Polysaccharide Applications in Textiles and Materials Technologies

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Abstract

The paper presents a summary overview of the research investigations undertaken in the four-year European Commission funded Marie Curie Initial Training Network: “STEP”.

Introduction

Polysaccharides, e.g. cellulose, starch, chitin, are among the polymers that make up the fundamental components of life and constitute a major proportion of the earth’s biomass. These carbohydrate polymers constitute the largest segment of all available polymers, and hence exhibit the greatest potential as alternative sources of raw material in efforts to replace petroleum-based polymers with those obtained in sustainable modes from renewable resources.

A primary challenge in sourcing of materials/products from renewable resources is the development of “selective efficient separation and conversion process-

Table 1. The consortium in the Initial Training Network “STEP”.

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<tr>
<th>Institution</th>
<th>Location</th>
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<tr>
<td>Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck</td>
<td>Dornbirn, Austria</td>
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<tr>
<td>Institute of Organic Chemistry and Macromolecular Chemistry, University of Jena</td>
<td>Jena, Germany</td>
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<td>Division of Food Sciences, School of Biosciences, University of Nottingham</td>
<td>Nottingham, United Kingdom</td>
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<tr>
<td>Institute of Biopolymers and Chemical Fibers</td>
<td>Lodz, Poland</td>
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<tr>
<td>Laboratory for Characterization and Processing of Polymers, University of Maribor</td>
<td>Maribor, Slovenia</td>
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<tr>
<td>East Thuringian Material Testing Company</td>
<td>Rudolstadt, Germany</td>
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<tr>
<td>Innovation and Business Development Textiles, Lenzing AG</td>
<td>Lenzing, Austria</td>
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<tr>
<td>Unilever Food and Health Research Institute</td>
<td>Vlaardingen, The Netherlands</td>
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were divided into the following broad categories: results pertaining to materials applications. The work in this paper, we present an overview of the project’s structure and properties. These two perspectives were integrated in the research investigations of the network. However, existing conversion processes are limited in scope by the predominant intra- and inter-molecular non-covalent interactions that characterize the supramolecular structures of polysaccharides. The non-covalent interactions impose constraints on polysaccharide conversion by restricting polymer solubility in solvents, limiting thermal processability and dictating the feasibility and extent of functionalization.

To gain understanding of these constraints and to utilize the knowledge in finding solutions for polysaccharide conversion to overcome them, was the focus of the joint research-training program of the Marie Curie Initial Training Network “Shaping and Transformation in the Engineering of Polysaccharides (STEP)”, formed by a consortium of industry and academic institutions (see Table I), and funded from the European Community’s Seventh Framework Program from October 2008 – September 2012.

Research Activities of the Network

Two major areas of polysaccharide application, foods and materials, were represented in the consortium. In both, conversions typically involve swelling or dissolution of polysaccharides in solvent; and hence, polysaccharide-solvent interactions are of vital interest. In foods, the focus is on polysaccharide influence on solution structure and properties; while in materials, attention is paid to solvent influence on polysaccharide structure and properties. These two perspectives were integrated in the research investigations of the network. In this paper, we present an overview of the project’s results pertaining to materials applications. The work was divided into the following broad categories:

- polysaccharide derivatization,
- mixing or blending polysaccharides with other components,
- polysaccharide shaping (i.e. dissolution and regeneration from solvents), and
- structure-property relationships in polysaccharides along with methods for their characterization.

The derivatization modes ranged from regioselective to non-specific reactions. 3-mono-O-alkyl cellulose bearing two different ether groups (methyl/ethyl, methyl/n-propyl or ethyl/n-propyl) were regioselectively synthesized with varying ratios of the two alkyl groups [2]. The mixed derivatives exhibit heat-induced self-association (i.e. thermogelation) in aqueous solutions at temperatures that vary with composition and proportions of the alkyl substituents [3-4], which is of interest as a means of controlling rheology in food and pharmaceutical formulations. Novel amino cellulose esters were synthesized through ring-opening reactions of lactam in BMIMCl with or without co-solvent, or in NMP/LiCl. Good yields of the derivative were obtained even with low molar ratio of reagent to cellulose, over a wide range of cellulose DPs [5]. Some derivatives were investigated for their utility as flocculants or thickeners as they have environmentally advantageous fate-after-use profiles [6], as well as surface-coating agents to modify properties of cellulose films [7]. Amino cellulose sulfate derivatives were synthesized in a novel route through tosyl cellulose intermediates [8]. The products are polyampholytic, exhibit pH dependent solubility and some antibacterial activity [9]. The derivatives could be added onto viscose to impart amphoteric properties to the fibers [10]. A method of introducing carbamate groups on woven celluloses in a continuous pad-dry-cure process was devised [11]. The reagents are inexpensive, non-toxic and commonly used in the textile and paper processing and pad–dry–cure treatments are routinely employed at both industries. Hence, the process may be adopted in existing commercial-scale operations without additional capital investment. The treated substrates, paper or fabrics, may be utilized as adsorbents for heavy metals from waste water or in the creation of flame retardant products. An additional use is in the creation of all-cellulose composites or membranes, by further treatment with alkali [12].

A method of improving polysaccharide properties is by mixing or blending with a second component. In ideal cases, the resulting combinations exhibit properties not available in either component individually, i.e. synergies are created. In STEP, investigations were conducted on combinations of polysaccharides with another polysaccharide, an organic component or an inorganic component. It was found possible to achieve sorption of anionic polysaccharides (pectin, alginate, xanthan) on cellulosic fibers by first treating the cellulosics with calcium salts [13]. Copper ions were inserted in cellulosic fibers from alkaline conditions of copper–D-gluconate complexes [14]. Copper salts precipitate in alkaline conditions, but copper complexes with D-gluconate remain soluble. The sorption of copper by cellulose from
complexes is believed to occur through ligand-exchange reactions, to extents depending on the strength of copper complexation with D-gluconate relative to that with cellulose. In experiments conducted to determine sorption profiles of silver ions on cellulosic fibers, the ions were found to reduce and form particles on substrates [15]. The treated substrates exhibited antimicrobial activity comparable to that reported for silver-nanoparticle-treated substrates – suggesting efforts towards nanoparticle synthesis may not be necessary to utilize the antimicrobial activity of silver on clothing and textiles. Methods were devised to incorporate calcium phosphates (hydroxyapatite powder, tricalcium phosphate nanoparticles) in chitosan fibers and sponges [16-17]. Composite fibers were produced with tenacity similar to that of pure-chitosan fibers. The composites also proved susceptible to enzymatic degradation. These properties are important in the envisaged utilization of the composites as scaffolds for cell-growth.  

A significant stage in the preparing polysaccharides for use in materials applications is the creation of appropriate shapes or forms, e.g. creating cellulosic fibers or films from wood pulp. The process, termed “shaping”, for polysaccharides is based predominantly on dissolving the purified polymer in solvent and then re-precipitating it in desired shapes. The investigations in STEP focused on the solvent (toxicity, thermal stability), polymer solubility, and potential for solvent recovery and reuse in processes. Ionic liquids – essentially ionic, salt-like materials that are liquid below 100° C – exhibit promise as solvents in cellulose processing. The safety and viability of their industrial-scale application were investigated for a wide range of ionic liquids [18-19]. The thermal stability of cellulose solutions in ionic liquids was determined to be comparable to that of the existing NMMO-system. Efficient recycling and reuse of ionic liquids, deemed necessary for achieving cost-competitiveness, remains a challenge. The difficulties arise due to high affinity of ionic liquids for cellulose as well as reduction of their thermal stability. It was found possible to blend cellulose with secondary components in NMMO or ionic liquids, but the latter are believed to possess advantages over NMMO for selected components [19-21]. There were indications that mechanical grinding renders cellulose susceptible to “cold-melting”, i.e. plasticization in absence of high temperature [22]. If confirmed in further work, these results point to potential for thermo-mechanical shaping processes for cellulose similar to those used for thermoplastic polymers. Localized, limited swelling operations, although not categorized as shaping, are used as activation pretreatments. Concentrated urea-salt mixtures were investigated for the purpose as alternatives to the traditional alkali-based treatments [23-24].

In addition to the identity of chemical species’ present in the chemical structure of polysaccharides, the physical arrangement of the long-chain molecules (i.e. supramolecular architecture) is also significant in determining the properties of these polymers. The determination of such structure-property relationships was the subject of some investigations in STEP, including the development or refinement of characterization methods. Model cellulose films were created from spun-coated trimethylsilyl cellulose for use in understanding mechanisms of biomolecule immobilization, water-cellulose interactions and structural rearrangement of cellulose on drying, as well as of enzymatic hydrolysis of cellulose [25-29]. By applying paramagnetic relaxation enhancement techniques in solid-state NMR spectroscopy of cellulose, it was found possible to obtain separable spectral contributions for crystallite cores, accessible and inaccessible surfaces of crystallites as well as solvent-accessible non-crystalline cellulose [30]. It was found possible, with a single fitting procedure, to simultaneously determine particle charges, polydispersity indices and intra-, inter-particle interactions in aqueous suspensions of nanocrystalline cellulose through small-angle x-ray scattering measurements with generalized indirect Fourier transformation [31]. The utility of perichromism was demonstrated in determining application-oriented properties of cellulose and its derivatives, e.g. solvent-polymer interactions and degrees of substitution [32-33].

An additional goal, of equal importance as the research, was the training of young researchers. A total of 16 PhD students and 6 postdoctoral researchers were recruited and trained in technical skills (instrumentation, analytical methodologies), on critical problem-solving, best-practice in management of Intellectual Property Rights, and on communicating research concepts and the results of investigations to a diverse audience by a variety of means (lectures, written reports, scientific publications etc.). More details on the project are available on its website: www.stepitn.eu

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References


