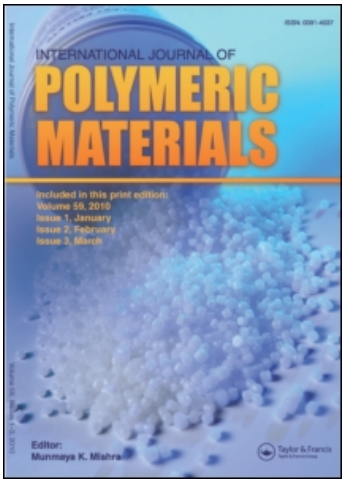

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The Activation Energy and Some Structural Parameters of Thermally Treated Polypropylene Suture Fibers

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Multiple-beam Fizeau fringes in transmission were used to study the changes in optical parameters of thermally treated polypropylene PP suture fibers. Changes in the refractive indices and birefringence have been measured interferometrically on thermally treated PP suture fibers at temperatures of 19 to 40 ± 0.5°C. From the optical parameters; the mean polarizability of monomer units, the density, stress optical coefficient, the thermal stress and the activation energy of PP sutures were calculated. The results of density and optical measurements were used to calculate the crystallinity and the specific refractivity of the isotropic dielectric. Additionally, we calculated the mean square density fluctuation, the segment anisotropy, the molar refractivity and form birefringence. Relations between evaluated and measured parameters are given for illustration. The present study throws light on the changes due to slight thermal treatments as an example of thermal human end uses. Curves are given for illustration.

Keywords: activation energy, crystallinity, form birefringence, interferometry, molar refractivity, orientation, polypropylene sutures

INTRODUCTION

Polypropylene suture fibers play an important role in biomedical applications. In recent years, due to increasing demand and the favorable mechanical properties and degradation characteristics of this synthetic fiber, much attention has been devoted to the study of its morphology, thermal and mechanical properties [1,2]. Sutures are subjected to stretching when in use, and this process gives rise to temperature increases with the rate of stretching.

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Recently, the interferometric methods applied to fibrous materials have been discussed extensively by many authors. For optically anisotropic fibers the refractive index and the double refraction are parameters that characterize the structure of the material.

The thermal treatment of polymer causes structural variations, which in turn lead to variations in physical properties. The changes in the optical anisotropy and orientation in polymer fibers due to heat treatment can be evaluated interferometrically by the measurement of refractive indices and birefringence of these fibers. These optical properties provide parameters that characterize the structure of the polymer on the molecular level. It is well known that birefringence is one of the most sensitive indicators of the anisotropy in polymers fibers; i.e., the degree of macromolecular orientation [3–10]. So, oriented polymers exhibit important changes on heating and produce thermal stress which may be an interesting method of characterizing fibers.

In this work the optical parameters and calculated values of density and crystallinity for PP suture fibers, under slightly different thermal conditions were used to calculate some structural parameters at temperatures ranging from 19 to $40 \pm 0.5^{\circ}$C.

THEORETICAL CONSIDERATIONS

Multiple-beam Fizeau fringes in transmission were used for the determination of the basic optical parameters of PP suture fibers. The experimental values of the refractive indices and polarizabilities were used to calculate the polarizability of the monomer unit at different temperatures by suitable equations given elsewhere [2,8,9].

Mean Polarizability of Monomer Unit

For a bulk polymer of density ρ and monomer unit molecular weight M, the number of monomer units per unit volume is $v = N_A\rho/M$, where N_A is Avogadro's number and M is 42.08 mole weight for PP fibers. The mean refractive index $\bar{n}$ of a polymer depends on the total polarizability of the molecules, which leads to the following Lorentz-Lorenz type equation [11]

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{v\bar{\alpha}}{3\psi} \tag{1}$$

where $\bar{\alpha}$ is the mean polarizability of a monomer unit, which is caused by the deformation of the electron clouds in and between the molecules of the dielectric under the influence of the effective field, i.e., internal field, and Ψ is the permittivity of free space ($8.85 \times 10^{-12}\,\mathrm{Fm}^{-1}$).

Stress-Optical Coefficient

The value of the stress-optical coefficient C_s depends on the chemical structure of the polymer. Also, the value of this coefficient depends solely on the mean refractive index and the optical anisotropy of the random link, as seen from the following equation [12]

$$C_s = \frac{2\pi}{45KT}\left[\frac{(\bar{n}^2+2)^2}{\bar{n}}\right][\alpha^{\|} - \alpha^{\perp}] \tag{2}$$

where $\alpha^{\|}$ and $\alpha^{\perp}$ are the polarizabilities along and across the axis of such units, K is Boltzmann's constant and T is the absolute temperature.

Determination of Thermal Stress

The transformation of initially crystalline and amorphous fibers by thermal treatment was known to introduce structural changes as polymer chains align in the direction of an applied thermal stress due to the mobility of the molecules. The average chain orientation of both the amorphous and crystalline regions in the network is measured by birefringence Δn in the present work, so that we can obtain the deformation thermal stress from the following equation

$$C_s = \frac{\Delta n}{\sigma} \tag{3}$$

From the above equations (2) and (3), it can be seen that the birefringence in elastomers is proportional to the applied stress.

The Segment Anisotropy

The segment anisotropy γ_s is related to the stress-optical coefficient, which leads to the following equation [13]

$$C_s = \frac{\gamma_s}{90\psi KT}\frac{[\bar{n}^2+2]^2}{\bar{n}} \tag{4}$$

Evaluation of the Activation Energy

Temperature coefficients of link anisotropy $\bar{\alpha}$ are readily obtained by the measurement of optical coefficients over a convenient range of

temperatures. As $\bar{\alpha}$ decreases with increasing temperature, it can be represented by an Arrhenius type equation, namely:

$$\bar{\alpha} = \mathrm{A}\ \exp^{(\mathrm{E/RT})} \tag{5}$$

where E is equivalent to an activation energy, T is the absolute temperature, R is the gas constant and A is a pre-exponential parameter.

The Molar Refractivity

The polarizability of a molecule is related to its refractive index by the Lorentz-Lorenz relation [14]

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\left(\frac{M}{\rho}\right) = N \tag{6}$$

where N is the molar refractivity.

The Specific Refractivity

The specific refractivity of the isotropic dielectric ($\varepsilon^{||}$, $\varepsilon^{\perp}$ cm^3/g) is proportional to the ρ ($\mathrm{g/cm}^3$) of the medium according to De Vries equations [11]

$$\varepsilon_{\|} = (n_{\|}^2 - 1)\rho^{-1}/(n_{\|}^2 + 2 + S(n_{\|}^2 - 1)) \tag{7a}$$

$$\varepsilon_{\perp} = (n_{\perp}^2 - 1)\rho^{-1}/(n_{\perp}^2 + 2 - 1/2S(n_{\perp}^2 - 1)) \tag{7b}$$

where S is the anisotropy index which equals 0.83 for PP fiber [11].

Calculation of the Surface Reflectivity

The surface reflectivity of a polymer for light at normal incidence can be estimated from Fresnel's equation [15] and knowledge of the mean refractive index. Thus, the reflection $\overline{R}$ (in air) is given by

$$\overline{R} = \left(\frac{\overline{n} - 1}{\overline{n} + 1}\right)^2 \times 100 \tag{8a}$$

The internal transmittance τ_{i} can be found from the following equation (transmittance transparency)

$$\tau_{\mathrm{i}} = 1 - \overline{R} \tag{8b}$$

Determination of Form Birefringence

The total birefringence Δn of a fiber is the sum of three terms

$$\Delta n = \chi_c \ \Delta n_c^\circ + (1 - \chi_c)\Delta n_a^\circ + \Delta n_f \tag{9}$$

where Δn is total birefringence, Δn_c° is the birefringence of a crystalline phase, Δn_a° is the birefringence of the amorphous phase ($\Delta n_c = 0.029$ and $\Delta n_a = 0.06$), χ_c is the crystalline regions and Δn_f is the form birefringence [16]. Form birefringence is a phenomenon arising from the interfaces between crystalline and amorphous regions.

Average Optical Orientation

The overall orientation F_{av} [17] was calculated from birefringence measurements of individual fibers. The average orientation F_{av} was calculated from the following equation

$$F_{av} = 2\Delta n/(\Delta n_c^\circ + \Delta n_a^\circ), \tag{10}$$

where the denominator is composed of the intrinsic birefringence of both the crystalline and the amorphous regions.

Mean Square Density Fluctuation

For a two-phase structure consisting of amorphous and crystalline regions with densities ρ_a and ρ_c, respectively, the mean square density fluctuation $\langle \eta^2 \rangle$ can be calculated from the following equation [18]

$$\langle \eta^2 \rangle = [\rho_c - \rho_a]^2 \chi[1 - \chi] \tag{11}$$

where $\rho_c = 0.936\,\mathrm{g/cm^3}$ and $\rho_a = 0.854\,\mathrm{g/cm^3}$ [19].

EXPERIMENTAL PROCEDURES AND RESULTS

Suture Material

This study uses nonabsorbable monofilament Polypropylene Suture PP, manufactured by Ethicon (Johnson and Johnson, NJ, USA), under the trade name Prolene. The suture diameter was measured using the method described in the United State Pharmacopoeia (USP); the diameter of PP suture is USP10/0 in size. The cross-section of PP sutures has been seen by a high-power optical microscope, and was found to be of circular shape and of diameter 88.93 μm.

Interferometric Measurements of the Optical Parameters

The optical system below was used to produce multiple-beam Fizeau fringes in transmission [20]. A parallel beam of plane polarized monochromatic light of wavelength 546.1 nm was used to illuminate a wedge interferometer placed on a microscope stage. The suture was immersed in a suitable liquid and its orientation was perpendicular to the edge of the wedge. Straight line fringes parallel to the edge of the wedge are formed in the liquid region. The amount, shape and direction of fringe shift crossing the fiber depends on the refractive index of the liquid, the refractive indices of the skin and core of the suture, and on the wavelength and the state of polarization of monochromatic light used. The interference pattern was recorded photographically at each value of temperature by CCD camera (from 19 to 40 $\pm$ 0.5°C), which were set by air conditioning throughout the laboratory.

Using these photographs, the mean birefringences of PP suture at various temperatures were calculated. Figure 1 shows the relation between the mean birefringence of PP suture with various temperatures. Figure 2 shows the stress-optical coefficient C_s at with different temperatures for PP suture.

Temperature coefficients of link anisotropy $\bar{\alpha}$ were readily obtained by measurement of optical coefficients over a convenient range of temperature. The value of the activation energy E may be obtained from a

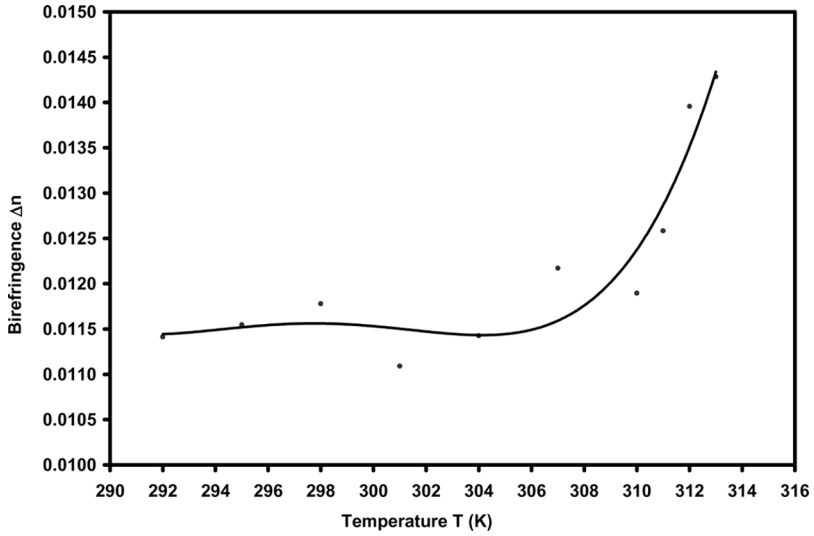

FIGURE 1 The mean birefringence of PP suture at various temperatures.

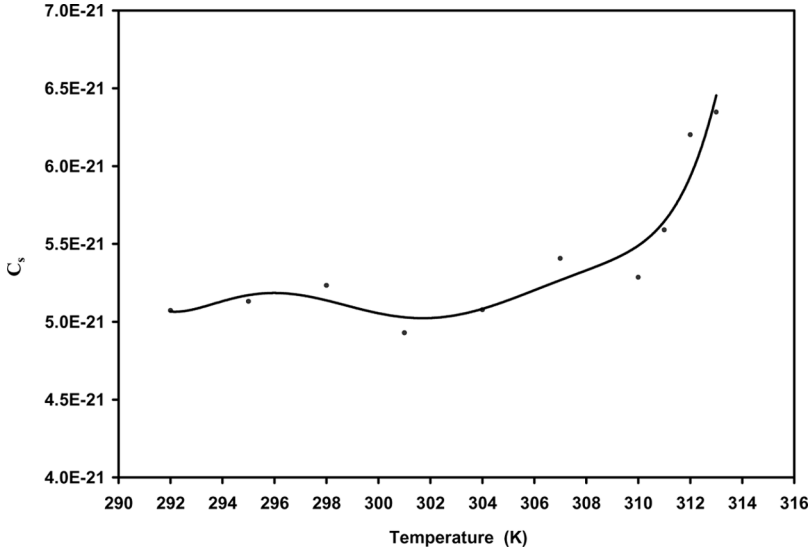

FIGURE 2 The optical stress coefficients C_s for PP sutures at different temperatures.

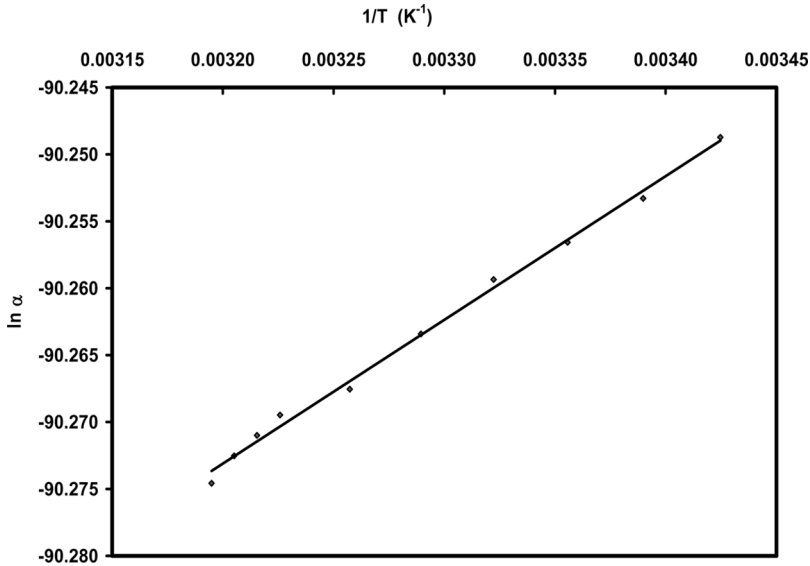

FIGURE 3 The relation between $\log \bar{\alpha}$ and T^{-1}, to obtain the value of the activation energy E.

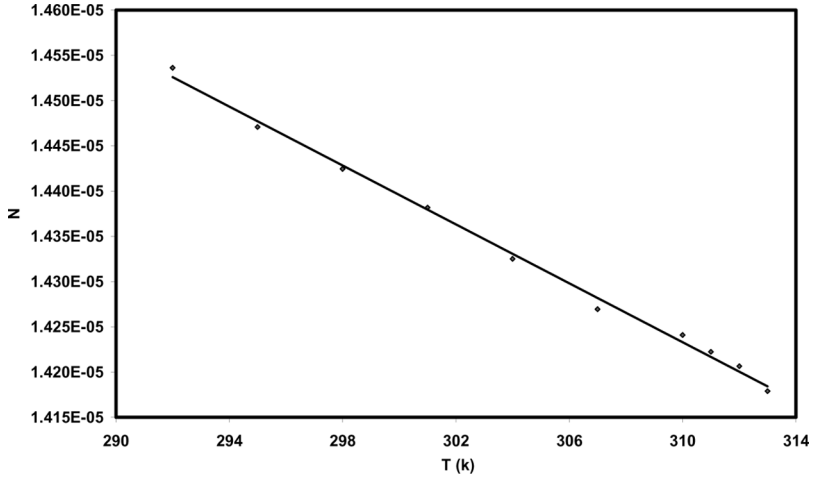

FIGURE 4 The molar refractivity N decreases with increasing temperature for PP suture.

plot of $\ln \bar{\alpha}$ against T^{-1} as show in Figure 3. The value of the activation energy E equals 213.404 cal/mol, and constant A equals −90.617 for PP suture fibers.

The molar refractivity N decreases with increasing temperatures for PP suture as shown in Figure 4.

Density Measurements

The density of the PP suture fibers was estimated by the Lorentz-Lorenz equation as discussed in detail elsewhere [21].

Crystallinity Equation

The degree of crystallinity χ, understood as the volume fraction of crystalline material, was determined by the relation [19]

$$\chi = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \times 100 \tag{12}$$

where ρ_c and ρ_a are the densities of the crystalline and noncrystalline regions and ρ is the experimentally measured values of density.

Table 1 gives the values of the density ρ, the degree of crystallinity χ, the mean square density fluctuation $\langle \eta^2 \rangle$, thermal stress σ and

TABLE 1 The Values of the Density ρ, the Degree of Crystallinity χ, the Mean Square Density Fluctuation $\langle\eta^2\rangle$, Thermal Stress σ and the Average Orientations F_{av} at Different Temperatures

Temp (k)	ρ (g/cm^3)	χ (%)	$\langle\eta^2\rangle \times 10^{-2}$	$\sigma \times 10^{18}$ Pa	F_{av}
292.0	0.8528	3.5194	−5.2326	2.2500	0.2565
295.0	0.8528	3.5838	−5.4706	2.2501	0.2595
298.0	0.8529	3.6726	−5.8076	2.2503	0.2647
301.0	0.8527	3.4729	−5.0634	2.2499	0.2492
304.0	0.8528	3.5977	−5.5225	2.2501	0.2567
307.0	0.8530	3.8541	−6.5267	2.2507	0.2735
310.0	0.8530	3.7780	−6.2204	2.2505	0.2673
311.0	0.8531	4.0039	−7.1511	2.2510	0.2828
312.0	0.8529	3.6853	−5.8566	2.2503	0.3137
313.0	0.8529	3.7061	−5.9370	2.2504	0.3209

the average orientations F_{av} at different temperatures. In addition, the value of the specific refractivity ($\varepsilon^{||}$, $\varepsilon^{\perp}$), the surface reflectivity $\overline{R}$, the internal transmittance τ_i and the form birefringence Δn_f at different temperatures are listed in Table 2.

DISCUSSION

In the present work, the physical characteristics of a suture are the cross-section, crystallinity, stress-optical coefficient, orientation and activation energy. At the same time, a polymer for medical uses needs to be connected to the micro structure which may be affected by thermal stresses when in use. Since we are dealing with viscoelastic materials, important information on their deformation can be obtained by

TABLE 2 Values of the Specific Refractivity ($\varepsilon^{||}$, $\varepsilon^{\perp}$), the Surface Reflectivity $\overline{R}$, the Internal Transmittance τ_i and the Form Birefringence Δn_f at Different Temperatures

Temp (k)	$\varepsilon^{||}$ (cm^3/g)	$\varepsilon^{\perp}$ (cm^3/g)	$\overline{R}$	τ_i	$\Delta n_f \times 10^{-2}$
292.0	0.2797	0.3892	4.0119	−3.0119	−4.759
295.0	0.2787	0.3872	3.9783	−2.9783	−4.744
298.0	0.2781	0.3856	3.9549	−2.9549	−4.718
301.0	0.2773	0.3846	3.9314	−2.9314	−4.793
304.0	0.2765	0.3827	3.9031	−2.9031	−4.756
307.0	0.2758	0.3807	3.8762	−2.8762	−4.674
310.0	0.2753	0.3800	3.8611	−2.8611	−4.704
311.0	0.2751	0.3791	3.8531	−2.8531	−4.628
312.0	0.2752	0.3781	3.8429	−2.8429	−4.500
313.0	0.2748	0.3771	3.8289	−2.8289	−4.467

evaluating the stress-optical coefficient. The changes in the optical anisotropy in suture PP fibers by heat treatments can be evaluated interferometrically by the measurement of refractive indices and density of these fibers.

These optical properties provide the parameters C_s, γ_s, R and Δn_f of these fibers. The stress birefringence of a crystalline polymer is given by the orientation of the amorphous chains between crystallites, the orientation of crystallites and the form birefringence arising from the interfaces between crystalline and amorphous regions [16]. The form birefringence was usually neglected. It is evident that birefringence yields reliable information about orientation in single-phase systems but additional information is required when two-phase systems were involved. If the sign of the birefringence in the spherulite is positive, then the layer refractive index lies along the radial direction. If the sign was negative, then the larger index lies at right angles to this along the tangential direction. The obtained values for the PP sutures form birefringence follow the negative sign; the form birefringence will in theory fall to zero when the refractive index difference between the phases is reduced to zero [8,22].

CONCLUSIONS

From the above, the following conclusions can be drawn:

1. The stress-optical coefficient C_s and the segment anisotropy γ_s change as temperature increased.
2. Measurement of the refractive indices indicates that the structure of the fiber along its axis is different from that across its axis.
3. The value of the activation energy E is 213.404 cal/mol and the constant A equals −90.617 for PP suture fibers.
4. The value of the calculated form birefringence in Table 2 changes for PP suture according to the ratio between the crystalline and amorphous regions, depending on the thermal conditions.
5. The surface reflectivity $\overline{R}$ and the molar refractivity decrease as the temperature increased.

In conclusion, the structural orientation changes due to thermal treatment as observed by multiple-beam technique. Also, our studies throw light on the influence of thermal effects on reorientation of PP suture fibers after surgical process.

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