Nitroxides in Cotton and Cellulose Physicochemistry and Technology. 42 Years of History

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Abstract:- Since pioneering works of Marupov and Likhtenshtein groups, nitroxides are widely used in solving a number of challenging problems of structure and functions of cotton fibres and cellulose. Methods of nitroxide spin labelling have been proved to be a powerful tool in this area. Covalent modification cotton fibres and cellulose by the labels and the use electron Spin Resonance (ESR) allow to establish the label location and motion the labelled samples which in turn is modulated 'by the polymers local molecular dynamics and its distribution. Data on dependencies of the fibres' molecular dynamics on origin, temperature, water and other plasticizing agents, nutrition, period of maturing, virus infection and radiation of seeds have been presented. Combination of ESR experiments and Zhurkov technique have revealed a strong dependence of fibres' resistance to stress (durability) on microscopic structural defects. In the fibres, the distribution of the molecular dynamics correlation time within $10^{-4} - 10^{-9}$ s temporal range was also established. Employing non-covalently bound nitroxides as spin probes provides a way for studies of effect of humidity on the supramolecular structure of cotton, local polarity and heterogeneous viscosity of two types of unprocessed cotton fibers, cellulose modification by nitroxide-mediated graft polymerization, composites of poly(lactic) acid reinforced with TEMPO-oxidized fibrillated cellulose, photo-lnduced macromolecular functionalization of cellulose via nitroxide spin trapping. The developed approach, the efficiency of which is demonstrated in this review, can be used in the investigation of molecular dynamics, microstructure polymers and other complex molecular objects.

Key words: cotton fibres, cellulose, nitroxide spin labels, luminescence labels, molecular dynamics, structural defects, stress resistance

1. Introduction

Cotton is one of the essential materials for the human civilization. The role of cotton fibres and cellulose in industry, medicine and human beings' everyday live is impossible to overestimate [1-3]. 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 being the most abundant organic raw material on the planet. The molecular structure dynamic properties

of these polymers form a base for their functional activity, technological characteristics, stability, compatibility, and so forth. Stable nitroxide radicals has proved to be effective tool in solving numerous problems in chemistry, physic sand biology at the molecular level. The theoretical and experimental data presented in [2-9] clearly demonstrate both the current progress and prospects for future developments within the nitroxide "empire". Thousands new nitroxides radicals, related nitrons and chromophore-nitroxide compounds of different chemical reactivity, redox potential, hydrophobic and hydrophilic properties, electrostatic charge, so forth have been synthesized and characterized.

Spin labelling methods are powerful tool for the investigation of the molecular mobility and structure of various objects [2-9]. The basic idea underlying this approach is the modification of the chosen sites of the object in question bynitroxide (NRO), whose properties make it possible to trace the state of the surrounding biological matrix via ESR technique. The principle advantage of the 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 objects.

According to the theory and large body of experimental data [4-6], the molecular motion of a label in a condensed phase are modulated to a great extent by the molecular dynamics of the surrounding molecules. Incorporation nitroxides in various biological and non-biological objects followed by using ESR and other physical methods allow to investigate molecular dynamics within a wide range of correlation times ($\tau_c = 10^2$-10^{-10} s) and
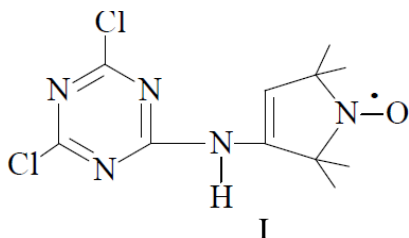
amplitudes (0.02- 0.1 nm) and to measure the distance between labeled groups up to 100 nm and depth of the radical immersion up to 4 nm. Special nitroxides intended for the measurement local pH, polarity, electrostatic potential, redox status, concentration of oxygen, antioxidants and functional groups were synthesized and successfully employed. Molecular mechanisms of polymerization, nitroxides mediated leaving polymerization in particular, photochemical and photophysical processes are subjects of interest from researchers employing nitroxides.

Since pioneering works [2, 3] nitroxides are widely used in solving a number of challenging problems of structure and functions of cotton fibres and cellulose. This review is intended to provide the physical principles of methods based on the use of the covalently bound and adsorbed nitroxides (spin labels and spin probe, correspondingly) and its applications in the investigation of cotton fibres and cellulose microstructure and molecular dynamics and it connection with it durability.. An arsenal of modern physical methods including electron spin resonance (ESR) and luminescence techniques is involved in investigation of the labelled samples. Involving nitroxide in chemical processes in this area is also considered.
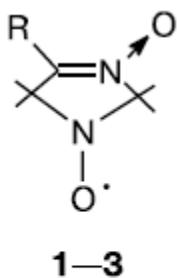
2. Spin labelling

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 [10-11].

I

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 X-Band continuous wave electron spin resonance (CW ESR) spectra were taken using PE-1301 and PE-1306 radiospectrometers.
Samples of cellulose labelled with stable nitroxyl radicals were prepared through mechanochemical synthesis [12].

1—3

R = Me (1), COOH (2),
CH$_2$Br (3)

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.

2.2 Microstructure and Molecular dynamics

Modern ESR techniques allows ones to access dynamic processes that are characterized by a wide range of correlation time, $\tau_c = 10^2 – 10^{-10}$ s [4-19]. For example, in the region of motion with τ_c $10^{-7} – 10^{-8}$ s the following equation, calculated the first harmonic ESR spectra in the 3-cm band (V_1), can be used [13]:

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

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. Spectra of the ESR spectra second harmonic (V_2) are sensitive to nitroxide motion in the temporal submicrosecond range $\tau_c = 10^{-4} – 10^{-5}$ s.

Experiments showed (Fig. 1) that the investigated cotton fibres consist of two factions: major (component h, $\tau_c \leq 10^{-8}$) and minor ((component h', $\tau_c \geq 10^{-8}$ s). Apparently, the latter is attributed to loose microscopic defects of the fibres. The contribution of these factions in different samples is 94 -98 and 6 -2 %, respectively. Contribution of the loose fraction enhances with increase of temperature.
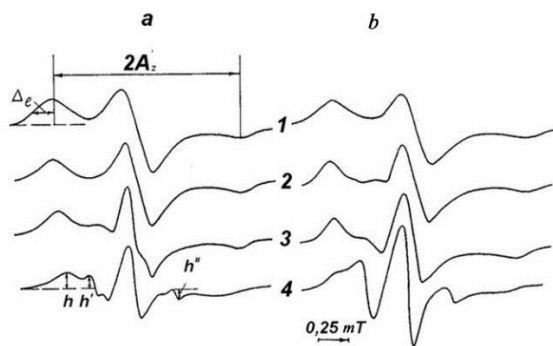
Figure 1. The first harmonic ESR spectra (V_1) for spin labeled cotton fibers a - «5595-B», b- "Tashkent 1" Temperature 1) 123 K, 2) 213 K, 3) 323 K, 4) 373 K. Relative humidity $P/P_0 = 0.96$ [20].

Temperature dependencies of parameter $2A_z^{'}$ for the nitroxide spin label I incorporated in different cotton fibres are presented in Fig. 2. The slight decrease of parameter $2A_z^{'}$ dependencies at temperatures from 153 to 210 K can be attributed to high frequency low amplitude vibration of the nitroxide fragment. Further decrease of $2A_z^{'}$ at temperature ≥ 210 K is caused by high amplitude motion with correlation time in the range $\tau_c = 10^{-7}$- 10^{-8} s. Narrowing of Δ_l at temperatures from 253 K to 263 K (not shown) may be explained by the effect of low-amplitude motion of nitroxide or surrounding protons. Final line broadening is most probably affected by the animation of the wobbling of the label nitroxide fragment at temperatures above 273 K
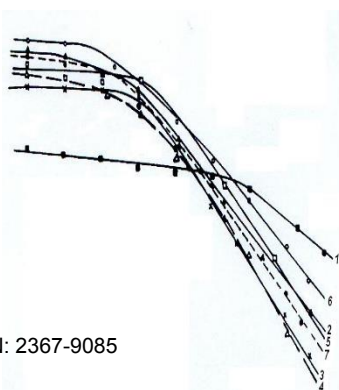

Figure 2. Parameters of the first harmonic spectra (V_1) $2A_z^{'}$ (a) and (Δ_l) (b) for different spin labeled cotton fibers versus temperature. - Relative humidity $P/P_0 = 0.96$ [20].

The dynamic behaviour of spin-labels with nitroxides located in samples of cotton fibre from "5595-B" at at relative humidity $P/P_s = 0.04$ was investigated with the use of high resolution, high-frequency (2-mm) ESR spectroscopy (Fig.3) [20-22]. The studies confirmed conclusions formulated on the base of the 3-cm band (V_1) ESR, namely, slight decrease of the $2A_z^{'}$ hps components in the temperature range 280 – 320 K and its significant change at T ≥ 320 K. In addition, the change of x component is different as compare with y and z components that indicates strong anisotropic of the label nitroxide fragment. Study of microcrystalline cellulose modified by the nitroxide spin label I by the ESR method showed that microstructure and molecular dynamics of this polymer are similar to that for the cotton fibers, while former is characterized higher contribution of loose fraction with higher mobility of the spin labels [14]. Change of the ESR second harmonic V_2 spectra taken starting from 273 K can be explained by the label motion with correlation time in submillisecond region [16] Notably, the nitroxide fragment dynamics in this temporal region and its nanosecond dynamics (Figs 2-5) occur in the same temperature region (273 – 373 K). These finding suggests distribution of the label dynamic parameters modulated by the fibres dynamics.
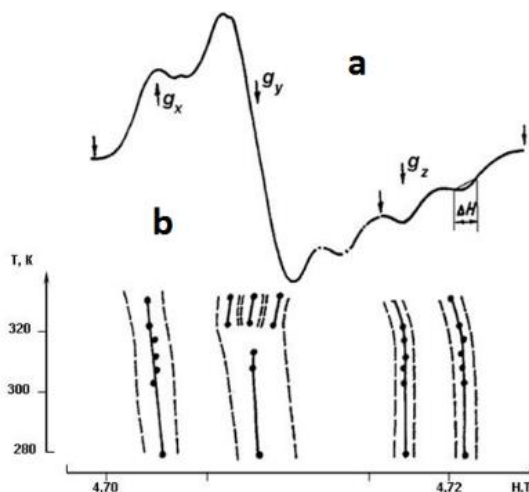
Figure 3. High resolution (2 mm) ESR spectrum of spin labeled cotton fiber «5595-B at relative humidity $P/P_s = 0.04$ and temperature 150 K (a); Dependence of parameters of g and A tensors on temperature (b) [22].

This conclusion was confirmed in study of molecular dynamics of cotton fibers by methods of fluorescence and phosphorescence labels [20, 23, 24]. 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 , τ_r in the samples under investigation. This conclusion is strongly supported by analysis of the experimental dependencies of the time of polar environment relaxation in the vicinity of excited chromophore (τ_r) [20, 22]. 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 estimate the energy activation of relaxation in the

distribution maximum (E_{max}) and the second moment of the distribution curve $(\Delta F^{\#})^2$. $(\Delta F^{\#2})$. The analysis gave the $\Delta F^{\#}$ value equal 10.5 kJ/mole and 6.7 kJ/mole for data on the relaxation shift in the fluorescent and phosphorescent spectra, respectively.

2.3. Immersion Depth of Nitroxide Fragment

At interpretation of data on spin label dynamics it is important to know it immersion death in molecular object of interest (r_{im}). 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 (T_{1e})·and is randomly distributed in the bulk of the vitrified sample [25-29].) In fact, the r_{min} value is equal to the radical immersion depth. The contribution of the dipole interaction of IR to the R·spin relaxation rate is expressed by the equation:

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

where $1/T_{1e}$ is the nitroxide spin-lattice relaxation rate, which is derived by analysis of ESR spectra saturation curves, 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, $A_d = 0.2$. The sensitivity of the ESR spectra saturation curves for spin-labelled cotton and cellulose fibres to the nature of the object and presence of ion-relaxator ferricyanide are shown in Fig.4.
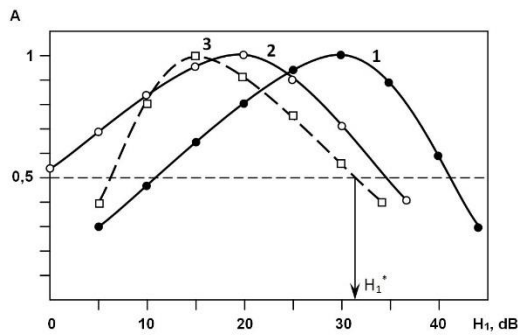
Figure 4. ESR spectra saturation curves of spin labeled fibers in water-glicerol mixture at 77 K: 1 a-cellulose (without ferricyanide); 2 a-cellulose ($3,9 \cdot 10^{-2}$ M ferrycyanide); 3—cotton fiber (without ferricyanide} A is intensity of center component of ESR spectra, H_1 is intensity of microwave field [29].

Values of immersion depth of spin label I in fibers (r_{min}, in nm) was found to be 1.0 and 1.1 for α-cellulose and cotton fiber cotton fiber, respectively [29]'. These values are close to the immersion depth of phosphorescence triplet label of about 0.8 nm [20]. Therefore, the labels' mobility reflects the molecular dynamics of the polymers chains in the vicinity of the label location.

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. The design, fabrication, testing, or an operation stage of a polymer product's life, and considering the use of predictive modeling to assess the seriousness and the likely consequences of the detected failure of polymers are in a great extend related to its durability.

A connection between durability of various samples of cotton fibers and its molecular properties was established using method of nitroxide spin labels (Table 1)]. The principle advantage of the labelling method is possibility to take direct information about local structure, mobility, micropolarity of molecular object of of interest. Widely accepted Zhurkov model, assuming the kinetic nature of bond destruction through the thermofluctation mechanism, enables one to obtain a simple, easy-to-use and physically meaningful formula for the evaluation of the durability of a material after the given time in operation at the given temperature and under the given stress [30-33]. According to this model, a sample durability (r) can be described with the following equation:

$$\text{r} = \tau_0 \, e^{\frac{U_0 - \sigma\gamma}{kT}} \qquad (2)$$

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. Analysis of ESR spectra of spinlabeling cotton fibers showed two fractions with different local mobility of the cotton and cellulose chains characterized by the different label rotation time τ: main rigid fraction with τ = $>10^{-7}$ s , and defects with τ = $10^{-8} - 10^{-9}$ s (Fig. 1). Apparent activation energies of rotation of spin labels localized in loose and rigid phases were found to be 19.3 and 51-7 kJ/mole, respectively. 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 Eq. 2 are presented in Table 1.

Table 1. 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 (Fig. 1); which characterizes a loosing of the polymer structure at temperature increase above 333 K [48'].

Fiber	n - defects fracture	ξ, K^{-1}	σ_p, MPa	U_0, kJ/моle	$\gamma 10^{-4}$, m^3/моle
«5595-B» «Taskent-1A» (	2±0,5% 6±2%	0,009 0,030	280±12 180±12	142±7 141±7	2,6 4,9
«Tashkent-1B»	2.8±2%	0,070	150±12	141±7	6,0

As is seen in Table 1, 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. Spin probing.

3.2 Microstructure and Molecular dynamics

EPR studies cellulose microstructure employing the nitroxide spin-labeled albumin, as spin probe entrapped in cellulose triacetate fibers, were carried out [35]. The experiments showed that within the fiber two phases are present: medium viscosity inside microcavities and more rigid phase. After entrapment, spin-labeled albumin is distributed mainly in the first phase, though some amount of it remains within the polymeric matrix. The behavior of the albumin incorporated inside the microcavities toward denaturating agents and pH change and that of the free albumin in solution is similar, while the minor differences noticed indicate a second-order interaction between the fiber and the protein. These data suggested existing microcavities in the cellulose triacetate fibers. To probe the entire amorphous zone of dry cotton the nitroxides (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO} and (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPOL) were deposit using ethanol and water [36]. To probe the fiber surface specifically toluene was used. Analysis of the probes ESR spectra indicated that in both regions the apparent micro viscosity is about 30 cP. A small proportion of the radicals deposits to an area of much higher viscosity. The spin probe method is extended via a simple electron spin polarization experiment.

The motion of TEMPOL contained within the nanopores of dry cotton at temperature 10º and 70º was conducted using ESR. At low loadings ($<3 \times 10^{-3}$ mol kg^{-1}), the radicals are in an equilibrium between a mobile state in the amorphous pores and adsorbed onto the crystallites. A loading dependence equilibrium enthalpy (ΔH^0) dropping from 75 to 50 kJ mol^{-1} and entropy (ΔS^0) from 0.25 to 0.20 kJ mol^{-1} K^{-1} between loadings of 2×10^{-4} and 3×10^{-3} mol kg^{-1} were established. The apparent viscosity of the amorphous region, obtained from the rotational correlation time of the mobile radicals, shows a dependence on loading rising from 20 to 35 cP between 2×10^{-4} and 3×10^{-3} mol kg^{-1} at 298 K. The effects are indicative of microdomains of different character with the preferred microdomains being those with pores of equivalent size to TEMPOL ($d \approx 1$ nm) and concentration of 4×10^{-4} mol kg^{-1}. At high loadings ($>3 \times 10^{-3}$ mol kg^{-1}), aggregation of the radicals occurs, when the number of radicals in a microdomain is double the number of pores.

The effect of water content on the physicochemical properties of the amorphous regions in cotton were investigated by measuring the electron paramagnetic resonance (EPR) of TEMPOL. Mobility of nitroxide radicals, deposited in cotton at different loadings, as a function of the relative humidity (RH) and temperature was investigated [38]. Three different components contribute differently to the experimental EPR spectra, corresponding to (a) mobile radicals absorbed in the bulk amorphous region, (b) slow moving radicals adsorbed on the crystallite surfaces in cotton, and (c) aggregated radicals. The polarity extracted from the analysis of the spectra dropped when the water content fell below approximately 3 wt %, indicating that water was removed from the bulk amorphous regions. At intermediate loading (10^{-4} - 10^{-3} mol kg^{-1} both mobile (fast) and adsorbed (slow) moving radicals were present, the fraction of which depended on the RH. The mobility of the adsorbed and mobile radical signals was smaller at higher loadings, indicating microdomains of different character, reflecting the variation in pore sizes (0.5-8 nm) and the relaxation behavior of the cellulose chains.

The method of nitroxide spin labels of different charges developed in [4] was employed to investigate the effect of charge on spin probe interactions and dynamics in the nanopores of cotton, using 4-amino-TEMPO (T−NH$_2$) and 4-carboxy-TEMPO (T−COOH) nitroxide radicals deposited on dry cotton [39]. Spectra are recorded as a function of probe loading (2×10^{-5} to 10^{-2} mol kg^{-1}), temperature (293−333 K), and relative humidity (RH, 6 and 75%) and compared to results from the neutral probe 4-hydroxy TEMPO (T−OH). The effective internal pH of the cotton was measured using codeposited indicator dyes. Three components contribute to the spectra, corresponding to (a) mobile radicals absorbed in the bulk amorphous regions, (b) slowly moving radicals adsorbed on the crystallite surfaces in cotton, and (c) aggregated radicals. The mobile T−NH$_3^+$ experience a highly polar aqueous-like environment at 75% RH, which became much less polar at 6% RH as water was removed from the cotton, while much smaller drop in polarity was found for T−COO$^-$, ascribed to the higher hydrogen-bonding ability of the probe, binding water more effectively. The enthalpy and entropy of

the adsorption equilibrium between mobile and adsorbed radicals extracted at 10^{-3} mol kg^{-1} were independent of humidity except for T−COO^{-}, because of its stronger interactions with water.

Spin probe ESR method was used to study local polarity and heterogeneous viscosity of two types of unprocessed cotton fibers, *G. hirsutum* and *G. barbadense* [40]..These fibers were loaded with two nitroxide probes that differ in polarity- TEMPO and its more hydrophilic derivative TEMPOL. A series of polar and non-polar solvents was utilized. Multiple resonance frequencies ESR techniques such as X-band (9.5 GHz) and W-band (94.3 GHz) were employed. Results demonstrated co-existence of cellulose nanodomains with different physicochemical properties, such as polarity and microviscosity, that are affected by solvents and temperature. Spin labeling studies also revealed a macroscopic heterogeneity in the domain distribution along the cotton fibers.

Works cited above confirmed conclusions on heterogenic character of structure of fibers of cotton and cellulose and distribution of molecular dynamics parameters in these materials obtained by methods nitroxide spin and luminescence methods [20, 23] and Section 2.2).

4. Nitroxide in Chemistry and Technology of Cotton and Cellulose

4.1 Miscellaneous Applications of Nitroxides Based on Spin Labeling

40 samples of cotton filaments from naturel and mutant plants spin-labelled by a nitroxide 2,2,5,5-tetramethyl-3-aminopyrrolidine-(3,5-dichlorotriazine)-1-oxyl (I), chemically bound by the cellulose hydroxyl group, were prepared [2]. According to ESR spectra of the nitroxide probes, in investigated samples there are two regions in cotton cellulose: ordered and disordered ones. Experiments revealed conformational changes of cotton cellulose grown from seeds exposed to different doses of gamma-irradiation Temperature dependence of rotation diffusion parameters of radical connected to different varieties of cotton fibers , isolated from normal and virus wilt affected cotton was studied [3]. For samples from wilt-affected plants temperatures at which structural transitions proceed were found to be higher as compared to the filaments taken from normal plants. This findings indicate higher micro rigidity of cotton fibers derived from the wilt-affected plants.

The spin-label investigation of flax shive cellulose structural and molecular dynamics properties in the process of its nitration using the spin label I revealed that the macromolecules packing density in the less ordered nitrate fields is higher than that of natural flax cellulose [34]. A correlation between the «order» and « disorder" relation in natural cellulose and in finite nitrogen products was established. The total content of less ordered fields of cellulose nitrate remains approximately constant at the intermediate states of the nutration and is defined by the stage of structural disordering at the beginning of nitration. The sharp decrease of the less ordered fields content at the final stage of nitration may be a consequence of the third termination stage of the formation

of the physical structure of nitrated cellulose, in which -generation of conformational ordering of side substituents occurs. In the nitration process, the spin label motion correlation time τ_c increases in 3 times saturates after 2-3 minutes of the processing. This finding indicated higher packing density in the nitrated areas in modified samples as compare of that in natural flax cellulose. The effect of H_2O, CH_3Cl, and EtOH solvents on temperature transitions of plasticized cellulose of cotton fibers employing 2,2,5,5-tetramethyl-3-aminopyrrolidine-(3,5-dichlorotriazine)-1-oxyl as spin label was studied by the ESR technique [41]. High-amplitude motion of the spin label with correlation time $\square_c \leq 10^{-7}$ s appeared at 0, -20, and -30° for H_2O, $CHCl_3$, and EtOH, respectively, that is associated with effect of the plasticizer on molecular dynamic state and microstructure of cellulose fibers. The plasticizing capacity of the solvents at 0° decreases through the EtOH, H_2O, $CHCl_3$ series.

4.2 Chemistry of Polymers

Grafting synthetic polymers onto cellulose is the straightforward method to improve its surface properties to overcome problems of using cellulose including its water-absorbing nature and its poor compatibility with other materials, for example, synthetic polymers [42-46].

A facile grafting to protocol based on the generation of radicals at the surface of cellulose by mild UV irradiation ($\lambda_{max} \sim 311$ nm) of an immobilized photoinitiator was conducted [42]. The generated radicals were trapped with a nitroxide-functionalized polymer (Fig. 5)

via a copper-catalyzed mechanism using atom transfer radical polymerization (ATRP)-made polymers to generate reactive radicals. Spin capturing was reported, using nitrones that after a first radical reaction generate a nitroxide able to undergo a second radical coupling. Composites of poly(lactic) acid (PLA) reinforced with TEMPO-oxidized fibrillated cellulose (TOFC) were prepared [43]. Acetylation of the TOFC prior to the fabrication of TOFC-PLA composite films provided the material dispersion and improved stress transfer. These composites displayed a significantly higher strain to failure compared to pure acetylated TOFC film, and dominated by the mechanics of the networks, and a shear-lag type stress transfer between fibers.
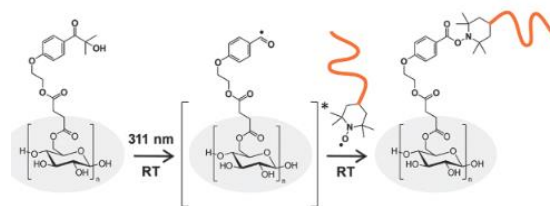

Figure 5. Scheme of Nitroxide Mediated Grafting [42].

.One possibility to solubilize cellulose is carrying out the nitroxide-mediated (NMP) polymerization in N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA) with 5 to 10 wt % of lithium salts (LiCl or LiBr) The aim of work [44] was to develop a model study of the stability of the SG1 nitroxide (Fig. 6) in organic media in the presence of unprotected glucose or cellobiose (used as a model of cellulose) and in the presence of lithium salts (LiBr or LiCl) in DMF or DMA. It was shown that SG1 is stable in the presence of unprotected sugar, even with an excess

of 100 molar equivalents of glucose. On the other hand, lithium salts in DMF or DMA degrade SG1 nitroxide. The conditions to perform an SG1-based nitroxide-mediated graft polymerization from cellobiose have been established
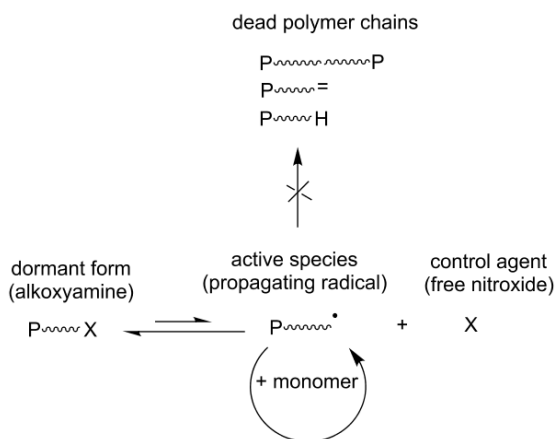

Figure 6. Key equilibrium between active and dormant species involved in the nitroxide-mediated (NMP) polymerization technique [44]
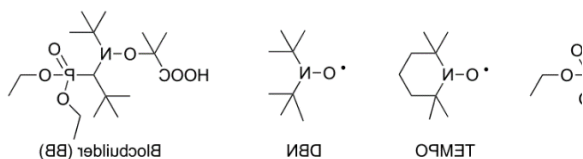

Figure 7. Structure of the SG1, TEMPO and DBN nitroxides and the BlocBuilder MA alkoxyamine [44].

A nitroxide amphiphilic block copolymer of poly(ethylene glycol)-b-poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl-methacrylate) block copolymer was used as a recoverable catalyst for selective catalytic oxidn. of cellulose [45]. This copolymer was easy to

recycle and the activity did not decrease to a noticeable level after 4 cycles. Using carbon dioxide, as the trigger to conduct the optical switching process, stimuli-responsive cellulose nanocrystals (CNC), whose surface properties can be reversibly switched, were synthesized [46]. The surfaces of polymers from cellulose nanocrystals (CNC) were modified using surface-initiated nitroxide mediated polymerisation (SI-NMP) with CO_2-responsive polymers poly(dimethylaminoethyl methacrylate), poly(diethylaminoethyl methacrylate), and poly(dimethylaminopropyl methacrylamide). In CNC carbon dioxide serves trigger to conduct the optical switching process.

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Conclusion

Physical labels, nitroxide radical and a chromophore, which exposed fluorescence and phosphorescence, were covalently tethered to cotton fibers and cellulose. It was found that both labels incorporated into cotton fibers and cellulose on immersion death of 0.8-1.0 nm. 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 a gradual animation of various molecular dynamic effects, such as low-amplitude high-frequency vibration wobbling in the submillisecond and nanosecond temporal region. At ambient temperature the fibres molecular dynamics can occur in both the submillisecond and nanosecond scales indicating broad distribution of dynamic correlation times. The free activation energy

distribution of mobility of the chromophore label were found to be 10,5 kJ/mole (data on fluorescence) and 6,7 kJ/mole (data on phosphorescence). The heterogenic domain micro structure of cotton fibers was confirmed in studies with the use nitroxide spin probes adsorbed in the fibers. The differences in the cotton fibers samples' duration, obtained in the framework of the Zhurkov model, were caused by differences in the fraction of structural defects, loose phase (n) detected by the ESR technique. The spin labelling method, owing to its ability to investigate molecular dynamics, was used to solve problems related to cotton fibre properties and technology such as effects of maturation nitrition, humidity, CH_3Cl, and EtOH solvents, cotton plant wilt affection, and growing from γ-irradiated seeds. Nitroxide involving in chemical processes of grafting of cotton fibers and cellulose including nitroxide-mediated polymerization was described.

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