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Characterizing The Effect of Thermal Annealing Process on the Physical and Structural Properties of Polybutester Suture Fibers.

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Abstract: In this work the effect of thermal annealing treatment on the different physical, optical and structural of surgical suture fibers were considered. Polybutester monofilaments suture fibers were thermally annealed at temperatures fluctuating from 50-130? for two different periods of 60 and 120 min. The thermal-treatment was supported using taut end settings. Multiple-beam Fizeau fringes in transmission and X-ray diffraction techniques were used to measure the physical and structural properties of the tested sutures. Such as refractive indices, birefringence, dielectric constant, polarizability, dielectric susceptibility and the crystallinity. From the obtained measured data , there was a noticeable increase in the physical properties and crystallinity throughout the annealing process for annealing time 120 min. which indicates that a new reorientation of Novafil suture molecules was performed, which will improve the mechanical properties of the sutures. This is a significant enhancement for these suture fibers to broaden their medical use and improve their clinical results. The new molecular reorientation of the Novafil surgical sutures was performed using the annealing process which demonstrates the polymer-chain relaxation during the thermal annealing process. Micro Interferograms were used to illustrate these findings.

Keywords: Crystallinity, Annealing Process, Refractive Indices, Orientations, Dielectric Constant

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1. INTRODUCTION

Suture fibers or materials are a vital part in the tissues wound healing process. The whole consideration of the physical and biological properties plays a significant part in the process of suture material selection. Polybutester suture fibers are new mono- filament fibers and non-absorbable. These fibers have a high-class stress-strain character. Thus, they rummage-sale mostly in the abdominal wound closure. Novafil is the trade name of Polybutester surgical sutures [1]. Novafil surgical sutures are a copolymer consisting of randomly segmented glycol and butylene. The absorbable monofilament Novafil surgical suture enactment such as a single suture material are used for shutting profound surgical defects, such as dermal tissue and the hypodermis, to provide satisfactory results[2]. During the time required for the healing of facial surgery defects, the Novafil surgical suture is absorbed [2]. Additionally, sutures have played a key role in ligating blood vessels and in hair transplant surgical procedures [3, 4]. Novafil suture is a useful quantifiable in the surgical field, and its degradation period is few weeks in the body. There are many compensations of Novafil surgical suture, such as its bio-compatibility, meta-bolizability, non-toxic, insoluble in organic solvents and high melting point [5]. To change the physical properties of polymers, which are caused by changes in the chemical and structural properties of the polymers, thermal handling can be used [6]. The thermal annealing process leads to reorganization of the molecular configuration to a molecular chain by the production of thermal energy [7, 8]. The refractive indices and the birefringence can be considered as a good pointer to the different physical properties of fibers materials. Such as the structural homogeneity and the diverse molecular orientations[9]. The crystallinity of the polymer is a temperature dependent parameter. The crystallinity can be measured using different techniques such as DSC, XRD, FTIR and NMR [10-13]. The chief goal of this work is to throw light on the effect of the thermal annealing treatment conditions on the diverse structure and physical properties of NOVIAL suture fiber. These properties were measured using multiple-beam Fizeau fringes in transmission technique and the XRD technique. Using these techniques, the refractive indices, birefringence, the molecular-orientation and the crystallinity were measured at different annealing temperatures for two different periods of annealing temperatures.

2. MATERIAL AND METHODS

The trade name of the sample used in this work was Novafil (Polybutester). Which is a copolymer of glycol and butylene. This fiber is a monofilament surgical suture [1]. Multiple beam Fizeau fringes system in transmission was used to measure the optical parameters of the sample under consideration [14]. The index of refraction of thermally annealed sample can be calculated using the following equation [15].

$$\boldsymbol{n^{\parallel} = n_L + \frac{F^{\parallel}\lambda}{2bA}} \quad (1)$$

where n_L is an immersion liquid refractive index. λ is the monochromatic light wavelength. A is the cross-sectional area of the thermal annealed sample. b is the interfering spacing. The enclosed area under the fringe shift is F. This equation can be used to determine parallel and perpendicular refractive indices of the sample. The double refraction (birefringence) can be calculated using the following equation [9, 14]:

$$\Delta n = n^{\parallel} - n^{\perp} \quad (2)$$

where $n^{\parallel}$, $n^{\perp}$ are the parallel and perpendicular refractive indices. Using the calculated values of the refractive indices the molecular polarizability (P_m) and the dielectric constant (DE) and the dielectric susceptibility (η) can be measured using the following equations [15].

$$P_m = \frac{3}{4\pi}\left(\frac{n^2-1}{n^2+2}\right) \quad (3)$$

$$DE_{\parallel} = n_{\parallel}^2 \quad (4)$$

$$\eta = \frac{DE-1}{4\pi} \quad (5)$$

To evaluate the crystallinity degree of thermally annealed NOVAIL suture fibers, XRD technique was used. The crystallinity of the samples can be measured with the aid of the following equation [16].

$$\chi = \frac{A_c}{A_c+A_a} \quad (6)$$

Where A_c, A_a are the enclosed areas under the crystalline and amorphous peak respectively.

The thermal annealing procedure can be used to improve the different physical and structural properties of semicrystalline polymers [17]. The taut end thermal annealing process for Novafil suture fibers were performed. The used electric oven in this process was adjusted at which its temperature can be modified and enhanced easily in the annealing process. Initially, the oven should be intense for 1 hour at least to make sure that the temperature is immutable. The selected temperatures of annealing were (50-130 °C) and with incrementing step of 10 °C. The selected durations were 1 and 2 hours. The selected temperatures of annealing were chosen taking into consideration the values of T_m and T_g. The melting temperatures of Novafil surgical suture is 200 -220°C. While the glass transition temperature ranged from -36 to 15°C [18]. The sample is held in the oven for the selected time in the chosen temperature. Then the sample is left in free space or at room temperature to be cooled.

3. RESULTS AND DISCUSSION

The obtained Micro Interferograms using the multiple beam interference technique was used to clarify the impact of the thermal annealing conditions on the physical properties of Novafil suture fibers as the refractive indices and the birefringence. The wavelength of the light used was $\lambda =$ 546.1 nm. The refractive indices of the two prepared immersion liquids were 1.533 & 1.476 for parallel and perpendicular directions respectively. Inorder to study the dependence of the refractive index and the birefringence on the annealing time and temperature a single filament of thermally treated Novafil surgical suture was fixed on the wedge of the interferometer, then relocated to the Fizeau system. The images of the thermally annealed Novafil suture specimen were captured in case of parallel and perpendicular components of the light electric field. Figure 1 (a-d) illustrate some of the obtained images by multiple beam Fizeau system in transmission for thermally annealed Novafil suture fibers at temperatures 50 and 130°C at annealing time T=60 min for light vibrating parallel (a, b) while (c, d) for light vibrating perpendicular to the fiber axis. Figure 2 (a-d) gives some of the obtained images using Fizeau system in transmission for thermally annealed Novafil suture fibers at temperatures of 50 and 130°C for annealing period T=120 min in case of light vibrating parallel (a, b) while (c, d) for light vibrating perpendicular to the fiber axis. From these figures, it is clear that the area enclosed under the fringe shift has been changed through the thermal annealing process. The refractive indices can be measured using these micro interferograms and equation (1) at each annealing temperature at the two durations (1 and 2 hour). Figure (3) gives the calculated values for parallel refractive index with the annealing temperature in case of the two periods (60 and 120 min). Figure (4) gives the calculated values for perpendicular refractive index with the annealing temperature in case of the two periods (60 and 120 min). The thermal annealing conditions (annealing temperature and annealing time) have a great effect on the sample refractive index. At which the parallel refractive index increasingly raised. While the perpendicular refractive index changed a little bit randomly.

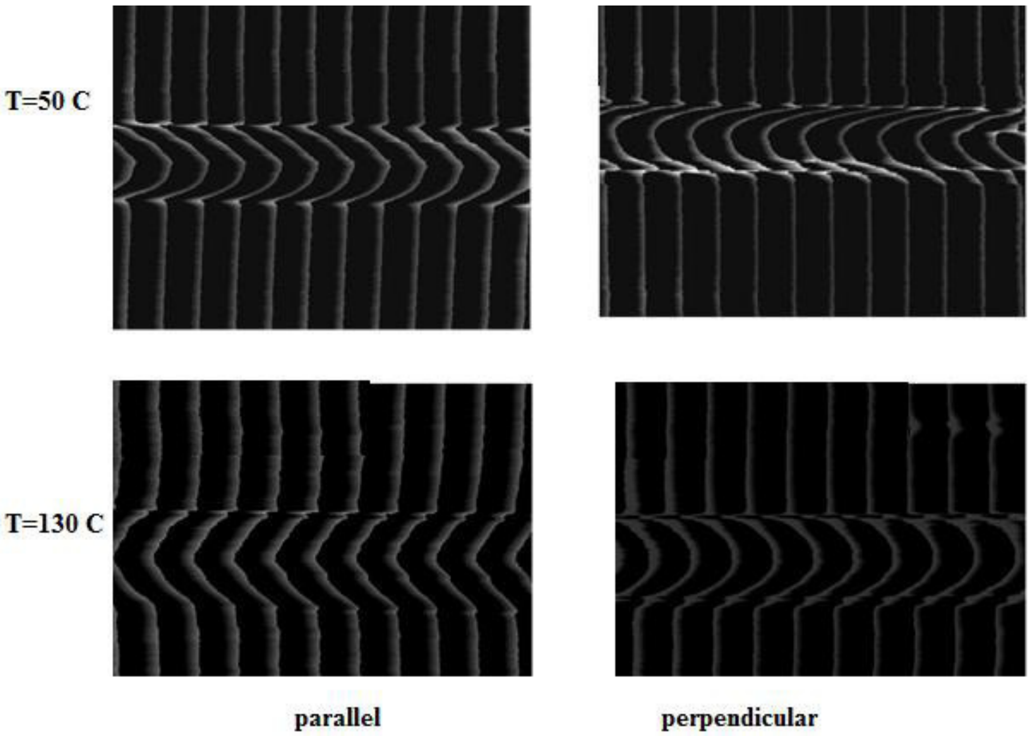

Fig 1 (a-d): Some of the obtained micro interferograms for thermally annealed Novafil suture fibers at temperatures 50 and 130°C at annealing time T=60 min for light vibrating parallel (a, b) while (c, d) for light vibrating perpendicular to the fiber axis.

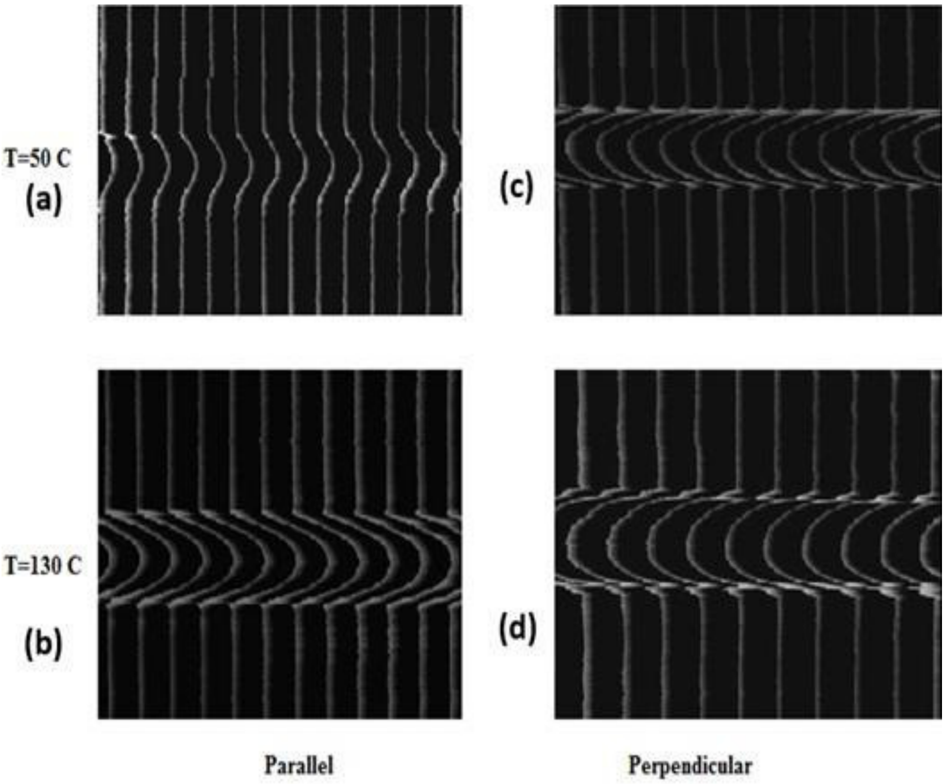

Fig 2 (a-d): Some of the obtained micro interferograms for thermally annealed Novafil suture fibers at temperatures 50 and 130°C at annealing time T=120 min for light vibrating parallel (a, b) while (c, d) for light vibrating perpendicular to the fiber axis.

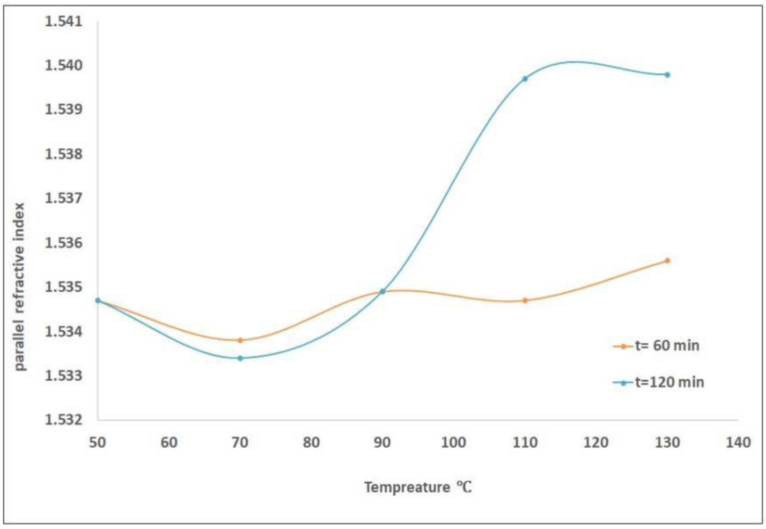

Fig (3) gives the calculated values for parallel refractive index with the annealing temperature in case of the two periods (60 and 120 min).

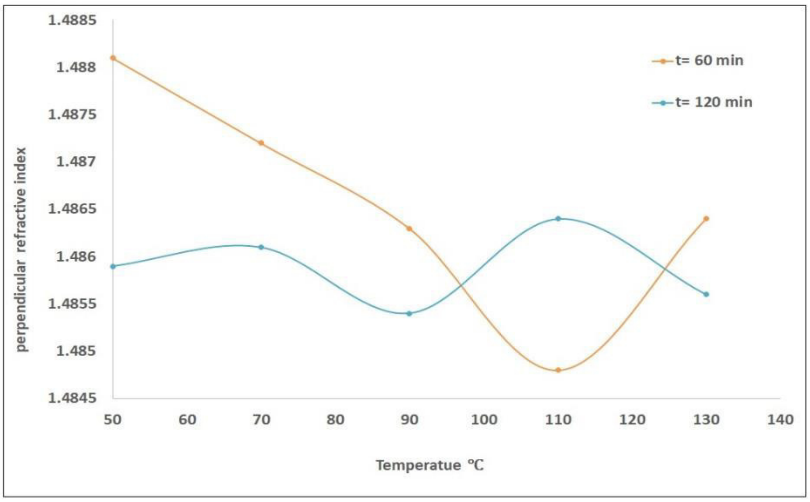

Fig (4): The calculated perpendicular refractive index with the annealing temperature in case of the two periods (60 and 120 min).

The birefringence has been measured by means of the calculated values of the refractive indices and with the aid of equation 2. The birefringence is the distinction between the indices of refraction, increased with increasing

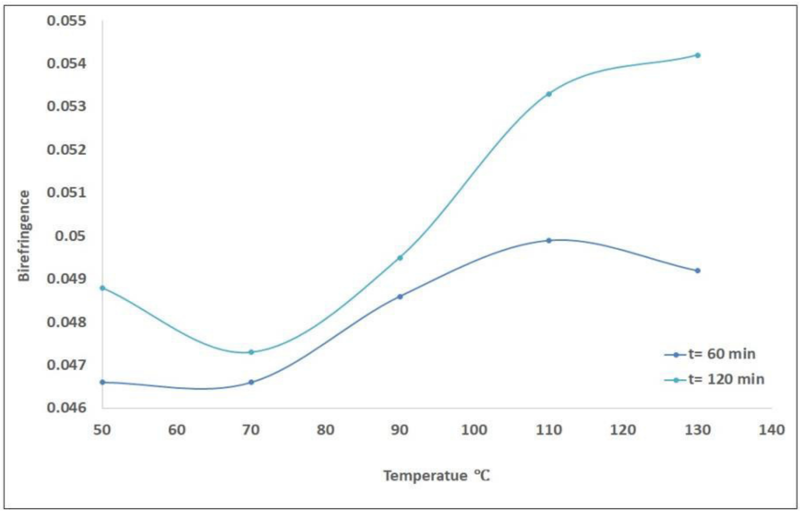

Fig (5) shows the calculated birefringence Δn of Novafil sutures with the annealing temperature for two periods (60 and 120 min) both of the annealing temperature and annealing period6,8,9.

It is clear that, for the annealing temperatures 50-90 °C, the changes of the birefringence values were minor for the different periods of time. To get more orientations of the chain of the polymer, the annealing process with low temperatures using more time is required [20]. Nonetheless in case of annealing temperatures greater than 90 °C, there was clear growth in the recorded values of the birefringence, particularly for annealing time t= 120 min. The chain orientation and the optical anisotropy increased as the annealing time increased[6,9]. So, the thermally suture fiber became more oriented. That will improve the polymer crystallinity and orientation. The rank of this improvement for bio-degradable suture fibers is to extensive its therapeutic request and advances the best clinical result [20]. The thermal annealing temperature touch the birefringence of Novafil surgical sutures and this outcome can be defined using the Arrhenius equation as follows [21]:

$$\Delta n = q\ exp\left[\frac{-E_a}{RT}\right] \quad (7)$$

where q is a constant. The energy of activation is E_a . It can be defined as the lowest energy obligatory for a chemical reaction to occur or response. R is the universal gas constant. The absolute temperature is T. This equation can be rewritten in a logarithmic form as in equation 8.

$$ln\ ln\ \Delta n = ln\ ln\ q - \frac{E_a}{RT} \quad (8)$$

The energy of activation can be evaluated using equation (8). Equation (8) gives a straight line joining between the logarithmic value of birefringence and the inverse of the absolute temperature selected for test. From the slope of this line, the energy of activation can be measured. Figure (6) gives the change in the logarithmic value of the double refraction of samples with the reverse of the absolute annealing temperatures in case of the two durations (60 and 120 min). From the slope of the obtained line, the activation energy can be measured[6]. The calculated value of the activation energy in case of annealing time 60 min was E_a= 0.967 kJ/mole. While its value for the annealing time 120 min was E_a= 1.738kJ/mole.

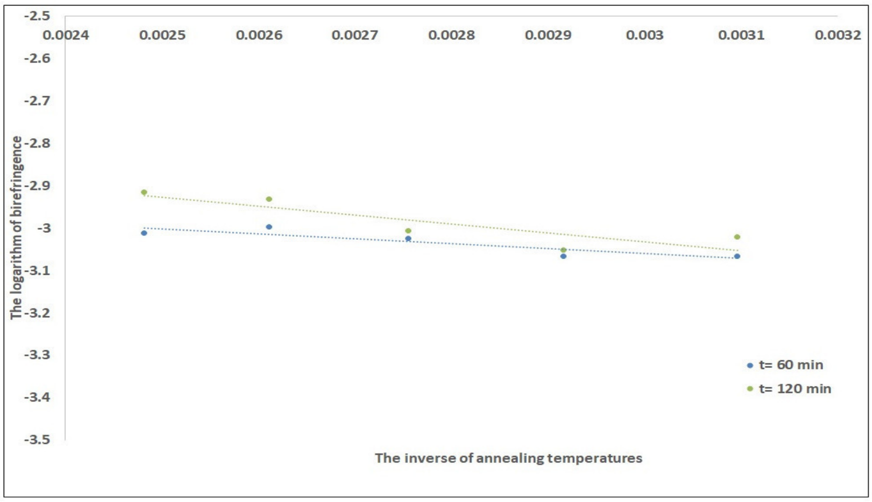

Fig (6) : The change in the logarithmic value of the double refraction of samples with the reverse of the absolute annealing temperatures in case of the two durations (60 and 120 min).

The variation in molecular orientation and the crystallization process that happened during the annealing time of 60 min originated gradually, that may be considered because of the low value of the activation energy. While the molecular orientation and crystallization increase at the annealing time of 120 min, so the value of the activation energy increases remarkably. The calculations are in a good arrangement with the polymer data[22,23]. Some of the physical parameters as, the dielectric susceptibility, the dielectric constant, and polarizability per unit volume of the Novafil suture fibers can be measured from the obtained results of the refractive indices. Figure (7) shows the calculated polarizability per unit volume of thermally treated Novafil suture when light vibrating parallel to the suture axis6. Figure (8) gives the polarizability per unit volume of Novafil suture for light oscillated perpendicular to the suture fiber axis. It is obvious that, as the annealing temperature rises, the values of the polarizability for parallel direction increased, but the values in the perpendicular direction decreased as the annealing temperature increased, which confirms that the preferential alignment of the polymer chains of the thermally treated Novafil fibers was the parallel direction to the fiber axis[6].

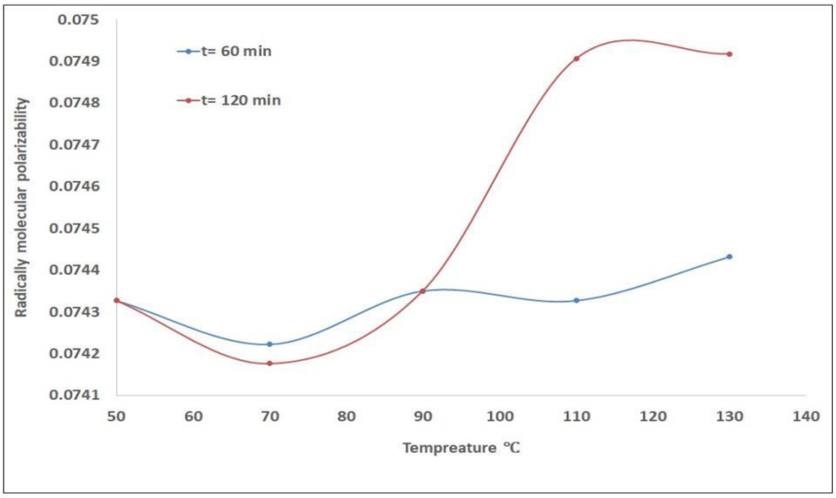

Fig (7): The calculated polarizability per unit volume of thermally treated Novafil suture when light vibrating parallel to the suture axis

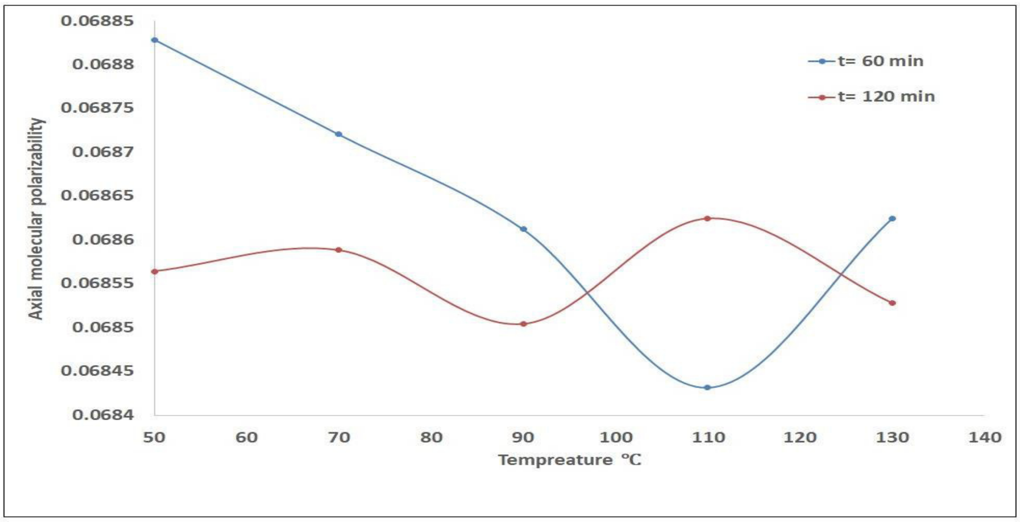

Fig (8): The polarizability per unit volume of Novafil suture for light oscillated perpendicular to the suture fiber axis.

For examining the structure of a given polymer, the inquisition of dielectric properties with the annealing temperature is acting as a precise method 6,22. To calculate the dielectric parameters of Novafil surgical sutures, the acquired outcomes of the refractive indices were used. Figure (9) and figure (10) show the variations in the dielectric constants of the Novafil suture for the two components of light polarization, parallel and perpendicular to the suture axis, respectively, with annealing temperature. The dielectric susceptibilities, $\eta_{\parallel}$ and $\eta_{\perp}$, of Novafil suture at different annealing temperatures are represented in figures (11) and (12), respectively. From these figures, one can conclude that the values of the dielectric constant and dielectric susceptibility at the parallel component of polarized light increased as the annealing temperature increased at steady annealing times 60 and 120 min [6,7,20]. Thus, the molecules embracing this surgical fiber are oriented laterally in the direction of the fiber axis. Subsequently, the consistent values for the light vibrating perpendicular to the fiber axis were decreased which shows that a new re-orientation of the thermally treated samples under study has been performed at the different annealing conditions[6,7].

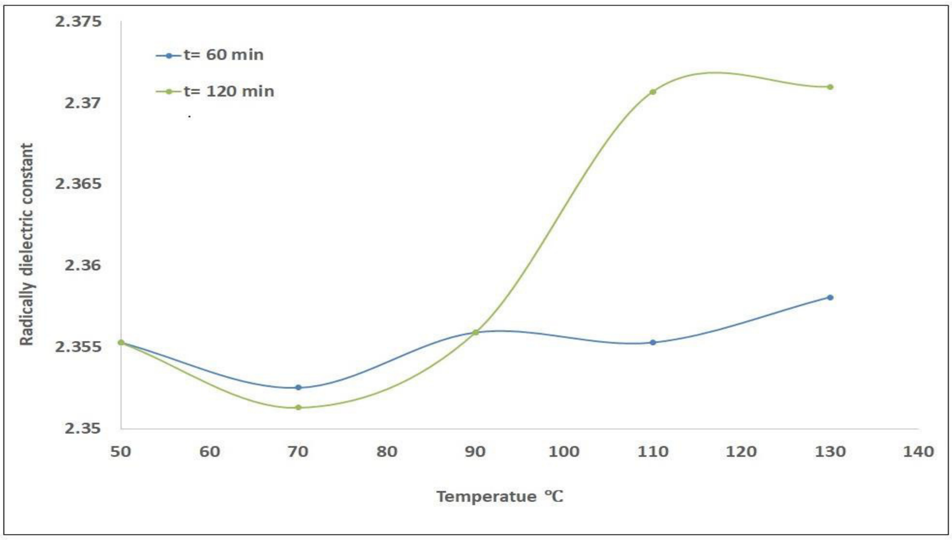

Fig (9) : The variations of the dielectric constants of the Novafil suture for the two components of parallel polarizatied light, with the annealing temperature.

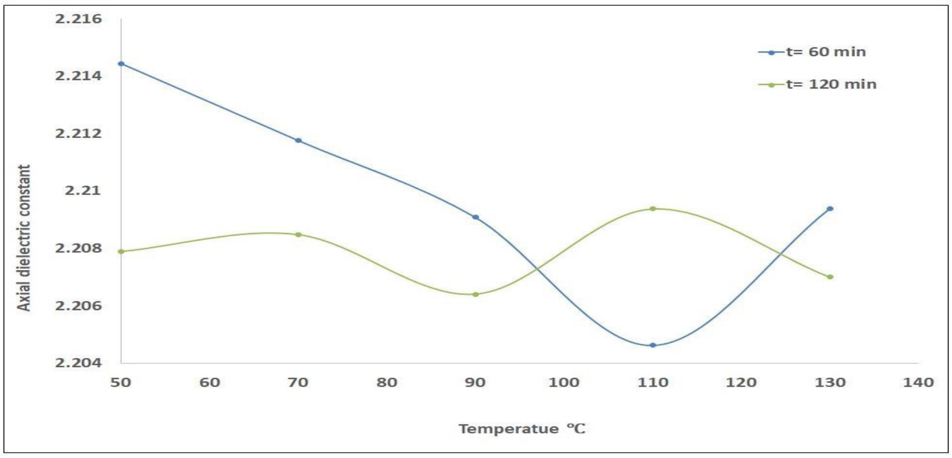

Fig (10): The variations of the dielectric constants of the Novafil suture for the two components of perpendicular polarizatied light, with the annealing temperature

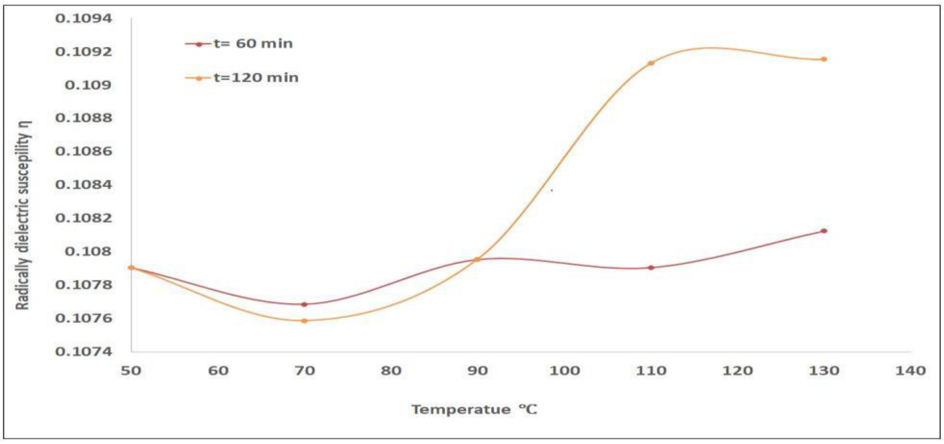

Fig (11): The parallel dielectric susceptibilities, η ‖of Novafil suture at different annealing temperatures

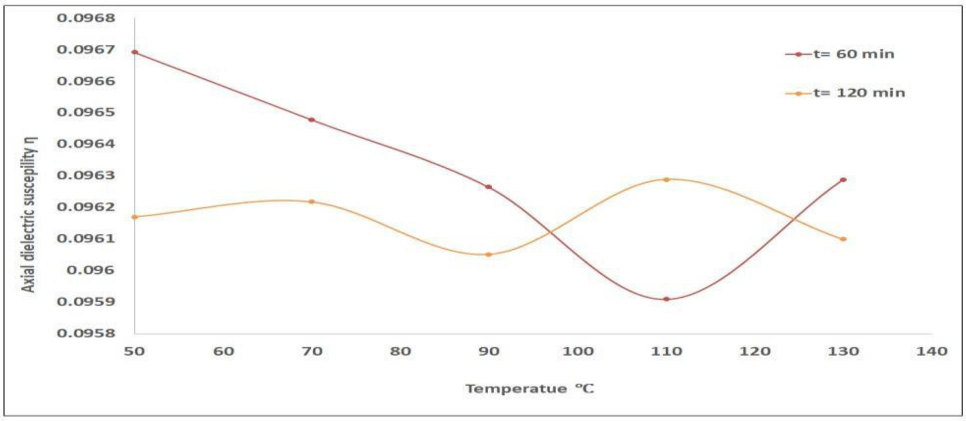

Fig (12): The perpendicular dielectric susceptibilities, η ‖of Novafil suture at different annealing temperatures.

The values of dielectric susceptibility, dielectric constant, and molecular polarizability per unit volume for annealing temperatures at two stable annealing times of 60 and 120 min were calculated. These measured properties are affected by the internal microstructure changes induced during the thermal annealing process [24-27.] To evaluate the effect of the thermal annealing conditions on the crystallinity of the thermally annealed samples under investigation the XRD techniques were used. The samples were taut end samples. Table (1) represents the measured data of the crystallinity at different annealing time 50-130 °C for the two different durations 60 - 120 min. The measured degree of crystallinity showed a slight increase at little annealing temperatures for both annealing periods before the plateau region. The recorded crystallinity values were higher for annealing time 120 min than for annealing time 60 min for the thermal treated suture fibers. The evaluated data show that the polymer chains relaxed as a result of the thermal annealing treatment causing an increase in crystallinity[23,25]

Table1: The measured crystallinity values for thermally annealed samples using XRD technique.

Annealing time	t= 60 min	t= 120 min
Annealing Temperature	Crystallinity χ %	Crystallinity χ %
T= 50 °C	32.34	33.31
T= 70 °C	33.12	34.76
T= 90 °C	34.56	36.76
T=110 °C	36.3	38.6
T=130 °C	36.76	39.54

4. CONCLUSION

In this study, by applying multiple Fizeau fringes in transmission and XRD techniques, the structural and physical properties of thermally annealed Novafil surgical sutures were measured. Some records can be developed from the obtained results:

1. The refractive indices and dielectric constant were strongly dependent on the internal microstructure changes induced during the thermal annealing treatment. The anisotropies of the measured optical parameters of the Novafil material across the sutures exhibited positive values. Consequently, the parallel orientation to the suture fiber axis was favored, and this orientation was temperature- time dependent.
2. Increasing the value of the activation energy with the annealing process means, that the thermal-stability of the Novafil suture increases as the crystallinity increases.
3. The measured crystallinity was higher at annealing time 120 min than that at time 60 min.
4. A new molecular reorientation of the Novafil surgical sutures was performed with the annealing process. Demonstrating relaxation of the polymer-chain during the thermal annealing process.

5. ACKNOWLEDGMENT

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6. AUTHOR CONTRIBUTION STATEMENT

Dr A. M Ali and Prof. Ali H Amin gathered the data of this work. Dr A. M Ali analyzed these data . Dr A. M Ali and Prof. Ali H Amin discussed the methodology and the results of this manuscript

7. CONFLICT OF INTEREST

Conflict of interest declared none.

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