

Article

Fiber Spinning from Cellulose Solutions in Imidazolium Ionic Liquids: Effects of Natural Antioxidants on Molecular Weight, Dope Discoloration, and Yellowing Behavior

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Abstract: Spinning of cellulosic fibers requires the prior dissolution of cellulose. 3-Alkyl-1-methylimidazolium ionic liquids have proven to be suitable solvents for that purpose, but the degradation of cellulose in the spinning dope can be severe. Suitable stabilizers are therefore required that prevent cellulose degradation, but do not adversely affect spinnability or the long-term yellowing behavior of the fibers. A group of twelve renewables-based antioxidants was selected for stabilizing 5% cellulose solutions in the ionic liquids and their effects on cellulose integrity, dope discoloration, and aging behavior were tested by gel permeation chromatography (GPC) and ISO brightness measurements. Propyl gallate (a gallic acid derivative), hydroxytyrosol (from olives), and tocopheramines (a vitamin E derivative) performed best in the three test categories, minimizing both cellulose degradation, chromophore formation in the spinning dope, and yellowing upon accelerating aging of the spun fibers. The use of these stabilizers for cellulose solutions in the imidazolium-based solvent system can therefore be recommended from the point of view of both performance and sustainability.

Keywords: aging; antioxidants; brightness; cellulose; fiber spinning; ionic liquids; molecular weight; yellowing

1. Introduction

The spinning of cellulosic fibers requires prior dissolution of the cellulosic pulp. This dissolution can be affected either by chemical means, i.e., permanently, or by temporary derivatization into soluble derivatives. Such a temporary cellulose modification for solution purposes is done, for instance, in the viscose (rayon) process, in which cellulose is converted into alkali-soluble cellulose xanthate, which can be spun and simultaneously re-converted into cellulose by removal of the xanthate groups. Alternatively, cellulose can be dissolved in “direct solvents” that, in theory, dissolve cellulose in a physical process. In real-world systems, accompanying chemical processes and side reactions cannot be prevented, only minimized. One example of this type of cellulose dissolution are processes based on *N*-methylmorpholine *N*-oxide monohydrate (NMMO) for Lyocell fiber production. About two decades ago, ionic liquids (ILs) were introduced as possible solvent alternatives. *N*-Alkyl-*N*-methylimidazolium ILs belong to the first generation of cellulose-dissolving ILs, which, at that time, were rather unsuccessful in diverse pulping and spinning scenarios because of overwhelming recycling and purification problems. These ILs were later

followed by approaches with higher-generation ionic liquids through which these obstacles were overcome. This eventually led to the development of the Ioncell[®] technology [1–5]. Recently, *N*-alkyl-*N*-methylimidazolium ILs paired with optimized recycling concepts have found renewed interest in the production of special high-strength cellulose fibers [6,7]. However, this dope system is also not free of side reactions and byproduct formation, and needs to be stabilized, which is the general topic of this account.

Side reaction and degradation of cellulose in spinning dopes can generally be categorized into two processes: reactions due to the solvent and reactions due to oxidative or autoxidative processes. The former class involves all reactions that might proceed by direct chemical interactions between solute (cellulose) and solvent or by interactions between solute and degradation products. There are illustrative examples in the literature; the solvent NMMO, as the basis of Lyocell fiber production, is an oxidant and might oxidize cellulose directly or even cause thermal degradation processes [8], while its degradation products can cause discoloration of the fibers [9]. The binary solvent mixture *N,N*-dimethylacetamide/LiCl, mostly used for analytical purposes in gel permeation chromatography of celluloses, is itself inert, but when heated above 100 °C, thermally produced *N,N*-dimethylketeniminium ions may specifically target and cleave glycosidic bonds, thus causing severe degradation. In addition, it suffers hydrolysis when a large amount of water is present [10]. The combination of phenyl isocyanate and DMSO, used for dissolution of cellulose derivatives, can generate oxidative *Swern*-type conditions and additionally introduce sulfur-moieties by side reactions. Evidently, all solvent-derived side processes are highly undesirable. In some cases, stabilizers can be used to suppress them (e.g., stabilizers for Lyocell spinning dopes); in other cases the conditions must be chosen in a way that the generation of reactive species is avoided (e.g., thermal stress in DMAc/LiCl or avoidance of DMSO in combination with isocyanates).

The second category of cellulose side reactions in spinning dopes, the (aut)oxidative processes, are generally caused by the involvement of oxygen and oxygen-derived reactive species, which involve both reactive radical species (e.g., hydroxyl, peroxy and other radicals) and non-radical compounds (e.g., hydrogen peroxide, peracids, ozone). They are typical autoxidative processes involving radical (homolytic) and ionic (heterolytic) contributors. In cases where the solvent or one of its components is an oxidant itself (such as NMMO in Lyocell manufacture), they are superimposed by redox reactions of this solvent. Antioxidants, mostly used in concentration ranges of 0.5–3% relative to the dissolved cellulose, are commonly used to minimize such autoxidative processes, quite similar to their use in the production of synthetic fibers [9]. While acting effectively against the typical species involved in autoxidation, antioxidants do not effectively mitigate hydrolytic effects on cellulose and direct reactions between cellulose and solvents.

The degradation products of 3-alkyl-1-methylimidazolium ionic liquids are known [11] and their reactions with celluloses have been established [12]. In addition to the general reaction of the cation, different side reactions with co-reacting anions, such as acetylation in the case of acetates, might occur. In general, side reactions in cellulose fiber spinning dopes are very complex and their effects on cellulose are generally hard to separate and assign to a particular process; cellulose degradation can be either caused by general (acidic) hydrolysis, by the effect of specific agents, or through the effect of oxidation and subsequent chain cleavage.

We hypothesized that both degradation of cellulose in imidazolium-type ionic liquids and discoloration of the spinning dopes are consequences of mainly hemolytic degradation processes, which can be suppressed by the addition of auxiliaries (stabilizers, antioxidants). In this study, we address the question of whether autoxidative processes in cellulose spinning dopes in *N*-alkyl-*N*-methylimidazolium ILs can be curbed by natural antioxidants and we identify their effects on cellulose integrity, discoloration of spinning dope, and the yellowing behavior of the resulting fibers.

2. Materials and Methods

Commercial chemicals from Sigma-Aldrich (Schnelldorf, Germany) were of the highest grade available and were used without further purification. Distilled water was used for all aqueous solutions.

Three cellulosic pulps were used, of which the parameters, i.e., number-average molecular weight (M_n), weight-average molecular weight (M_w), DP, and dispersity ($\bar{D}$, M_w/M_n), are shown in Table 1. The data were determined by size exclusion chromatography according to the published standard protocol [13]. α -Cellulose contents were 97.0–97.5% according to the manufacturer. Imidazolium acetate ionic liquids were obtained from Nippon Nyukazai Co., Ltd. (Tokyo, Japan) and imidazolium chloride ionic liquids from Sigma-Aldrich (Tokyo, Japan and Schnelldorf, Germany).

Table 1. Molecular weight parameters of the three pulps used.

Pulp	M_n (kDa)	M_w (kDa)	DP	$\bar{D}$	$^{\circ}\text{ISO}$
A	49.7	125.9	776	2.54	79
B	62.6	200.6	1272	3.29	81
C	99.3	362.7	2237	3.65	82

UV/Vis spectra were recorded in the range of 400 to 700 nm at a scanning speed of 480 nm min^{-1} on a LAMBDA 45 UV/Vis spectrophotometer (Perkin Elmer, Waltham, MA, USA), in which quartz glass cuvettes ($l = 1.0 \text{ cm}$) were used for all measurements.

2.1. Preparation and Aging of Spinning Dopes

The specified amount of antioxidant to be tested (2 wt% rel. to the mass of cellulosic pulp to be dissolved) was dissolved in the ionic liquid at room temperature. The cellulosic pulps were dried at 100°C for 3 h. In a stainless-steel vessel, a pulp aliquot was added to the respective ionic liquid containing the stabilizer and stirred at room temperature for 1 h. The mixture was heated to 100°C under stirring to affect the dissolution of the pulp, producing spinning dopes with cellulose contents of 5 wt%. Higher cellulose contents are achievable, but contents of 5 wt% were preferred, as they afforded solutions that can be readily stirred and handled. Complete dissolution was confirmed using a polarized optical microscope (Olympus BHT-P, Tokyo, Japan) under crossed Nicols. The mixture was stirred for different times and in different atmospheres (see main text) at 100°C . Aliquots of 1 mL were taken in regular intervals for analysis (see main text).

2.2. Dry-Jet Wet Spinning

Spinning was carried out according to a dry-jet wet spinning process as reported previously [6]. At a temperature of 100°C , the spinning dopes were extruded through the spinning nozzles into an air gap (15 cm) with water as the coagulation bath, at a constant throughput speed of 0.1 mL min^{-1} and a constant winding speed of 107 m min^{-1} . The resulting fibers were thoroughly washed in water, loosely coiled on bobbins, agitated in water overnight to remove solvent and byproduct residues, and dried at room temperature.

2.3. Rheology

The rheological and tensile properties of the spinning dopes were determined as previously reported [6,7]. The measurements were performed in steady-flow mode with a shear rate ($\dot{\gamma}$) of $0.1\text{--}100 \text{ s}^{-1}$, or in oscillation mode in a frequency-sweep range of $0.6283\text{--}62.83 \text{ rad s}^{-1}$. Zero-shear viscosity (η_0) was calculated according to the three-parameter Cross model [14] by data fitting. For tensile data, data from at least 15 measurements were accumulated.

2.4. Molecular Weight Distribution

For size exclusion chromatography, sample dissolution and measurement were conducted according to Potthast et al. [13]. Activated samples were placed in 4 mL vials and an *N,N*-dimethylacetamide (DMAc)/lithium chloride solution (1 mL, 9% *w/v*) was added to each sample. The vials were vortexed for 20 s and placed in a rotary shaker again for over 20 h to dissolve the samples; then, the samples were diluted to 1:3 with pure DMAc and filtered through PTFE syringe filters (0.45 μm) before SEC-MALS analysis. The SEC-MALS system was described in detail previously [13]. The calculations were based on a refractive index increment for cellulose of 0.136 mL g^{−1}.

Viscometry measurements were performed in the solvent cupriethylene diamine (cuen) according to a previously published protocol [15] that incorporates a reduction step to reduce errors due to β -elimination reactions, which produce underestimated values, especially for pulps with higher degrees of oxidative damage.

2.5. Accelerated Aging of the Fibers

Hand sheets were prepared from 2 g of fibers suspended in distilled water (500 mL) on a Büchner funnel, followed by pressing and drying at 92 °C for 5 min. Brightness was measured before and after aging according to ISO 2470 (2009) [16], detecting UV/Vis remission at 457 nm. Continuous aging was performed either under dry conditions according to the TAPPI method UM 200 (105 °C, 40% rel. humidity, 4 h) [17] or under humid conditions according to Paptac E.4P (100 °C, 100% rel. humidity, 1 h) [18]. The aging progress was monitored by UV/Vis (brightness reversion) to follow the kinetics of chromophore generation.

3. Results and Discussion

3.1. Side Reactions in the Spinning Dope: Solvent-Derived vs. Autoxidative Processes

To study the effect of antioxidants in the imidazolium-IL/cellulose system, we had to eliminate—or at least minimize—possible side reactions between solvent and cellulose, which are not autoxidative. Therefore, freshly purified solvents were used, in which ionic or hydrolytic degradation of cellulose in the absence of oxygen was very insignificant. The recommended purification process and the effect of IL degradation products on cellulose integrity will be discussed elsewhere. We then compared the degradation of cellulose in an inert atmosphere (argon), in ambient air, and eventually in oxygen, expecting very limited autoxidation for the Ar environment and a strongly enforced autoxidation for the oxygen atmosphere. To render the results comparable between the three sample pulps used and the four imidazolium-ILs tested, we used the relative decrease of the molar mass, i.e., the molar mass after the dissolution treatment related to the starting molar mass of the pulp.

Cellulose was largely stable in the purified and degassed ionic liquid over 12 h at 100 °C in an argon atmosphere, with molar mass (*M_w*) losses of less than 8% after 5 h (Figure 1). Degradation after 5 h at 100 °C ranged between 22 and 28% working under ambient air and without degassing, i.e., under conditions usually present, and became rather severe when working in an oxygen atmosphere: between 56 and 54% (Figure 1). This outcome clearly demonstrates the important contribution of autoxidation processes to cellulose degradation in the IL/cellulose system and confirms the need to counteract these processes with the addition of stabilizers (antioxidants). Under ambient conditions in air, corresponding to the “usual” non-stabilized cellulose/IL system, the dope clearly experienced stronger degradation than the dope in an inert atmosphere. The molar mass decrease in oxygen was overly drastic, as expected. The special conditions used for these experiments (purified ILs, change of atmospheres)—although obviously impractical in everyday fiber production operations—allowed the distinction of autoxidation effects from non-autoxidative side reactions, i.e., to sort out the different contributors to cellulose degradation and to clearly demonstrate the involvement of autoxidation in the complex set of side reactions.

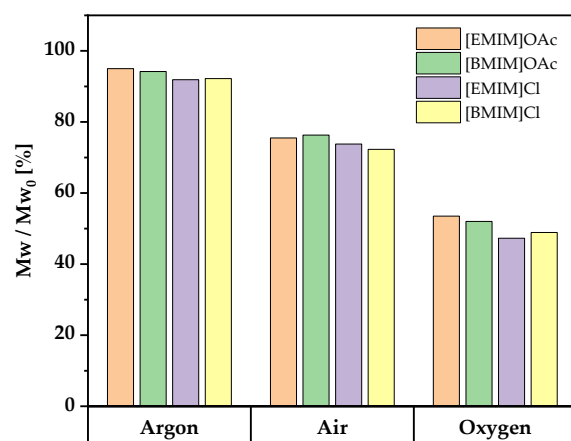


Figure 1. Cellulose (5 wt%, pulp A) degradation after 5 h in four different 3-alkyl-1-methylimidazolium ILs at 100 °C in different atmospheres, indicating the involvement of autoxidative degradation processes. For good comparability, the molar mass loss relative to the starting molar mass is given: M_w/M_{w_0} . M_w = molar mass determined, M_{w_0} = starting molar mass of the pulp. M_w values were obtained by cuen viscometry [15].

3.2. Selection of Antioxidants

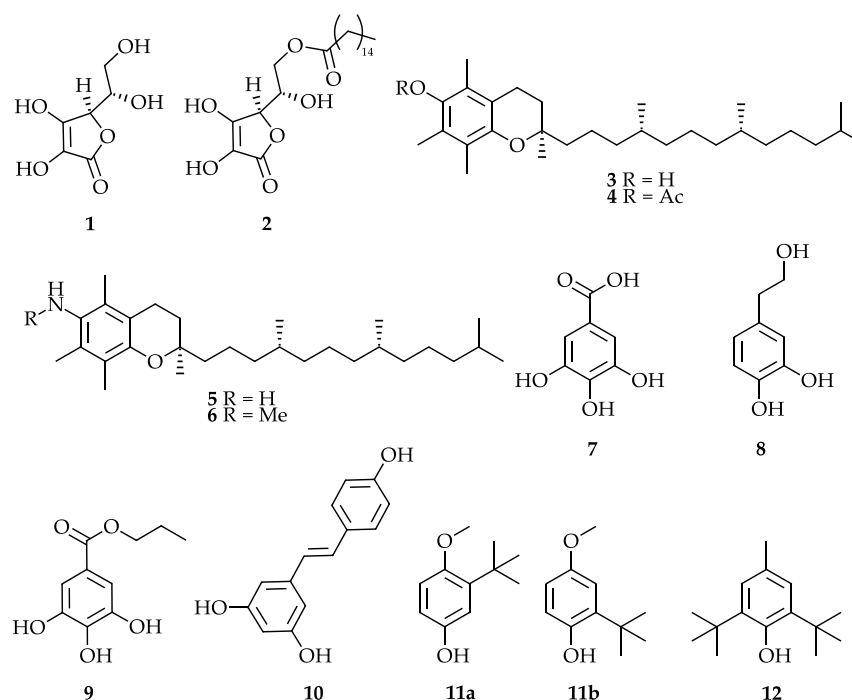
In our study, we intended to focus on natural antioxidants or their derivatives, which have no health or environmental concerns at all; it would be unreasonable to sacrifice the advantage of a sustainable cellulose fiber by adding fossil-based or even toxicologically questionable antioxidants. Still, to assess their effect, a reference was needed, and we selected butylated hydroxyanisole (BHA, **11**) and butylated hydroxytoluene (BHT, **12**) for this purpose. Both are synthetic, fossil-derived standard antioxidants, which are widely used in dyes, plastics, cosmetics, and packaging, as well as in food and feed (E320 and E321, respectively), although there have been severe toxicological concerns (see Table 2).

As antioxidants, we employed the compounds shown in Scheme 1. Table 2 lists relevant compound data and pertinent literature. The compounds are either natural antioxidants, such as ascorbic acid (vitamin C, **1**), α -tocopherol (vitamin E, **3**), gallic acid (**7**), hydroxytyrosol (**8**), and resveratrol (**10**), or their derivatives, such as ascorbyl palmitate (**2**), α -tocopheryl acetate (**4**), α -tocopheramine (**5**), *N*-methyl- α -tocopheramine (**6**), or propyl gallate (**9**). All these compounds have been proven to have health-promotive effects and to be non-allergenic; none of them are classified as a compound of concern or even as a hazardous chemical, unlike several fossil-based antioxidants, such as the BHA/BHT comparisons. Most of the natural antioxidants in Table 1 and Scheme 1 are widely used as nutraceuticals, food supplements, and even in baby food formulations. Apart from that, they are increasingly used as a replacement for conventional fossil-based stabilizers in the versatile material applications mentioned above. In addition to these pure compounds, two antioxidative compound mixtures were tested: olive mill wastewater (OMWW) and standardized green tea extract (SGTE); see Table 2.

We deliberately excluded compounds that had an intensive color (yellow curcumin, red carotenoids, red grape extracts) or intensive odor (cinnamic acid) on their own. Similarly, compound mixtures with largely unknown or strongly changeable compositions were excluded, as their effect would not be assignable to a particular compound and may vary with composition (tannins, lignins, plant extracts). The wastewater from olive oil production (lyophilizate) and the standardized green tea extract (lyophilizate) both show a largely constant, known composition of antioxidants.

Table 2. Natural antioxidants, antioxidant derivatives, and mixtures used to stabilize cellulose solutions in 3-alkyl-1-methylimidazolium ionic liquids against autoxidation processes.

Stabilizer	CAS	Molar Mass (g mol ⁻¹)	E-Number	References
Ascorbic acid (1)	50-81-7	176.13	E 300	General: [19–21], mechanism: [22], in polymer processing: [23–26], in ionic liquids: [27,28], in fiber spinning: [29–35]
Ascorbyl palmitate (2)	137-66-6	414.53	E 304	General: [36], mechanism: [37,38], transport: [39,40], safety: [41], stability: [42], in fibers: [43,44]
α -Tocopherol (3)	10191-41-0	430.71	E 307	General: [45,46], mechanism: [47–49], in fibers: [50–54]
α -Tocopheryl acetate (4)	7695-91-2	472.76		General: [55], transport and stability: [56,57], in fibers: [58,59]
α -Tocopheramine (5)	7666-00-4	429.70		General: [60], mechanism: [61]
N-Methyl- α -tocopheramine (6)	4869-06-1	443.73		Synthesis: [62], mechanism/metabolism: [63], products: [64,65]
Gallic acid (7)	149-91-7	170.12		General: [66], metabolism: [67], in polymers: [68,69], biological action: [70], in fibers: [71–73]
Hydroxytyrosol (8)	10597-60-1	154.16		General: [74,75], biology: [76,77], in polymers: [78–80], in fibers: [81,82]
OMWW lyophilizate	Compound mixture			General: [83–85], otherwise see hydroxytyrosol (8), which is the main active component
Propyl gallate (9)	121-79-9	212.20	E 310	General: [86,87], application in fibers: [88,89]
Resveratrol (10)	501-36-0	228.25		General: [90–92], in fibers and textiles: [93–97]
SGTE lyophilizate (mixture)	Compound mixture			General: [98,99], biological action: [100,101] in fibers: [102–106]
BHA (11)	25013-16-5	180.24	E 320	General: [107], toxicology: [108–110]
BHT (12)	128-37-0	220.35	E 321	As above for BHA (11)

**Scheme 1.** Formulae of antioxidants 1–12 used in the study. The lyophilizates of olive mill wastewater (OMWW) and standardized green tea extract (SGTE) are multi-component mixtures; BHA is a mixture of the two regioisomers 11a and 11b.

3.3. Cellulose Degradation in the Spinning Dope

We used a constant ratio of 2 wt% stabilizers relative to the air-dried cellulosic pulp, of which, in turn, 5 wt% was dissolved in the ionic liquid. This corresponds to a stabilizer charge of 1‰ relative to the mass of the spinning dope. The auxiliary was added to the ionic liquid and dissolved before the pulp was added. It should be noted that far higher contents of pulps can be dissolved in the ionic liquids, especially in the case of pulps with lower molar mass, but for practical reasons, comparability, and lower viscosities, 5 wt% was chosen. Molar ratios were not used because potential effects of the auxiliaries on the spinnability and dope rheology are mass-dependent and would not be comparable if equal molar ratios of antioxidants—but, consequently, different masses—were added. Non-consumed antioxidant was present in all cases after the test time, as confirmed by GC/MS analysis of methanol/chloroform extracts of the dopes (data not shown). Thus, it was safe to assume throughout that the added antioxidant mass was never a limiting factor and that only a minor error was introduced by using the same masses but different molar ratios. Moreover, the application of stabilizers in fiber production on large scale is also based on weight ratios.

The molar mass of the cellulose in the spinning dope was determined after swelling the air-dried pulp in the ionic liquid at room temperature for 1 h and stirring the dope at 100 °C for 3 h. The cellulose was precipitated in excess water/ethanol (4:1, *v/v*) and its molar mass was measured by viscometry [15]. The relation to the starting molar mass of the pulp and the comparison with the stabilizer-free behavior allow an easy, yet quite accurate assessment of the effectivity of the stabilizer. The results are summarized in Figure 2. All measurements were done in triplicate, with standard deviations below 2.5% for all values.

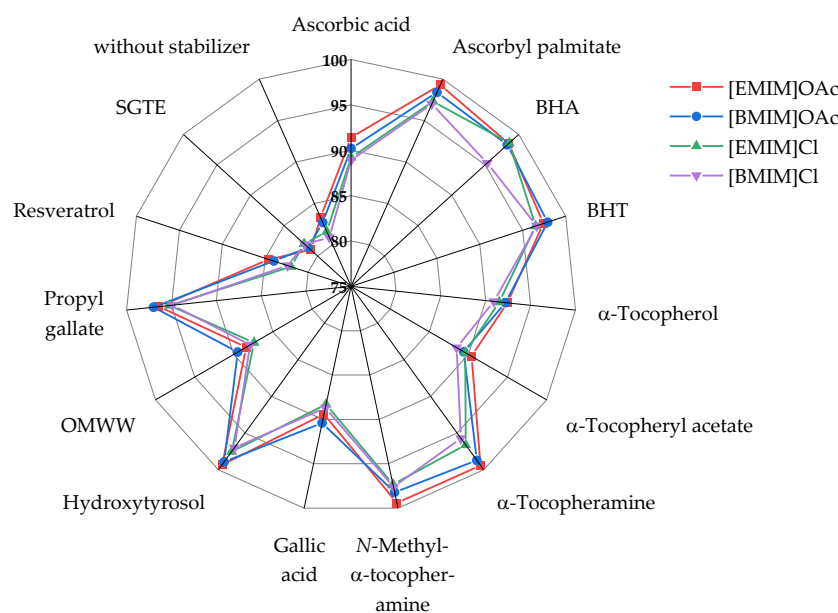


Figure 2. Cellulose degradation in spinning dopes of 5 wt% cellulose (pulp B) in four different 3-alkyl-1-methylimidazolium ionic liquids by thermal treatment for 3 h at 100 °C, depending on the added stabilizers (0.1 wt% rel. to dope, 2% rel. to dissolved pulp), expressed as molar mass loss relative to the starting molar mass: $(Mw_0 - Mw)/Mw_0$ [%]. Mw = molar mass determined, Mw_0 = starting molar mass of the pulp.

Four general trends were evident:

- (1) All employed antioxidants had a protective effect on cellulose integrity. The molar mass loss was in all cases smaller than without additive. In some cases, the protective effect was better than working under an inert argon atmosphere (cf. Figure 1), which demonstrated that the protective atmosphere was able to limit, but not fully eliminate the autoxidation processes. Cellulose degradation during the first hour of swelling at

room temperature was not detectable (data not shown), which indicated that the side reactions are mainly connected with elevated temperatures.

- (2) All antioxidants used were chemically compatible with the ionic liquids and with the cellulose solute. No violent reactions, signs of pronounced degradation of solvent or solute, phase separations, or precipitates were observed. The effects of antioxidant addition on dope viscosity and spinnability were insignificant, which can be related to the very low content of the additives (2 wt% rel. to the dissolved pulp (5 wt%) corresponding to 0.1 wt% of the dope).
- (3) The differences between the four ionic liquids were minor. For a given antioxidant, the same effectiveness category (A, B, or C, see below) was obtained for all four ILs, without a single exception. On average, degradation in the two imidazolium chloride ILs was 2–3% (relative molar loss) stronger than in the imidazolium acetate ILs, independent of the antioxidant used.
- (4) The results were very similar for all three pulps used. The relative molar mass losses for the pulps at a given pair of antioxidant and IL differed by less than 4%. The values in Figure 2, determined for pulp B, are thus also fully representative for pulps A and C, so it appears possible to draw a general conclusion from the test set.

For a more detailed evaluation, we used a simple categorization: “A = very effective” (relative mass loss less than 5%, i.e., more than 95% of the starting molar mass retained), “B = medium effective” (relative mass loss less than 15%, i.e., more than 85% of starting molar mass retained), and “C = less effective” (relative mass loss more than 15%, i.e., molar mass less than 85% of the starting value). Figure 2 shows that ascorbyl palmitate (2), α -tocopheramine (5), *N*-methyl- α -tocopheramine (6), hydroxytyrosol (8), and propyl gallate (9) belonged to group A, with a very good performance with regard to the protection of cellulose integrity. The beneficial effects of ascorbic acid (1), α -tocopherol (3), α -tocopheryl acetate (4), and gallic acid (7) and the lyophilizate of olive mill wastewater were significantly smaller (category B), while resveratrol and green tea lyophilizate were rather ineffective (group C). The fossil-based antioxidants BHA (11a and 11b) and BHT (12), used for comparison, ranged in the “very effective” category A, but were in no way superior to the other renewables-based representatives in this group. The data for the non-stabilized dope, included in Figure 2 for comparison, corresponds to that in Figure 1 for a 5 h thermal treatment in ambient air. Noteworthy, the two derivatives, ascorbyl palmitate (2) and propyl gallate (9) (both group A), performed better than their respective parent compounds ascorbic acid (1) and gallic acid (7) (both group B). The (slightly) inferior behavior of the chloride-containing ILs compared to the acetate counterparts can be attributed to the fact that, in reaction systems involving autoxidative processes, the conversion of chloride into chloro radicals might additionally participate in homolytic reactions, while analogous processes would not exist for acetate.

3.4. Discoloration of the IL Spinning Dope

A progressing discoloration of the spinning dope and differences between the stabilizers indicated side reactions under the involvement of the antioxidants. This discoloration of the dope, if not overly pronounced, an expected process and not a concern with regard to product quality: consider as supporting examples the brown color of Lyocell spinning dopes or the dark orange hue of rayon spinning dopes, from which bright white fibers are produced in both cases. Cellulose fibers usually undergo intensive washing and, in most cases, a mild bleaching step after spinning so that satisfactory brightness levels are easily obtained from colored dopes. Nevertheless, too dark a discoloration of the spinning dope is disadvantageous for several reasons: the recycling and purification of the solvent are made more difficult, the initial brightness of the fibers is negatively affected, and bleaching must be more severe (at higher temperatures or with higher dosages of bleaching agents). Evidently, these purification and bleaching issues are also directly related to process costs.

Significant differences in the discoloration of the spinning dope were seen depending on the stabilizer added, whereas the type of pulp had no significant influence (Figure 3).

Chloride ILs showed, on average, a slightly darker discoloration than the acetate ILs, which corresponds to the slightly more pronounced cellulose degradation in the chloride ILs (see above). The discoloration of the pulp originates from two general contributions: chromophoric degradation products from cellulose and solvent, and degradation products from the stabilizer. On the one hand, the stabilizer regulates the formation of chromophoric degradation products from cellulose [111] and solvent; on the other hand, it might itself become a source of chromophores by forming chromophoric byproducts. An illustrative example is propyl gallate, used inter alia to stabilize cellulose solutions in NMMO; the colorless compound is effective as a radical scavenger and antioxidant, but, in this process, it is converted into a slightly yellowish intermediate ellagic acid and further to a dark black oxidation product, the bis(*ortho*-quinone) derivative of ellagic acid [9].

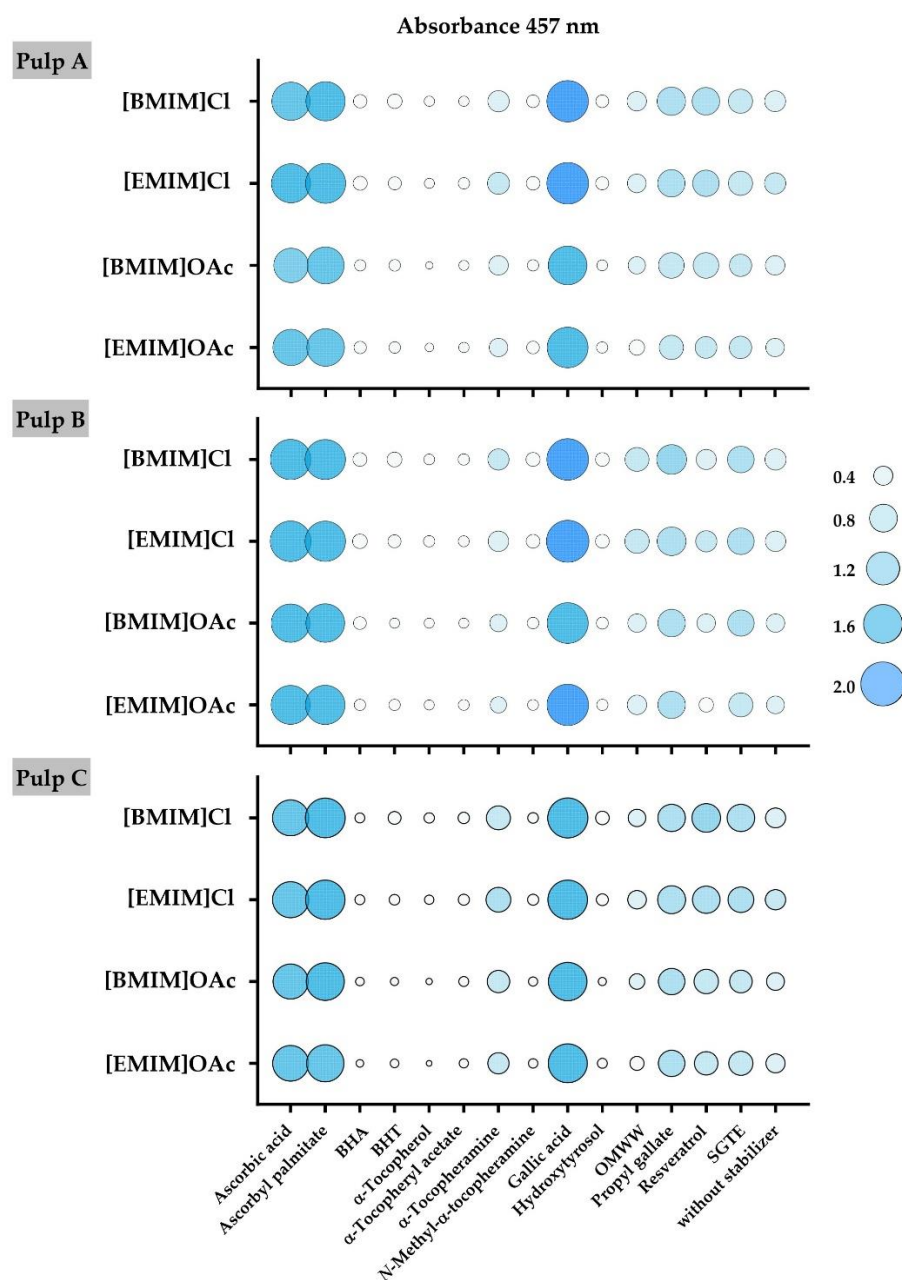


Figure 3. Discoloration of spinning dopes of 5 wt% cellulose in 3-alkyl-1-methylimidazolium ionic liquids depending on added stabilizers (0.1 wt% rel. to dope, 2% rel. to dissolved pulp), upon thermal stress (100 °C) for 5 h, measured as UV-absorbance at 457 nm of a diluted aliquot (1:10 with water), relative to the fresh solvent. Top: pulp C, middle: pulp B, bottom: pulp A.

Among the stabilizers tested, α -tocopherol (3), α -tocopheryl acetate (4), *N*-methyl- α -tocopheramine (6), hydroxytyrosol (8), the lyophilizate of olive mill waste, and the two references BHA and BHT showed relatively little discoloration of the spinning dope (Figure 3), which was yellowish to light brown, even after 5 h of thermal treatment. The discoloration effect was stronger for α -tocopheramine (5), propyl gallate (9), resveratrol (10), and green tea lyophilizate, which produced dark red and dark brown dopes, respectively. Furthermore, the non-stabilized dope was dark brown after the aging time. Ascorbic acid (1), ascorbyl palmitate (2), and gallic acid (7) caused a rather strong and rapid discoloration, which caused the dope to turn black already after two to three hours. A further darkening upon longer thermal treatment was confirmed spectrophotometrically, but was impossible to detect visually. To compare and quantify the discoloration, an aliquot of the dope was mixed with the 10-fold amount of water and filtered, and the UV absorbance at 457 nm, analogous to the ISO brightness determination of pulps and papers, was determined (Figure 3).

It was noticeable that the anion of the IL had a small, but reproducible influence, with chloride as the anion causing a more pronounced discoloration than acetate. There was no discernible systematic effect of the pulp type and the 3-alkyl substituent in the ILs' cation. Although, as mentioned above, the color of the dope cannot be translated directly into a brightness loss of the fiber or reduced bleachability, it was obvious that the stabilizers causing the blackening of the dopes would be of little value for application on a larger scale, considering the progressive accumulation of the chromophores during recycling of the IL and difficulties in their removal. While the discoloration in the case of non-stabilized pulps only originates in cellulose-derived and solvent-derived chromophores, the additional, more pronounced color of several stabilized dopes must have been caused by potent stabilizer-derived chromophores.

3.5. Yellowing Behavior of the Spun Fibers upon Accelerated Aging

Cellulose fibers were spun from the obtained dopes following a previously published protocol [6]. While spinnability was already good after two hours—one hour of swelling at room temperature, one hour of kneading/stirring at 100 °C, plus one additional hour of resting time at 100 °C—in this case, we used the dopes after 5 h because these dopes had also been used for the above dope-discoloration experiments. The spun fibers were thoroughly washed and dried (see experimental part) and subjected to accelerated dry-aging according to the TAPPI method UM 200 (105 °C, 40% rel. humidity, 24 h); the brightness was determined according to ISO 2470 (2009), measuring the remission of UV/Vis light at 457 nm of a hand sheet-type dry fiber mat. The results are displayed in Figure 4.

It was evident that the type of IL had no influence on the brightness reversion of the fibers (less than 2 brightness points), which is understandable since a well-washed fiber should be essentially free of adhering IL. Therefore, Figure 4 does not list four separate curves for the four ILs used, but rather the respective averaged values. The observed differences in brightness loss after aging thus either come from differences in the pulps (molar mass, degree of oxidative damage, α -cellulose content) or from reactions of adhering residual stabilizers and degradation products, not from differences in the IL per se.

Only the fibers from dope stabilized with *N*-methyl- α -tocopheramine (6), hydroxytyrosol (8), propyl gallate (9), green tea lyophilizate, and lyophilizate of olive mill wastewater showed satisfying behavior with regard to the prevention of brightness loss, i.e., a drop of less than five ISO brightness points. The yellowing of the fibers from dopes with α -tocopherol (3), α -tocopheryl acetate (4), α -tocopheramine (5), and ascorbyl palmitate (2) was still acceptable (loss of 5–20 ISO brightness points), while fibers with the stabilizers ascorbic acid (1), resveratrol (10), and gallic acid (7) showed a fast and very pronounced brightness loss (>20 ISO points). Because of their inferior aging behavior, spun fibers in the last group would thus be considered of poor quality and their dope stabilizers unsuitable (Figure 4). Interestingly, the fossil-based reference stabilizers, BHT and BHA, ranked only

among the medium group, not the best-performing one. The good performance of the two lyophilizates (olive mill wastewater and green tea extract) can be explained by the fact that these mixtures contain polyphenolic oligomers, which precipitate much better on the cellulose during fiber formation than low-molar mass compounds. The amount of active, antioxidatively acting stabilizers on the fiber is thus higher in these two cases than for the other low-molar mass auxiliaries, which explains the good brightness loss prevention.

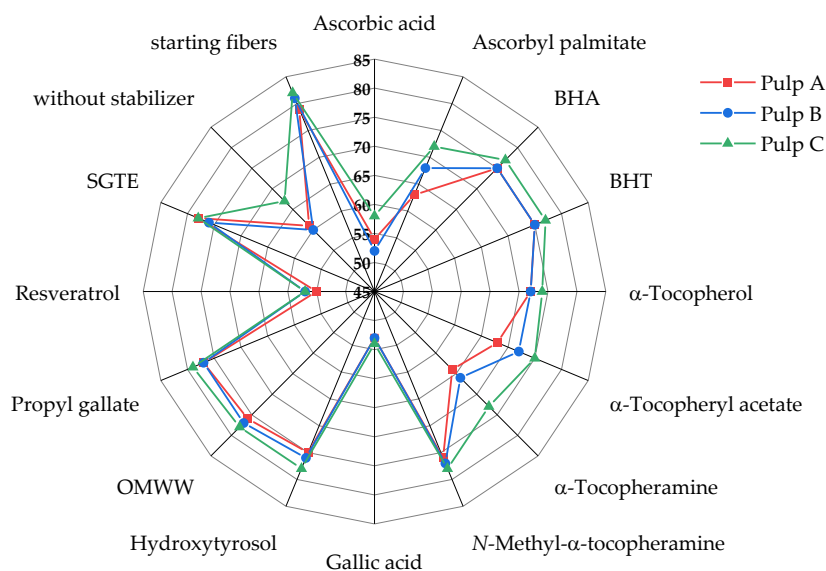


Figure 4. Thermal aging (105 °C, air, 40% rel. humidity, 12 h) of fibers spun from spinning dopes of 5 wt% cellulose in 3-alkyl-1-methylimidazolium ionic liquids depending on added stabilizers (0.1 wt% rel. to dope, 2% rel. to the dissolved pulp), measured as ISO brightness points (UV absorbance at 457 nm). The ISO values of starting fibers from pulp A, B, and C (before accelerated aging) were 78, 81, and 82 °ISO. The brightness of the non-stabilized fibers is given for comparison. Values are averages of the four ILs used.

4. Conclusions

Ten natural antioxidants were screened in terms of their performance as antioxidatively acting stabilizers in spinning dopes of cellulosic pulps in 3-alkyl-1-methylimidazolium ionic liquids. The effectiveness was evaluated according to three parameters: (a) prevention of autoxidative side reactions that cause degradation (loss of molar mass) of cellulose (cf. Figures 1 and 2), (b) discoloration of the spinning dope (Figure 3), and (c) brightness reversion (yellowing) behavior of the spun fiber upon accelerated aging (thermal stress). Even when taking three simple categories—A: very effective, B: effective, and C: less effective—as the basis of the conclusions, there was quite a clear picture of which stabilizers performed best. Compounds that “failed” (category C) in one of the three parameters were not considered promising for further optimization; compounds that performed optimally in all three evaluation classes were regarded as the best candidates for such work. Table 3 summarizes the conclusions as to the suitability of the stabilizers. The three best-performing compounds are printed in italics.

In conclusion, hydroxytyrosol (8) and *N*-methyl- α -tocopheramine (6) showed the best overall performance and are obviously promising candidates for further testing and optimization. Propyl gallate (9), the stabilizer used in Lyocell (NMMO) solutions, also gave satisfying results, comparable to the fossil-based BHA/BHT antioxidants, which were employed only as a reference. The other vitamin E derivatives (3–5) and OMWW hydrolysate should be excluded in further studies. The latter mixture, of which hydroxytyrosol (8) is the main antioxidative component, might be interesting, as it has been a waste product thus far that now could find a utilization. Gallic acid (7), resveratrol (10), and green tea lyophilizate were evidently unsuitable as stabilizers in the system studied.

Table 3. Natural antioxidants, antioxidant derivatives, and mixtures used to stabilize cellulose solutions in 3-alkyl-1-methylimidazolium ionic liquids against autoxidation processes (category A: very effective, B: effective, and C: less effective; the three best-performing compounds are printed in *italics*).

Stabilizer	Cellulose Degradation	Dope Color	Yellowing upon Aging	Remarks
Ascorbic acid (1)	B	C	C	Inferior at chromophore formation
Ascorbyl palmitate (2)	A	C	B	Inferior at chromophore formation
α -Tocopherol (3)	B	A	B	Very similar to acetate (4)
α -Tocopheryl acetate (4)	B	A	B	Very similar to parent phenol (3)
α -Tocopheramine (5)	A	B	B	Good cellulose protection
<i>N-Methyl-α-tocopheramine (6)</i>	<i>A</i>	<i>A</i>	<i>A</i>	<i>Superior overall performance, better than parent amine (5)</i>
Gallic acid (7)	B	C	C	Inferior overall performance
<i>Hydroxytyrosol (8)</i>	<i>A</i>	<i>A</i>	<i>A</i>	<i>Superior overall performance</i>
OMWW lyophilizate (mixture)	B	B	A	Mixture, highly economical, better than tocopherols
<i>Propyl gallate (9)</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>Good besides dope color, better than parent acid (7)</i>
Resveratrol (10)	C	B	C	Inferior overall performance
SGTE lyophilizate (mixture)	C	B	A	Mixture, little protective effect
BHA (11)	A	A	B	Fossil-based, used for comparison
BHT (12)	A	A	B	Fossil-based, used for comparison

Further work must now concentrate on processing parameters regarding the stabilizers. Of particular interest are the chromophoric degradation products formed and their removal from the recycled solvent, the amount of stabilizer retained in the spun fiber, and the (economically important) question of minimizing the stabilizer concentration without sacrificing performance. It was obvious that renewables-based stabilizers are a viable alternative to their fossil-based counterparts with regard to performance in cellulose/IL spinning. Availability in sufficient quantities would be given for all tested compounds. Although this statement is not intended to present detailed economic analysis, the economic side also does not seem to be a major obstacle to the utilization of the stabilizers.

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