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Feature Article

Grafting of cellulose by ring-opening polymerisation – A review

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A B S T R A C T

In this review, homogeneous and heterogeneous grafting from cellulose and cellulose derivatives by ring-opening polymerisation (ROP) are reported. Cellulose is biorenewable and biodegradable as well as a stiff material with a relatively low specific weight, foreseen to be an excellent replacement for synthetic materials. By utilising ROP of monomers such as ε-caprolactone or L-lactide from cellulose, composite materials with new and/or improved properties can be obtained. Grafting of solid cellulose substrates, such as cotton, microfibrillated cellulose (MFC) or cellulose nanocrystals, renders cellulose that can easily be dispersed into polymer matrices and may be used as reinforcing elements to improve mechanical and/or barrier properties of biocomposites. A surface grafted polymer can also tailor the interfacial properties between a matrix and the fibrillar structure of cellulose. When derivatives of cellulose are grafted with polymers in homogenous media, amphiphilic materials with interesting properties can be achieved, anticipated to be utilised for applications such as encapsulation and release.

Contents

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1. Introduction

Cellulose, being the most abundant naturally occurring polymer on earth, is a highly interesting material due to its renewability, low price, high availability, and good mechanical properties [1–4]. Cellulose is composed of repeating units of glucose joined together by hydrogen bonds to form sheets. The sheets in turn form microfibrils, which aggregate. These aggregates form layers with different orientation in the cell wall, see Fig. 1 [1–3,5]. The high molecular weight and numerous hydroxyl groups bring about strong inter- and intra-molecular interactions due to hydrogen bonding, so strong that cellulose is practically insoluble in water, although highly hydrophilic. Furthermore, these hydrogen bonds give cellulose fibres excellent mechanical properties, [1,2] similar to those of synthetic fibres.

The interest in cellulose has reawakened due to the concern for the environmental impact of synthetic polymers and fibres, and as the price of the raw material for production of synthetic polymers is rapidly increasing. Since cellulose is both biorenewable and biodegradable, several studies have focused on the modification of cellulose, to investigate it as a replacement material for synthetic polymers [1,6,7]. The hydroxyl groups can act as chemical handles and cellulose can either be modified with small organic molecules [2,4,8] or by grafting of polymer from the cellulose backbone. Grafting of polymer chains can be performed by several different methods, either by "grafting from", "grafting to" or "grafting through" [1,4,8]. There are several reports in the literature of the grafting of cellulose by free radical polymerisation, coupling chemistries, controlled radical polymerisation etc. [1,7,9]. The focus of this review is, however, the grafting of polymers from cellulose and cellulose derivatives utilising Ring-Opening Polymerisation (ROP). The review is divided into heterogeneous (i.e. from solid cellulose fibres and fibrils), homogeneous (i.e. from soluble cellulose derivatives and dissolved cellulose) and enzymatic grafting, as well as in "grafting to" and grafting from", referring to the way the polymer is anchored to the substrate. Furthermore, for every method, each substrate of cellulose is described separately. A short introduction to the different cellulosic substrates that have been utilised for ROP is given below.

2. Cellulosic substrates

There are several natural sources of cellulose; plants (major sources are wood and cotton), some animals, bacteria, and fungi [3,6,10]. Depending on the source, molecular properties such as molecular weight and crystallinity will differ. Wood pulp is the most important of all cellulosic raw materials, which is used in the paper industry. Only around 2% of the wood pulp is modified to be used for production of regenerated fibres and chemically modified fibres. The molecular weight of cellulose in wood pulp varies with the source of the pulp, but it typically has a degree of polymerisation (DP) in the region of 300–1700 [2].

2.1. Nanocelluloses

Recently, much research has focused on the investigation and disintegration of cellulose into its nanostructural components. Microfibrillated cellulose (MFC), also called nanofibrillated cellulose (NFC), is cellulose that has been

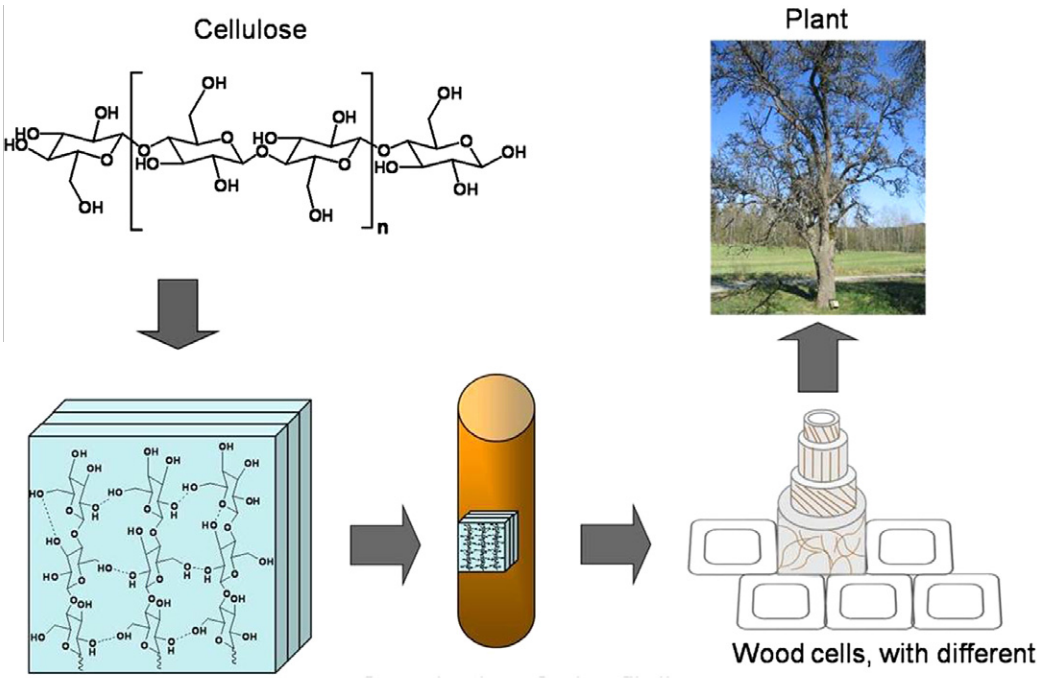

Fig. 1. The hierarchical structure of cellulose from wood. Reproduced from Ref. [5].