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Sustainable optics? A critical insight into biopolymer-enabled optics

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ABSTRACT

The use of biobased polymers or natural inorganic materials in place of synthetic polymers or liquid crystals derived from petroleum to fabricate optical components establishes the concept of "sustainable optics", at least for what concerns the environmental dimension of sustainability as these polymers are renewable and often biodegradable or compostable. To identify the main obstacles to be addressed prior to industrial uptake of these polymeric resins in the optics industry, we focus on two promising and widely studied biobased polymeric materials, namely nanocellulose and poly(limonene carbonate). The conclusions have implications also for the emerging bioeconomy and the undergoing reshaping of the chemical industry driven by sustainability megatrend.

1. Introduction

In the last two decades biopolymers and biopolymer-based composites have been widely studied for biomedical and biological applications such as implants [1], drug delivery [2], wound dressings [3], soil modification [4,5], and also for optic, photonic and optoelectronic devices [6]. Many naturally derived polymers indeed present favorable optical properties, including high transparency and light guiding efficiency.

Compared with polymers of petroleum origin, biopolymers are often (but not always) biodegradable and biocompatible, whereas the presence of functional groups in their structure (amino-, carboxy-, hydroxy- and other groups) opens up ways for their chemical modification to impart properties such as conductivity, and the ability to change color under external stimuli or the desired refractive index [7,8].

New advanced applications of biopolymers for electronics and photonics include living waveguides and biocompatible wearable biosensors [9,10]. Several nano- and living materials have been combined with biopolymers to add new functionalities to meet the requirements of emerging novel technologies that need a combination of optical, mechanical, electronic and stimuli-responsive properties, as well as sustainability and environmentally friendly processes of fabrication [10].

In pure form, e.g. without fillers, biopolymer can be used for fabrication of waveguides or microlenses by template techniques or molding [11,12]. More often, biopolymers are used as a matrix for nanoparticles (NPs) or mixing with synthetic polymers, to obtain high refractive index materials for waveguides [13], microlenses [14], photonic stimuli-responsive materials, and optical sensors [15].

Metal and metal oxide NPs are used as spread filler for biopolymer-based composite to tune their optical properties, in particular their refractive index, optical transparency and scattering [16,17]. These type of NPs are introduced in biopolymer matrices either *in situ* starting from salt precursors or by mixing prepared NPs with biopolymer solution [18,19].

Concluding that the knowledge of the assembly mechanism and the control of physical/chemical interactions at the matrix/filler interface is still limited, recently Martucci and Colussi published a review on biopolymer and biopolymer composite applications in optics and electronics [20].

The use of biobased polymers or natural inorganic materials, being renewable and often biodegradable or compostable, in place of synthetic polymers or liquid crystals derived from petroleum to fabricate optical components establishes the concept of "sustainable optics". What are the main obstacles that remain to be addressed prior to industrial uptake of these polymers in the optics industry?

To answer these questions, we focus on two highly promising and widely studied biomaterials, namely nanocellulose and poly(limonene carbonate). Many other biopolymers, such as silk and chitosan, have been used to fabricate optical components and continue to be widely investigated. Furthermore, natural inorganic materials such as abundant and recyclable layered 2D mineral vermiculite sourced via eco-friendly (zero-waste) method using water only, have been lately developed to replace organic liquid crystals with mineral liquid crystals of excellent optical performance (to modulate transmitted light in a broad spectrum and sensitive magneto-birefringence response) [21].

In addition, optics also includes a wide scope, such as birefringence, transparent film, photochromism and many other applications. Excellent reviews have been recently published for example in the field of wood- and plant-derived biomaterials in optics, electronics and energy applications [22,23].

Others concern the use of chitosan [24] (nanochitin)-based materials and nanocellulose [25] fibres to develop photonic materials for toxic anions, heavy metal pollutants or even biomolecules.

The aim of this work, however, is not to provide a comprehensive review articles concerning poly(limonene carbonate), nanocellulose, or vermiculite-based optical and photonics components. The study rather aims to answer the aforementioned questions on the technical and

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economic feasibility of optics based on polymers and materials sourced from biological resources.

Its conclusions, which encompass other natural sources of the optical materials such as minerals, have implications also for the development of the emerging bioeconomy and the undergoing reshaping of the chemical industry driven by sustainability megatrend [26].

2. Biopolymer-based optical devices

Optical elements, we briefly remind, are used for transmitting, detecting and converting light. They include waveguides (a physical structure that conducts electromagnetic waves of the optical spectrum), lenses (elements designed to focus or scatter light), optically active coatings such as sensors, photonic coatings, Bragg reflectors, and several other devices.

The materials for the manufacture of optical elements must have the function of controlling or changing electromagnetic radiation in the ultraviolet (UV), visible and infrared (IR) spectral regions [27]. For use in photonics, materials must also have certain mechanical, chemical and biological (biocompatibility in biomedical applications) characteristics.

In general, the most important properties for the selection of optical material are the degree of transparency and refractive index, and their spectral dependence [27]. Materials with high transparency have relatively low reflection, absorption and scattering of light, thus leading to low optical losses. On the other hand, biopolymers strongly absorb light at short wavelengths of 250–400 nm, which is typical for many organic molecules and imposes limitations on the optical usage of biopolymer-based materials.

Scheme 1 displays the typical biopolymer structure alongside their typical applications in optics and photonics.

Biopolymers suitable for optical applications include poly(limonene carbonate), silk fibroin, chitosan, gelatin, nanocellulose, alginate, polylactic acid and polyhydroxyalkanoates.

The presence of abundant functional groups and the possibility of controlling the supramolecular organization of the biopolymers facilitate the fabrication of materials with new functionalities and tunable properties. Nanocellulose and poly(limonene carbonate) offer two instructive examples.

2.1. Nanopaper

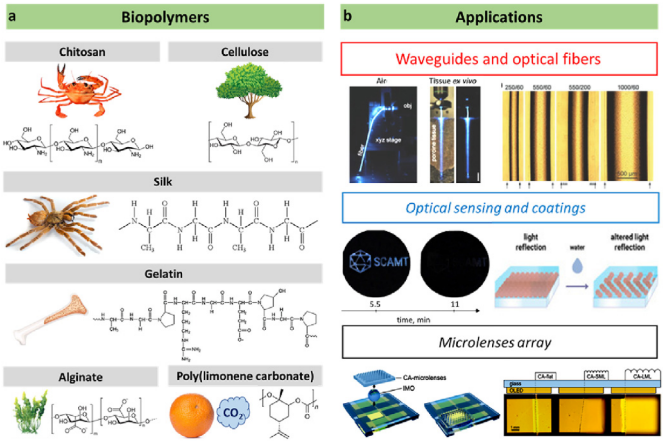
Comparing transparent TEMPO-oxidized microsized wood fiber paper to a differently fabricated nanopaper made of randomly arranged microfibrils, in late 2013 a joint team reported the discovery of a transparent nanopaper of exceptional optical transparency (~96%) and optical haze (~60%; haze is the percentage of light diffusely scattered through a transparent surface from the total light transmitted) [30].

In detail, the team mixed 5 g of wood fibers with a 1% suspension of softwood pulp in water. The mixture underwent partial oxidation using de Nooy's TEMPO/NaBr/NaClO oxidation system at alkaline pH to selectively oxidise the primary hydroxyl groups in polysaccharides to carboxyl groups [31], followed by processing the TEMPO-oxidized wood fiber solution using a Microfluidizer processor. The new transparent paper was readily obtained by vacuum filtration with a filtration time of less than 1 h (for comparison, the filtration time required to filter a piece of nanopaper of similar thickness consisting of TEMPO-oxidized nanofibers was more than 8 h).

De Nooy's oxidation system relying on the TEMPO (2,2,6,6-tetramethyl-1-piperidine-*N*-oxy radical)-mediated oxidation at alkaline pH [31] introduces in the suspended cellulose fibrils about 10% of carboxylate groups which weaken the hydrogen bonds between the cellulose fibrils and cause the partly oxidized cellulose fibrils freed in suspension following a mechanical treatment to swell up and become stable in aqueous suspension [32,33].

The team led by Hu showed that significantly enhanced light scattering and enhanced transparency of the new transparent paper are due to the high packing density of the TEMPO-oxidized wood fibers, while a significant amount of small fragments in the pulp fill in the voids within the paper causing less light scattering to occur within the TEMPO-treated paper and allow more light to pass through it (Fig. 1) [30].

Commenting the achievement, Professor Hu highlighted how the newly developed nanopaper "is formed from much less energy intensive processes that enable low cost paper devices" [34]. Claiming interest in the manufacturing of the nanopaper, Hu highlighted the team's interest



Scheme 1. Scheme of typical biopolymer structure (a) and their application in optics (b). [Adapted from Refs [28,29,11], with kind permission].

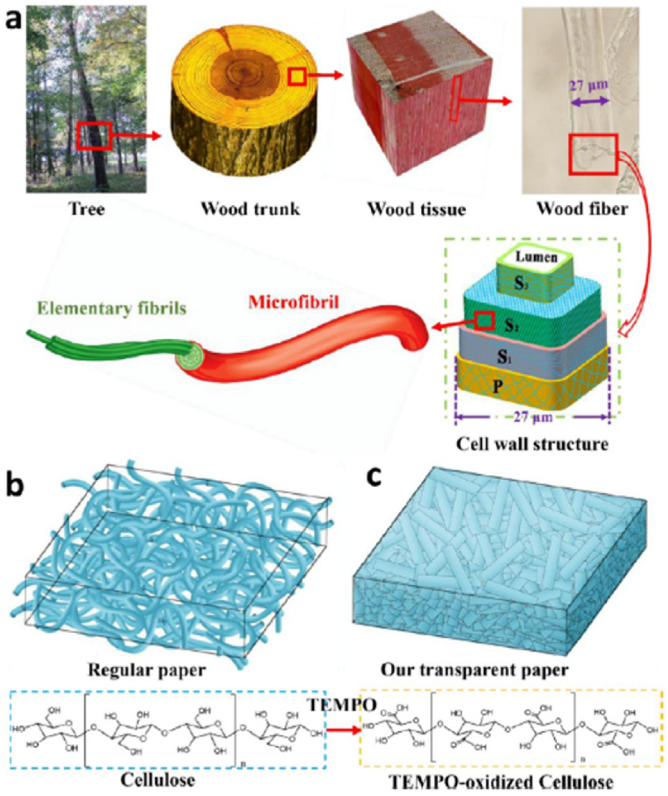


Fig. 1. (a) Hierarchical structure of a tree. A schematic of cellulose and paper before and after TEMPO-mediated oxidation. (b) Top left, regular paper; bottom left, molecular structure of cellulose. (c) Top right, transparent paper made of TEMPO-oxidized wood fibers; bottom right, TEMPO-oxidized cellulose with carboxyl groups in the C6 position. [Reproduced from Ref. 30, with kind permission].

"to work with solar cell and display companies to evaluate the applications" [34]. Nearly a decade after its invention, however, the production of this remarkable transparent paper has not yet been commercialized [35].

Once similar nanopaper films will be made available at low cost in a form resistant to humidity (nanopaper films are highly sensitive to humidity, swelling and losing their optical properties for instance under rain), highly transparent and high haze nanopaper films will become commercially viable.

The production process involves the de Nooy's TEMPO-mediated oxidation of primary wood fibers (bleached sulfate softwood pulp) with NaOBr generated *in situ* by adding NaOCl to a 10 wt% NaBr solution under stirring for 8 h at pH 10.5, followed by extraction of the 5–30 nm nanofibers using a high-pressure homogenizer (operated under a pressure of 1360 atm) producing the higher shear rates required for mechanical disintegration of the aggregated nanofibrils.

Drawing on independent work carried out by academic and industrial researchers, some of us have recently shown elsewhere that the polysaccharide nanofiber production costs incurred in the TEMPO-mediated oxidation followed by homogenization requires the replacement of the homogeneous carboxylation process mediated by expensive (and toxic) TEMPO catalyst in solution with a solid catalyst [36]. The heterogeneously catalyzed process indeed affords in one-pot (and in one step only) insoluble polysaccharide nanofibers of superior quality, eliminating the high costs of processing waste generated in the multi-step homogeneous process [37]. In the heterogeneously catalyzed process, indeed, at the end of the reaction the residual hypochlorite is quenched with 0.3% ascorbic acid, while CNF is separated from the solid catalyst via simple filtration, and the catalyst recovered and reused [36].

All this dramatically reduces polysaccharide nanofiber production costs and opens the route to mass-scale production and uptake of cellulose nanofibers in a variety of functional products, including transparent nanopaper, whose practical applications so far have been limited chiefly by its high production cost [36].

2.2. Lenses, luminaries and breathing glass with PLimC

Obtained via the alternating copolymerization of *trans* 1,2-limonene oxide and CO_2 mediated by Zn(II) or Al(III) catalysts under relatively low pressure (6–20 bar) and temperature (up to 73 °C), poly(limonene carbonate) (PLimC) is a biobased polycarbonate of exceptional optical, thermal, and gas permeability properties that make it ideally suited as glazing material for the production of "breathable" windows and greenhouses [38].

Compared to the main commercial glazing material, bisphenol A (BPA)-polycarbonate, PLimC is lighter and shows higher transparency and pencil hardness besides being orders of magnitude more permeable to O_2 and CO_2 gas molecules [39]. However, its high melt viscosity restricts most engineering applications of pure PLimC since its melt processing results only in brittle and colored objects.

However, it is enough to simply compound PLimC with 7.5 wt% ethyl oleate (EtOL) to control the glass transition temperature (T_g) and melt viscosity of the resulting composite polymer affording melt-processed PLimC/EtOL objects of excellent optical quality (Fig. 2) [40].

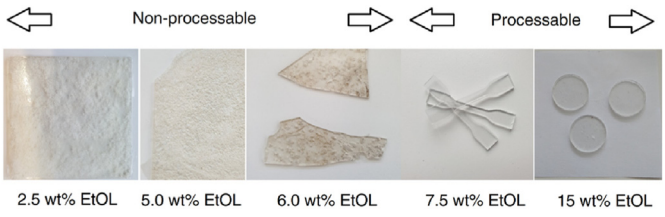


Fig. 2. Optical appearance of hot-pressed PLimC/EtOL compounds with different EtOL contents. The respective EtOL contents are given below the images. [Reproduced from Ref. 40, with kind permission].

The addition of EtOL results in an increase in the haze, for values ≤15%. Still, high transmission (of about 90%) and clarity (85%) comparable to those for commercial polycarbonate (BPA-PC), can be reached even for the composite with 15 wt% EtOL. Further contributing to the overall sustainability of the new composite, the PLimC/EtOL composites can be melt-processed a second time without significant loss of mechanical and optical properties.

Given the paucity and high cost of limonene, some of us have suggested that the first applications of PLimC will be in high-revenue, advanced uses where the higher cost of PLimC will be justified in light of its superior mechanical, thermal, and optical properties [41].

The high cost of PLimC would not stem from the catalytic synthesis using a low cost Zn or Al catalyst and readily available CO_2, but rather from the high (and increasing) selling price of limonene, today nearly entirely obtained from orange peel prior to fruit squeezing to extract the juice, and the limited yearly availability barely exceeding 20,000 t/a [42].

Clearly, the use of limonene as a platform chemical for the chemical industry requires to commercialize its microbial production [43]. In 2020, Scrutton and co-workers estimated at 0.7 kg/(m^3·h) the minimum productivity for the limonene microbial process starting from glucose to be economically viable (Fig. 3).

The minimum limonene price for the economically viable production rapidly declines with increasing productivity reaching $16.29/kg at 1 kg/($m^3$·h) [43]. According to the team, who used the highest fermentation productivity achieved to 2014 over engineered *Escherichia coli* in bench-top bioreactor system of 0.02 kg/(m^3·h) using glycerol as bacterial feed [44], economic viability would require a 20-fold improvement in productivity [43].

Nearly a decade later, however, the productivity of the microbial synthesis of limonene has more than tripled, with low cost and highly stable engineered *Saccharomyces cerevisiae* fungi replacing *E. coli* bacteria [45], and low cost glucose juice obtained from hydrolyzed cardboard waste successfully replacing pure glucose (or pure glycerol) as substrate [46], further lowering production costs.

In brief, whereas in the case of nanocellulose its large scale production has been hindered by the high production costs, in the case of PLimC, its industrial production is restricted by the limited supply and high cost of limonene. The latter terpene, however, today has so many usages and applications beyond its original use as biosolvent [42,47], that the large

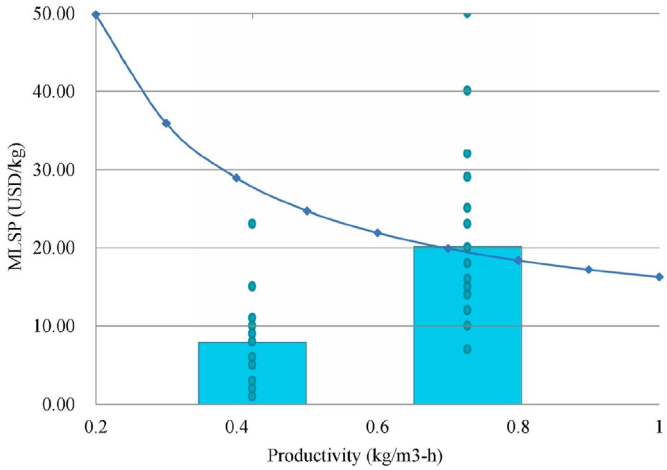


Fig. 3. Variation of minimum limonene selling prices over a range of limonene fermentation productivity (connected scatter plot). Averaged upper and lower bound prices for limonene (96 wt%) are indicated with bars, with the distribution of prices shown by scatter plots. [Reproduced from Ref. 43, with kind permission].

and rapidly increasing demand will shortly drive commercialization of the fermentation route.

Similarly, once the emerging green routes to nanocellulose will be commercialized [48], production costs will drop, opening the route to multiple applications of this exceptional bionanomaterial, including the production of transparent nanopaper [49], that so far have been limited by nanocellulose high cost and limited supply.

Seen from the economic viewpoint, the replacement of oil-derived polymers with biobased polymers in optical devices will not need government incentives as was the case for biodegradable and compostable bags and disposable cutlery derived from bioderived polymers [50]. Biobased polycarbonates would indeed replace significantly more expensive polymers when compared to polyethylene and other commodity polymers.

Besides being more versatile, biopolymers such as PLimC have superior thermal and optical properties: a distinctive advantage in the three-dimensional (3D) printing of optical devices. Therefore, the first segment of the optics industry that will uptake 3D printing biopolymers, we forecast, will be the lighting industry, wherein additive manufacturing was termed "the next frontier for the LED lighting industry" already in 2018 [51].

For example, recently 3D printing allowed to create in two weeks an elegant and effective lens array fitting into the LED lighting fixture. The array eliminated light losses at the surface by halving the beam angle from the wide 120°–60° and nearly eliminated glare [52].

Typically relying on transparent oil-derived UV-curable polymers such as (oligo)methacrylate, acrylate, or styryl moieties 3D printing of optical components [53], digitally controlled 3D printing can be used to develop any shape surface, including large area objects, dramatically reducing the cost and improving the quality of manufacturing optical components thanks to significantly higher precision (resolution), less material consumption, and higher fabrication speed when compared to conventional manufacturing [54,55].

Lamenting the poor availability of a sufficient number of suitable resins, recently Li and co-workers highlighted that the major limitation in developing 3D printing of functional optical structures are the transparency and the variation in material properties during the three-dimensional printing process [56]. Filling this gap, bioderived polymers are particularly well suited used to produce optics via additive manufacturing (3D printing) because they are easily imparted with new functionalities and tunable properties.

3. Outlook and perspectives

Focusing on nanocellulose and poly(limonene carbonate) potential use to produce optical components, we have attempted to identify what is required for the industrial uptake of biobased polymers in the optics industry. Not only biopolymers with both enhanced optical properties and declining cost, however, are promising and applicable in the optical industry to improve its overall sustainability. Natural minerals such as recyclable layered 2D mineral vermiculite mined in 600 million t yearly, can also be used to replace synthetic, organic liquid crystals with enhanced optical performance (to modulate transmitted light in a broad spectrum and sensitive magneto-birefringence response) [21].

Since more than 60 years, the latter industry heavily relies on transparent polymers made available by the chemical industry. Both industries are highly profitable. The chemical industry nearly entirely relies on oil-derived feedstocks to produce all of its polymers.

Why then, realistically, should biopolymers start to replace affordable and reliable synthetic polymers with which the optics industry profitable makes its components including optoelectronic substrates?

The driving force, we argue, will not be "the non-renewability and non-biodegradability of plastics" [49] that would cause a "huge threat to the environment caused by their use" [49]; but rather the enhanced performance of the optical devices that can be produced using polymers such as certain biopolymers having better mechanical, thermal, and optical properties, such as is the case of nanocellulose and PLimC.

The latter biobased polymers currently are expensive and even commercially not available in the case of PLimC. Yet, completely new manufacturing technologies such as additive manufacturing (3D printing) [53], enable to minimize losses and to produce optical devices based on customer demand (namely without accumulating unsold goods that greatly damage any business profitability).

The first optics companies commercializing biobased optical components will likely add "green" certification labels to their product packages highlighting the sustainability of their products. Yet, their customers will select (and pay) the new optical components derived from biobased polymers (or from natural minerals sustainably sourced and processed) based on enhanced performance, and not on "sustainability" metrics.

For example, transparent windows made of PLimC will show unique permeability to O_2 and CO_2 molecules with significant health benefits in a number of utilization of said glazing based on "breathing glass" [38,39].

The concept can be generalized: advanced applications of biopolymers such as those in the optics industry are those that chemical and bioeconomy companies evaluating production of said biopolymers should target [57].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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