

Chapter 2

Chemical Functionalization of Cellulose Derived from Nonconventional Sources

V. K. Varshney and Sanjay Naithani

Abstract Chemical functionalization of cellulose aims to adjust the properties of macromolecule for different purposes, particularly, as a chemical feedstock for production of cellulose derivatives for a variety of applications. The conventional sources of cellulose include cotton linters and wood pulp which now-a-days are discouraged on account of the cost of the former and environment conservative regulations associated with the latter. Further, renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies. In this regard, cellulose-rich biomass derived from the nonconventional sources such as weeds, fibers, bamboos, and wastes from agriculture and forests, etc. acquires enormous significance, as alternative chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical functionalization. Etherification of cellulose through methylation, carboxymethylation, cyanoethylation, hydroxypropylation, single or mixed, is one of the most important routes of cellulose functionalization. Chemical composition and rheological characteristics make possible the selection of the modified cellulose to serve special applications. Prompted by above facts, possibility for chemical functionalization of cellulose rich biomass derived from bamboo, *Dendrocalamus strictus* (DCS), and noxious weeds – *Lantana camara* (LC) and *Parthenium hysterophorus* (PH) for their utilization was examined and results are reported. Proximate analysis of these materials was conducted and processes were standardized for production of α -cellulose on 1 kg batch scale. The percent yield, Av. DP, and the percentage of α -cellulose content of the obtained celluloses were found in the range of 35–40, 400–825, >90 (Brightness 80% ISO), respectively. Processes were optimized for production of water-soluble carboxymethyl cellulose (DCS, LC, and PH), cyanoethyl cellulose (DCS) and water-soluble hydroxypropyl cellulose (DCS and PH). The optimized products were characterized by IR spectra. Rheological studies of 1% and 2% aqueous solutions of the optimized carboxymethyl celluloses and hydroxypropyl celluloses showed their non-Newtonian

V.K. Varshney (✉)

Chemistry Division, Forest Research Institute, Dehra Dun 248 006, India

e-mail: varshney2000@yahoo.com

pseudoplastic behavior. Thus, abundantly available biomass from *Dendrocalamus strictus* bamboo and the weeds – *Lantana camara* and *Parthenium hysterophorus* seem to be a potential feedstock for production of α -cellulose and its subsequent functionalization into cellulose derivatives for variety of applications. This was also demonstrated that these noxious weeds could also be managed by their utilization into products of commercial importance.

Keywords Bamboo · Cellulose · Cellulose ethers · Chemical functionalization · Lantana · Parthenium

Contents

2.1	Introduction	45
2.1.1	Cellulose and Its Sources	45
2.1.2	Chemical Functionalization of Cellulose	46
2.1.3	Applications of Cellulose Derivatives	48
2.2	Status of Research on Chemical Functionalization of Cellulose Derived from Nonconventional Sources	49
2.3	Chemical Functionalization of Cellulose Derived from Nonconventional Biomass <i>Dendrocalamus strictus</i> (DCS) and Noxious Weeds <i>Lantana camara</i> (LC) and <i>Parthenium hysterophorus</i> (PH)	50
2.3.1	Proximate Analysis of Biomass	51
2.3.2	Isolation of α -Cellulose	52
2.3.3	Etherification of α -Cellulose	53
2.3.4	Characterization and Rheology of the Optimized Derivatives	56
2.4	Conclusion	57
	References	58

Abbreviations

AGU	Anhydroglucose unit
AN	Acrylonitrile
CEC	Cyanoethylcellulose
CMC	Carboxymethyl cellulose
CMHEC	Carboxymethylhydroxyethylcellulose
DCS	<i>Dendrocalamus strictus</i>
DP	Degree of Polymerization
DS	Degree of Substitution
HDP	Hypochlorite/Chlorine dioxide/Peroxide
HEC	Hydroxyethylcellulose
HP	Hydroxypropoxyl content
HPC	Hydroxypropyl cellulose
HPMC	Hydroxypropylmethylcellulose
IR	Infra Red

ISO	International organization for standardization
LC	Lantana camara
MC	Methylcellulose
MCA	Monochloroacetic acid
MS	Molar Substitution
PH	Parthenium hysterophorus
PO	Propylene oxide

2.1 Introduction

2.1.1 Cellulose and Its Sources

Cellulose, the most abundant renewable and biodegradable polymer, is the promising feedstock for the production of chemicals for their applications in various industries. Annual production of cellulose in nature is estimated to be 10^{11} – 10^{12} t in two forms, partially in a pure form, for example seed hairs of the cotton plant, but mostly as hemicelluloses in cell wall of woody plants (Klemm et al. 1998). The versatility of cellulose has been reevaluated as a useful structural and functional material. The environmental benefits of cellulose have become even more apparent (Hon 1996a). Cellulose is revered as a construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. The value of cellulose is also recognized as a versatile starting material for subsequent chemical transformation in production of artificial cellulose-based threads and films as well as of a variety of cellulose derivatives for their utilization in several industries such as food, printing, cosmetic, oil well drilling, textile, pharmaceutical, etc. and domestic life.

Cellulose can be derived from a variety of sources such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valonica ventricosa*), and bacteria (*Acetobacter xylinum*) (Nevell and Zeronian 1985). *A. xylinum* can synthesize extracellular pellicles of cellulose from glucose. Some simple marine animals such as tunicates deposit cellulose in their cell walls (Coffey et al. 1995). Besides cellulose, these materials also contain hemicelluloses, lignin, and a comparable small amount of lignin. Wood and cotton are the raw materials for commercial production of cellulose. Cellulose serves as a structural material within the complex architecture of the plant cell walls with variation in its content. In wood, it constitutes about 40–50%; in leaf fibers: sisal fibers (55–73%), in bast fibers: flax 70–75%, hemp 75–80%, jute 60–65%, ramie 70–75%, kenaf 47–57%, in canes: bamboo 40–55%, baggase 33–45%, and in cereal straw: barley 48%, oat 44–53%, rice 43–49%, rye 50–54%, wheat 49–54%. Cotton seed hairs, the purest source, contain 90–99% of cellulose (Hon 1996b; Han and Rowell 1996).

2.1.2 Chemical Functionalization of Cellulose

Among the polysaccharides, the structure of cellulose is unique and simple. However, this influences its chemical reactions significantly. Cellulose being rigid, highly crystalline, and insoluble in common organic solvents is an ideal structural engineering material (Hon 1996b; Mathur and Mathur 2001). Cellulose is a polydisperse, linear, syndiotactic polymer. Its basic monomeric unit is D-glucose (anhydroglucose unit, AGU), which links successively through a β -configuration between carbon 1 and carbon 4 of adjacent units to form a long chain 1,4 glucans (Mathur and Mathur 2001). Two glucose molecules react to form a cellobiose which is the basic chemical unit of a cellulose molecule. The pyranose rings are in the 4C_1 conformation, which means that the $-\text{CH}_2\text{OH}$ and $-\text{OH}$ groups as well as glycosidic bonds are all equatorial with respect to the mean planes of the rings. The hydroxyl groups at both ends of the cellulose chain show different behavior. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxyl group is nonreducing.

When the cellulose molecule is fully extended it takes the form of a flat ribbon with hydroxyl groups protruding laterally and capable of forming both inter- and intramolecular hydrogen bonds. Intramolecular hydrogen bonding between adjacent anhydroglucose rings enhances the linear integrity of the polymer chain and affects the reactivity of the hydroxyl groups, particularly of the C-3 hydroxyl group, which hydrogen binds strongly to the ring oxygens on adjacent anhydroglucose units. The surface of ribbons consists mainly of hydrogen atoms linked directly to carbon and is therefore hydrophobic. These two features of cellulose are responsible for its supramolecular structure, and this in turn determines many of its chemical and physical properties. In the fully extended molecule adjacent chain units are oriented with their mean planes at an angle of 180° to each other. Thus the repeating unit in cellulose is the AGU and the number of repeating units per molecule is half the Degree of Polymerization (DP) (Nevell and Zeronian 1985).

The size of cellulose molecule occurring in nature is indicated by its chain length or DP, which is average value of the number of monomer units. The DP of cellulose can be determined by various physical methods such as intrinsic viscosity measurements, light scattering, etc. DP of cellulose is heavily dependent on source. For example, cellulose obtained from cotton fibers, cotton linters, baggase, and wood fibers have DP 8,000–14,000; 1,000–6,500; 700–900; and 8,000–9,000, respectively. The DP or molecular weight distribution in many cases profoundly influences the mechanical, solution, biological, and physiological properties of cellulose and has given very useful clues for the designing of effective cellulose derivatives (Hon 1996b).

The abundance of hydroxyl groups and concomitant tendency to form intra- and intermolecular hydrogen bonds results in the formation of linear aggregates. In the solid state, highly ordered crystalline areas are interspersed between less ordered amorphous zones. These amorphous zones are regions in which the hydroxyl groups are more readily available for reaction than in the more highly ordered crystalline areas, which are less reactive (Coffey et al. 1995). The ratio of amorphous cellulose to crystalline cellulose is called degree of crystallinity which depends upon the species

and pretreatment of the sample (Fink et al. 1995). For instance, the degree of crystallinity of cellulose derived from bacteria, cotton, and *Valonia* algae is about 75%, 40–45%, and 93%, respectively (Kulshreshtha and Dweltz 1973; Yamamoto and Horii 1993; Osullivan 1997).

Degree of crystallinity plays an important role in chemical functionalization of cellulose. Cellulose contains 31.48% by weight of hydroxyl groups (one primary and two secondary per AGU), accessibility of these present enormous opportunities for preparing useful derivatives. Reactivity of these hydroxyl groups varies according to the reaction medium in which functionalization is done. For example, the order of reactivity for etherification performed in an alkaline medium is $2 > 6 > 3$ while the primary hydroxyl group (OH-6) is the most active in esterification (Hon 1996b). The type, distribution, and uniformity of substituents groups determine the properties of derivatives. (Nicholson and Meritt 1985). The average number of hydroxyl groups replaced by the substituents is the degree of substitution (DS); the maximum is three. For example, in a cellulose ether with a DS 1.5, 50% of the hydroxyl groups are etherified and 50% are free, to average 1.5 substituent moieties per anhydroglucose unit. When the side chain formation is possible, as for example in hydroxypropylation, molar substitution (MS) is used to denote the length of the side chain, and the value can exceed three. If the DS value is known for a substitution, the average chain length of the ether side chain can be calculated from the ratio of MS to DS (Hon 1996b).

In 1838, Payen recognized cellulose as a definitive substance and coined the name cellulose (Zugenmaier 2008). The functionalization of cellulose was utilized extensively, even when its polymeric nature was not determined and understood, as evidenced from the discovery of cellulose nitrate by Schonbein (1846), the preparation of Schweizer's reagent, that is, a cuprammonium hydroxide solution, the first cellulose solvent (Schweizer 1857) in 1857, the synthesis of an organosoluble cellulose acetate by Schutzenberger in 1865 (Cross and Bevan 1907), and artificial fibers in 1892 (Menachem 2006). The partially nitrated ester of cellulose is well known among the first polymeric materials used as a "plastic" under the trade name of celluloid. Cellulose nitrates of higher N-content have been used extensively for military purposes. Cellulose nitrate is the only inorganic cellulose ester of commercial interest (Balsler et al. 1986). Other derivatives such as methyl-, ethyl-, hydroxyalkyl ethers, mixed ethers/esters like ethylhydroxyethyl, hydroxypropyl methyl cellulose, cellulose acetopropionates, and acetobutyrate are still important, many decades after their discovery.

Chemical functionalization of cellulose include reactions of hydroxyl groups such as esterification, etherification, intermolecular crosslinking reactions, and macrocellulosic free radical reactions, particularly in the formation of graft cellulose copolymers (Arthur 1986) to increase the usefulness of cellulose by altering its properties. These cellulose derivatives are grouped according to the processes and substituents, for instance, esters- cellulose acetate through esterification and ethers- methyl cellulose/cyanoethyl cellulose/carboxymethyl cellulose (CMC) via etherification. Chemical functionalization continue to play a dominant role in improving the overall utilization of cellulosic polymers. The accessibility to hydroxyl groups and their reactivity open prospects for preparation of specific molecular structures for

future applications. Broader and more specialized applications of advanced and trend setting materials based on this unique and renewable macromolecule will increase the demand for more diverse synthesis paths and derivatives (Heinze and Liebert 2001).

The esters of cellulose with inorganic and organic acids were the first chemically modified cellulose derivatives (Klemm et al. 1998). Among the more than 100 cellulose esters developed, only a few of them including nitrates, acetates, and mixed esters of acetic acid and propionic acid, acetic acid and butyric acid, and acetic acid and phthalic acid have industrial applications (Hon 1996b). Cellulose acetate is extensively used in fibers, plastics, and coatings and thus becomes the universally recognized and the most important organic ester of cellulose.

2.1.3 Applications of Cellulose Derivatives

Cellulose derivatives, being of natural origin, have diverse physicochemical properties because of the kind of substituents, DS, molecular weights and DP and are revered for their large scale use mainly as additives of fine/special chemicals in textile, pharmaceutical, cosmetic, food, and packaging industries (Balsler et al. 1986; Barndt 1986). Cellulose derivatives of commercial importance belong to water or organic solvents such as soluble ethers or esters (Table 2.1). Nevertheless, cross linked and graft copolymers of cellulose are also of significant industrial importance.

Despite the large variety of cellulose derivatives that have been made, there is continuous expansion in the worldwide market of cellulose ethers because of their availability, economic efficiency, easy handling, low toxicity, and great variety of types. Combined effects of flow control, stabilization, water retention, film formation, etc. provided by cellulose ethers are not generally obtainable by the use of fully synthetic polymers. Cellulose ethers such as CMC, hydroxypropyl cellulose (HPC), cyanoethylcellulose (CEC), ethylcellulose (EC), methylcellulose (MC), hydroxyethylcellulose (HEC), hydroxypropylmethylcellulose (HPMC), carboxymethylhydroxyethylcellulose (CMHEC), etc. have gained their position in the market due to their multifunctional properties. The worldwide annual production of cellulose ethers is estimated to be over 300,000 metric ton (Schweizer and Sorg 1995). They exhibit useful properties of thickening, thermal gelation, surfactancy, film formation, and adhesion. Further they are kinetically and thermodynamically more stable and appear easy to prepare and characterize. These characteristics earn them applications in areas such as pharmacy, cosmetics, food, oil drilling, paper, paint, textiles, construction, and adhesives (Davidson 1980; Whistler and BeMiller 1973; Nicholson and Meritt 1985). Among cellulose derivatives, cellulose ethers constitute the only food allowed group of modified celluloses.

Crosslinking of cellulose, in heterogeneous systems, with formaldehyde or formaldehyde adducts of urea, melamine, or carbamates impart dimensional stability to cellulosic textile and paper products (Nicholson and Meritt 1985). A range of polymers, to obtain a better balance of properties for the commercial application of

Table 2.1 Some commercially marketed cellulose esters and ethers (Arthur Jr 1986)

Cellulose derivatives	DS range	Solubility	Product applications
Cellulose esters			
Nitrate	1.5–3.0	MeOH, PhNO ₂ , ethanol-ether	Films, fibers, explosives
Acetate	1.0–3.0	Acetone	Films, fibers, coatings, heat and rot resistant fabrics
Cellulose ethers			
Methyl	1.5–2.4	Hot H ₂ O	Food additives, films, cosmetics, greaseproof paper
Carboxymethyl	0.5–1.2	H ₂ O	Food additives, fibers, coatings, oil-well drilling muds, paper size, paints, detergents
Ethyl	2.3–2.6	Organic solvents	Plastics, lacquers
Hydroxyethyl	Low DS	H ₂ O	Films
Hydroxypropyl	1.5–2.0	H ₂ O	Paints
Hydroxypropylmethyl	1.5–2.0	H ₂ O	Paints
Cyanoethyl	2.0	Organic solvents	Products with high dielectric constants, fabrics with heat and rot resistances

polymeric materials, can be synthesized by graft copolymerization of cellulose. By minimizing degradation, copolymerization reactions of cellulose could result in retaining of the desirable properties of the natural molecule giving it additional properties through the added polymer. Cellulose graft copolymers find a wide array of applications in construction (wood plastic composites), furniture and industrial parts, sporting goods, woodcarving, textiles, and pulp and paper. They are also used as thickeners, absorbents, and in making ion exchange fibers and extrudable composites (Hebeish and Guthrei 1981).

2.2 Status of Research on Chemical Functionalization of Cellulose Derived from Nonconventional Sources

Renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies, escalating cost and problem of nonbiodegradability of petroleum-based polymers, and the recent environment-conservative regulations. The chemical industry is estimated to meet about 10% of its raw material needs from the renewable raw materials (Clasen and Kulicke 2001). Natural polymers are of renewable nature, hence, environment-friendly and cost-effective technologies can be developed by functionalization of these polymers. In this regard, cellulose rich biomass acquires enormous significance as chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical functionalization (Barkalow and Young 1985). The limitation of insolubility of cellulose in water can be overcome and spectrum of its industrial applications can be widened by functionalized to water-soluble forms. Various polymer analogous reactions could be used to modify the cellulose and its derivatives can be used as substitutes of petrochemicals in getting some important polymers including thermoplastics.

The conventional sources of cellulose are wood pulp and cotton linters. However, global efforts are going on to search for cellulose biomass from other sources as a feedstock as an alternative to expensive cotton linters, and wood pulp which now-a-days are discouraged due to environment conservative regulations. Annual plants are considered as potential resource because of their higher yield of cellulose than wood (McDougall et al. 1993; Atchison 1996; Han 1998), lower lignin contents, looser fibril structure than wood, consumption of less pulping chemicals and energy (McDougall et al. 1993; Han and Rowell 1996; Oggiano et al. 1997), have same main chemical components as woody plants, i.e., cellulose, hemicellulose, lignin, and extractives, ease of cultivation, harvesting and transportation (McDougall et al. 1993). Under the consideration of the economical objective, the environment influence, the sufficient supply, and the higher yield of cellulose, annual plants are now gradually substituting woods as alternative resources of cellulosic products. Investigations have shown that annual plants such as *Miscanthus sinensis*, *Cynara cardunculus*, flax, hemp, jute, sisal, and abaca could be used as new alternative sources for production of methyl cellulose (Daiyong 2005).

Agricultural wastes, for example, rice straw, sugarcane bagasse, saw dust, cotton stables (Hebeish, et al. 1984), orange mesocarp (Akaranta and Osugi 1997), and weeds, *Eichoria crassipes* (Barai et al. 1997), have been used as a base material for production of CMC differing in their DS and properties using different set of reaction conditions depending upon the DP and composition of the cellulosic material. Reactivity of fibers of *Agave lechuguilla* and *Agave fourcroydes* toward chemical functionalization such as carboxymethylation, sulfation, acetylation, tritylation, and subsequent carboxymethylation as well as oxidation and grafting has been studied, which has demonstrated the suitability of the agave fibers as a potential feedstock for producing cellulose derivatives for a variety of applications (Vieira et al. 2002; Ramos et al. 2005; Cruz et al. 1999). Graft copolymerization of acrylonitrile and methyl methacrylate onto jute fibers and pineapple leaf fibers has been examined (Patra and Singh 1994; Patnaik et al. 1989; Ghosh and Ganguly 1994; Samal and Bhuyan 1994). Low-quality woods as well as industrial wastes of wood have been utilized to produce a thermoplastic material through cyanoethylation (Khalil and El-Wakil 2000). The goal of these functionalizations is to increase the utilization of this abundantly available cellulose biomass from nonconventional sources.

2.3 Chemical Functionalization of Cellulose Derived from Nonconventional Biomass *Dendrocalamus strictus* (DCS) and Noxious Weeds *Lantana camara* (LC) and *Parthenium hysterophorus* (PH)

Identification of biopolymers from different plant sources, their isolation, and subsequent chemical functionalization for varied applications has been one of the research programs of the Chemistry Division, Forest Research Institute, Dehra Dun

(Sharma 2003; Gupta 2005; Bhatt 2004; Bansal 2005; Rana 2006; Sharma 2007; Pandey 2008; Goyal 2008). A technology for production of α -cellulose of high DP (800–3,000), high purity (>95%), and high brightness (>80%) derived from cotton linters, bamboo, eucalyptus, and bagasse was developed.

L. camara L. (Verbenaceae) and *P. hysterophorus* L., (Helianthae: Asteraceae) are noxious weeds, which have imposed a great threat to land productivity, grazing livestock, human health, biodiversity, and consequently to the overall ecology (Sharma et al. 1988; Pass 1991; Evans 1997). Attempts to manage these weeds using mechanical, chemical, and biological means have been made but met with limited success on account of their inbuilt limitations such as high cost, impracticability, environmental safety, temporary relief, etc (Sharma 2004; Jayanth 1987; Jayakumar et al. 1989). Alternatively, luxuriant growth and vigorous survival make these weeds of potential economic value for utilization of their abundantly available biomass into value added products offering thereby an efficient and effective method for their management. During the last few years, research has been conducted to utilize the lantana biomass for development of furniture products, baskets, mulch, compost, drugs, and other biologically active agents (Sharma and Sharma 1989; Inada et al. 1997; Sharma 2004).

Bamboo, belonging to the grass family Poaceae, is an abundant renewable natural resource capable of producing maximum biomass per unit area and time as compared to counterpart timber species (Tewari 1995). The chemical composition of *D. strictus* has been studied, which was found to contain Cross and Bevan cellulose 68.0% and lignin 32.20% (Singh et al. 1991). Its hemicellulose (18.8%) has also been shown to consist of xylose 78.0%, arabinose 9.4%, and uronic acid 12.8% (Tewari 1995).

Driven by the challenges to explore and increase the usefulness of cellulosic biomass from nonconventional sources, possibility for chemical functionalization of cellulose rich biomass derived from bamboo, *D. strictus* (DS) and noxious weeds – *L. camara* (LC) and *P. hysterophorus* (PH) for their utilization was examined.

2.3.1 Proximate Analysis of Biomass

L. camara and *P. hysterophorus* used in the study were collected from the field of the institute's campus. All the chemicals used were of laboratory grade. Plant materials were reduced to chips of 1–2 in. size and air dried. Chips were reduced to dust, and the dust passing through 40 mesh and retained on 60 mesh were taken for studies. Proximate chemical composition of the plant material was studied using the standard methods to assess the quality and solubility of raw material for further processing and results of the analysis are presented in Table 2.2.

Table 2.2 Proximate chemical composition of *Lantana camara* (LC) and *Parthenium hysterophorus* (PH)

Sl. No.	Parameters	Value%		Method used
		LC	PH	
1	Hot water solubility	7.0	11.25	APPITA P 4 M-61
2	1% NaOH solubility	18.0	22.5	APPITA P 5 M-61
3	Alcohol–benzene solubility	4.45	5.89	APPITA P 7 M-70
4	Holocellulose	71.34	78.0	TAPPI 9 m-54
5	α -cellulose	64.91	65.0	TAPPI T-203 OM 88
6	Pentosans	13.0	15.86	TAPPI T-203 OM 84
7	Lignin	27.25	17.2	TAPPI T-222 OM 88
8	Ash	1.8	2.1	APPITA P3 M-69

2.3.2 Isolation of α -Cellulose

The air-dried chips were subjected to following treatments. The conditions at each stage were optimized and 1 Kg production of α -cellulose [yield 35% (DCS), 38.76% (LC), and 37.4% (PH) and Brightness 80% (DS), 81.0% (LC), and 80.0% (PH) ISO] was carried out under optimized conditions.

2.3.2.1 Water Prehydrolysis

The chips were prehydrolyzed in autoclave keeping bath ratio 1:4 at 100°C for 30.0 min (DCS and LC)/1:5 at 100°C for 30.0 min (PH). The yield after prehydrolysis was 96.5%, 95.5%, 92.2%, respectively.

2.3.2.2 Alkali Hydrolysis

Water prehydrolyzed chips were treated with 2% alkali as NaOH. The bath ratio was maintained 1:4 (DCS)/1:4 (LC)/1:5 (PH) and heated in autoclave to 130°C (DCS)/120°C (LC)/130°C (PH) for 60 min. The yield was 94.4%, 85.9%, and 87.4%, respectively.

2.3.2.3 Pulping

The pulping of alkali hydrolyzed chips was carried out with 20% (DCS)/20% (LC)/18% (PH) alkali as NaOH at 170°C for 120 min (DCS)/90.0 min (LC)/60 min (PH). The kappa number of the pulp was 24, 26, 23 and pulp yield was 45.8%, 48%, and 45.6% with 3.2–3.8%, 1.2% screen rejects, respectively.

2.3.2.4 Bleaching

Bleaching was carried out using HDP sequence.

Table 2.3 Characteristics of the cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Characteristics of cellulose	Value (%)			Method used
	DCS	LC	PH	
α -cellulose	90.09	94.80	90.82	TAPPI T2003 OM-88
β -cellulose	3.9	2.5	3.2	
γ -cellulose (by difference)	5.0	1.42	1.2	
Lignin	0.44	0.80	4.0	TAPPI T-222
Ash	0.56	0.48	0.98	APPITA P3 M-69
Av. DP	816	430	661.5	SCAN 15

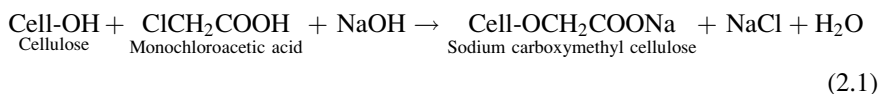
Cellulose obtained as above was characterized for its DP and composition and are presented in Table 2.3 DP was determined by CED viscosity method using following formula:

$$DP^{0.905} = 0.75 (\eta), \text{ where } \eta \text{ is intrinsic viscosity.}$$

2.3.3 Etherification of α -Cellulose

2.3.3.1 Carboxymethylation

A typical carboxymethylation method involving given below two competitive reactions was followed.



Carboxymethylation was conducted in two steps alkalization and etherification under heterogeneous conditions and the process was optimized with respect to DS by varying the reaction parameters such as concentration of NaOH, monochloroacetic acid (MCA), temperature, and duration of reaction. Each of these parameters was varied one by one keeping the remaining parameters constant as shown in Table 2.4. The alkalization consisted of addition of varied amount of aqueous NaOH to vigorously stirred slurry of α -cellulose (3 g) in iso-propanol (80 ml)/12.5% aq. iso-propanol (in case of PH) over a period of 30 min. Stirring was continued for another 60 min. Then varied amount of monochloro acetic acid dissolved in 10 ml iso-propanol was added under continuous stirring and the reaction mixture was heated upto the desired temperature and stirred at that temperature for fixed duration. After neutralizing the excess alkali with acetic acid, the CMC samples were filtered, washed with 70% aq. methanol, followed by absolute methanol, and dried at 60°C in oven. Yield: 110–124% (DCS), 110–133% (LC), and 140–150% (PH). Using the optimized set of reaction conditions as presented in Table 2.5,

Table 2.4 Reaction parameters for carboxymethylation of α -cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	LC	PH
Aq. NaOH concentration, temp. (°C)	2.5–12.5M 28	3.24 (mol/AGU); 10–40%; 25	3.89 (mol/AGU); 18–70% 25
MCA (mol/AGU)	1.80–2.55	1.55–2.30	0.98–2.48
Temperature of carboxymethylation (°C)	35–65	35–65	45–65
Duration of carboxymethylation (h)	1.5–5.5	1.5–4.5	3–6

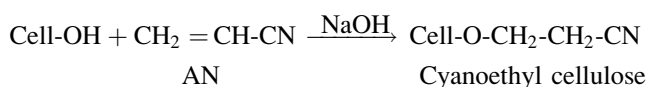
Table 2.5 Optimized reaction parameters for preparing CMC from α -cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	LC	PH
Aq. NaOH concentration, temp. (°C)	10M	3.24 (mol/AGU); 20%	3.89 (mol/AGU); 60%
MCA (mol/AGU)	1.80	2.05	1.98
Temperature of carboxymethylation (°C)	4.5	3.5	5.0
Duration of carboxymethylation (h)	55	55	55

water-soluble Na-CMC of degree of substitution 0.98 (DCS), 1.22 (LC), and 1.33 (PH) could be prepared (Varshney et al. 2005; Khullar et al. 2007).

2.3.3.2 Cyanoethylation

A typical cellulose etherification involving Michael addition of an activated C=C bond of acrylonitrile (AN) to a partially anionized cellulosic hydroxyls in an aqueous alkaline medium represented below was employed.

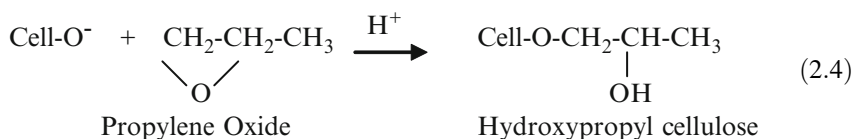
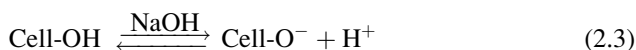


Cellulose (2 g) obtained from bamboo was cyanoethylated by first converting it into alkali cellulose using 20 ml of aqueous sodium hydroxide solution (8–14% by weight) for 1 h at temperature varying between 20 and 40°C followed by squeezing alkali from alkali cellulose up to three times the weight of the cellulosic material. The alkali cellulose was then dispersed in a large excess of acrylonitrile (70–90 mol/AGU) and reacted at a certain temperature for a fixed duration varying from 45 to 60°C and 0.5 to 1.25 h, respectively. During this reaction, the cyanoethylcellulose is dissolved in an excess of acrylonitrile to yield a homogenous solution. Each of these parameters was altered one by one keeping the remaining parameters constant in the reaction in order to optimize the reaction conditions for the production of CEC of maximum degree of substitution. The reaction was stopped by adding an excess of 10% aqueous acetic acid and was subsequently precipitated from this still

homogenous reaction mass by an excess of ethanol/water mixture (1:1, v/v), filtered, washed first with hot and then with cold water followed by drying in vacuum at 60°C (Yield: 124–145%). Using the optimized set of conditions, viz aqueous NaOH concentration 12%, alkalization temperature 20°C, acrylonitrile concentration 90 mol/AGU, cyanoethylation time 0.75 h, and temperature 55°C, an organosoluble CEC of DS 2.2 could be prepared (Khullar et al. 2008).

2.3.3.3 Hydroxypropylation

A typical hydroxypropylation reaction shown below was used.



The reaction was carried out in two steps – alkalization and etherification of cellulose under heterogeneous conditions and the process was optimized with respect to percent hydroxypropoxyl content (% HP) by varying the process parameters such as concentration of NaOH and propylene oxide (PO), temperature, and duration of reaction and studying their effect on the hydroxypropoxyl content. Each of these parameters was varied one by one keeping the remaining parameters constant in the reaction as shown in Table 2.6. The alkalization was carried out by adding varying amount of aqueous NaOH to slurry of finely pulverized cellulose (1.0 g) in iso-propanol (10 ml) at ambient temperature, with continuous stirring for 1 h (DS), while in case of PH for 0.5 h. Alkali cellulose thus formed was pressed to remove alkali and transferred to a three-necked round-bottom flask of capacity 250 ml, fitted with a coiled condenser and nitrogen inlet. Ice-cold water was circulated in the condenser throughout the reaction. Varied amount of propylene oxide (PO) in iso-propanol (50 ml) and water (2 ml) were added and the reaction was allowed to proceed at desired temperature for fixed duration. After neutralizing the excess alkali with acetic acid, the synthesized HPC samples were dissolved in water and precipitated in acetone, filtered and washed in acetone, and dried at 60°C in oven [Yield: 110–130% (DCS), 105–144% (PH)]. The standardized reaction

Table 2.6 Reaction parameters for hydroxypropylation of α -cellulose isolated from *Dendrocalamus strictus* (DCS) and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	PH
Aq. NaOH concentration (w/v%)	14–26	18 (0.5–2.0 mol/AGU)
Propylene oxide (mol/AGU)	11.6–29	11.6–38.9
Temperature of hydroxypropylation (°C)	30–60	60–80
Duration of hydroxypropylation (h)	2–5	2–4

Table 2.7 Optimized reaction parameters for hydroxypropylation of α -cellulose isolated from *Dendrocalamus strictus* (DCS) and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	PH
Aq. NaOH concentration (w/v%)	22	1.0 mol/AGU; 18%
Propylene oxide (mol/AGU)	17.4	34.77
Temperature of hydroxypropylation ($^{\circ}$ C)	50	70
Duration of hydroxypropylation (h)	4	3

conditions as shown in Table 2.7 afforded to produce water-soluble HPCs [soluble content 82%, 80.5% and hydroxypropoxyl content 65.89%, 67.75% (DCS and PH, respectively)] (Sharma et al. 2008).

2.3.4 Characterization and Rheology of the Optimized Derivatives

The IR spectra of all the optimized CMCs, CEC, and HPCs were recorded in KBr pellets. Typical absorptions of the cellulose backbone as well as bands at $1605\text{--}35\text{ cm}^{-1}$ [ν_{as} (COO $^{-}$); $1420\text{--}21\text{ cm}^{-1}$ ν_{s} (COO $^{-}$)] characterized for carboxymethyl ether group were observed in all the CMCs. Besides the typical signals of cellulose backbone (ν_{OH} $3,443\text{ cm}^{-1}$, ν_{CH} $2,862\text{ cm}^{-1}$, $1,415\text{ cm}^{-1}$, ν_{COC} $1,057\text{ cm}^{-1}$, ν_{β} -linkage 890 cm^{-1}), the IR spectra of the optimized CEC displayed a characteristic absorption band at $2,253\text{ cm}^{-1}$ for the nitrile group ($\text{--C}\equiv\text{N}$) introduced and the intensity of the band at $2,891\text{ cm}^{-1}$ characteristic for --CH_2 group is increased, furnishing thereby the evidence that cyanoethylation has occurred. The IR spectra of the optimized HPC displayed, besides the typical signals of cellulose backbone (ν_{OH} $3,398\text{ cm}^{-1}$, ν_{CH} $2,890\text{ cm}^{-1}$ and $1,419\text{ cm}^{-1}$, ν_{COC} $1,060\text{ cm}^{-1}$, ν_{β} -linkage 890 cm^{-1}), a shoulder at $2,974\text{ cm}^{-1}$, which was assigned to the --CH stretching of the methyl group characteristic for the hydroxypropyl group, furnishing thereby the evidence that hydroxypropylation has occurred. Further evidence of hydroxypropylation was revealed by comparing the Scanning Electron Microscope images for parent and the HPC obtained at magnification 1,000 and 5,000 (Sharma et al. 2008), which depicted the transformation in surface morphology of bamboo cellulose on hydroxypropylation. The parent bamboo cellulose exhibited a relatively smooth surface compared with HPC and deposition of PO on the surface and in the intercellular region of the bamboo cellulose fiber was clearly visible.

The DS of the CMC (LC and PH) samples determined by the standard method (Green 1963) was found to be 1.22 and 1.33, respectively, while in case of CMC derived from bamboo cellulose (DCS), this was calculated from its mole fractions after complete depolymerization of polymer chains by HPLC (Heinze et al. 1994) as 0.98. The DS of the optimized CEC sample was calculated from the N content using the equation $\text{DS} = 162 \times \%N/1,400 - (53 \times \%N)$ was 2.2. Nitrogen content was determined by the Kjeldahl's method. The percent hydroxypropoxyl content in HPCs determined by UV spectrophotometric method (Jhonson 1969) were found to be 65.89% (DCS) and 67.75% (PH).

One of the most important properties of CMC and HPC utilized in their wide range of practical applications is their ability to impart viscosity to the aqueous solutions. Each polymer chain in a dilute solution of CMC is hydrated and extended, and exhibits a stable viscosity. In aqueous solution, it represents a complex rheological system as it forms aggregates and associations, and hence higher-level structures (Kulicke et al. 1999). The viscosity is greatly influenced by polymer concentration, temperature, salt content, molecular structure, and the presence of surfactants (Edali et al. 2001; Kulicke et al. 1996; Ghannam and Esmail 1997). Consideration of the end uses for CMC and HPC make it immediately apparent that the rheological properties of the solutions of these cellulose derivatives are of prime importance. Rheological studies of the optimized CMCs and HPCs were, therefore, carried out by measuring apparent viscosity (η_{app}) of its 1% and 2% aqueous solutions using a Brookfield Digital Viscometer model “RVTD,” Stoughton, USA at different shear rates ranging from 3.4 to 34 s^{-1} at $25 \pm 10^\circ C$. The values of η_{app} (cps) of the solutions of the optimized products at both the concentrations [CMCs 75, 795 (DCS), 600, 7,500 (LC), 260, 2,255 (PH); HPCs 120–1,105 (DCS), 75, 745 (PH)] were observed to be dependent upon shear rate and decrease with increasing shear rate. No time effects were detected and the viscosity obtained with decreasing rate was identical with that obtained with increasing shear rate. Thus, the solutions of the optimized products exhibited non-Newtonian pseudoplastic behavior.

2.4 Conclusion

Continuously depleting limited fossil supplies, rising price, problem of nonbiodegradability of petroleum-based polymers, and the recent environment-conservative regulations have triggered search for nonconventional sources of cellulose biomass as feedstock for production of cellulose and its derivatives. Having initiated efforts in this direction, isolation and characterization of cellulose and its chemical functionalization to ethers from some nonconventional biomass were studied. The study contributed to find appropriate conditions for production of α -cellulose from bamboo, *D. strictus*, and two noxious weeds – *L. camara* and *P. hysterophorus* and its carboxymethylated, cyanoethylated, and hydroxypropylated derivatives. The present work demonstrated that these plants have the capacities to produce α -cellulose and its ethers for varied applications. The industry can utilize these biomass as an alternative feedstock to produce cellulose ethers. Therefore, a lot of wood will be saved. The work has also paved the way for management of these noxious weeds through their utilization into products of commercial importance.

Acknowledgments We duly thank the Director, Forest Research Institute, Dehra Dun, for encouragement and providing necessary facilities to carry out study. Financial support from the Indian Council of Forestry Research and Education (ICFRE), Dehra Dun, Department of Biotechnology (DBT), New Delhi, and World Bank under the KANDI IWDP (Hills II) scheme is gratefully acknowledged.

References

- Akaranta O, Osugi LC (1997) Carboxymethylation of orange mesocarp cellulose and its utilization in drilling mud formulation. *Cellulose Chem Technol* 31:195–198
- Arthur JC Jr (1986) In: Allen G, Bevington JC (eds) *Comprehensive polymer science*, Vol 6. Pergamon, Oxford
- Atchison JE (1996) Twenty-five years of global progress in nonwood plant fiber repulping. *TAPPI J* 79(10):87–95
- Balser K, Hoppe L, Eicher T, Wandel M, Astheimer HJ, Steinmeier H, Allen JM (1986) Cellulose esters. In: Gerhartz W, Stephen YY, Thomas CF, Pfefferkorn R, James F (eds) *Ullmann's encyclopedia of industrial chemistry*. Wiley, New York
- Bansal A (2005) Structural investigation of *Cassia tora* Linn. seed polysaccharides. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Barai BK, Singhal RS, Kulkarni PR (1997) Optimization of a process for preparing carboxymethyl cellulose from water hyacinth (*Eichornia crassipes*). *Carbohydr Polym* 32:229–231
- Barkalow DG, Young RA (1985) Cellulose derivatives derived from pulp and paper mill sludge. *J Wood Chem Technol* 5:293–312
- Barndt L (1986) Cellulose ethers. In: Gerhartz W, Stephen YY, Thomas CF, Pfefferkorn R, James F (eds) *Ullmann's encyclopedia of industrial chemistry*. Wiley, New York
- Bhatt A (2004) Chemical investigation of *Kydia calysina* Rox. bark. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Clasen C, Kulicke W-M (2001) Determination of viscoelastic and rheo-optical material functions of water soluble cellulose derivatives. *Prog Polym Sci* 26:1839–1919
- Coffey DG, Bell DA, Henderson A (1995) *Food polysaccharides and their application*. Marcel Dekker, New York
- Cross CF, Bevan EJ (1907) *Researches on cellulose*. Longman Green, London
- Cruz RA, Mendoza AM, Vieira MC, Heinze Th (1999) Studies on grafting of cellulosic materials isolated from *Agave lechuguilla* and *A. fourcroydes*. *Angew Makromol Chem* 273:86–90
- Daiyong Ye (2005) Preparation of methylcellulose from annual plants. Ph.D. Dissertation Graduate School of Rovira i Virgili University
- Davidson RL (1980) *Handbook of water soluble gums and resins*. McGraw-Hill, New York
- Edali M, Esmail MN, Vatistas GH (2001) Rheological properties of high concentrations of carboxymethyl cellulose solutions. *J Appl Polym Sci* 79:1787–1801
- Evans HC (1997) The potential of fungal pathogen as classical biological control agents for management of *Parthenium hysterophorus* L. In: Mahadevappa M and Patil VC (eds) *First international conference on Parthenium management*. Dharwad University of Agricultural Sciences, Dharwad, Karnataka, India
- Fink HP, Hofmann D, Philipp B (1995) Some aspects of lateral chain order in cellulose from X-ray scattering. *Cellulose* 2:51–70
- Ghannam MT, Esmail MN (1997) Rheological properties of carboxymethyl cellulose. *J Appl Polym Sci* 64:289–301
- Ghosh P, Ganguly PK (1994) Polyacrylonitrile (PAN)-grafted jute fibers: some physical and chemical properties and morphology. *J Appl Polym Sci* 52:77–84
- Goyal P (2008) Chemical modification of tamarind kernel powder. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Green JW (1963) Carboxymethyl cellulose. In: Whistler RL (ed) *Methods in carbohydrate chemistry*, vol III. Academic, New York
- Gupta S (2005) Chemical modification of *Cassia occidentalis*. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Han JS (1998) Properties of nonwood fibers. In: 1998 Proceedings of the Korean society of wood science and technology annual meeting 3–12
- Han JS, Rowell JS (1996) Chemical composition of fibers. In: Rowell RM, Young RA, Rowell J (eds) *Paper and composites from agrobased resources*. CRC, London

- Hebeish A, Guthrei JT (1981) The chemistry and technology of cellulosic copolymers. Springer, Berlin
- Hebeish A, Abou-Zied NY, Waly A, Higazy A (1984) Chemical modification of flax cellulose via etherification, esterification, and crosslinking reactions. *Cellulose Chem Technol* 22:591–605
- Heinze T, Liebert T (2001) Unconventional methods in cellulose fictionalization. *Prog Polym Sci* 26:1689–1762
- Heinze Th, Erler U, Nehls I, Klemm D (1994) Determination of the substitution pattern of heterogeneously and homogeneously synthesized carboxymethyl cellulose by using high-performance liquid chromatography. *Angew Makromol Chem* 215:93–106
- Hon DNS (1996a) Cellulose and its derivatives. In: Dumitriu S (ed) *Polysaccharides in medicinal applications*. Marcel Dekker, New York
- Hon DNS (1996b) Chemical modification of lignocellulosic material. Marcel Dekker, New York
- Inada A, Nakanishi T, Tokuda H, Sharma OP (1997) Antitumor activities of lantadenes on mouse skin tumors and mouse hepatic tumors. *Planta Med* 63:476–478
- Jayakumar R, Mahadevappa M, Joshi S, Prasad TG (1989) Dormancy studies in *Cassia sericea* seeds. *Seed Res* 17(2):118–121
- Jayanth KP (1987) Introduction and establishment of *Zygomma bicolorata* on *P. hysterophorus* at Bangalore, India. *Curr Sci* 56(7):310–311
- Jhonson DP (1969) Spectrophotometric determination of the hydroxypropyl group in starch ethers. *Anal Chem* 41:859–860
- Khalil EMA, El-Wakil NA (2000) Infrared absorption spectra of cyanoethylated cellulose fibers. *Cellulose Chem Technol* 34:473–479
- Khullar R, Varshney VK, Naithani S, Heinze T, Vieira-Nagel GPK, Naithani S, Soni PL (2007) Carboxymethylation of cellulose isolated from bamboo (*Dendrocalamus Strictus*) and its rheology. *Cellulose Chem Technol* 40(7):545–552
- Khullar R, Varshney VK, Naithani S, Soni PL (2008) Study of the influence of reaction conditions for production of cyanoethylcellulose from cellulosic material from bamboo (*Dendrocalamus strictus*). *J Nat Fibers* 5(2):138–147
- Klemm D, Phillip B, Heinze T, Heinze U, Wagenknecht W (1998) *Comprehensive cellulose chemistry*, vol 2. Wiley, Weinheim
- Kulicke WM, Kull AH, Thielking H, Engelhart J, Pannek JB (1996) Characterization of aqueous carboxymethylcellulose solutions in terms of their molecular structure and its influence on rheological behavior. *Polymer* 37(13):2723–2731
- Kulicke WM, Reinhardt Fuller UGG, Arendt O (1999) Characterization of the flow properties of sodium carboxymethylcellulose via mechanical and optical techniques. *Rheol Acta* 38:26–33
- Kulshreshtha AK, Dweltz NE (1973) Para crystalline lattice disorder in cellulose – 1. Reappraisal of the application of the two-phase hypothesis to the analysis of powder x-ray diffractograms of native and hydrolyzed cellulosic materials. *J Polym Sci* 11:487–497
- Mathur NK, Mathur V (2001) *Chemical Weekly*, July Edition, 155
- McDougall GJ, Morrison IM, Stewart D, Weyers JDB, Hillman JR (1993) Plant fibres: botany, chemistry and processing. *J Sci Food Agric* 62:1–20
- Menachem L (2006) *Handbook of fiber chemistry*. CRC, USA
- Nevell TP, Zeronian SH (1985) *Cellulose chemistry and its applications*. Ellis Horwood, Chichester York
- Nicholson MD, Meritt FM (1985) Cellulose ethers. In: Nevell TP, Zeronian SH (eds) *Cellulose chemistry and its applications*. Ellis Horwood, Chichester
- Oggiano N, Angelini LG, Cappelletto P (1997) Pulping and paper properties of some fibre crops. *Ind Crops Prod* 7(1):59–67
- Osullivan AC (1997) Cellulose: the structure slowly unravels. *Cellulose* 4:173–207
- Pandey N (2008) Chemical modification of alpha cellulose from *Lantana camara*. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Pass MA (1991) Poisoning of livestock by Lantana plants. In: Keeler R, Tu AT (eds) *Handbook of natural toxins*, vol 6. Marcel Dekker, New York

- Patnaik S, Sarangi S, Mohanty AK, Singh BC (1989) Graft copolymerization of acrylonitrile onto jute fibers (Studies on Ce (IV)- hippuric acid redox system). *J Appl Polym Sci* 37: 2099–2107
- Patra CM, Singh BC (1994) Influence of N-acetylglycine on the kinetics of ceric ion-initiated graft-copolymerization of acrylonitrile and methyl-methacrylate onto jute fibers. *J Appl Polym Sci* 52:1557–1568
- Ramos LA, Frollini E, Heinze Th (2005) Carboxymethylation of cellulose in the new solvent dimethyl sulphoxide/tetrabutyl ammonium fluoride. *Carbohydr Polym* 60:259–267
- Rana V (2006) Chemical investigation of *Dalbergia sissoo* Rox. laef polysaccharides. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Samal RK, Bhuyan BL (1994) Chemical modification of lignocellulosic fibers. 1. Functionality changes and graft polymerization of acrylonitrile onto pineapple leaf fibers – their characterization and behavior. *J Appl Polym Sci* 52:1675–1685
- Schweizer E (1857) Das Kupferoxyd-Ammoniak, ein Auflösungsmittel für die Pflanzenfaser. *J Prakt Chem* 72(1):109–111
- Schweizer D, Sorg C (1995) Cellulose ethers for cement extrusion. In: Kennedy JF, Phillips GO, Williams PA, Picullel L (eds) *Cellulose and cellulose derivatives: physico-chemical aspects and industrial applications*. Woodhead, England
- Sharma BR (2003) Chemical modification of polysaccharides for industrial applications. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Sharma S (2004) Lantana-whose weed any way! Developing strategic directions for integrated utilization and control. In: Workshop on *Lantana camara*: Problems and Prospects (Volume of abstracts), organized by IIT, Delhi, HESCO, Dehra Dun and Department of Science & Technology (DST), Govt. of India at Dehra Dun from 10–11 Feb 2004
- Sharma R (2007) Studies on chemical modification of cellulose of different DP and their rheology. Ph. D. thesis, Forest Research Institute, Deemed University, Dehradun, India
- Sharma OP, Sharma PD (1989) Natural products of lantana plant – the present and prospects. *J Sci Ind Res* 48:471–478
- Sharma OP, Makkar HPS, Dawra RK (1988) A review of the poisonous plants *Lantana camara*. *Toxicon* 26:975–985
- Sharma R, Varshney VK, Naithani S, Chauhan GS, Soni PL (2008) Hydroxypropylation of cellulose (Av. DP 816) isolated from bamboo (*Dendrocalamus strictus*) with respect to hydroxypropoxyl content and rheological behavior of hydroxypropyl cellulose. *J Appl Polym Sci* 113(4):2450–2455
- Singh SV, Rai AK, Dhawan R (1991) *Advances in pulp and paper research in India*. ICFRE Publication 15, Dehra Dun
- Tewari DN (1995) A monograph on bamboo. International Book Distributors, Dehra Dun
- Varshney VK, Gupta PK, Naithani S, Khullar R, Bhatt A, Soni PL (2005) Carboxymethylation of α -cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behavior. *Carbohydr Polym* 63(1):40–45
- Vieira MC, Heinze Th, Antonio-Cruz R, Mendoza-Martinez AM (2002) Cellulose derivatives from cellulosic material isolated from *Agave lechuilla* and *A. fourcroydes*. *Cellulose* 9:203–212
- Whistler RL, BeMiller NJ (1973) *Industrial gum, polysaccharides and their derivatives*. Academic, New York
- Yamamoto H, Horii F (1993) CPMAS carbon-13 NMR analysis of the crystal transformation induced for Valonia cellulose by annealing at high temperatures. *Macromolecules* 26:1313–1317
- Zugenmaier P (2008) *Crystalline cellulose and derivatives: characterization and structures*. Springer, Berlin