Thermally Induced Microstructural Changes in Cotton Fibers: A Free-Volume Study

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ABSTRACT: I measured positron lifetime in natural polymer–cotton fibers as a function of isochronal annealing temperature in the range 27–290°C. The variations in the positron results indicated structural changes occurring in the cotton fibers and determined the glass-transition temperature as 80°C. Activation energies were measured separately for the crystalline and amorphous regions, indicating the versatility of the technique. These values were close to the O—H bond dissociation energy, suggesting O—H bond dissociation, the most probable process occurring under thermal treatment. As an extension of the positron results, the molecular weight of the cotton fibers was determined to be 1,200,000 based on free volume, which was within the range suggested for cotton. There seemed to be an indication that crosslinking changed the spiral structure of cotton fibers to the network type. However, this needs to be validated by other measurements. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3336–3345, 2002

Key words: activation energy; fibers; viscoelastic properties; molecular weight

INTRODUCTION

Over 50% of the total organic matter in the living world is cellulose. Cotton is a natural fiber, which is cellulosic in composition and finds extensive use in the textiles, paper, and plastics industries. Cotton fibers contain the highest percentage of cellulose (90–92%) with small amounts of other substances such as protein (0.9%), pectin (0.9%), and water (6–8%). Cotton cellulose is a high polymer, containing units of hydroglucose with the empirical formula $(C_6H_{10}O_5)_n$, where n is the degree of polymerization, which ranges as high as 4000–5000, giving molecular weights up to 800,000 or more. Because of the polymolecular nature of cotton cellulose, molecular weights determined by different methods give different values.[1,2] Because cotton fiber is essentially cellulosic in nature, its organochemical structure is best described as that of cellulose: poly(1,4-β-D-anhydroglucose),[3,4] which is shown in Figure 1. The chains in cellulose are closely packed and, in view of the strong intermolecular hydrogen bonds, are characterized by a high degree of crystallinity. Its high stereoregularity is also a contributory factor for this high crystallinity.[5] Cotton cellulose is also polymorphic, that is, it crystallizes into different forms like cellulose I (cotton cellulose), which is the most common natural structure, and cellulose II, which is the product usually formed when a swelling reagent is added and then removed. For example, cellulose II occurs in mercerized cotton. Cellulose III and IV do not occur in nature and are not well characterized like cellulose I and cellulose II.

X-ray diffraction studies of cellulose reveal the presence of both amorphous and crystalline regions, suggesting the semicrystalline nature. It contains up to 70–80% crystallinity. The crystalline and amorphous regions may be mixed or may exist alternately along the fibrillar length. The interesting point in favor of cotton fibers is that it can be folded and unfolded several times without loss of strength. In comparison to silk, cotton is a better conductor of heat and has an excellent moisture absorption capability. These two properties make it an ideal clothing material for humid summer weather.

The crystalline regions in the cotton fibers do not swell with water; instead, water is embedded in the matrix of the amorphous regions, and hence, the regions restrict the swelling of the fibers, acting as crosslinks of the polymer network.[6] The mechanical properties of cotton cellulose are highly dependent on the fibrillar orientation, and this classifies them as stiff, strong, and relatively extensible. Cotton is hydrophilic with an equilibrium moisture regain of approximately 7–8%. This is considerably below that of a regenerated cellulose fiber because of the high degree of lateral order or molecular packing, which prevents many of the hydroxyl groups from being accessible to moisture or other swelling agents. However, the hydroxyl groups, which are involved in moisture sorption, provide excellent dyeing sites. As a result, cotton may be dyed with a variety of dyestuffs.[4]

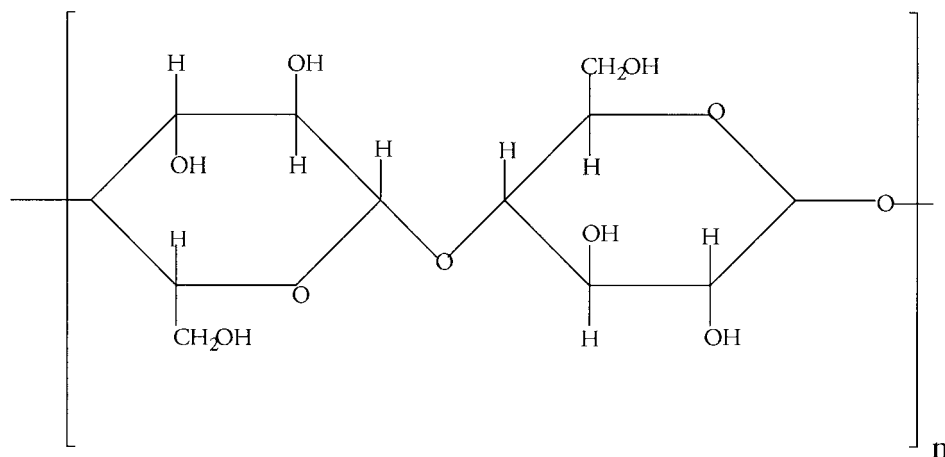*Correspondence to:* C. Ranganathaiah (crang1@excite.com).

Figure 1 Chemical structure of cellulose.

Both natural and synthetic fibers are polymers. The natural polymers are readily biodegradable, abundantly available, and ecologically friendly. In contrast, the synthetic polymers are durable and sustainable but not biodegradable in the environment; thereby, they cause pollution after their end use. Environmentally conscious citizens are, therefore, reverting to the use of natural polymers wherever possible in place of synthetic ones to minimize pollution. It is, therefore, necessary to improve the characteristic properties of these natural polymers by various physical and chemical treatments.[7] The molecular motion in cotton cellulose is strongly restricted by intermolecular and intramolecular hydrogen bonding.[8] Below a certain temperature that is characteristic of a given sample, the number of possible junction points the hydrogen bonds can be assumed to have remains practically unchanged over a relatively narrow range of the volume fraction of the polymer. Beyond this temperature, the junction points are broken down to a certain extent, depending on the amount of moisture absorbed and also on the arrangement of the molecules in the disordered regions. For cotton fibers, this temperature seems to be in the vicinity of 50°C. This temperature corresponds to the transition from a glassy to a partially rubbery state. When cotton cellulose is subjected to heat treatment, free radicals may be formed, and decomposition occurs at about 217°C. The free radicals may initiate crosslinking and provide dimensional stability, which is very useful for making paper and textile products. It seems possible to produce crosslinking by heating to a temperature of around 127°C.

These interesting properties of cotton fibers motivated me to investigate them to understand their thermal behavior at the molecular level in terms of free-volume fraction with a novel technique such as positron lifetime spectroscopy (PLS). I hoped that a thermal study of the cotton fibers would provide use-ful information about the glass temperature; thermally induced processes, such as thermal expansion of free-volume holes and coagulation of free-volume holes; and the activation energies involved in such processes.

Microstructural changes due to thermal treatment in polymers have been studied by various research groups with PLS because this technique is sensitive to free-volume changes and is nondestructive.[9–14] Positrons have been successfully used for materials research, as they are extremely sensitive to defects, phase transitions, and inhomogeneties. The following is a brief outline of PLS technique. The utility of positrons in the study of polymers is enhanced by the fact that the positron can capture an electron and form a bound system called positronium (Ps). Ps can exist in two forms. The first form is ortho-positronium (o-Ps), where the positron and electron spins are parallel and have a mean lifetime of 142 ns in free space. The second form is para-positronium (p-Ps), where the spin of both the particles is antiparallel and which decays with a lifetime of 123 ps. In condensed-media-like polymers, the o-Ps lifetime is shortened to few nanoseconds or less because of the pick-off process in which the positron of o-Ps picks an electron of antiparallel spin from the surrounding medium and annihilates it. Still, this has a relatively long lifetime compared to p-Ps, and hence, its component is well defined in the lifetime spectrum. Therefore it is possible to make a precise measurement of the o-Ps lifetime and its intensity (the fraction of positrons that annihilate as o-Ps). Another aspect of o-Ps annihilation in polymers is that this species is preferentially trapped or formed in regions of low electron density, or what we call free-volume holes or cavities. Because the o-Ps annihilation rate is proportional to the overlap of the positron and pick-off electron wave functions, it is natural to expect that the o-Ps lifetime is strongly dependent on the size of the free-volume cavities. It has also been shown that the intensity of o-Ps, or in

other words, the probability of o-Ps formation, is related to the number of free-volume sites in the polymer.[9] Therefore, with pick-off annihilation of o-Ps in a polymer around the glass-transition temperature (T_g), it can be interpreted as the indicator of the change of the cavities and the change in the number of such cavities. A detailed theoretical description of the positron annihilation process can be found in refs. 9–11.

EXPERIMENTAL

Cotton fiber strands were wound on a centrally holed (1.5 cm diameter) aluminum sheet to a thickness of 1.5 mm. Two pieces of this type were used for positron lifetime measurement in sandwich geometry. I performed isochronal annealing of the samples by keeping the sample for a fixed time of 1 h in a tubular oven and then quenching them in an ice water bath to preserve the structure at the annealing temperature. The samples were then thoroughly dried before use in lifetime measurements. The oven temperature was controlled to within ±1°C with a proportional temperature controller. Isochronal annealing of the samples was done in the temperature range 27–290°C.

The positron lifetime spectrometer consisted of a fast–fast coincidence system with a time resolution of 340 ps, determined by measurement of the coincident γ photons from a ^{60}Co source with a 40% energy window setting to receive ^{22}Na events. The lifetime spectra were collected so as to have at least 1 million counts under each spectrum. I repeated the experiment at each annealing temperature to check the reproducibility of the measurements. A detailed description of this PLS system can be found elsewhere.[15,16] With the PATFIT-88 program,[17] measured PLS spectra were analyzed with appropriate source and background corrections. The source and background corrections were determined from a lifetime spectrum taken with a defect-free aluminum sample and analyzed with the Resolution program.[17]

RESULTS AND DISCUSSION

All positron lifetime spectra were subjected to two-, three-, and four-lifetime component analyses. Invariably, the three-lifetime component analysis gave better χ^2 values and standard deviations than the two-lifetime and four-lifetime component analyses. Hence, the results of the three-lifetime component analysis are discussed here. The attribution of the three lifetimes to various states of positron annihilation was as follows: The first, short-lived component (τ_1) with intensity I_1 was attributed to p-Ps and free annihilations. There seems to some difference of opinion with regard to the assignment of the intermediate-lifetime component (τ_2) with intensity I_2. I followed the prescription

of Goldanski et al.,[18] according to which, this component is thought to arise due to the trapping of positrons in the defects present in the crystalline regions or in the crystalline–amorphous interface regions. The longest lived component (τ_3) with intensity I_3 was attributed to pick-off annihilation of the o-Ps in the free-volume sites present in the amorphous regions of the polymer matrix.[9–11]

As described earlier, the free-volume cavity radius (R) is related to the o-Ps pick-off lifetime (τ_3) by a simple relation. This relation is based on the quantum mechanical model first developed by Tao[19] for molecular liquids. This was later modified for solid polymers by Eldrup et al.[20] and Nakanishi et.al.[21] The underlying assumption in the formulation of this relation is that o-Ps atom in a free-volume cell can be approximated to a particle in a potential well of radius R_o. The potential is infinite if $r > R_o$ and constant for $r \leq R_o$. Further, it is assumed that there is an electron layer in the region $R < r < R_o$, with $R_o = R + \delta R$, where δR represents the thickness of the electron layer. The o-Ps in the electron layer has a spin-averaged lifetime of 0.5 ns. The expression connecting R (in nm) and the o-Ps pick-off lifetime τ_3 (in ns), according to Nakanishi et.al.,[21] is

$$(1/\tau_3) = 2\left[1 - (R/R_o) + (1/2\pi)\sin(2\pi R/R_o)\right] \quad (1)$$

where the value of $\delta R = 0.1656$ nm was determined by fitting experimental τ_3 values to data from molecular materials with well-known hole sizes, such as zeolites.[11] With this value of R, the free-volume size (V_f) is calculated as $V_f = (4/3)\pi R^3$. The fractional free volume (F_v) is then calculated as

$$F_v = C\,I_3 V_f \quad (2)$$

where the structural constant C for cotton fibers is evaluated by first determining the free-volume expansion coefficient (α) from positron results as $\alpha = 6.16 \times 10^{-4}$ K^{-1}; with this, C for cotton fibers turns out to be 0.006/Å.^{3}

Thermal behavior of free-volume sites in the amorphous regions

From the positron results, plots of o-Ps τ_3, average V_f and o-Ps intensity (I_3) were made as a function of annealing temperature and are shown in Figures 2(a) and 2(b), respectively. Similarly, τ_2 and its intensity (I_2) were plotted as a function of annealing temperature and are shown in Figures 3(a) and 3(b), respectively. F_v, calculated from eq. (2), is also shown in Figure 4. Figure 2(a) shows that τ_3 and, hence, V_f initially increased with annealing temperature up to 60°C, then decreased, and then changed slope at 80°C. Beyond 80°C, it increased up to 170°C and, thereafter,
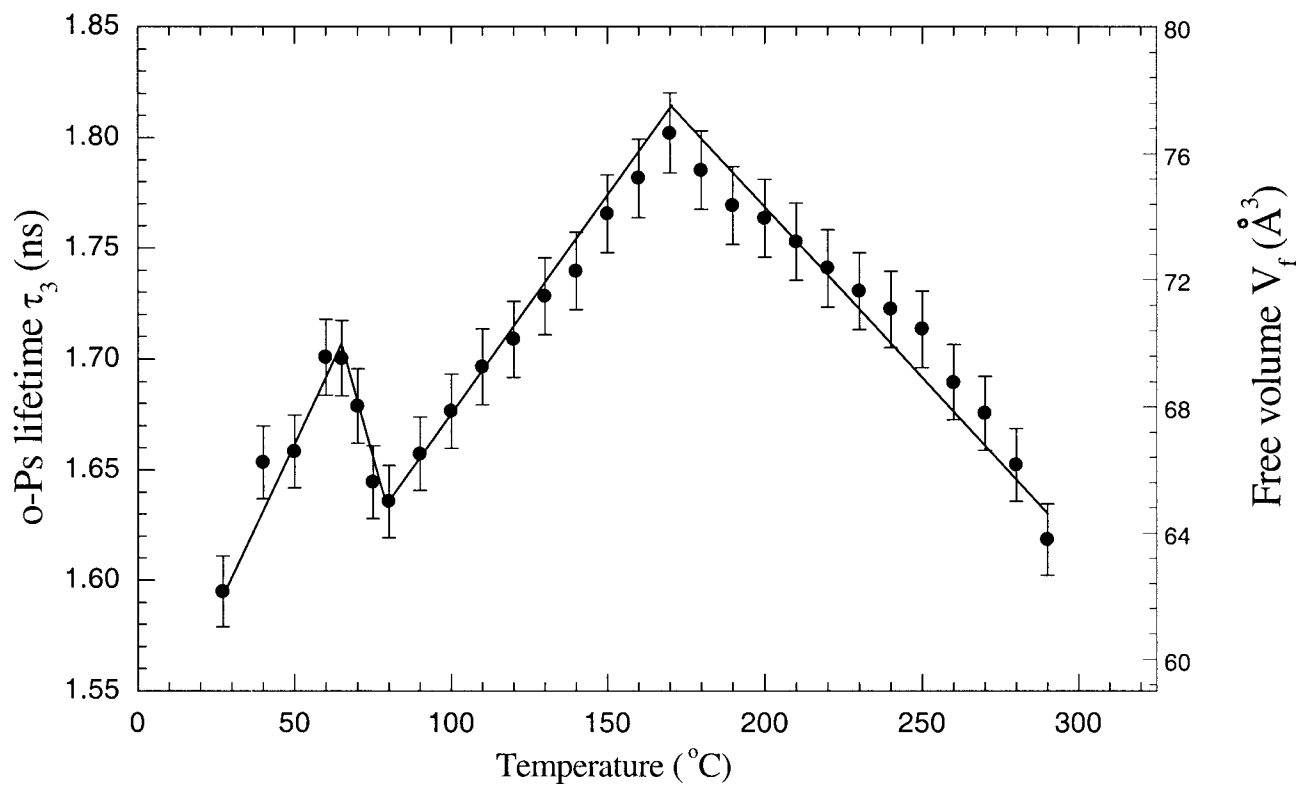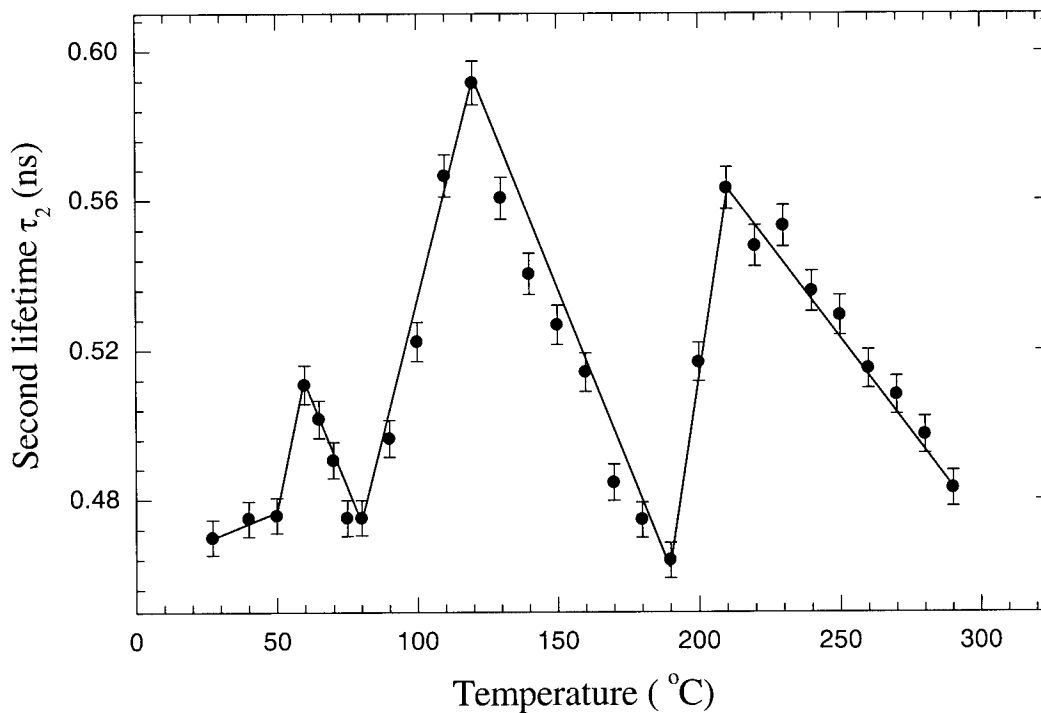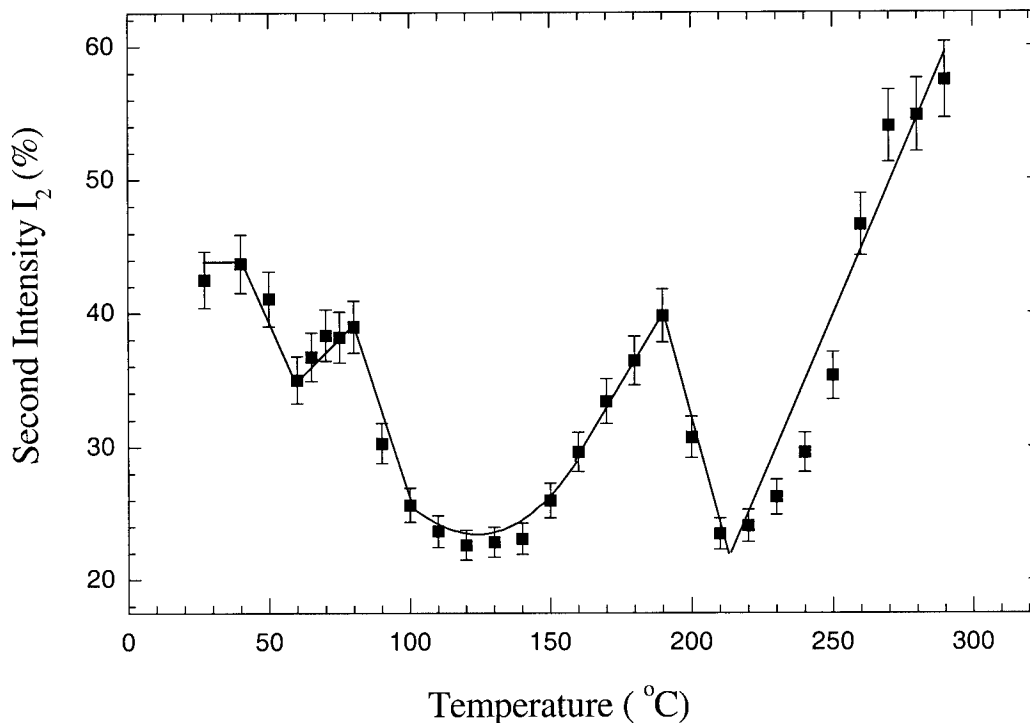
(a)
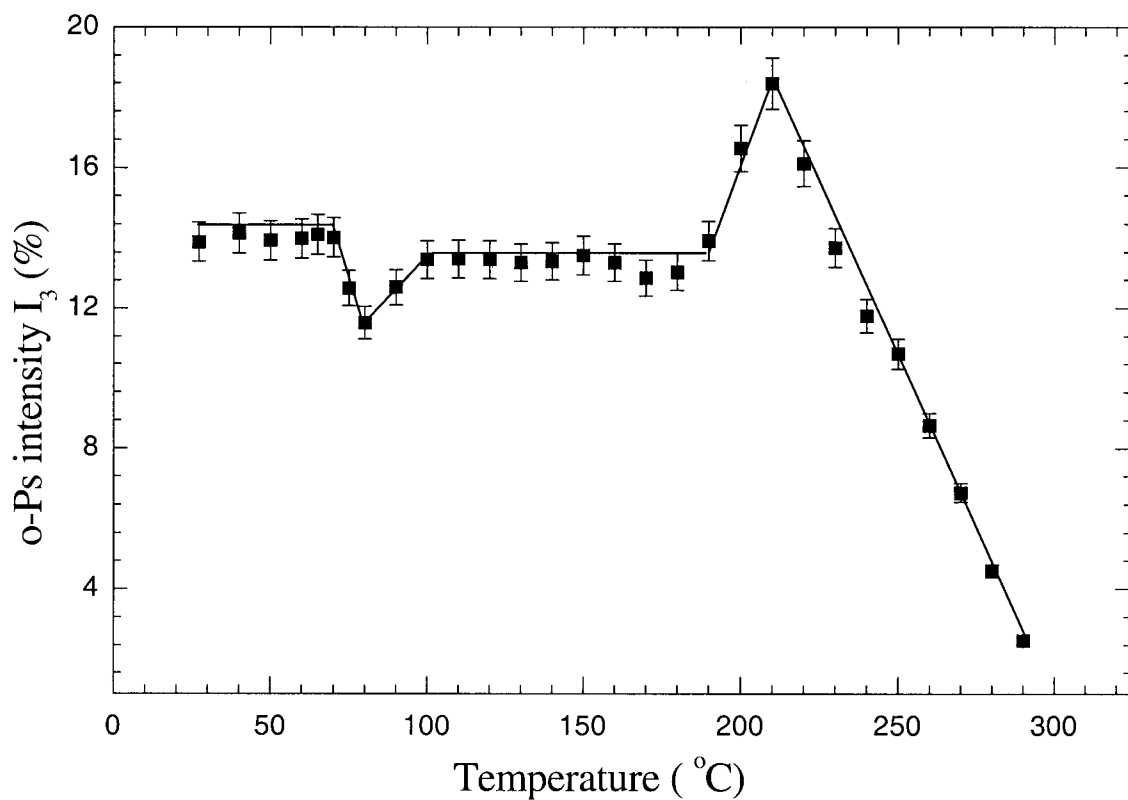
(b)

Figure 2 Variation of o-Ps (a) lifetime τ_3 and V_f and (b) intensity (I_3) as a function of annealing temperature. The solid lines are to guide the eye.

(a)

(b)

Figure 3 Variation of (a) second lifetime (τ_2) and (b) its intensity (I_2) as a function of annealing temperature. The solid lines are to guide the eye.

decreased continuously throughout the final stages of annealing. The o-Ps intensity, on the other hand, decreased slowly until 80°C was reached, then increased a little, and remained constant until 170°C was reached. Thereafter, it increased up to 210°C, beyond which it fell continuously until the end. Plausible explanations for these variations in positron results follow. As described in the Introduction, water is a con-
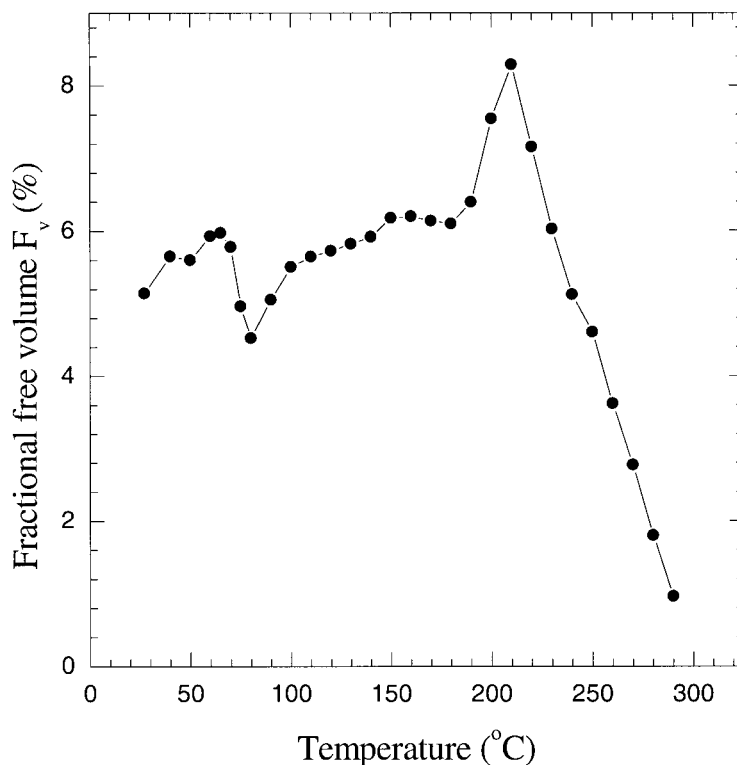
Figure 4 Variation of F_v as a function of annealing temperature. The solid line is to guide the eye.

stituent of the cotton fibers. These water molecules are mostly embedded in the amorphous regions of the fiber matrix; their removal seems to result in contraction of the fibers.[22] With an increase in annealing temperature, we expect the removal of water to increase further. As this happens, V_f, and the o-Ps lifetime, is expected to increase lifetime. This seemed to be possible in the initial stages of annealing. Second, the contraction of cotton fibers has an effect on the number density of free volume such that some of the fibers coagulate, leading to a decrease in their number, and hence, the o-Ps intensity is expected to decrease. This is what I observed up to 80°C.

After 60°C, the o-Ps lifetime and V_f began to decrease up to 80°C. Normally, T_g is characterized by the onset of cooperative motion of the molecular segments, more so in the amorphous regions. Below T_g, only limited local motion of a small fraction of the molecules is possible.[23] In this case, it appeared that this type of motion actually started from 60°C, and at each annealing temperature, some free-volume holes allowed fewer molecular segments to diffuse into them, leading to a decrease in the average V_f and their number density. The variation in τ_3, V_f, and I_3 supported this argument up to 80°C.

At 80°C, all three parameters, τ_3, V_f, and I_3, changed slope and started increasing. All these variations indicated that the T_g of the cotton fibers was 80°C. The differential scanning calorimetry (DSC) scan shown in

Figure 5 supported the positron results. Above T_g, the segmental motion in the fiber increased. This led to an increase in the average V_f, and hence, an increase in τ_3 was observed up to 170°C. As pointed out earlier, it was reported that the junction points (possibly hydrogen bonds) get broken under thermal treatment around this temperature.[6] Thus, the delinking of these junctions resulted in increased free volume, allowing greater segmental mobility. Interestingly, this long-range motion of the segments had very little effect on the number of free-volume sites. Beyond 170°C, τ_3 decreased monotonically, whereas I_3 increased up to 210°C and then decreased. This might have been due to crosslinking in cotton fibers by thermal treatment. This change is also interpreted as a change of structure from spiral to a three-dimensional network, which results in a more rigid material.[24–26] On account of crosslinking, a decrease in free volume[27] and an increase in the number density was observed. Beyond 210°C, all three parameters showed decreasing trends, indicating possible thermal degradation or decomposition of the cotton fibbers. This was supported by the DSC scan, which showed a transition at 213°C and is shown in Figure 5. Another plausible explanation for the changes in free volume in the final stages of annealing could be the following: temperature-induced crystallinity changes may have also changed the free-volume fraction of the cotton fibers. Crystallinity and free-volume fraction are inversely related.[11] I calcu-
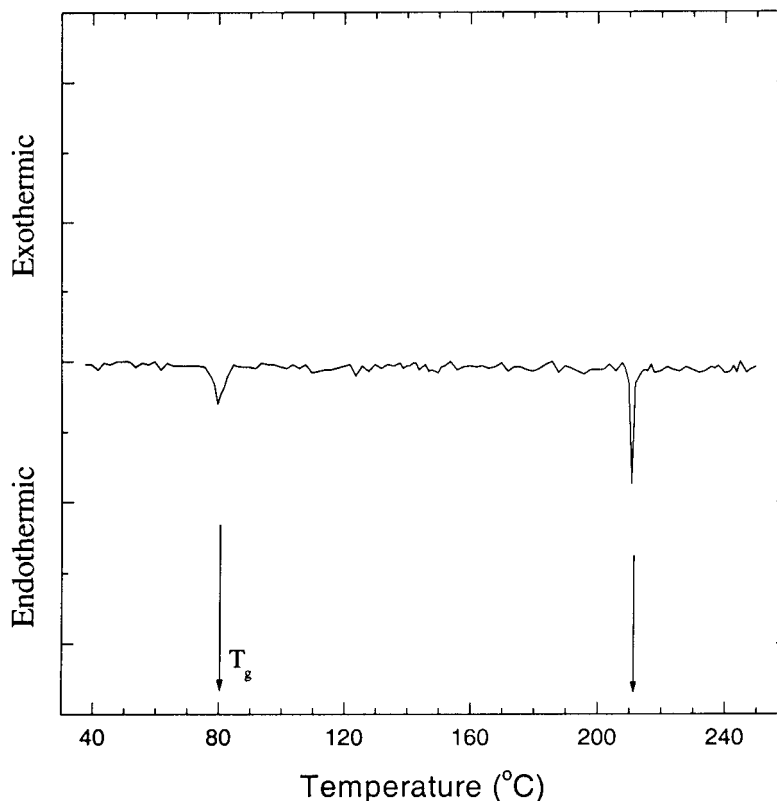
Figure 5 DSC scan of cotton fibers. Arrow marks indicate T_g and the decomposition temperatures.

lated crystallinity as $I_2/(I_2 + I_3)$[18] and plotted it as a function of annealing temperature; this graph looked exactly like that of F_v change (Fig. 4), suggesting that the crystallinity of cotton fibers increased with temperature, thereby reducing the F_v in the final stages of annealing.

Thermal behavior of crystalline and crystalline–amorphous interface regions

Figure 3(a,b) shows the variation of τ_2 and I_2 as a function of annealing temperature. These changes corresponded to the crystalline regions as per the treatment of Goldanski et al.[18] The molecular chains in cotton fibers take ordered arrangement and somewhat stable in the presence of water.[8] Because water molecules are present in the amorphous regions, as the removal of water molecule starts, the strain on the crystalline regions will be withdrawn,[28] and the chains get some freedom to rearrange. This rearrangement may give rise to larger size crystalline defects, as such an increase in τ_2 is expected. This arrangement also leads to a decrease in the number of these defects, and so I_2 is expected to decrease. The observed results were in tune with this explanation. Below T_g, local motion is frozen, and the changes in τ_2 and I_2 are due to the influence of changes in the amorphous regions. Our results showed that τ_2 and I_2 showed such behav-

ior up to 80°C. Beyond 80°C, intermolecular and intramolecular hydrogen bond breakage or dissociation may have taken place similar to that in amorphous regions, suggesting coagulation of crystalline defects. This resulted in increased defect size, which continued up to 120°C. After 120°C, thermally induced crosslinking seemed to occur, which was in agreement with the literature results, which showed that at 127°C, thermally induced crosslinking occurs in cotton fibers. The crosslinking seemed to cease at 190°C. Beyond this temperature, the changes in τ_2 and I_2 suggested that crosslinking changed the fiber structure from spiral[29] to a three-dimensional network.[24] After 210°C, the thermal degradation of the cotton fibers took place. Because I_2 is not an independent parameter like I_3, a definitive conclusion in terms of crystallinity change could not be drawn based on I_2 alone.

Activation energies

Positron results were further used to estimate the activation energies corresponding to the ordered regions (crystalline regions) and disordered regions (amorphous regions). To do this, I used Goldanski et al.'s[18] kinetic relations corresponding to the two regions of the fiber matrix. They are

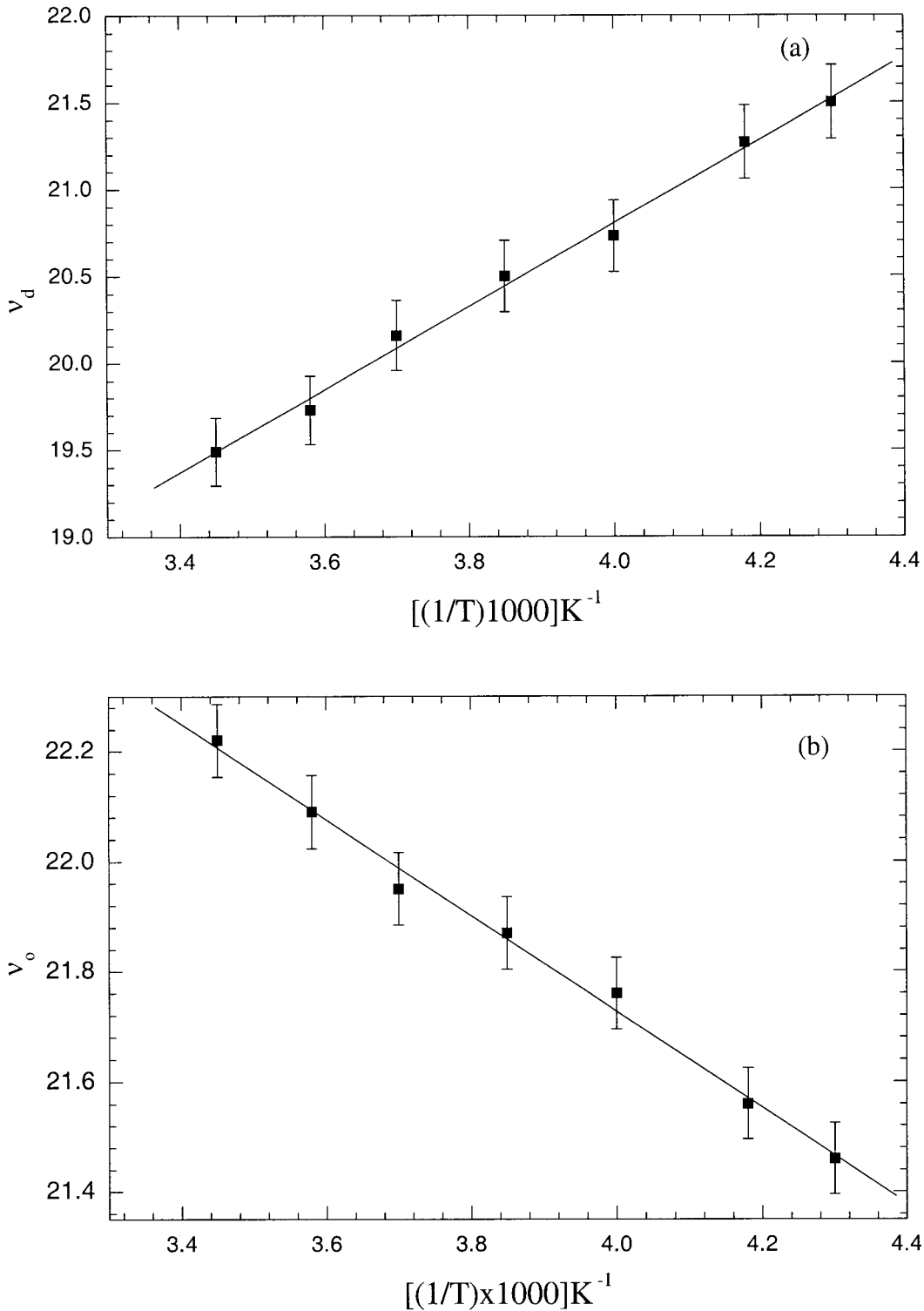$$\nu_o = [I_2/(1 - I_2)]*[1/\tau_1 - 1/\tau_2] \qquad (3)$$

Figure 6 Arrhenius plots for (a) disordered and (b) ordered regions The solid lines are fit to the experimental data.

$$\nu_d = 4I_3[1/\tau_1 - 1/\tau_3]/(3 - 4\,I_3 - 3\,I_2) \qquad (4)$$

where ν_o and ν_d are the trapping rates for positrons and Ps in ordered and disordered regions, respectively. Arrhenius plots of trapping rates as a function of $1/T$ for disordered and ordered regions are shown in Figures 6(a) and 6(b), respectively. The activation energies obtained from the slopes of these plots were $E_d = 20$ kJ/mol and $E_o = 8$ kJ/mol, where E_d is the activation energy for the disordered regions and E_o is the activation energy for the ordered regions. These activation energies corresponded to the temperature

region above T_g. The total activation energy turned out to be $|E_d| + |E_o| = 28$ kJ/mol. The energy required for hydrogen bond dissociation (O—H) is around 29 kJ/mol. Good agreement between these two values suggested that the O—H bond dissociation was the most probable process that occurred in the cotton fibers under thermal treatment.

Molecular weight estimation

The molecular weight of a polymer is an average quantity relative to the molecular weight of its individual macromolecules. This is one of the fundamental properties that distinguishes polymers from low-molecular-weight substances because the latter have absolutely definite values of molecular weight. The degree of polymerization, that is, the number of monomer units in a macromolecule determines the molecular weight of a polymer that is usually very large for polymers, such as cotton and silk. Many of the polymer properties depend on molecular weight, for example, tensile and impact strength, T_g, free-volume fraction, crosslinking, and viscosity. Experimentally, one can determine the molecular weight of the polymer by methods such as cryoscopy, membrane osmometry, gel permeation chromatography, and viscometry. All these methods require the polymer samples to be in solution form, and they are concentration dependent.[5] To the best of my knowledge, currently there is no method to determine the molecular weight of a polymer in solid form experimentally. Here, I made an attempt, which was nondestructive in character, to extend the positron measurements to estimate the molecular weight of the natural polymer–cotton fibers by exploiting the connection between free volume and viscosity. Free volume is inversely proportional to the viscosity, which in turn, is related to the molecular weight through the well-known Mark–Houwink relation.[5] For this purpose, I plotted free-volume cell size as a function of molecular weight for different polymers (data collected from literature[2,30−34]), and these data fit well to a power relation of the type

$$V_f = AM^{-\beta} \tag{5}$$

where A is a constant, M is the molecular weight, and β is the exponent. These were evaluated from the fit, and their values were 5287 and 0.32, respectively, with a correlation coefficient of.93. Using these values and the free-volume cell size from these measurements, I estimated the molecular weight of the cotton fibers to be 1,200,000. This value lies in the range 800,000–3,000,000 that is suggested for cotton.[2,3] However, there is no independent measurement with which to compare these results.

CONCLUSIONS

1. I demonstrated that PLS is a versatile tool in probing the thermal behavior of cotton fibers through free-volume measurement.
2. PLS measured the T_g of cotton fibers at 80°C, which was in good agreement with the DSC result.
3. On the basis of free volume, the molecular weight of the cotton fibers was determined to be 1,200,000, which lies within the range suggested for cotton.
4. Activation energies were measured separately for the crystalline and amorphous regions, thereby demonstrating the versatility of the technique. The values corresponded to the O—H bond dissociation energy, suggesting O—H bond dissociation.
5. There seemed to be an indication that crosslinking changed a spiral structure to a network type in the cotton fibers. However, to support this observation, validation is needed from other techniques.

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