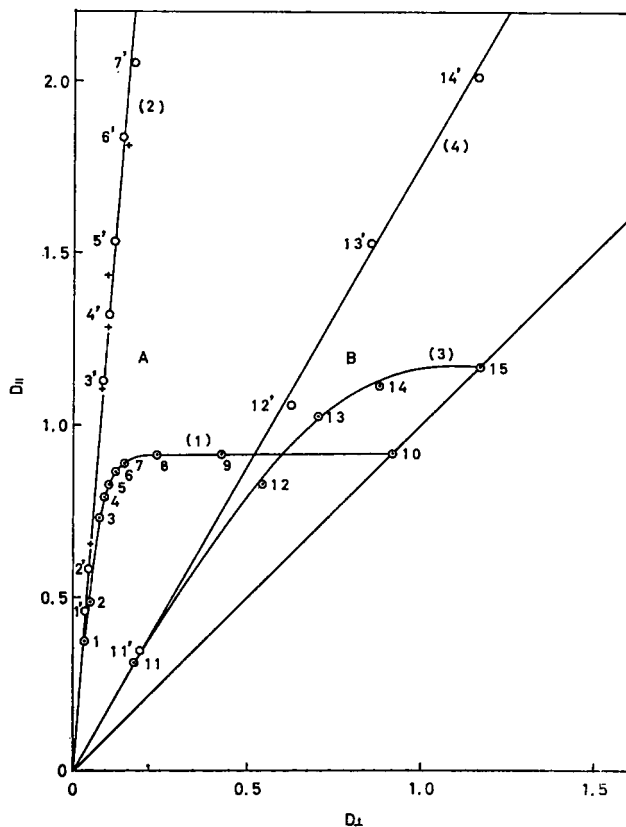


Fig. 3. Over-dyeing phenomenon of filaments: (1) cellulose (3) poly(vinyl alcohol), and the corrected relation (2) for cellulose and (4) for poly(vinyl alcohol).

These phenomena lead to the opinion that the over-dyeing may be due to the edge effect, i.e., to the incomplete cutting off of the stray light. Then eqs. (1) and (2) should be corrected as indicated by eqs. (3) and (4) respectively, where the primed quantities are corrected values and I_r is the absolute intensity of the stray light,

$$10^{-D_{||}} = I_{||} / I_0 \quad (1)$$

$$10^{-D_{\perp}} = I_{\perp} / I_0 \quad (2)$$

$$10^{-D_{||}} = (I_{||}' + I_r) / (I_0' + I_r) \quad (3)$$

$$10^{-D_{\perp}} = (I_{\perp}' + I_r) / (I_0' + I_r) \quad (4)$$

and consequently

$$(10^{-D_{\parallel}'} + \alpha)/(1 + \alpha) = 10^{-D_{\parallel}} \quad (5)$$

$$(10^{-D_{\perp}'} + \alpha)/(1 + \alpha) = 10^{-D_{\perp}} \quad (6)$$

where α is I_r/I_0' .

When the incident light is absorbed almost completely by a very deeply dyed filament, I_{\parallel}' is negligibly small compared with I_r , and the apparent value of I_{\parallel} can be taken to be equal to I_r . Therefore the true absorbances D_{\parallel}' and D_{\perp}' are obtained by eqs. (3) and (4), respectively, by subtracting I_r from I_{\parallel} and I_{\perp} .

In Figure 3, curve 1 is the relation obtained on a cellulose filament with birefringence 0.048, where the over-dyeing phenomenon can be clearly seen. D_{\parallel} of points 8, 9, and 10 level off. So this limiting I_{\parallel} can be taken as I_r . When D_{\parallel} and D_{\perp} of the points 1-7 are corrected with this I_r , the corresponding points 1'-7' fall on line (2).

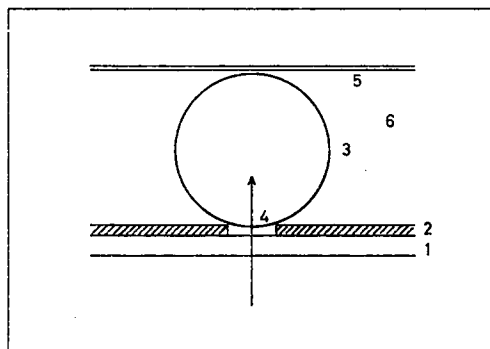


Fig. 4. A method for elimination the stray light directly: (1) deck glass; (2) silver mirror; (3) filament specimen; (4) narrow and sharp slit; (5) cover glass; (6) immersion liquid.

B is another example of a poly(vinyl alcohol) filament, where curve (3) and the straight line (4) correspond to (1) and (2), respectively. Here I_{\parallel} of point 15 on curve (3) was taken as equal to I_r , and the correction was applied. The value of α is 0.139 in the former example and 0.0718 in the latter.

By a slit method, parallel and perpendicular absorbances can be obtained directly by eliminating stray light. One side of a deck glass was coated with a silver mirror, on which a line was drawn with the sharp edge of a safety razor blade, then a narrow and sharp slit could be obtained on the deck glass. When a dyed filament is placed parallel to this line slit and a reading is made as usual, only a narrow beam of light can pass through the sample as shown in Figure 4, and stray light can be cut off by reflection; consequently, parallel and perpendicular absorbance can be measured directly. The five points indicated by the plus symbol (+) in Figure 3

were obtained by this slit method on the same filament. These lie on the same line (2) and prove the rationality of the consideration.

In Table III, perpendicular absorbance remained unchanged even when parallel absorbance increased as the readings advanced inward from the edges. This can be explained by the fact that I_r is negligibly small compared with I_{\perp}' and I_0' but is comparable with I_{\parallel}' . When the observation

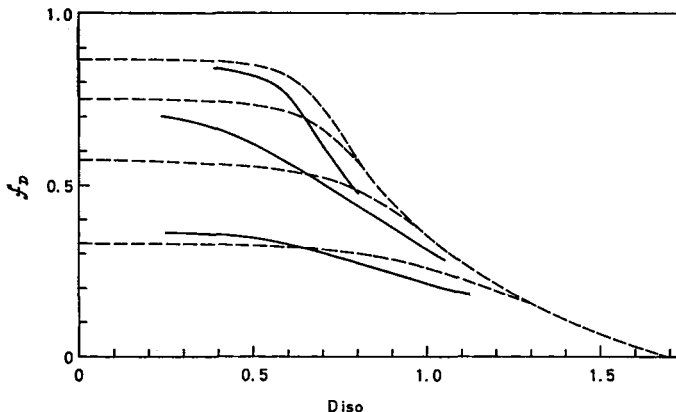


Fig. 5. Relation between apparent dichroism and dye contents: (—) Heikens' curves (---) curves calculated by eqs. (5) and (6) for $\alpha = 0.02$.

is made more than 1 mm. from the edges of a strip, I_r decreases and the edge effect vanishes.

DISCUSSION

It was verified that the over-dyeing phenomenon was due to stray light at least in the present authors' previous observation, where the determination of dichroism was, however, carried out from the slope of the linear portion of the $D_{\parallel}-D_{\perp}$ curve and the values seem to be almost equal to the correct ones.⁴

The observations of other authors also may be open to question from this standpoint, although the precise experimental conditions are not clear. For example Heikens² has shown the relation of dichroism and D_{iso} as seen in Figure 5, where D_{iso} is equal to $(D_{\parallel} + 2D_{\perp})/3$ and is used as a measure of dye content. The broken lines are the same relation calculated by the present authors by using eqs. (5) and (6), α being taken as 0.02. Heikens' curves are closely akin to the calculated ones, so the same explanation holds for his experiments.

Over-dyeing is then an apparent phenomenon. When the correct absorbance is measured, the Lambert-Beer's law holds good over the range of the possible dye contents. Therefore the orientation of the dye molecules in polymer is independent of the amount of the dye up to saturation. This suggests also that the dye molecules are held very firmly parallel to

cellulose or poly(vinyl alcohol) and perhaps unimolecularly. Of course it is shown by x-ray examination that dye crystals do not exist even in the most intensely dyed samples, i.e., those containing 120% dyestuff. The denial of the over-dyeing and the non-existence of the crystalline Congo Red in these samples may be curious in the current concept of dyeing, but the next rough consideration supports for the above opinion.

The length of a Congo Red molecule is estimated to be 27 Å. and that of a glucose residue of cellulose molecule is 5.15 Å. When Congo Red molecules are absorbed parallel to the segments of cellulose molecules, a Congo Red molecule should occupy 6 glucose units. Then the weight of the absorbed dye per 100 g. cellulose amounts to about 70 g., provided that the cellulose is 100% accessible to the dye. In our cellophane the maximum dye uptake was 22%, so the accessibility to the dye is calculated to be 31%. Taking into consideration that the water accessibility of the regenerated fibers is usually estimated to be 80–85%, this accessibility to the dye is not unreasonable. This seems to support the unimolecular absorption of dye molecules.

In the case of poly(vinyl alcohol) the unit length is 2.52 Å. and the length of a Congo Red molecule corresponds to 11 units of poly(vinyl alcohol); then the ratio of the dye to poly(vinyl alcohol) is 144:100 by weight at 100% accessibility. Considering the experimental conditions of preparing the dyed films, 100% accessibility is to be assumed. The fact that the constancy of dichroism holds good for poly(vinyl alcohol) film containing 120% dye is very significant from the above consideration.

References

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Résumé

Un dichroïsme dans le visible reflète une orientation de la région amorphe du polymère; ainsi donc le dichroïsme du polymère doit être constant indépendamment de la quantité de colorant attaché au polymère. On admet généralement toutefois que l'échantillon de fibre ne doit pas être trop fortement teinté de façon à pouvoir mesurer quantitativement le dichroïsme. Le dichroïsme de la cellulose et de l'alcool polyvinylique, colorés au moyen de rouge congo a été mesuré soigneusement et la cause de ce phénomène a été étudiée. Le phénomène de surcoloration est apparent. Lorsque l'absorbance correcte est mesurée, a loi de Lambert-Beer reste valide sur l'entier domaine des pourcentages en colorants possible. L'orientation des molécules de colorant dans polymère est indépendante de la teneur en colorant jusqu'à saturation.

Zusammenfassung

Dichroismus in Sichtbaren spiegelt die Orientierung des amorphen Bereiches von Polymeren wieder, daher sollte der Dichroismus eines Polymeren unabhängig von der Farbstoffmenge in Polymeren konstant sein. Es wird aber allgemein angenommen, dass die Faserprobe zur quantitativen Messung des Dichroismus nicht überfärbt werden

darf. Der Dichroismus von Cellulose und Polyvinylalkohol wurde bei Anfärbung mit Kongorot sorgfältig gemessen und die Ursachen dieser Erscheinung untersucht. Das "Über-Färbungs"-phänomen ist augenfällig. Bei Messung der korrekten Absorption gilt das Lambert-Beer'sche Gesetz im Bereich des möglichen Farbstoffgehaltes. Die Orientierung der Farbstoff-moleküle im Polymeren ist bis zur Sättigung vom Farbstoffgehalt unabhängig.

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