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Determination of the compensation band due to birefringence with dispersion and large phase differences

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The simple measurement of birefringence by means of a tilting compensator becomes difficult and unreliable when large phase differences must be compensated in samples in which dispersion of birefringence differs from that of the compensator. The problem is treated experimentally and theoretically. The result is a simple correction formula with only one parameter. A method to obtain this parameter is presented. Measurements on polycarbonate, polyethylene and polyurethane support the assumptions of the theoretical calculations.

1. Introduction

It is usual, to investigate the birefringence of polymeric materials in order to obtain the degree of orientation. For this purpose, a polarizing microscope and a compensator such as a Berek [1], Babinet or Ehringhaus [2] is mostly used. With monochromatic light it is impossible to identify the zero-order band, because all interference fringes are indistinguishable. A correct value of the phase difference and therefore the birefringence is only achieved with the use of the right compensation band. It is therefore customary to apply white light, because the zero-order-fringe is then nearly black. It is only exactly black when the sample and the compensator consist of the same material or if they have the same dispersion of birefringence. This condition is not fulfilled for polymeric materials and a Calcit, magnesium difluoride or quartz compensator. It is the aim of this paper to develop a theory of compensation with white light, accounting for dispersion of birefringence and the spectral sensitivity of the human eye.

2. Theory

A polarizing microscope with compensator and sample operates as follows. Parallel light, emitted by a bulb, passes a polarizer. This linear polarized light beam splits in the sample (which is oriented 45° to the polarization plane) into two equi-intensive beams propagating with different refractive indexes. Therefore an optical path difference results

$$\Gamma_s = \Delta n_s d_s \quad (1)$$

d_s is the thickness of the sample and Δn_s the birefringence. The compensator is oriented 90° to the sample therefore reducing the optical path difference by

$$\Gamma_c = \Delta n_c d_c \quad (2)$$

with Δn_c as the effective birefringence and d_e the effective thickness of the compensator plate. The excess optical path difference, OPD, of sample and compensator yields

$$\mathrm{OPD} = \Gamma_c - \Gamma_s \quad (3)$$

and the intensity of monochromatic light, I, after the analysor, which is oriented 90° to the polarisor, is then given by

$$I(\mathrm{OPD}(\lambda)) = \tfrac{1}{2} I_0(\lambda)\left[1 - \cos\left(\frac{2\pi}{\lambda}\mathrm{OPD}(\lambda)\right)\right] \quad (4)$$

With a variable compensator, the value of Γ_c can be changed and therewith the optical path difference. Equation 4 describes exactly the variation of light intensity that is seen, when turning at the compensator. It is impossible to distinguish the optical path difference zero, and an integral multiple of the wavelength. Let us now introduce the simplest dependence of birefringence on wavelength. We write for sample and compensator

$$\Delta n_{s,c}(\lambda) = \Delta n_{s,c}(\lambda_{ref}) + \alpha_{s,c}(\lambda - \lambda_{ref}) \quad (5)$$

$\alpha_{s,c}$ are the derivatives of birefringence with respect to λ at λ_{ref}, the wavelength at which we want to know the phase difference. With Equations 1 to 3 and 5 this yields

$$\mathrm{OPD}(\lambda) = \mathrm{OPD}(\lambda_{ref}) + (\lambda - \lambda_{ref})(d_c\alpha_c - d_s\alpha_s) \quad (6)$$

The argument of the cosinus function in Equation 4 is an integral multiple of 2π, when

$$d_c\alpha_c - d_s\alpha_s = n \quad (7)$$

and with the same n

$$\mathrm{OPD}(\lambda_{ref}) = n\lambda_{ref} \quad (8)$$

with n as a positive or negative integer. This result is independent of wavelength. In any of these cases the resulting intensity vanishes and the fringe, according to the conditions, is the darkest one. But this is not the zero-order fringe, because the zero-order fringe fulfills the condition

$$\mathrm{OPD}(\lambda_{ref}) = 0 \quad (9)$$

The compensation band is therefore n fringes below

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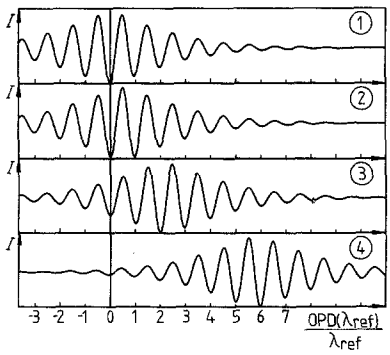

Figure 1 The dependence of subjective intensity of light on the optical path difference at $\lambda_{ref} = 546\,nm$ is numerically calculated (Equation 10) with $\lambda_{ultra} = 350\,nm$, $\lambda_{infra} = 750\,nm$, $T = 3000\,K$ and the following values of $(d_c\alpha_c - d_s\alpha_s)$: ① 0; ② 0.5; ③ 2.2; ④ 5.8. The compensation band is, in all cases, at $OPD(\lambda_{ref}) = 0$ and the darkest fringe is at $OPD(\lambda_{ref}) = [d_c\alpha_c - d_s\alpha_s]_Z\lambda_{ref}$.

the darkest fringe. This effect is called "fringe jumping" [3, 4]. Focusing on the darkest fringe yields to a "phase-difference" Γ_{dark}, which is $n\lambda_{ref}$ above the correct value $\Gamma(\lambda_{ref})$. In order to see what happens when $d_c\alpha_c - d_s\alpha_s$ is not an integral, the intensity can be calculated numerically with the aid of

$$I(OPD(\lambda_{ref})) = \int_0^\infty \varrho(\lambda, T)\,\mathrm{sens}(\lambda) \times \left(1 - \cos\left\{\frac{2\pi}{\lambda}[OPD(\lambda_{ref}) + (\lambda - \lambda_{ref})(d_c\alpha_c - d_s\alpha_s)]\right\}\right) d\lambda \quad (10)$$

$\varrho(\lambda, T)$ is the black-body intensity distribution [5]

$$\varrho(\lambda, T) = 2hc^2 \Big/ \lambda^5\left[\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right] \quad (11)$$

with T the absolute temperature, c the speed of light, h the Planck constant and k_B the Boltzmann constant and sens(λ) is a approximation for the spectral sensitivity of the human eye [6]

$$\mathrm{sens}(\lambda) = \frac{\delta^2}{[(\lambda - \lambda_{max})^2 + \delta]^2} \quad (12)$$

with $\lambda_{max} = 555\,nm$ and $\delta = 4000\,nm^2$. The intensity integral in Equation 10 was computed from the lower limit λ_{ultra} to the upper limit λ_{infra} only, because the other wavelengths do not contribute due to the sensitivity of the human eye. The results are drawn in Fig. 1.

With thin samples the factor $d_c\alpha_c - d_s\alpha_s$ is very small in comparison to unity and therefore the darkest band is the zero-order fringe. When, on the other hand, α_c and α_s are equal or nearly equal, this factor is also very small and the darkest band and compensation band are identical. But when the samples, and therefore the compensation plate, are thicker and have a different dispersion of birefringence, the factor $d_c\alpha_c - d_s\alpha_s$ increases. When it is equal to 0.5 there are two fringes in the interference pattern, both considered to have the same darkness. If the factor is in the range between 0.5 and 1.5, the darkest fringe is one order above the compensation band, etc. (see Fig. 1).

The phase difference can therefore be calculated according to

$$\Gamma(\lambda_{ref}) = \Gamma_{dark} - [d_c\alpha_c - d_s\alpha_s]_Z\lambda_{ref} \quad (13)$$

with the square bracket defined as

$$[x]_Z \equiv \text{integral number next to } x \quad (14)$$

For simplicity we can introduce

$$d_c \propto \Gamma_{dark}; \quad \text{and} \quad d_s \propto \Gamma_{dark} \quad (15)$$

This is a reasonable assumption, because a sample twice as thick needs a compensator with twice the effective thickness. Therefore, the results of measurements, focusing on the darkest fringe, yield twice the "phase difference". Thus Equation 13 yields

$$\Gamma(\lambda_{ref}) = \Gamma_{dark} - \left[\frac{\Gamma_{dark}}{\Gamma_{c,s}}\right]_Z \lambda_{ref} \quad (16)$$

where $\Gamma_{c,s}$ is a constant which depends on the material of the compensator and the sample.

$\Gamma_{c,s}$ can be measured using the following method. The thickness of the sample is increased until two "equi-dark" fringes are observed for the first time. In this state the term in the square brackets in Equation 16 is equal to 0.5 and therefore

$$\Gamma_{c,s} = 2\Gamma_{dark} \quad (17)$$

To obtain greater accuracy of the value of $\Gamma_{c,s}$ the thickness can be increased until there are two "equi-dark" fringes again and the term in the square brackets is equal to 1.5, 2.5, 3.5, . . . , etc. Once the value of the correction constant $\Gamma_{c,s}$ for a combination of compensator and sample is determined, further measurements can be obtained with this combination by using Equation 16.

3. Experiments

In polymers there exists an easier way to increase the path difference continuously. During stretching the polymer molecules become oriented and therefore birefringence occurs, increasing with the strain [7].

Samples of polycarbonate of bisphenol A (Macrolon 2304), low-density polyethylene (LDPE 1810) and polyurethane (chemical components and their weight fractions: polyethylene-adipate ($M \simeq 2000$): diphenylmethane-4,4′di-isocyanate: 1,4 butanediol = 1 : 8.45 : 7.22; 57.7% hard segments) are stretched under a microscope (Leitz Orthoplan Pol). The phase difference is measured simultaneously with a compensator after Berek [1] (Leitz 1054 K, Calcit). This compensator has a maximum phase difference of about 18 000 nm (33 orders). Larger phase differences have been compensated with additional quartz plates (11 000 nm, 20 orders; 23 000 nm, 42 orders). The dispersion of birefringence of Calcit and quartz is nearly the same. The number of fringe jumps is measured dependent on the phase difference of the darkest fringe. The results are drawn in Fig. 2.

Fringe jumping was observed up to a difference of ten orders (polycarbonate) between the compensation band and the darkest fringe.

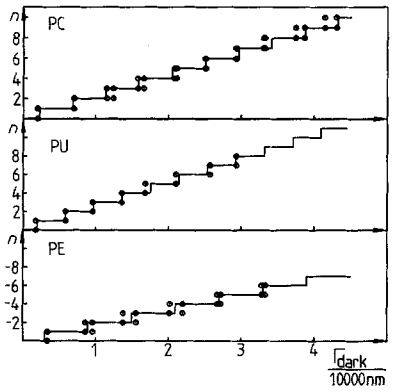

Figure 2 The dependence of the number of fringe jumps on Γ_{dark} for polycarbonate (PC), polyurethane (PU) and polyethylene (PE). (●) Experimentally observed jumps at several samples from the lower to the upper point, (——) calculated using Equation 16 and the parameters listed in Table I. $\Gamma_{C,PE}$ is negative and so therefore is the value of Γ_{dark} below $\Gamma(\lambda_{ref})$.

4. Results and discussion

From the plots in Fig. 2 one can calculate the compensator–sample specific constant $\Gamma_{c,s}$. The results are given in Table I. The observed jumps (Fig. 2) are fairly well reproduced by the calculations (Equation 16).

On first sight it seems to be better to measure the point where both fringes are "equi-dark" with an objective method, such as a photosensitive device. But this is not the usual method of obtaining the phase differences. Furthermore, the spectral sensitivity of the human eye may differ from that of the photosensitive device and therefore different correction constants are observed. This advantage compensates the subjectiveness of the measurements with the eye.

With the developed method there need be no knowledge of the dispersion of birefringence in order to measure the birefringence. Other methods need this information to calculate the fringe jumps [8] or count the order of interference from the end of a wedge-shaped sample [9].

TABLE I Correction constants for polycarbonate (PC), polyurethane (PU), polyethylene (PE) and a Calcit (C) compensator

$\Gamma_{C,PC}$	+4550 nm
$\Gamma_{C,PU}$	+3900 nm
$\Gamma_{C,PE}$	−6000 nm

The assumption of a linear dispersion of birefringence dependent on the wavelength is not critical, because of the broad spectral sensitivity of the human eye and the average linear dispersion of birefringence. There is a good agreement between the experimental results and calculations.

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