

Strain-optical behavior of polyethylene terephthalate film during uniaxial stretching investigated by Mueller matrix ellipsometry



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ABSTRACT

Polyethylene terephthalate (PET) has gained widespread applications in various flexible devices where its optical properties after drawing process in manufacturing play a great importance in the performance of devices. In this work, the strain-optical behavior of pre-oriented polyethylene terephthalate (PET) film during uniaxial stretching is studied utilizing a proposed anisotropic model and Mueller matrix ellipsometry (MME). In the biaxial anisotropic model, the molecular chain orientation is correlated to the change of refractive indices and strain-induced birefringence, while the rotation of molecular chains is directly characterized by the rotation of principal optical axis. According to this model, the refractive indices, extinction coefficients and Euler angles extracted from measured Mueller matrix spectra can be used to interpret the micro-structural response of PET. A set of tensile tests have been carried out, with loading direction being varied. The results show that the strain-induced birefringence is linearly correlated to strain, while loading direction significantly affects the slope of achieved birefringence-strain curve. Meanwhile, the birefringence exhibits a positive linear relation with the orientation estimated by extinction coefficients. Through the analysis of the Euler angle ϕ_E , the principal optical axis rotating towards the tensile direction is accurately observed. Our results show that MME can provide a deep and systematic understanding of strain-optical behavior which can give accurate control of the optical properties of polymer films during deformation.

1. Introduction

Polyethylene terephthalate (PET), a widely used polymeric material, serves as a common flexible substrate in functional devices as the substitute for conventional rigid substrates due to its exclusive advantages such as flexibility, transparency and low weight [1,2]. During the manufacturing process, the PET film typically undergoes a stretching process to achieve the necessary thickness and enhance the mechanical and optical properties. Often, the film is uniaxially stretched in machine direction (MD) and then in transverse direction (TD). The stretching procedure results in the preferential rearrangement of the molecular

chains towards the stretching directions, thus leading to the anisotropy in mechanical and optical properties [3,4]. The anisotropic optical characteristics play a great role on the performances of flexible devices, such as organic light emitting diode (OLED) [5–7], polymeric liquid crystal display (LCD) [8,9] and solar cell devices [10]. For instance, the electroluminescence quantum efficiency in polymeric OLEDs depends strongly on the refractive indices and birefringence [11,12] and the in-plane birefringence of polymeric film alters polarization state of the emitted light [13,14]. Furthermore, considering the scenarios of flexible devices usages, loading conditions including stretching and bending, are usually applied. Therefore, understanding the relationship between

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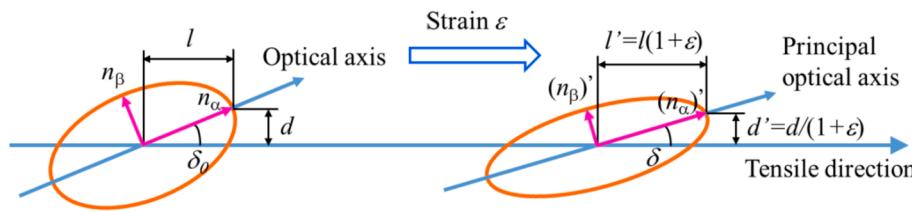


Fig. 1. The evolution of the refractive ellipsoid in 2D plane during uniaxial stretching. n_α and n_β represent the principal refractive indices in sample plane.

mechanical and optical properties is a critical issue for controlling the mechanical and optical properties of the PET films to ensure optimal performance in its applications. The strain-optical behavior, which contains the refractive indices, birefringence, molecular orientation and optical axis during deformation, can give a systemic comprehension to that issue.

Great efforts have been made to reveal the optical properties of the PET film using different methods, such as FTIR spectrometer [15], UV spectrometer [16], polarized Raman spectroscopy [17], conoscopy [18] and Abbe refractometer [19]. Utilizing these methods, the correlation between strain, stress and birefringence of loaded PET films have been intensively investigated. As early as 1942, the classical stress-strain-birefringence behavior of a rubber was originally interpreted on the basis of Gaussian distribution by Kuhn and Grün [20]. After that, extensive work has been done to further investigate such a behavior of PET in more detail. For instance, the relation between molecular orientation and birefringence in PET and PEN fibers was revealed utilizing polarized Raman spectroscopy [17]. Using the conoscopy, the birefringence and optical orientation of biaxial stretched PET and PEN films were measured [18]. The mechanical and optical anisotropy and the polymer molecular orientation in PET fibers with a range of drawn ratios using an interference microscope were investigated [21–24]. The stress-optical and strain-stress behavior of a drawn PET was demonstrated by a Monte-Carlo approach based model and the experimental studies with the help of Abbe refractometer and infra-red spectroscopy [25]. The real-time true stress-strain-birefringence behavior of PET film in rubbery state during biaxial stretching and relaxation was investigated by self-designed equipment [26,27], integrating polarized white light and optical spectrometer [28]. These techniques provide intuitive measurements to determine the birefringence or refractive indices and orientation of polymer films, which are of primary importance not only in their practical applications, but also in their large area molding process. However, most of the research was mainly focused on the strain-stress-birefringence behavior of PET films based on the assumption of initially isotropic properties. The commonly pre-oriented PET films which exhibit more anisotropic characteristics undergoing deformation are rarely investigated.

Spectroscopic ellipsometry (SE) is an optical metrology technique, which uses polarized light to characterize the optical constants of both layered and bulk materials, has been applied to characterize the polymer films [29–31], including PET films [32–35] due to its advantages such as broad spectral range, high precision, and no destruction. Compared with conventional SE that can only acquire two ellipsometric parameters, Mueller matrix ellipsometer (MME) can provide all 16 elements of the 4×4 Mueller matrix. Consequently, MME exhibits superior capability on the characterization of anisotropic materials due to the rich information acquired [36]. Therefore, the MME has been successfully employed to characterize the polymer films which often exhibit distinct optical anisotropy [37–39].

In this work, with the high precision MME, the strain-optical behavior of the pre-oriented PET film during uniaxial deformation is investigated when the tensile loading is applied in different directions. The principal optical constants in different directions and the Euler angles (ϕ_E) are extracted from the measured Mueller matrix spectra using the 4×4 matrix method based on a biaxially anisotropic model.

Corresponding to the deformation of the molecules during uniaxial stretching, the strain-optical behavior of pre-oriented PET film can be mainly divided into two phenomena, namely, the strain-induced birefringence and the rotation of the principal optical axis. The effects of the strain on the refractive indices and birefringence in plane are discussed when the film is stretched in different directions. A linear relation between the birefringence and the orientation of molecular chains defined with the extinction coefficients is revealed during different-direction stretching. Characterized by ϕ_E , the rotation angle of the optical axis towards the tensile direction is quantitatively determined.

2. Theoretical model

Frequently, the PET films are biaxially stretched during the fabrication with different ratios of biaxial tension to get designed physical properties and thickness. When a tensile loading is applied, more molecular chains will also orient along the tensile direction with the strain increasing [40]. For the smaller drawing ratio in machine direction (MD) than that in transverse direction (TD), the orientation degree of molecular chains in TD is higher than that in MD, leading to the inherent anisotropy in PET films. While, due to the existence of shear stress, the principal optical axis may do not completely coincide with TD during the biaxial stretching process, which has also been mentioned in the literatures [18,40].

When the PET film is subjected to a uniaxial stretching after biaxial stretching, the molecules, already oriented in different direction, are further deformed by the uniaxial tension, and the orientation in the tensile direction increases, while decreases in perpendicular direction. Thus, the refractive indices in different directions change accordingly and the orientation degree of the PET film is also affected. Besides, due to the deviation between the tensile axis and the direction of molecules, the chains gradually rotate towards the tensile direction under the shear stress.

In polymer films, their optical properties are highly affected by the orientation of molecular chains. For the PET film, after biaxially stretched, can be regarded as biaxially optical material with its principal optical axes lie in the sample plane and perpendicular to the plane. During uniaxial stretching, the deformation of molecular chains in plane can be characterized by the evolution of the refractive ellipsoid in 2D plane, as shown in Fig. 1. The optical behavior under the uniaxial stretching can be divided into two effects: (1) the variations of the refractive indices and birefringence, which are attributed to the orientation of molecular chains; (2) the change of the principal optical axis coinciding with the rotation of molecular chains due to the uniaxial tension.

The orientation of polymer films varies with the motion of molecular chains when tensile loading is applied. The mechanical orientation function factors $\langle P_2(\cos \theta) \rangle$ and $\langle P_4(\cos \theta) \rangle$, only the function of drawn ratio, are usually adopted by most of the researchers to characterize the orientation of molecular chains during uniaxial stretching [41–43]. Though these factors can give the accurate description of orientation, the polymer films have to be initially assumed amorphous and isotropic. Therefore, it is insufficient to estimate the orientation degree of pre-oriented films which can exhibit noticeable anisotropy by the orientation function factors. Benefit from the directly measured

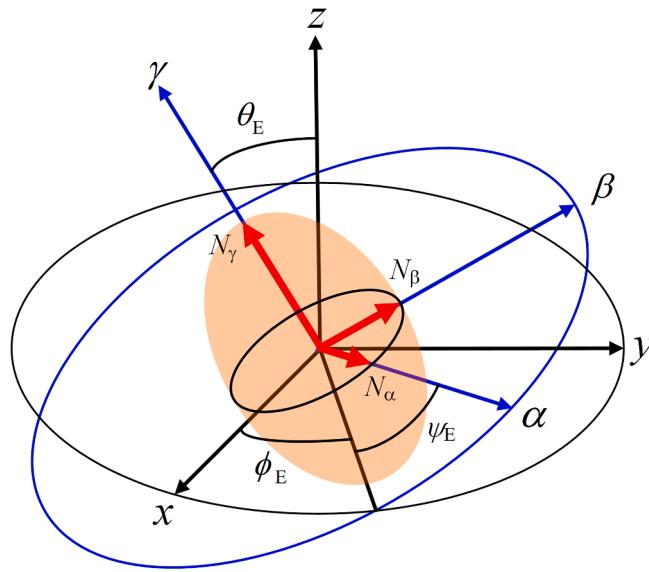


Fig. 2. Definition of the Euler angles (ϕ_E , θ_E , ψ_E) for uniaxial anisotropic materials in the laboratory coordinate system (x , y , z).

extinction coefficients using MME, the orientation of polymer film can be quantified using an orientation parameter S , which is defined as [44, 45].

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \frac{k_e - k_o}{k_e + 2k_o}, \quad (1)$$

where θ is the angle between the molecular long axis and the extraordinary axis and $\langle \cdot \rangle$ indicates the ensemble average, k_e and k_o are the

$$B = \begin{pmatrix} \cos\phi_E \cos\psi_E & -\cos\phi_E \sin\psi_E & \sin\phi_E \sin\psi_E \\ \sin\phi_E \cos\psi_E & -\sin\phi_E \sin\psi_E & -\cos\phi_E \sin\psi_E \\ \sin\theta_E \sin\psi_E & \sin\theta_E \cos\psi_E & \cos\theta_E \end{pmatrix}.$$

extraordinary and ordinary extinction coefficients at the peak wavelength, respectively. $S = 1$ means the molecules are completely parallel to extraordinary axis; $S = 0$ means the molecules are randomly orientated; and $S = -0.5$ means the molecules are completely parallel to ordinary axis.

Given that the optical axis is coincident with the main molecular chain, the azimuth of the principal optical axis along the direction of larger refractive index can be roughly predicted according to the rotation of the molecular chains under uniaxial deformation. As shown in Fig. 1, the in-plane optical axis will rotate towards the tensile direction which leads to smaller angles $\delta' < \delta$. The volume of the PET film is assumed a constant ($\mathbf{l}' \bullet \mathbf{d}' \bullet \mathbf{t}' = \mathbf{l} \bullet \mathbf{d} \bullet \mathbf{t}$) where t is the thickness of the PET film. If one can assume that $t' \approx t$, the angle δ' with the strain ϵ can be calculated as

$$\delta' = \tan^{-1} \left[\tan \delta_0 / (1 + \epsilon)^2 \right]. \quad (2)$$

3. Method

Since ellipsometry is an indirect metrology, appropriate models must be constructed to describe the optical properties of samples. According to the theoretical model, the investigated PET films can be regarded as an anisotropic material, more specifically, biaxially optical material with its principal optical axis parallel and perpendicular to the sample

plane which has been reported in the literatures [15,32,38]. Simply described by the principal dielectric constants, the dielectric tensors of the studied PET film can be simplified and expressed as

$$e_{\text{Die}} = \begin{pmatrix} e_\alpha & 0 & 0 \\ 0 & e_\beta & 0 \\ 0 & 0 & e_\gamma \end{pmatrix} = \begin{pmatrix} N_\alpha^2 & 0 & 0 \\ 0 & N_\beta^2 & 0 \\ 0 & 0 & N_\gamma^2 \end{pmatrix}, \quad (3)$$

where $(e_\alpha, e_\beta, e_\gamma)$ refer to the principal dielectric constants. $e_{\text{Die}} = e_1 + ie_2$ and $N = n + ik$ represent the dielectric function and complex refractive index, respectively. e_1 and e_2 are the real part and imaginary part of the dielectric function, n and k are the refractive index and extinction coefficient and can be solved from the dielectric functions according to the following equations

$$n = \left\{ \left[e_1 + (e_1^2 + e_2^2)^{1/2} \right] / 2 \right\}^{1/2}, \quad (4)$$

$$k = \left\{ \left[-e_1 + (e_1^2 + e_2^2)^{1/2} \right] / 2 \right\}^{1/2}. \quad (5)$$

Mathematically, anisotropy is generally described by a principal axes of index ellipsoid coincide with the (α, β, γ) coordinates. However, the principal axes are not necessarily parallel to the (x, y, z) coordinates, which are called the laboratory coordinates basically defining the coordinate system of ellipsometric measurement. Under this condition, it is algebraically practicable to express the dielectric tensor with a general rotation transformation from the (x, y, z) coordinates to the (α, β, γ) coordinates using the Euler angles $(\phi_E, \theta_E, \psi_E)$ depicted in Fig. 2. The optical properties of the PET films are represented, in the principal axis system, by three principal indexes $(N_\alpha, N_\beta, N_\gamma)$. Without loss of generality, the rotation transformation from the (α, β, γ) coordinates to the (x, y, z) coordinates is represented by a matrix B . Thus, the rotation matrix B can be obtained

$$\begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix} = B \begin{pmatrix} e_\alpha & 0 & 0 \\ 0 & e_\beta & 0 \\ 0 & 0 & e_\gamma \end{pmatrix} B^{-1}, \quad (7)$$

Through the introduction of rotation matrix B , the dielectric tensor in the (x, y, z) coordinate system can be obtained as follows

$$\begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix} = B \begin{pmatrix} N_\alpha^2 & 0 & 0 \\ 0 & N_\beta^2 & 0 \\ 0 & 0 & N_\gamma^2 \end{pmatrix} B^{-1}, \quad (7)$$

where B^{-1} is the inverse transformation matrix of B .

Since the principal optical axis highly coincident with the main chain segments orientation, are perpendicular and parallel to the sample plane, and the optical axis in plane is not completely collinear with TD, the Euler angle ϕ_E which shows the position of the optical axis can be set as a fitted parameter while the other two Euler angles are set to be constant values, $\theta_E = 0^\circ$, $\psi_E = 0^\circ$. Based on the established optical model, the complex optical constants $(n_\alpha, n_\beta, n_\gamma, k_\alpha, k_\beta, k_\gamma)$ and Euler angle (ϕ_E) of the investigated PET film can be determined from the best-fitted Mueller matrix spectra by Levenberg-Marquardt algorithm using the 4×4 matrix method [46,47].

4. Experimental procedures

4.1. Material

The studied PET films were manufactured by DuPont Teijin Films

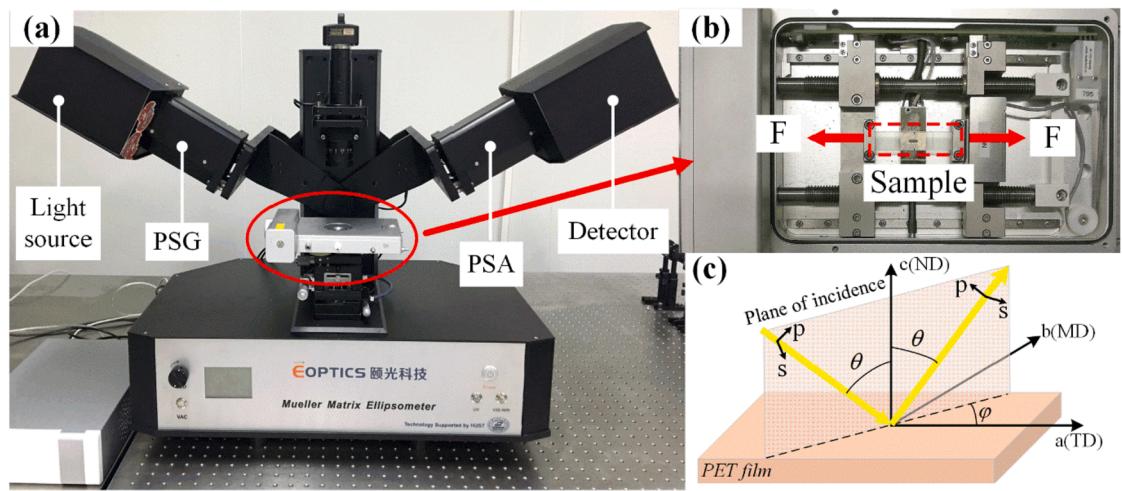


Fig. 3. Schematic diagram of experimental setup. (a) Photograph of the experimental setup in the MME configuration; (b) specimens uniaxial stretching device; (c) principle of ellipsometry for PET film in reflective mode.

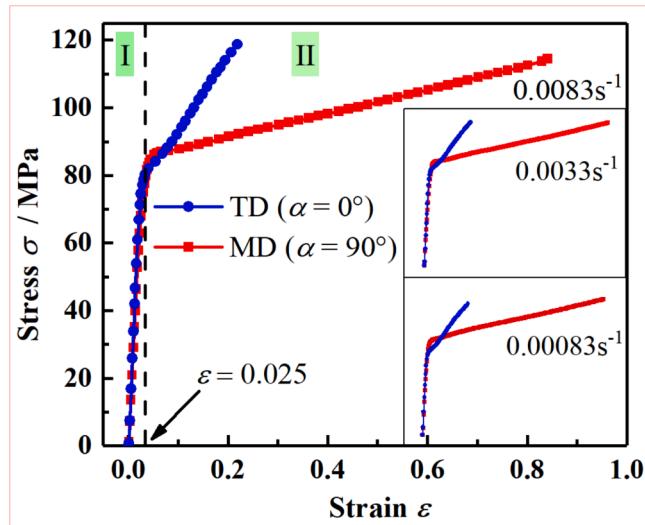


Fig. 4. Mechanical properties of uniaxial stretched PET films in TD and MD, respectively.

and had a biaxially pre-stretching process with a thickness of 170 μm . The initial draw ratios in MD and TD are $\lambda_{\text{MD}} = 3$ and $\lambda_{\text{TD}} = 3.6$, respectively. They are semi-crystalline films and their density is $\rho = 1.38 \text{ g/cm}^3$. The glass transition temperature T_g is around 120 $^\circ\text{C}$ and the melting temperature is $T_m = 255 \text{ }^\circ\text{C}$ measured by differential scanning calorimetry. The crystallinity ratio is calculated $\chi_c = 0.34$, where the heat of fusion of 100% crystalline PET was taken as 120 J/g [27,48].

4.2. Stretching process

The specimens were cut into strip shapes with a length of 53 mm and a width of 10 mm. The long side has an angle to the direction of TD, which is defined as the stretching angle α , and the angle varied from 0° (TD) to 90° (MD) with an increment of 15°. With a maximum limitation of 200 N, the PET films were uniaxial stretched at room temperature, 23 $^\circ\text{C}$ approximately, using Tensile Stress Testing Stage (TST350, Linkam, UK). The effective drawing length is 40 mm and the tension was applied parallel to the long side. All specimens were stretched at the rate of 0.0083 s^{-1} (20 mm/min).

The tensile forces were recorded in real time during the stretching.

The engineering stress and strain were defined by the following equations

$$\sigma = F/S_0, \quad (8)$$

$$\varepsilon = (l - l_0)/l_0, \quad (9)$$

where F and l are the recorded tensile force and length in real time, S_0 and l_0 are the initial cross section area and length, respectively.

4.3. Mueller matrix ellipsometry characterization

Fig. 3a and **Fig. 3b** show the whole experimental setup configuration. The Muller matrix spectra of the specimens were measured at different strains by a dual-rotating compensator MME (ME-L, Wuhan Eoptics Technology Co., Wuhan, China), over the wavelength of 200–1000 nm. **Fig. 3c** shows the principle of ellipsometry for PET film in reflective mode. The incident angle θ of polarized light is chosen as 50°, 55° and 60°. The azimuth angle φ between the incident plane and the direction of TD was maintained at 45° for the highest measurement sensitivity. In order to eliminate the contribution of the back reflection, the backside of the PET films were fully roughed in which case no back interface would occur in measured spectra.

5. Results and discussion

5.1. Mechanical behavior

The mechanical behaviors of the PET films are depicted in **Fig. 4** when tensile loadings in directions of TD and MD are applied, respectively. The mechanical response consists of two regions: I - the elastic region and II - the plastic region. Ranging from $\varepsilon = 0$ to $\varepsilon = 0.025$, the elastic region holds a coincident linear shape no matter in which direction the tension imposed. The Young's modulus was calculated at 2777 MPa approximately and the yielding point was measured about 86 MPa. The plastic region in both directions shows a strain hardening process and less sharp linear shape than that in the elastic region. The mechanical anisotropy becomes noticeable in plastic domain. This phenomenon is created by the more orderly rearrangement of molecular chains in TD than that in MD. When the chain is stretched, the molecular arrangement is packed more closely in TD. Thus, mutual attraction between chains becomes larger. As a result, larger tensile stress is required to achieve the slippage and disentanglement of chains since more non-covalent interactions need to be disrupted [49]. In addition, the mechanical properties of the other two stretching rates 0.0033 s^{-1} and

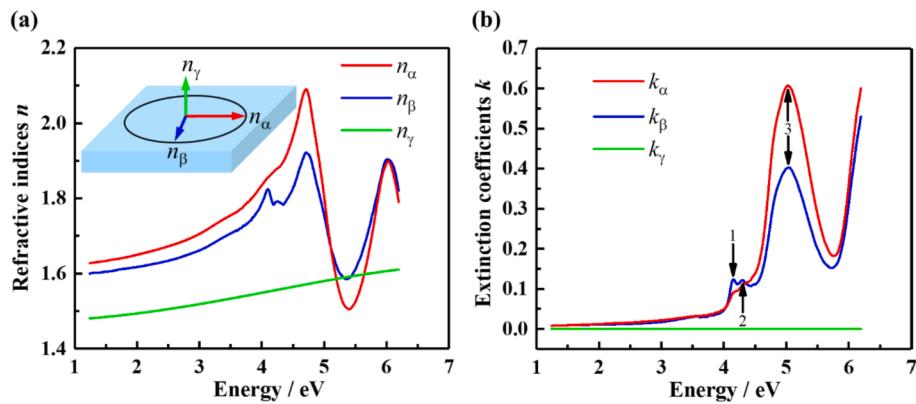


Fig. 5. Optical constants of undrawn PET film: (a) in-plane refractive indices n_α and n_β and out-of-plane refractive index n_γ ; (b) in-plane extinction coefficients k_α and k_β and out-of-plane extinction coefficient k_γ .

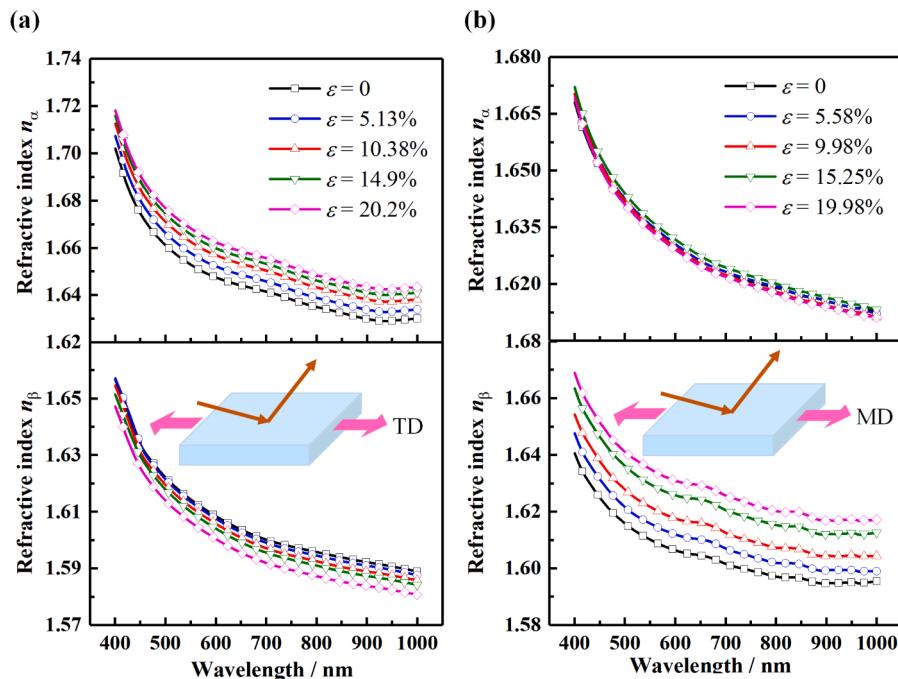


Fig. 6. The effects of strain on the in-plane refractive indices when stretched in (a) TD and (b) MD.

0.00083 s^{-1} are also shown. It can be seen that the stress-strain curves are similar which indicates the same deformation mechanisms of microstructure at different stretching rates. Therefore, the following results are based on the drawing rate of 0.0083 s^{-1} , but for other different drawing rates they are also considered to be valid.

5.2. Optical properties of original PET film

Fig. 5 presents the complex optical constants of the original undrawn PET film under the principal directions of the optical anisotropy. It can be observed from **Fig. 5a** that the out-of-plane refractive index n_γ is significantly less than the in-plane refractive indices over the most spectra due to phenylalanine's group preferential alignment in the sample plane. The in-plane anisotropy is also evidently since the refractive index n_α is larger than n_β . This in-plane anisotropy is attributed to the preferential alignment of chain segments in the biaxially stretching process during manufacturing. The in-plane refractive indices change dramatically in the ultraviolet region while keep gentle in the visible and near-infrared regions. The out-of-plane refractive index has a

gradual increment with photon energy increasing. Furthermore, the obtained Euler angle ϕ_E is not equal to zero, which indicates that the optical axis deviates from TD. As illustrated in **Fig. 5b**, the values of the extinction coefficients in plane are considerable in ultraviolet region and close to zero in visible and near-infrared regions, while extinction coefficient out of plane always keeps zero, indicating no absorption of light. Similar to the results reported in literatures [33,50,51], three significant absorption peaks (numbered as 1, 2 and 3 and corresponding to 4.15 eV , 4.30 eV , and 5.03 eV respectively) in the extinction coefficient k_β are observed. The main peak 3 can be attributed to the spin-allowed, orbitally-forbidden $^1A_{1g}\rightarrow ^1B_{1u}$ electronic transition ($\pi\rightarrow\pi^*$ transition) in molecular orbitals of benzene rings [16]. Peaks 1 and 2 can be attributed to the electronic transition of the nonbonded electron of the carbonyl O atom ($n\rightarrow\pi^*$ transition). It can be obviously seen that both the in-plane extinction coefficients have the absorption peak 3, while peaks 1 and 2 have vanished in the curve of k_α .

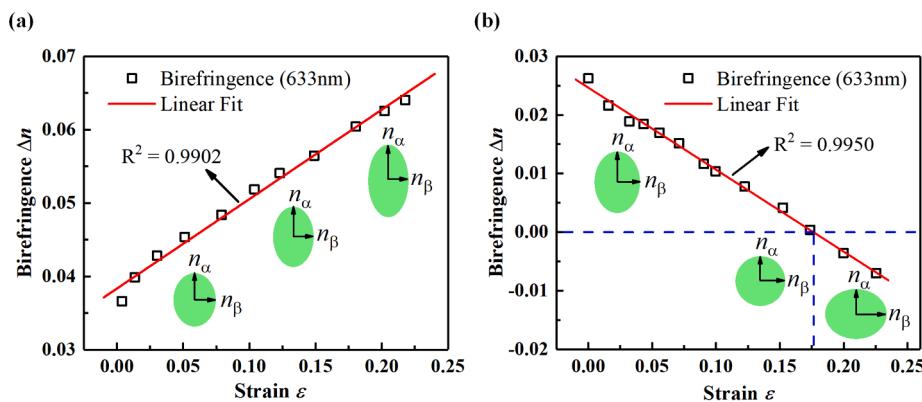


Fig. 7. The in-plane birefringence of the uniaxial stretched PET film as a function of the strain. The PET films were uniaxial stretched in (a) TD and (b) MD respectively.

5.3. Refractive indices during stretching

During uniaxial stretching, the molecular chains will orient towards the tensile direction, leading to changes in the refractive indices. In this work, since the investigated PET films have been biaxially stretched, the molecular chains are mainly lying in-plane. In this respect, uniaxial tension has little effect on the structure of the molecular chains in out-of-plane direction. Thus, the out-of-plane optical constants are assumed to be invariant and only in-plane optical properties varying with uniaxial loadings are discussed.

Fig. 6 shows the effects of uniaxial strain on the in-plane refractive indices of the PET films when stretched in TD and MD, respectively. As shown in Fig. 6a, when the PET film was stretched in TD, the refractive index n_{α} , which is closer to TD, also the tensile direction, increases significantly with the increase of strain, while the refractive index n_{β} , approaching the direction perpendicular to the tensile direction, changes little. When stretched in MD, the refractive index n_{α} is significantly increased, and refractive index n_{β} is basically invariant, as depicted in Fig. 6b. The effect of uniaxial strain on the refractive indices during TD stretching is just the opposite of that during MD stretching. Therefore, it can be concluded that the refractive index approaching the tensile direction increases with the strain increasing, while the refractive index in perpendicular direction hardly changes. The refractive indices corresponding to the uniaxial stretching can be related to the orientation of molecular chains. For polymeric materials, the refractive index is highly depended on molecular polarizability and a molecular chain has an anisotropic polarizability from its asymmetric chemical structure. When a uniaxial tension is applied, chains extend and orient towards the tensile direction by stress, while chains in the perpendicular direction are less affected since less stress occurs in this direction. According, polarizability becomes larger in tensile direction and hardly changes in the perpendicular direction, and thus the refractive indices show consistent changes with molecular polarizability [52].

5.4. Strain-induced birefringence

The phenomenon that the refractive indices are different in different directions is called birefringence, and the in-plane birefringence of the PET films can be defined by the difference between n_{α} and n_{β} as

$$\Delta n = n_{\alpha} - n_{\beta}, \quad (10)$$

Fig. 7 shows the birefringence (wavelength at 633 nm was chosen) of the uniaxial stretched PET film as a function of the strain. It can be observed that the birefringence is distinct even though no deformation occurred. The original birefringence is mainly depends on the orderly orientation of amorphous and crystalline chains along stretching direction during manufacture, which is also known as orientation birefringence [53]. The experimental data is well consistent with the linear

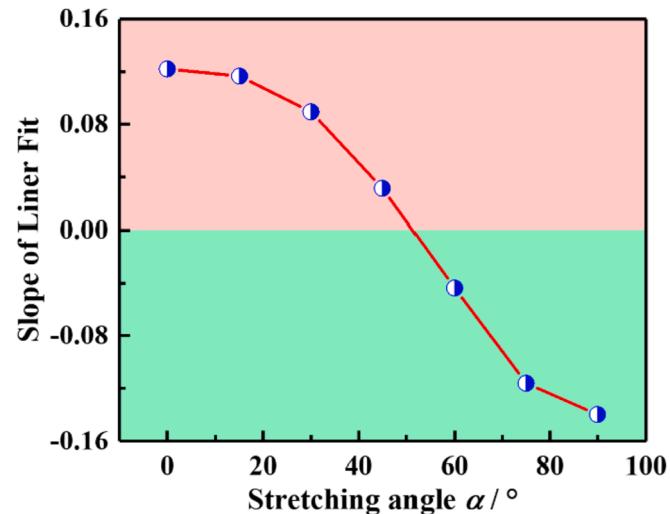


Fig. 8. The slopes of fitted curve between the birefringence and strain as a function of the stretching angle α .

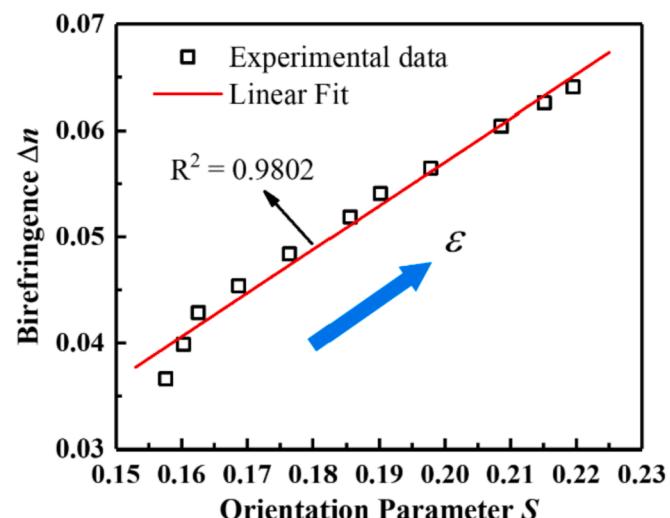


Fig. 9. The relation between the birefringence and orientation parameter during uniaxial stretching at $\alpha = 0^{\circ}$.

Table 1

Results of the linear fits for the curves of the birefringence and orientation parameter stretched at different stretching angles.

Stretching angle $\alpha(^{\circ})$	0	15	30	45	60	75	90
Fitting model	$y = k^*x + b$						
Slope	$k > 0$						
R^2	0.9802	0.9969	0.9713	0.9693	0.9808	0.9989	0.9862

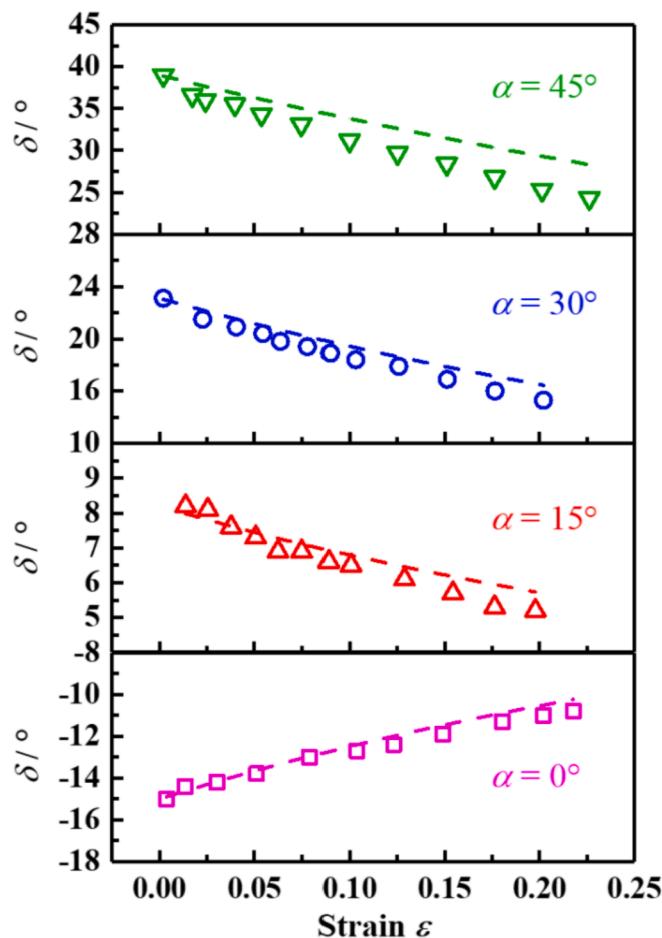


Fig. 10. The angle δ between the optical axis and the tensile direction during uniaxial stretching. The shapes (\square , \triangle , \circ , ∇) represent measured data obtained from the Euler angle ϕ_E and the dotted lines are theoretical calculations based on Eq. (2).

fit with the coefficient of determination $R^2 > 0.99$, indicating that the birefringence varies linearly with strain both in TD and MD. As illustrated in Fig. 7a, birefringence always increases with the strain when tensile loading is applied in TD. This can be explained by the continuous increase of n_o and little change of n_β , as exhibited by the refractive index ellipsoid in 2D plane.

On the contrary, the value of the birefringence always decreases with the strain increasing in MD, as shown in Fig. 7b. The magnitude of the birefringence decreases linearly as strain increasing. For the strain ϵ up to 0.18, the birefringence is equal to zero which means the isotropy in optical properties. When the strain ϵ exceeds 0.18, the birefringence turns to the increasing trend again but the value is negative since n_β is larger than n_o .

Also, the effects of other loading directions on the birefringence are considered. Good linear relationship between birefringence and loading strain has been achieved, and the slopes of fitted curve are shown in Fig. 8. It can be also noticed that the slopes of the fitted curve are positive when $\alpha \leq 45^{\circ}$, while the slopes become negative when $\alpha > 45^{\circ}$.

Furthermore, the effect of the strain on birefringence is more significant when α is closed to 0° or 90° while the effect is the smallest at $\alpha = 45^{\circ}$ according to the absolute value of the slope.

With the help of tension, molecules and lamellae will move and orient towards the tensile direction, thus, the orientation degree of polymer films is controlled by the strain. In fact, the birefringence, in polymer films, is directly related to the orientation degree. Fig. 9 shows the relationship between the measured birefringence and the calculated orientation parameter based on Eq. (1) during uniaxial stretching at $\alpha = 0^{\circ}$. As can be seen, the degree of orientation increases with strain increasing which states that more chain segments are oriented along the in-plane optical axis. Moreover, a good linear relationship between the birefringence and orientation can be observed. When the loading direction is varied, the more results of the fitted curves are listed in Table 1. Similarly, good positive linear correlations between the birefringence and orientation have been observed in all the test cases. The relation shown in Table 1 demonstrates that the birefringence can be an excellent indirect measure of average orientation of the pre-oriented polymer films, even stretching takes place in different direction.

5.5. Rotation of principal optical axis

According to the anisotropic optical model, the principal optical axis position of the PET film can be determined by the Euler angle ϕ_E . Fig. 10 shows the angle δ between the principal optical axis and tensile direction under uniaxial deformation when loading direction is varied ($\alpha \leq 45^{\circ}$). The measured δ is obtained by subtracting the azimuth angle φ from the extracted Euler angle ϕ_E . It can be seen that the theoretical calculations agree well with the experimental measurements. As the strain increases, the absolute value of δ decreases, indicating that the optical axis is turning toward the tensile direction. For the larger initial angle δ between the tensile direction and the optical axis, the optical axis rotates more remarkably with strain. When the stretching angle $\alpha = 0^{\circ}$, the angle δ shows negative values, while δ turns to positive values at $\alpha \geq 15^{\circ}$. This result means that the optical axis is located in plane between $\alpha = 0^{\circ}$ and $\alpha = 15^{\circ}$.

6. Conclusions

MME was introduced to study the strain-optical behavior of pre-oriented PET film during uniaxial stretching at different directions. The refractive indices, extinction coefficients as well as the Euler angles are determined by the 4×4 matrix method based on the anisotropic model. The strain-optical behavior can be decomposed into two effects: the variation of the refractive indices including the birefringence and the rotation of the principal optical axis. During uniaxial stretching, the refractive index parallel to the tensile direction changes notably, while the refractive index perpendicular to the tensile direction hardly changes. The birefringence keeps a linear response to the strain with the different tensile directions being considered. The orientation of molecular chains, estimated by the extinction coefficients, shows a positive linear relation with the birefringence which gives the indirect measure of the average orientation. Due to the discrepancy between the principal optical axis and the tensile direction, the rotation of the optical axis towards the tensile direction is accurately observed using the Euler angle ϕ_E . The present work shows that the molecular chains orientation and optical properties of polymer films during deformation can be accurately detected, which makes it possible to control these properties during

deformation, and MME can be a good candidate for such a tool on line.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare no competing financial interest.

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