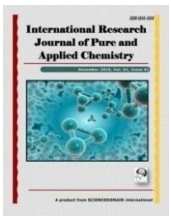

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Study of Microstructure and Molecular Dynamics of Cotton and Cellulose Fibers by Methods of Physical Labels

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Authors' contributions

This work was carried out in collaboration between both authors. Authors ILG and YIK designed the study and wrote the protocol. Author YIK performed experiments and calculations and prepared illustrations. Both authors discussed, wrote and approved the final manuscript.

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Review Article

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ABSTRACT

Methods of physical labelling have been proved to be a powerful tool for solving a number of problems in chemistry, physics and biology at a molecular level. This review concisely describes all the principle aspects of the application methods of nitroxide spin and luminescence labelling for the investigation of cotton fibres and cellulose: Chemical modification by the labels, with the use of Electron Spin Resonance (ESR) and fluorescence and phosphorescence techniques for the measurement of molecular dynamic parameters of the labelled samples' molecular dynamics, their distribution, and the label location in objects of interest. Experimental data on dependencies of the fibres' molecular dynamics on origin, temperature, water and other plasticising agents, nutrition, period of maturing and radiation have been presented. ESR experiments have revealed a strong dependence of fibres' resistance to stress on microscopic structural defects. The developed combined spin and luminescence labelling approach, the efficiency of which is demonstrated in this

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review, can be used in the investigation of molecular dynamics, microstructure polymers and other complex molecular objects.

Keywords: Cotton fibres; cellulose; nitroxide spin labels; luminescence labels; molecular mobility; structural defects; stress resistance.

1. INTRODUCTION

The role of cotton fibres and cellulose in industry, medicine and human beings' everyday lives is impossible to overestimate. Cotton is used to make a number of textile products, gunpowder (nitrocellulose), cotton paper and other plant fibres. Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and oomycetes [1-9].

The molecular dynamic properties of a vast number of objects, including liquids, polymers, organic and inorganic materials, and biological systems in particular, are a base for their functional activity, technological characteristics, stability, compatibility, and so forth. Physical labelling methods have been proved to be a powerful tool for the investigation of the molecular mobility and structure of various objects [10-23].

The basic idea underlying this approach is the modification of the chosen sites of the object in question with specific compounds, commonly nitroxide (NRO), fluorophores, Mössbauer atoms and electron density compounds which are bound covalently (labels) and/or non-covalently (probes), whose properties make it possible to trace the state of the surrounding biological matrix via appropriate physical methods. The principle advantage of the physical labelling method is possibility to take direct information about local structure, mobility, micropolarity, acidity, redox status and electrostatic potential of certain parts of the molecular object of any molecular mass and optical density. Developments in synthetic chemistry have provided researchers with a wide assortment of labels and probes, and have paved the way for the specific modification of molecular objects.

According to the theory and large body of experimental data, the rotation and intramolecular motion of a molecule including a label in a condensed phase are modulated to a great extent by the molecular dynamics of the surrounding molecules. This phenomenon is caused by the relatively tight packing of molecules of liquids and solids on the one hand and the existence of static and dynamic defects in these systems of the other. Essential knowledge about the microstructure and molecular dynamic state of the system under investigation can be derived from the measurement of static and dynamic spin-spin interactions between nitroxides and other paramagnetic compounds at its encounters. Similar independent information can be obtained from data on quenching exited singlet and triplet states of fluorescent and phosphorescent labels.

This review is intended to provide the physical principles of methods based on the use of the above mentioned nitroxide spin, fluorescence, phosphorescence, Mössbauer and mercury electron density labels and its applications in the investigation of cotton fibres and cellulose.

2. NITROXIDE SPIN LABELLING

2.1 Chemical Modification of Cotton Fibres and Cellulose with Nitroxide Spin Labels

The covalent modification of an OH group of cotton and cellulose fibres performed with correspondent nucleophilic reactions using nitroxide spin labels was described in detail in [24-26].

Formula 1

In a typical experiment, 25 mg of a cotton or cellulose fibre in 0.8 ml dimethylformamide in the presence of pyridine was treated with 0.1 ml of radical I or II solutions in acetone at a concentration of 10^{-2} M. The mixture was incubated for 48 hours at a temperature of 300 K and then two hours at 340 K. After rinsing with water, acetone and ethanol and incubation at a certain relative humidity, the continuous wave electron spin resonance (CW ESR) spectra were taken using PE-1301 and PE-1306 radio spectrometers.

Samples of cellulose labelled with stable nitroxyl radicals were prepared through mechanochemical synthesis [27].

Formula 2

The samples were studied by IR and EPR spectroscopy, X-ray phase analysis and electron microscopy. The EPR spectral patterns indicate a uniform distribution of paramagnetic centres over the cellulose macromolecule chains. Methods of modification of cellulose were recently described in [28].

2.2 Nitroxide Molecular Dynamics

Any motion of a nitroxide radical is greatly influenced by the molecular dynamics of surrounding molecules. A widely-employed parameter which characterises the molecular motion of nitroxide is the rotational diffusion correlation time (τ_c), the time of rotation by one radian. Nitroxide radicals in different solvents and at different pressures display a functional correlation between τ_c and the viscosity of the solution (μ) that follows from the Stokes-Einstein equation. The values of effective energy activation of nitroxide rotational diffusion (E_{eff}) in pure liquids and water-glycerol mixtures are approximately equal to the values of activation energy for viscosity in these systems. These data provide a way in which to investigate the properties of the molecular dynamics of cotton and cellulose fibres in the vicinity of attached nitroxide labels.

A widely-employed parameter which characterises the molecular motion of nitroxide is the rotational diffusion correlation time (τ_c), the time it takes for a molecule to rotate by one radian.

Modern ESR techniques allows ones to access dynamic processes that are characterized by a wide range of correlation time, τ_c = 10^2–10^{-10} s. Fig. 1 shows the effect of a nitroxide rotation on its first harmonic ESR spectra (V_1), theoretically calculated in the frame of 3 mm X-band ESR spectroscopy. Analysis of experimental spectra allows the calculation of the correlation time value.

For example, in the region of motion with τ_c 10^{-7} – 10^{-8} s the following equation can be used [19]:

$$\tau_c = ax\left(1-\frac{A_{zz}}{A_{zz}^0}\right)^b \qquad (1)$$

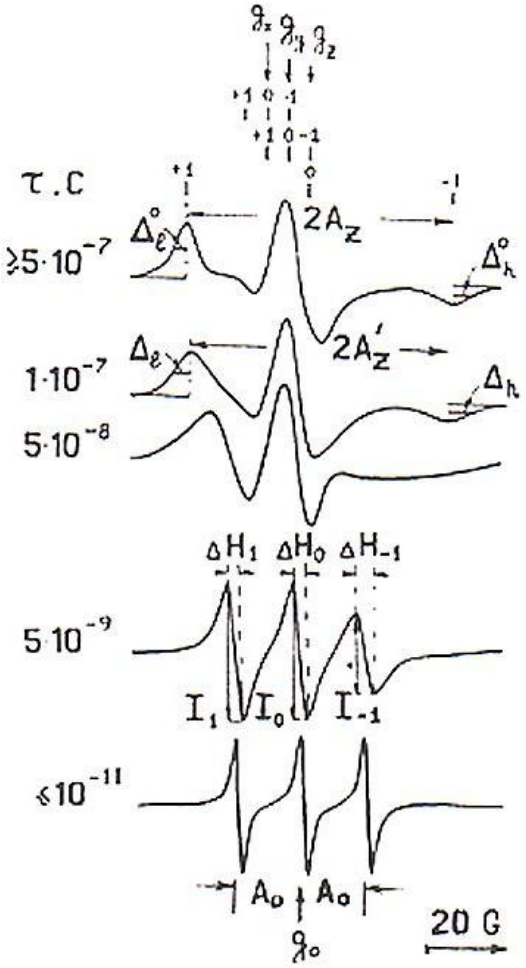

Fig. 1. Theoretically calculated the first harmonic ESR spectra in the 3-cm band (V_1) at different values of the nitroxide rotation correlation time. [16 and references therein]

where A_{zz}^0 an and A_{zz} are the z-components of A-tensor for immobilised (determined from the rigid limit spectrum) and mobile nitroxide, respectively. The coefficient *a* was found to be 5.4×10^{-10} and 2.6×10^{-10} s for systems modelling isotropic and anisotropic Brownian diffusion, respectively, and *b* was found to be –1.36 and –1.39 for the aforementioned models. Spectra of the ESR spectra second harmonic (V_2) are sensitive to nitroxide motion in the temporal range τ_c = 10^{-4}–10^{-5} s. According to theory the line form of nitroxide ESR spectrum is affected by the low-amplitude high-frequency vibration of radical and surrounding molecules.

Figs. 2 and 3 showed the effect of temperature on V_1 and V_2 for different kinds of cotton fibres. The component h' in the spectra at 373 K is caused by the appearance of a small fraction of structural defects in which fast rotation ($\tau_c \approx 10^{-9}$ s) occurs (Fig. 2).

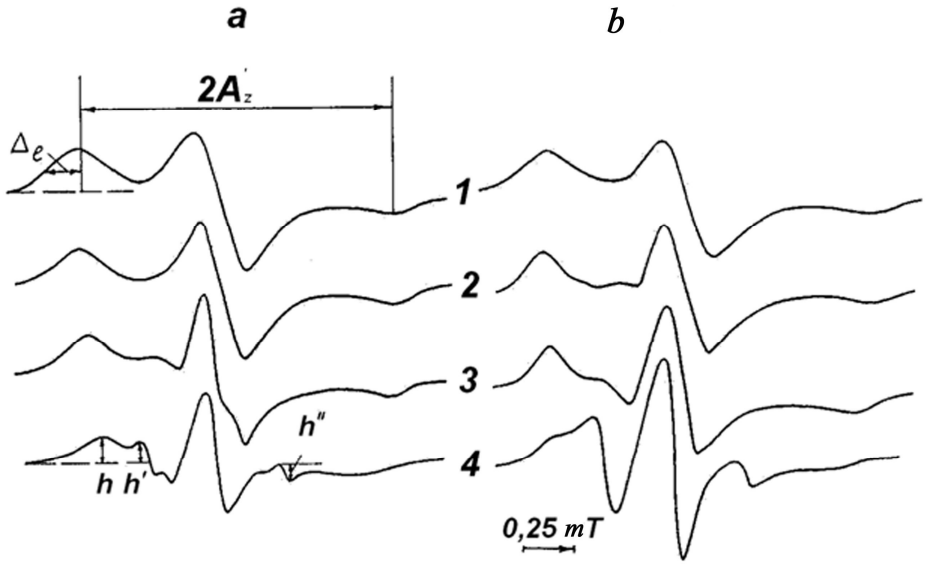

Fig. 2. The first harmonic ESR spectra (V_1) for spin labeled cotton fibers a - «5595-B», b- "Tashkent 1" Temperature 1) 123 K, 2) 213 K, 3) 323 K, 4) 373 K. Relative humidity P/P_0 = 0.96 [26]

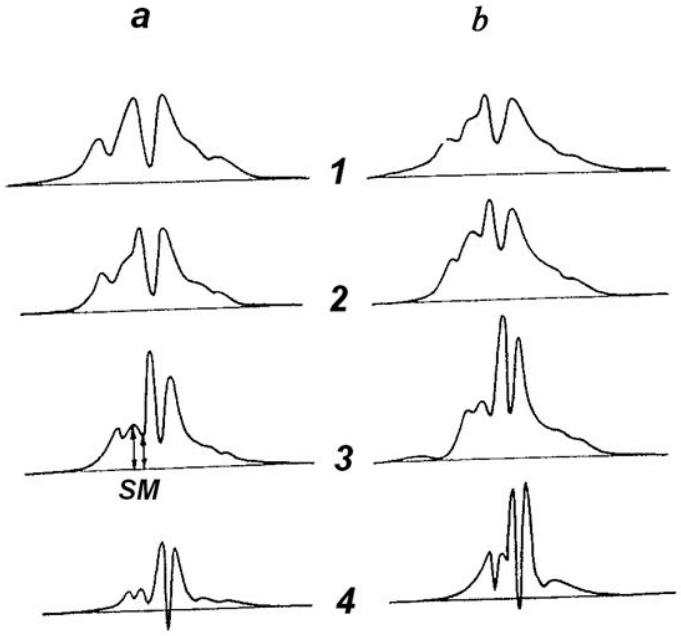

Fig. 3. The second harmonic spectra (V_2) for spin labeled cotton fibers a - «5595-B», b- "Tashkent 1"Temperature 1) 123 K, 2) 213 K, 3) 323 K, 4) 373 K. Relative humidity P/P_0 = 0.96 [26]

Change of the V_2 spectra starting from 213 K (Fig. 3) can be explained by the label motion with correlation time in submillisecond region [16, pages 24-29].

Temperature dependencies of parameter $2A_z^{'}$ for the nitroxide spin label I incorporated in different cotton fibres are presented in Fig. 4a. The $2A_z^{'}$ dependencies at temperatures above ≈ 210 K are caused by high amplitude motion with correlation time $t_c < 10^{-7}$s. Narrowing of Δ_l at temperatures from 253 K to 263 K (Fig. 4b) can be explained by the effect of low-amplitude vibrations, while further the line broadening is most probably affected by the animation of the wobbling of the label nitroxide fragment at temperatures above 273 K.

A decrease of parameter $2A_z^{'}$ (Fig. 4a) starting from T = 210 K indicates an animation of the nanosecond wobbling of nitroxide radicals incorporated in cotton fibre. A temperature increase up to 393 K leads to the motion intensification in the nanosecond region of correlation time. All investigated samples of cotton fibres demonstrated a similar tendency in their dynamic behaviour. Nevertheless they are distinguished by some details.

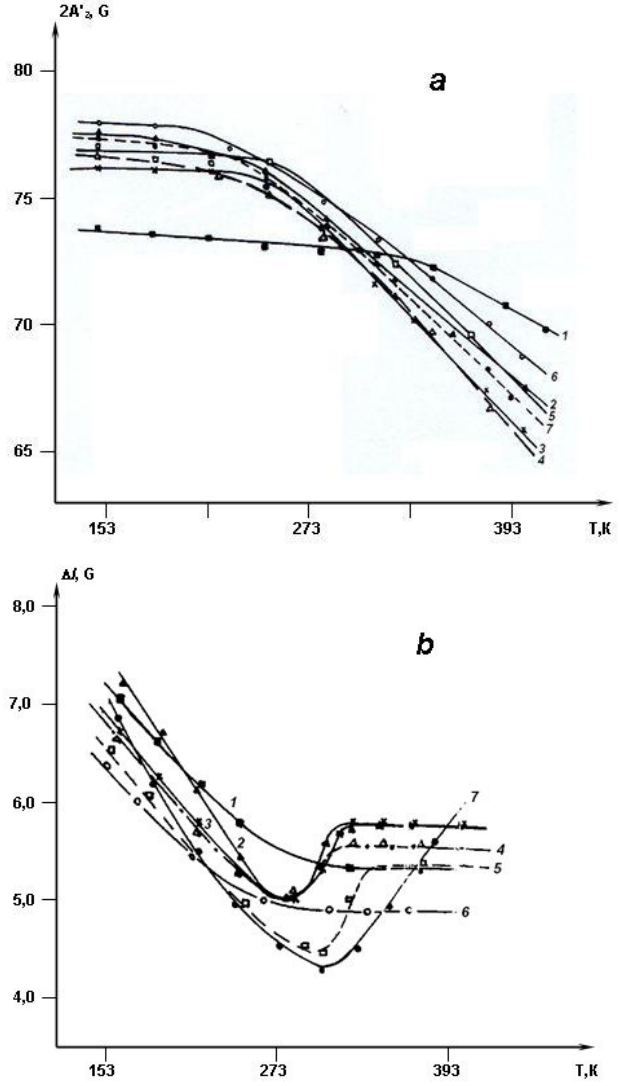

Fig. 4. Temperature dependences of parameters of ESR spectra, $2A_z^{'}$ (a) and Δ_l (b) at relative humidity P/Ps = 0,96 for various samples of cotton fibres [29]

High resolution, high-frequency 2-mm ESR spectroscopy provides a unique possibility to derive the values of g- and hyperfine structure (hfs, $A_{x,y,z}$) tensors directly from ESR spectra (Fig. 5) [30]. Detection of the hpf tensor allows detailed information to be obtained about the mechanism and intensity of nitroxide anisotropic motion.

The dynamic behaviour of spin-labels with nitroxides located in dry samples of cotton fibre from “5595-B” was investigated with the use of high resolution, high-frequency (2-mm) ESR spectroscopy [31].

ESR spectra of microcrystal cellulose derived from thinfiber cotton at temperatures 293 (1), 333 (2) и 373 K (3) and relative humidity P/P_s= 0,96 are shown in Fig 6. On the basis of the examination of the spin probes’ temperature dependence over the range150 –320 K it was concluded that within the temperature range 280–300 K only a slight change in the nitroxide ESR parameters occurred while above about 300 K nitroxide rotation is essentially anisotropic with correlation time $\tau_c = 10^{-7} – 10^{-8}$ s. The temperature dependencies of dynamic parameter 2 Azz for different samples of microcrystal cellulose (MCC) are similar to that for cottons. MCC from thin fibre cotton is characterised by higher stability at T > 273 K than other samples. Nevertheless, ESR spectra of the labelled MCC from thin fibre cotton show a significant contribution of the h' component caused by a high concentration of structural defects.

2.3 Labels Location

2.3.1 Depth of immersion of nitroxide

In the investigation of the molecular dynamics of a polymer using a physical label, it is necessary to know the depth of the label’s immersion. Under certain circumstances the ESR paramagnetic centres will respond suitably to the approach of other centres. Two types of spin-spin interaction can be distinguished:

Two types of spin-spin interaction can be distinguished: (1) Dipole dipole interaction associated with the fact that the magnetic dipole of one paramagnetic group induced a local magnetic field at the site of another paramagnetic group; (2) Exchange interaction caused by overlap of orbital of unpaired electrons as paramagnetic particles approach to each other [33-38].

These phenomena were the basis of the method for the measurement of distance between compounds bearing spin.

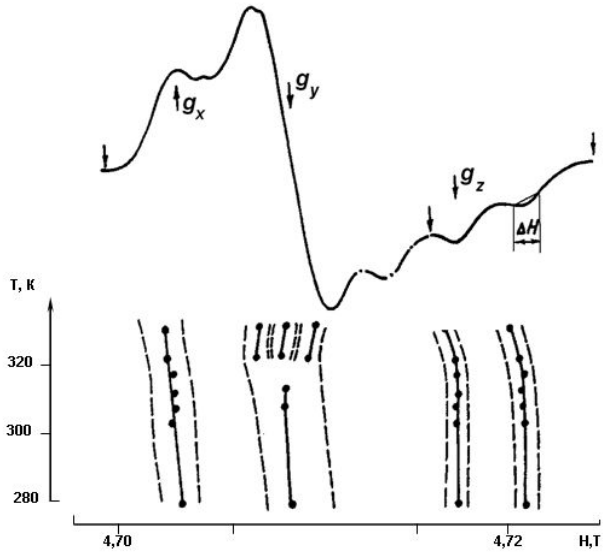

Fig. 5. High resolution (2 mm) ESR spectrum of spin labeled cotton fiber «5595-B at relative humidity P/P_s = 0.04 and temperature 150 K (a); Dependence of parameters of g and A tensors on temperature (b) [31]

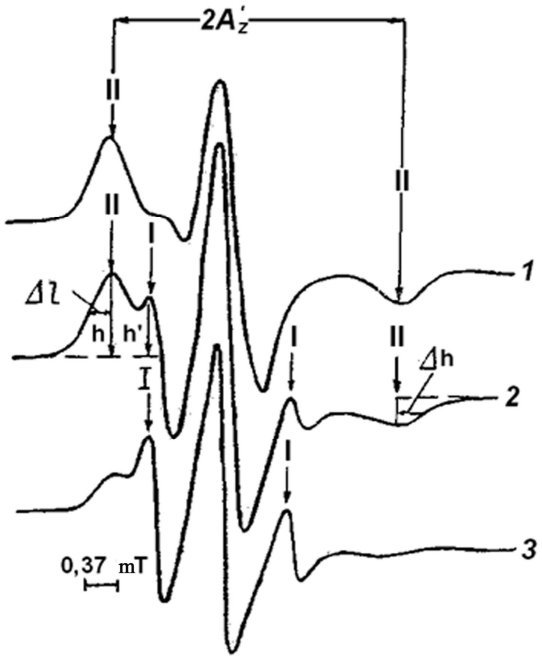

Fig. 6. ESR spectra of microcrystal cellulose derived from thinfiber cotton at temperatures 293 (1), 333 (2) и 373 K (3) and relative humidity P/Ps= 0,96. Arrows I and II indicate positions of components related to fast and slow rotating radicals, correspondingly [32]

A method was developed for determining the nearest distance (r_{min}) between a stable radical (R·) and an ion of paramagnetic metal, an ion-relaxator (IR), which has effects on the spin-lattice relaxation time of R· and is randomly distributed in the bulk of the vitrified sample [39-43]. In the case of R· penetration into an impermeable matrix (macromolecule, membrane, so forth), the r_{min} value is equal to the radical immersion depth. If the centre resides at a sufficient depth, $r_{min} > r_{av}$, where the latter value is the average distance of radicals, the contribution of the dipole interaction of IR to the R· spin relaxation rate is expressed by the equation:

$$\Delta\left(1/T_{1e}\right) = \frac{A_d \mu^2 \gamma^2 \tau_{1e} C}{r_{\min}^3} \qquad (2)$$

where $1/T_{1e}$ is the nitroxide spin-lattice relaxation rate, C is the IR concentration, μ and τ_{1e} are magnetic moment and the spin relaxation rate of the IR, respectively, and A_d is a factor that depends on the geometry of the surface. For example, if the surface is flat, A_d = 0.2. Equation 2 predicts the linear dependencies of the enhancement of the spin relaxation rate upon C in the case of NR immersion at different depths. The value $\Delta(1/T_{1e})$ can be derived by analysis of ESR spectra saturation curves (ESRSC), which are a dependence of the intensity of ESR spectra on the intensity of a microwave field, in the presence of ion-relaxator. The immersion death rim values can be derived plotting $\Delta(1/T_{1e})$ versus the IR concentration.

The sensitivity of the ESR spectra correlation curves for spin-labelled cotton and cellulose fibres to the nature of the object and presence of ion-relaxator ferricyanide are shown in Fig. 7.

Table 1 shows values of the spin label I depth immersion of spin label one in fibers (r_{min}). Thus the nitroxide fragment of spin label I is immersed in the structure cotton fibre and *a*-cellulose at a distance of roughly 0.1 nm. Thus the nitroxide fragment of spin label I is immersed in the structure cotton fibre and *a*-cellulose at a distance of roughly 0.1 nm. This fact has to be taken in consideration in a discussion of experimental data on molecular dynamics and mechanical properties of fibers under investigation using spin label I.

2.4 Microstructure of Cotton Fibres and Its Durability

The role of the microstructure of organic and nonorganic materials in its stability under tensile stress is a basic challenge and applied problem. According to the widely accepted kinetic theory by S.N. Zhurkov [45-47], a sample durability (r) can be described with the following equation:

$$r = \tau_0 e^{\frac{U_0 - \sigma\gamma}{kT}} \qquad (3)$$

where U_0 is the energy activation of mechanic destruction, τ_0 is the frequency of atomic vibration, σ is the applied tention and γ is the activation volume sensitive to the sample structure.

The effect of the defects in the microstructure of cotton samples detected by spin labelling methods was investigated using a Zhurkov device. The samples were prepared as 0.5 mg, 10 mm long strips and were put under gradually increased stress. The obtained parameters of Equation 3 are presented in Table 2.

Table 1. Values of the spin label l depth immersion of spin label one in fibers (r_{min}) [44]

Fiber	Paramagnetic complex	Solvent	r_{min}, нм
α-cellulose	$K_3Fe(CN)_6$ $Co(AA)_2 \cdot 2H_2O$	water glycerol (1:1) ethanol	0,1
Cotton fiber	$K_3Fe(CN)_6$	water glycerol (1:1)	1,05

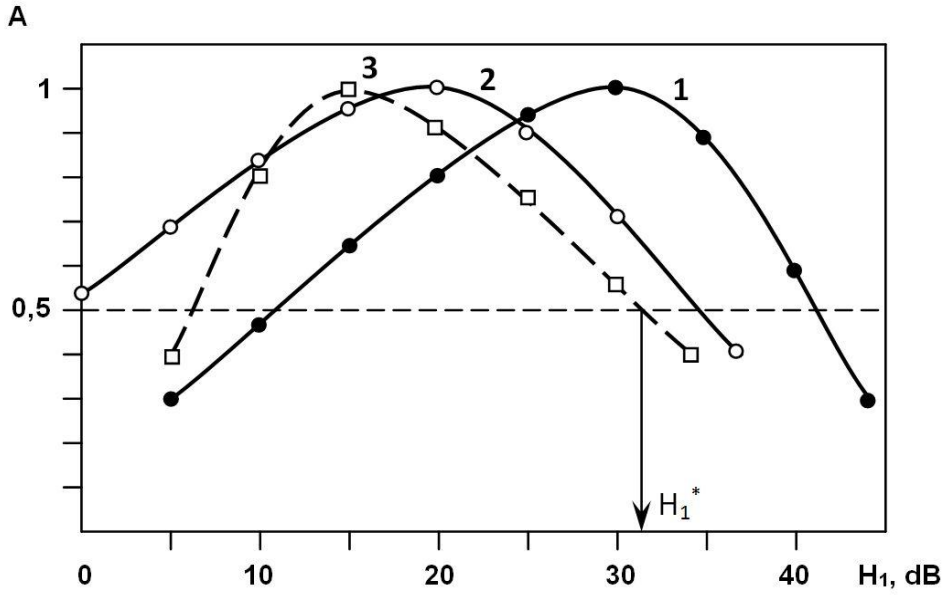

Fig. 7. ESR spectra saturation curves of spin labeled fibers in water-glicerol mixture at 77 K: 1 *a*-cellulose (without ferricyanide); 2 *a*-cellulose ($3{,}9 \cdot 10^{-2}$M ferrycyanide); 3—cotton fiber (without ferricyanide} A is intensity of center component of ESR spectra, H_1 is intensity of microwave field [44]

Table 2. Parameters of the Zhurkov Eq. 3. Loose phase (defects) fracture of cotton fibers (n) derived by the spin labeling and Zhurkov parameters for the samples at T = 300 K; $\xi = d(h'/h)/dT$ is the rate of increase of parameter 'h/h; which characterizes a loosing of the polymer structure at temperature increase above 333 K;[48']

Fiber	n –defects fracture	ξ, K^{-1}	σ_p, мн/м^2	U_0, kJ/mole	$\gamma \cdot 10^{-4}$, м^3/mole
«5595-B»	2±0,5%	0,009	280±12	142±7	2,6
«Taskent-1A»	6±2%	0,030	180±12	141±7	4,9
(«Tashkent-1B»	28±2%	0,070	150±12	141±7	6,0

As is seen in Table 2, the energy activation of mechanic destruction is practically the same for all samples, which indicates that the process occurs as a break in chemical bonds. The difference in the samples' duration is caused by differences in fracture structural defects (n). The larger n is, the smaller ξ and σ_p are, and the higher γ is – this equates to lower sample durability.

3. FLUORESCENCE AND PHOSPHO-RESCENCE LABELLING

3.1 Molecular Dynamics of Cotton Fibres

Because of their high sensitivity, fluorescence and phosphorescence techniques are especially suited to solving many problems of structure and dynamics of the molecular system [16,22]. The

excitation of a chromophore group is accompanied by a change in the electron dipole moment of the molecule. This involves a change in the interaction energy with the surrounding molecules, which manifests itself by a shift of the time-dependent frequency maximum of the fluorescence spectra, (relaxation shift).

The value of characteristic (relaxation) time of the polar environment relaxation in the vicinity of excited chromophore (τ_r) can be derived from an analysis of the temperature (T) dependencies of the relaxation shift using the following equation [16,49,50]:

$$\Delta\nu_{\max}(T) = \frac{[\nu_{\max}(0) - \nu_{\max}(\infty)]\tau_f}{[\tau_f + \tau_r(T)]} \quad (4)$$

Where $\Delta\nu_{max}$ *(T)* is the relaxation shift in the steady-state fluorescence (phosphorescence) spectra, τ_f is the fluorescence (phosphorescence) life time and indexes 0 and ∞ are related to maximal relaxation shift. A gradual increase in temperature results in the gradual decrease of the τ_r. The experimental $\Delta\nu_{max}$ *(T)* – T dependence can be used for the estimation of τ_r*(T)* at each temperature if τ_f is known.

In real systems (viscose liquids, polymers, proteins, membranes, etc.) there is, as a rule, a set of τ_r values, relaxation energy and entropy activation, and other parameters. This is because the analysis of the experimental data on relaxation shifts in such systems requires special approaches [16]. For instance, if one assumes a Gaussian distribution over the free activation energies of the reorientation of surrounding particles ($\Delta F^{\#}$), it is possible to find an expression to relate the energy activation of relaxation in the distribution maximum (E_{max}) to the second moment of the distribution curve (ΔF_0^2).

$$E_{app}(T) = E_{\max} - \frac{\Delta F_0^{\,2}}{RT} \quad (5)$$

where E_{app} (T) is the experimental value of apparent energy activation derived from the Arrhenius plot, log $\Delta\nu_{max}$ (T) – 1/T. Eq. 5 allows the estimation of E_{max} and (ΔF_0^2) plotting E_{app}(T) versus 1/T.

To investigate the molecular dynamics of cotton fibres, samples of interest were covalently modified with erythrosine thiocynate, which in an excited state can emit fluorescence and phosphorescence [51].

As one can see from Fig. 8, starting from T = 100 K a decrease in intensity of erythrosine phosphorescence J_{ph} (1.1') and fluorescence J_{fl} and a parallel increase in the position of the maximum of phosphorescence λ_{ph}^{max} (2.2') and fluorescence λ_{fl}^{max} (4.4') take place. Taking into consideration that the phosphorescence parameters are sensitive to processes of molecular dynamics in the submillisecond range, while fluorescence parameters are sensitive in the nanosecond range, we can come to a conclusion about the distribution of polar relaxation times, $\tau_r$in the samples under investigation. This conclusion is confirmed by analysis of the experimental dependencies of the time of polar environment relaxation in the vicinity of excited chromophore (τ_r), derived from Eq. 4. Plotting values of apparent energy activation E_{app} = 2.3 R$[\frac{dlg\tau_r}{d(\frac{1}{T})}]$ versus 1/T (Fig. 9) allowed the calculation of the energy activation of relaxation in the distribution maximum (E_{max}) to the second moment of the distribution curve for the free activation energies of the reorientation of the surrounding particles ΔF_0 using Eq.5. The obtained values of E_{max}, taken from data on relaxation shift of fluorescence and phosphorescence, were found as 42 kJ/mole and 67 kJ/ mole, correspondingly. The analysis gave the ΔF_0 value equal 10.5 kJ/mole and 6.7 kJ/mole for data on the relaxation shift in the fluorescent and phosphorescent spectra, respectively.

3.2 Depth of immersion of Phosphorescence Label in Cotton Fibre

To elucidate the location of a phosphorescent label (erythrosine) covalently incorporated in cotton fibre, which was also a source of information about the fibre's local dynamics, a method for determining the depth of the immersion of a luminescence chromophore (r_{im}) was employed [52]. The method is based on experimental measurements of rate constants of quenching luminescence in conditions of free access between chromophore and quencher (k_{qd}) and between immersed chromophore and free quencher (k_{qk}) [21,40,53].

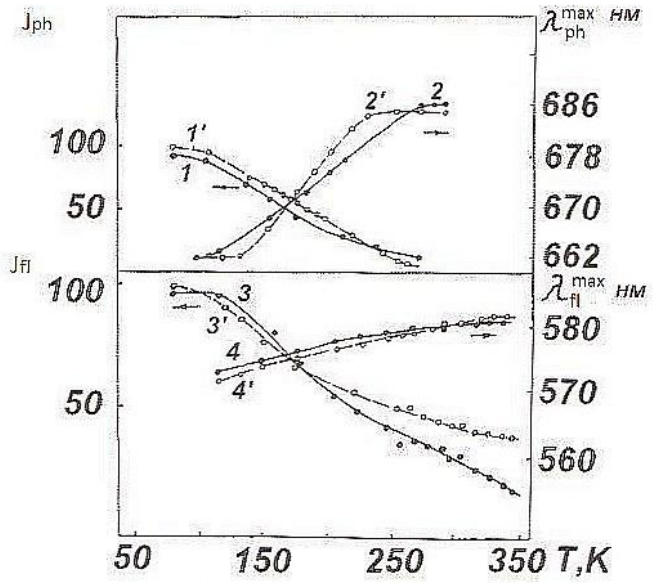

Fig. 8. Temperature dependence of intensity of phosphorescence J_{ph}(1,1') and fluorescence J_{fl} (3,3'), position of maximum of phosphorescence λ_{ph}^{max} (2,2') and fluorescence λ_{fl}^{max}(4,4') spectra of erythrosine thiocyanide covalently bound to cotton fibers of Tashkent 1 (bold line) and Tashkent 1a (dotted line) [52]

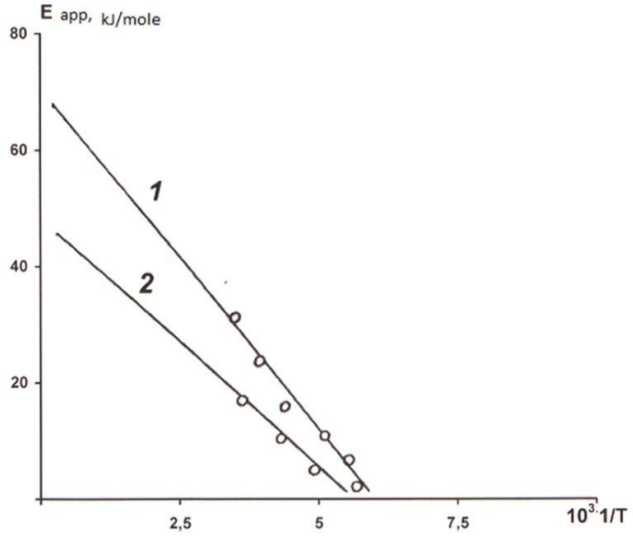

Fig. 9. Dependence of apparent energy activation E_{app} = 2.3 R[$\frac{dlg\tau_r}{d(\frac{1}{T})}$] on 1/T. on 1/T. The relaxation time values □*r(T)* were derived from temperature dependence of λ_{ph}^{max} and λ_{fl}^{max}, respectively [52]

For the measurement of r_{im}, the following equation can be used

$$\frac{k_{qd}}{k_{qk}} = \tau_c^2 10^a \exp 2(-\beta(R_0 - r_V) \quad (6)$$

where β = 2 and 1.3$Å^{-1}$ and *a* = 28 and 26 for the intersystem crossing (ISC) and electron transfer (ET) quenching mechanisms, respectively, and τ_c ≈ 10^{-10} s is the encounter complex's life time. This equation was used to determine a phosphorescent label immersion depth $r_{im} = (R_0 - r_v)$, where R_0 is the Van der Waals distance between chromophore and quencher and r_v is the distance between immersed

chromophore and quencher in the encounter complex.

Fig. 10 shows the effect of various concentrations of a quencher on the initial decay of phosphorescence of erythrosine covalently attached to cotton fibre "Tashkent 1A", which allows the value of phosphorescence life time, *tph*, to be obtained for each concentration of the quencher followed by the calculation of the quenching constant k_{qd} and (k_{qk}) using Stern-Volmer dependencies. The ratio (k_{qd})/(k_{qk}) (Table 3) was employed for the determination of the label depth immersion in the cotton fibre (Table 4).

Table 3. Rate constants of phosphorescence quenching of free eosin and erythrosine after attachment to cotton fibers by radical 3 in water solution and T =293 K [53]

№№	Fiber	*kq*
1.	Eosin in solution	$5{,}9 \cdot 10^9$
2.	"Tashkent A"	$2{,}2 \cdot 10^6$
3.	"Tashkent B"* ----------"	$5{,}3 \cdot 10^6$

According to the data presented in Tables 3 and 4, the depth of the immersion rim of nitroxide spin label 1 and triplet label 4 into cotton fibres was found to be 10 Å and 8 Å, respectively. Therefore the labels' mobility reflects the molecular dynamics of the polymers chains in the vicinity of the label location.

The spin labelling method, owing to its ability to investigate molecular dynamics, was used to solve problems related to cotton fibre properties and technology. ESR investigation of spin-labelled flax shive cellulose undergoing nitration revealed that the packing density of macromolecules in the less ordered nitrated regions was higher than that of virgin flax [54]. The following consequence of structural change during nutrition was found: The total amount of the less ordered regions in cellulose nitrate, approximately constant in the intermediate nitration stages, which depended on the degree of structural disorder in the sample at the beginning of nitration, was approximately constant in the intermediate nitration stages and sharply decreased during the final nitration stages because of conformational ordering of the side-chain substituents.

The conformational mobility of macromolecule chains of various cotton fibres which have different moisture contents was studied in the temperature range 77-363 K using a spin labelling technique [55]. The frequency of rotational motion of macromolecular segments increased with the increase in temperature and moisture content and correlated with the deterioration of fibre durability. Cotton grown from γ-irradiated seeds showed changes in the ESR spectrum which indicated mutational changes in the structure of the cellulose [56]. Nitroxide sin label I was used with ESR to study of the effect of H_2O, CH_3Cl, and EtOH solvents on temperature transitions of plasticised cellulose of cottonfibres [57]. It was found that the high-amplitude motion of the spin label in the nanosecond temporarily region appeared at 0°, –20°, and –30° for H_2O, $CHCl_3$, and EtOH, respectively. The plasticising capacity of the solvents at 0° decreases through the EtOH, H_2O, $CHCl_3$ series. It was found that the tensile strength and parameters of the Zhurkov equation for origin and wilt-damaged spin-labelled cotton fibres correlate with the concentration of loose structure defects and chain mobility measured by ESR at –150° to +100° [47].

Table 4. Values of immersion depth of phosphorescence $r_{im} = (R_0 - r_v)$ for label EIC in cotton fibers calculated by Eq. 6 using data of Table 3 [53]

№	Label/fiber	Quenching mechanism		
		ICHA	ET	Average
1	Eosin in solution	6,6	8,3	7,4
2	Label x – "Tashkent A"	6,9	8,8	7,8
3	Label x – "Tashkent B"*			

** Fibers derived from cotton infected with virus Vilton*

High resolution spin-labelling EPR at 95 GHz was used to characterise hydrogen bonding, viscosity and local polarity effects [58]. It was shown that loading of the two types of cotton fibres with hydrophobic probe Tempo and more hydrophilic probe Tempol indicate the presence of multiple compartments with different probe solubility, dynamics, and polarity. Loading cotton with a specific solvent followed by introduction of a small nitroxide through a gaseous phase resulted in different distributions of the probe in cellulose domains/compartments.

Miscellaneous applications of nitroxide radicals in the area of cotton fibres and cellulose which are not related directly to its molecular dynamics can be found in [59-62].

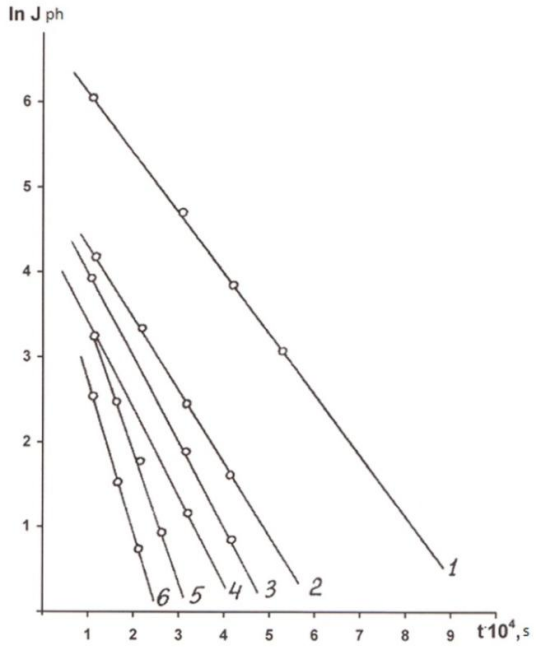

Fig. 10. Time dependence of logarithm of phosphorescence of covalently erythrosine J_{ph} incorporated in the cotton fiber "Tashkent 1" in the presence of quencher R III at different concentration (in M) 1 – 0; 2 – 2.10^{-3}M; 3 – 4.10^{-3} M; 4 – 6.10^{-3} M; 5 – 8.10^{-3}M; 6 – 10^{-2} M. Water solution, T = 293 K [53]

4. CONCLUSION

It was shown that physical labels, nitroxide radical and chromophore, which exposed fluorescence and phosphorescence, immerse to cotton fibers and cellulose on 8-10 Å.

Therefore the labels' mobility reflects local molecular dynamics of the fibre chains in the vicinity of the labels' location. Starting from the temperature of liquid nitrogen, the ESR and luminescence experiments have revealed an animation of various molecular dynamic effects, such as low-amplitude high-frequency vibration and wobbling in the submillisecond temporal region, while at an ambient temperature the molecular dynamics occur in the nanosecond scale.

The free activation energy distribution of mobility of the chromophore label were found to be 10,5 kJ/mole (data on fluorescence) and 6,7kJ/mole (data on phosphorescence).

The fibres and cellulose of various origin showed similar properties of molecular dynamics, while they were different in details. Water and other plasticising agents caused the intensification of the nanosecond mobility of the samples. ESR experiments indicate a change of the parameters of molecular dynamics in the steps of in the steps of plants maturation and at gamma-radiation. The energy activation of mechanic destruction was found to be practically the same for all samples that indicate that the process occurs as a break of chemical bonds. The differences in the samples' duration were caused by differences in the fraction of structural defects (n) detected by the ESR technique.

The developed combined spin and luminescence labelling approach, the efficiency of which is demonstrated in this review, can be used in the investigation of molecular dynamics and microstructure polymers and other complex molecular objects.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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