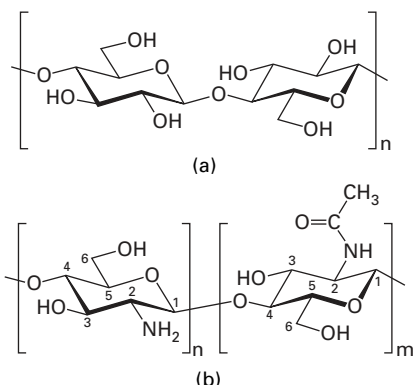# Conversion of cellulose, chitin and chitosan to filaments with simple salt solutions

H S W H A N G, N A M I N U D D I N, Fiber and Polymer
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12.1 Introduction

The biomaterials available in the largest quantities on the Earth are cellulose and chitin, being easily isolated and processed into many articles and chemical forms. The manufacture of wood pulp is a worldwide business and the conversion of shellfish waste into chemical chitin is now an established industry. These materials are closely related polysaccharides and are found in nature as structural materials; cellulose is found in the cell walls of plants; and chitin is found in the shells of marine crustaceans. These structures are indicated in Fig. 12.1.

12.1 The structural comparison of chitin and chitosan to cellulose. The structure of cellulose is shown in (a). In (b), when m > n, the structure is not soluble in aqueous acid and is called chitin. When n > m, and the copolymer is soluble in aqueous acid, then it is called chitosan.

The conversion of cellulosic wood pulp into a textile fiber dates to the earliest periods of synthetic fiber manufacture; viscose rayon and lyocell processes are well known. However, it is still conceivable to improve upon

the environmental impact of these existing methods by the development of new solvent systems which are less toxic and more easily recycled. In the case of chitin, and its deacetylated form, chitosan, much more work is needed to find a truly suitable method for the manufacture of filaments from nontoxic systems and that have adequate mechanical properties.

In this chapter we describe the use of simple ionic liquids based on ammonium salts with ammonia or other amino compounds, to dissolve cellulose and extrude filament. In the second section, the conversion of chitin and chitosan to filaments with other salt solutions is described. Both of these methods involve the direct dissolution of the polymer without derivatization. The solvent components include simple inorganic salts which can either be recovered and recycled back into the spinning process or used as fertilizer.

12.2   Cellulose in liquid ammonia/ammonium thiocyanate solutions

Cellulose is a natural, high molecular weight polymer. As well as being renewable and biodegradable, it is the most abundant naturally occurring organic polymer. Its β-(1 → 4)-glucopyranose structure favors close packing of the chains to form fibrous crystals. Due to its complex crystalline and amorphous morphology, considerable hydrogen bonding, and very high molecular weight, cellulose does not melt nor does it dissolve readily in many solvents. For this reason, cellulose has not been exploited to its fullest potential. Hence, any process which affects, simplifies or hastens the dissolution of cellulose represents a significant step forward in the development of cellulose as a viable, ecologically favorable polymer source. Furthermore, the ability of cellulose and its derivatives to form liquid crystalline solutions in certain solvents has resulted in many attempts to develop high-performance cellulosic fibers.

The terms 'liquid crystal' and 'mesophase' are interchangeable. *Meso*, in Greek, means 'between', so a fluid can be called a mesophase if it has some properties that are characteristic of crystals. The ability of the fluid to form a liquid crystal is due to the molecules' ability to align with each other and create local ordering. So, liquid crystalline polymers are those polymers that form liquid crystalline phases either in solution or in the melt. Molecules that form a mesophase are usually rod-like or disc-like. In the case of rod-like polymers, such as poly(*p*-phenyleneterephthalamide) (PPTA), the rigidity of the backbone is primarily responsible for the formation of a mesophase. The rigidity is, of course, dependent on a variety of factors such as the nature of the solvent used, the temperature of the solution, and the chemical structure of the molecule.

Presently there are only a few solvents that can directly dissolve cellulose without involving a chemical derivative of cellulose: *N*-methyl morpholine-

N-oxide/water (NMMO/H_2O); lithium chloride/dimethyl acetamide (LiCl/DMAc); trifluoroacetic acid/methylene chloride (TFA/CH_2Cl_2); calcium thiocyanate/water (Ca(SCN)$_2$/H_2O); ammonia/ammonium thiocyanate (NH$_3$/NH$_4$SCN); zinc chloride/water (ZnCl$_2$/H_2O); and sodium hydroxide/water (NaOH/H_2O). Two newly reported solvents are also of interest: one based on an ionic liquid, namely, 1-butyl-3-methylimidazolium chloride [1]; and a polar fluid/salt solvent, ethylene diamine/KSCN, discussed in Section 12.4.

12.2.1 Preparation of filament

Ammonia/ammonium thiocyanate (NH$_3$/NH$_4$SCN) is a powerful solvent for cellulose. Scherer [2] was first to observe the dissolution of cellulose in this mixture of liquid ammonia and ammonium salt, and this solvent was later rediscovered by Hudson and Cuculo [3, 4], which effectively dissolves cellulose by taking advantage of the powerful swelling character of liquid ammonia on cellulose. Cuculo *et al*. [5, 6] investigated the mechanism of dissolution and observed the transformation of cellulose polymorphs during dissolution. They observed during dissolution of cellulose I, that it experienced polymorph transformation from cellulose I → II → III → amorphous in solution. Once in solution, the cellulose can attain the most extended chain conformation to accommodate the formation of the anisotropic phase [7]. The anisotropic phase has been shown to occur in solution with cellulose concentration above 12% (w/w). Another attribute of the solvent is that it neither reacts with nor degrades cellulose [7]. These attributes are important; this solvent system can potentially form cellulose fibers of exceptional properties via the anisotropic solution without the need for regeneration of cellulose and with no degradation of the cellulose itself.

   The formation of high concentration cellulose solutions in this solvent, however, may be somewhat impeded by the presence of gel which in turn affects the anisotropic phase formation. Fortunately, the gelation is thermoreversible and it has been possible to form gel-free anisotropic solutions [8]. Frey *et al*. [9, 10] investigated the mechanism of gelation of cellulose in this solvent. Gelation usually forms in solutions with cellulose concentration greater than 10% (w/w) and it is rapid at temperatures below the gel melting point (*circa* 28°C). The cellulose gel consists of a three-dimensional fibrillar network, stabilized by hydrogen bonds which can be broken at temperatures above the gel melting point. Therefore, the anisotropic solution can be obtained gel-free at temperatures above the gel melting point. Also, the solvent can tolerate significant amounts of water without losing its dissolving power. Solvent, with addition of water, representing as much as 15% by weight of cellulose, was shown to dissolve cellulose completely. This is an interesting observation considering that water is a non-solvent for cellulose.

   Previous work has shown that the formation of anisotropic solutions is

thermodynamically driven [11], thus, the anisotropic phase formation is expected to be instantaneous with dissolution. The anisotropic phase formation of the cellulose/NH_3/NH_4SCN system was found to be consistent with this expectation; the anisotropic phase formed instantaneously, without any storage or aging period. Frey [12] constructed a theoretical phase diagram for this cellulose-solvent system, shown in Fig. 12.2. Solutions with cellulose concentration at 12% were observed to be birefringent. Observation under a polarizing microscope of this cellulose solution revealed isotropic regions with a few anisotropic domains. As the cellulose concentration was increased to 14% and 16%, the number of anisotropic domains increased. These observations are consistent with the predicted phase diagram; this concentration range is located within the narrow biphasic chimney region [12].
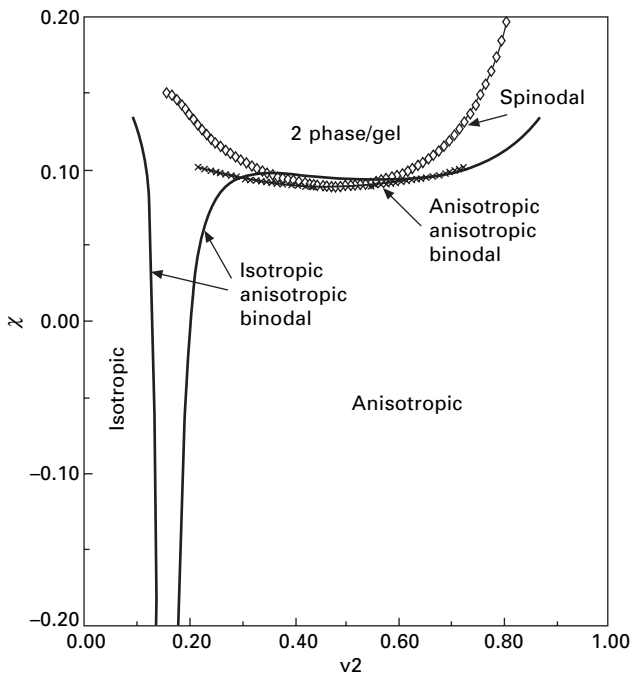
12.2 Phase diagram for cellulose in 24.5/75.5 w/w NH_3/NH_4SCN solvent. Rigid rod model x = 61.4.

Measurements of water content showed that undried cellulose pulp contained approximately 7% bound water. Cellulose containing 7% of both added and bound water can form high concentration and anisotropic cellulose solutions. The flow rate behavior of cellulose solutions, containing 7% water (both added and bound water), were similar to that of solutions prepared with pre-dried cellulose. This means that the presence of water up to 7% did not affect

the flow rate behavior, hence viscosity, of the cellulose solutions. This cellulose/ NH_3/NH_4SCN system has demonstrated a high potential as a viable commercial solvent: cellulose can be dissolved easily to prepare gel-free concentrated, anisotropic solutions. Anhydrous conditions are not required.

Measurements of the steady shear viscosity in the Newtonian or linear regime yields valuable information on molecular interactions. The molecular weight (Mw) and polymer concentration (C) dependence of the zero-shear viscosity, η_o, of cellulose solutions, exhibits two distinct regions. The dilute regime shows a linear increase of zero-shear viscosity with respect to CM_W. In the semi-dilute region, the CM_W is no longer linearly proportional to η_o. It is well established for linear, flexible polymer chains that η_o is proportional to $(CM_W)^{3.4}$ [13]. This proportionality for cellulose in the NH_3/NH_4SCN solvent is different than that of a flexible polymer. The result is similar to that of a rod-like polymer, which further supports that cellulose behaves as a semi-rigid polymer in the NH_3/NH_4SCN solvent.

A dynamic rheological investigation by Cuculo *et al.* [9], Frey *et al.* [10] on the formation and the behavior of the gel has shed some light on the so-called 'window of spinnability' of the anisotropic cellulose in this solvent. Steady state shear rheology shows that cellulose solutions possess a linear region at low shear rates and this is followed by a transition to a non-linear region at higher shear rates. This behavior shows that the cellulose in this solvent behaves as a true polymer solution. The zero-shear rate viscosity dependence on concentration and molecular weight further confirms that the cellulose in this solvent behaves as a semi-rigid polymer. The steady shear rate viscosity of cellulose solutions as a function of shear rate for degree of polymerization (DP) 760 is shown in Fig. 12.3. A region of Newtonian behavior is observed for solutions with lower concentrations. In this region, the viscosity is independent of the shear rate. The viscosity continues to decrease monotonically with increasing shear rate and this region is called the non-Newtonian region. The transition point between the linear and non-linear regions corresponds to the onset of molecular orientation and the break-up of entanglements. This point is described by the characteristic relaxation time, λ [14].

The plots in Fig. 12.4 show that under the extant conditions of cellulose DP and concentrations and solvent composition, liquid crystal formation occurs at *circa* 10% concentration. Near this point the cellulose/NH_3/NH_4SCN system starts to experience the drop in viscosity with increasing cellulose concentration. Observe the lower viscosity of the 10%, 12% and 14% solutions relative to that of the 9% solution and also observe that this behavior became evident only at the high shear rate range. Another advantage of using anisotropic solutions is the molecular ordering in the solution from which fiber can be obtained. This molecular chain ordering translates to superior mechanical fiber properties.
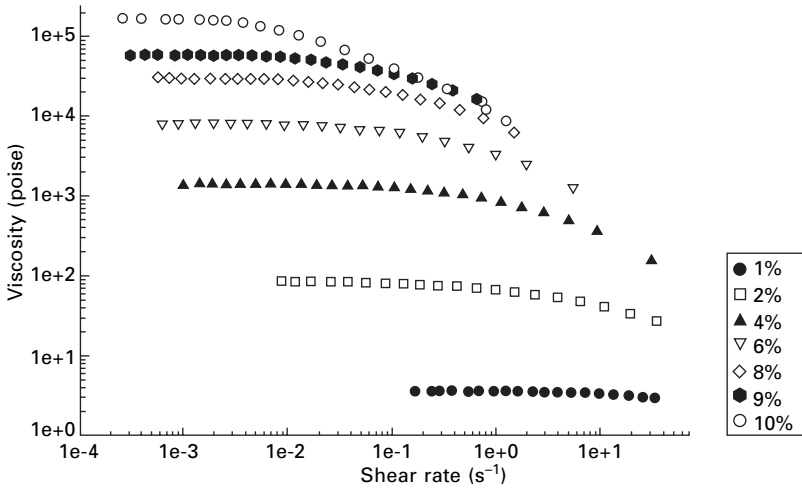
12.3 The viscosity dependence on shear rate for cellulose DP760 in NH$_3$/NH$_4$SCN at various concentrations.
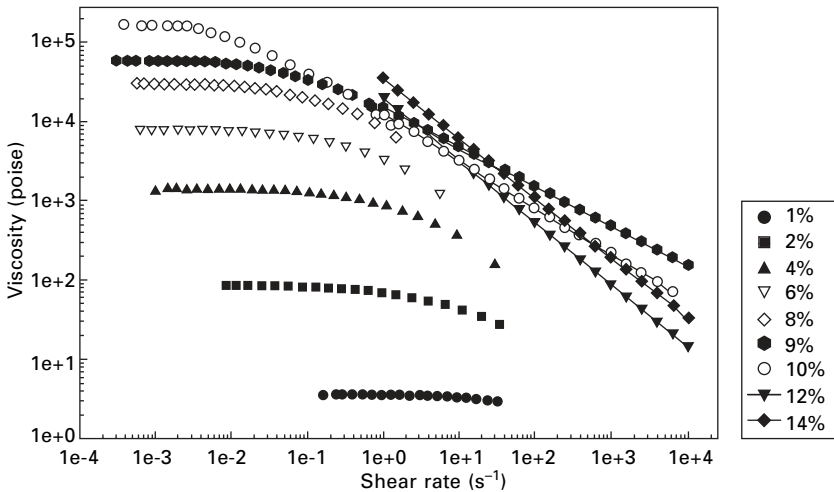
12.4 The viscosity in the linear and non-linear regions for cellulose solutions at different concentrations.

The physical properties of fibers produced from precursor liquid crystalline solutions are generally superior to those obtained from the corresponding isotropic solutions. Probably the most well-known commercial fiber derived from a lyotropic system is Kevlar®, produced by Du Pont. Cellulose fibers have not yet been produced commercially from mesophase solutions using the direct solvent route [15]. Tencel®, the commercialized cellulose fibers by

Courtauld, however, have shown marked improvement in physical properties as compared to its predecessor, rayon. Tencel® has a tensile strength of *circa* 4.5 g den^{-1}.

The difficulty associated with extruding mesophase cellulose solutions to produce high-strength fibers remains a perplexing problem. Navard and Haudin [16] indicated that one of the problems of spinning liquid crystalline cellulose solutions in the NMMO/water system was the instability or solution fracture of the solutions during extrusion. This instability resulted in uneven fiber dimensions with correspondingly poor physical properties. In 1980, Chanzy *et al.* [17] also reported fiber formation from lyotropic cellulose solutions in NMMO/H$_2$O.

Fibers obtained from a coagulated polymer solution, may be produced by two spinning methods, namely, wet spinning or dry-jet wet spinning. In the former, the solutions are forced through the spinneret directly into a coagulant. The coagulant is a nonsolvent for the polymer. In the coagulant bath the solvents diffuse out of the extrudate while the fiber is further stretched and washed and post treated. In the dry-jet wet spinning method, the solution is extruded into air and immediately proceeds into the coagulant. Post-treatments are then applied to the resulting fibers. The purpose of the air gap is to provide extensional flow to the extrudate to increase orientation across the fiber cross-section. The air gap also allows the temperature of the polymer solution to be different (usually higher) from that of the coagulant, as is the case in the production of Kevlar®.

Fibers from the anisotropic phase of cellulose/NH$_3$/NH$_4$SCN solution have been spun. High mechanical properties have been obtained with these cellulose fibers giving tenacity above 4.5 g den^{-1} and modulus above 200 g den^{-1}. The solutions were extruded by the dry-jet wet spinning method. A schematic of this process is displayed in Fig. 12.5. The temperature of the solution was adjusted to 30°C by using a heater block and heater sleeves.
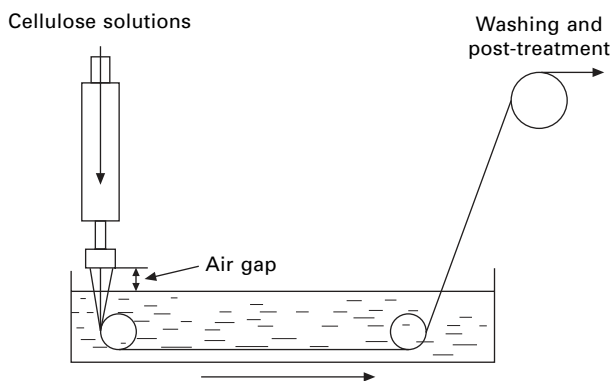
12.5 Dry-jet wet spinning process.

Three spinnerets were used in this study. They all had a single hole with 60° convergence angle and with capillary diameter of 0.127 mm but each spinneret had a different length. The spinnerets used had a ratio of length to diameter (L/D) of 2, 5 and 10. The temperature of the coagulant was held at –4°C and the washing stage was done by two methods; (a) online washing; (b) no tension washing. Water at ambient temperature (*circa* 21°C) was used in both washing methods. For the online washing method, a second bath containing water was used in the threadline. The fiber was washed immediately, under tension, prior to winding on the bobbin. The bobbin was then immersed in water overnight to further remove any solvent left on the fiber. For the no tension washing, the fiber was collected on the bobbin immediately after the coagulation bath. The bobbin was then immersed in water overnight. Finally, fibers collected by both washing methods were dried at room temperature for 24 hours.

One of the most important aspects in solution spinning is the choice of coagulant. In this study, methanol was primarily used. Liu *et al*. [18] reported that this coagulant at low temperature would provide a circular cross-section, a denser fiber and higher initial modulus for cellulose in this solvent system. Thus the temperature of the coagulant was kept at –4°C. The length of the air gap was maintained constant at 25.4 mm (1 inch), ambient conditions and no shroud was used. The length and the atmospheric condition of the air gap are influential in the cellulose/NMMO/water system of lyocell production affecting the defibrillation of the fibre. In this study attention is focused on obtaining the best mechanical properties of fibers, thus, variation of the air gap to affect the fiber properties was not a priority.

The draw-down ratio was varied in attempts to enhance the mechanical properties of the fibers. The draw-down ratio, D_r, affects the linear density of the fiber, which has effects on the tenacity and the initial modulus of the fiber. D_r, is the ratio of the take-up speed, V_i, to the extrusion speed, V_o. Therefore, D_r was changed by varying either V_o or V_i. The fiber properties that were obtained for these different spinning conditions are discussed below.

12.2.2 Fiber performance and characterization

The processing of the solution affects the morphology of the fiber. This in turn influences the mechanical properties of the fiber. The morphology of cellulose solutions has been investigated by Frey *et al*. [10]. In their study of the gelled morphology of cellulose/NH_3/NH_4SCN solutions, they observed spheroid structures connected to fibrils. They credited this morphology formation to the removal of the solvent by ethanol during the samples' preparation via critical point drying. The morphology was formed by the phase separation of the cellulose solution during the removal of the solvent into solvent-rich isotropic and polymer-rich anisotropic phases. Apparently,

the spheroid nodules were thought to form during the ethanol exchange where the cellulose in the isotropic phases collapsed due to the removal of the NH_3/NH_4SCN solvent. The fibrils, however, were formed due to the molecular alignment in the anisotropic phases. It was also observed that these spheroid nodules were connected to the fibrils because the long cellulose chains are able to participate in both isotopic and anisotropic phases. Note that the preparation of the gelled samples was conducted without any tension or stress applied on the samples.

Similar morphology, Fig. 12.6, was observed on the cross-section of the extrudate obtained from the spinning of the solutions, without any tension or stress applied along the threadline. The fiber's cross-section shows a defect zone which consists of elongated fibrils connected to spheroid nodules with average diameter in the range of 0.3–0.5 µm. These nodules are evenly distributed along the fiber's cross-section. The formation of the nodules may be attributed to the collapse of the cellulose structures in the isotropic phase during the removal of the solvent by the coagulant. These structures would contribute to the fiber's low tenacity. Also, instability of the extrudate is thought to originate in the entrance zone of the spinneret. In this zone the geometry of the entrance and the stress applied on the solutions provide no opportunity for alignment of the chains thus, resulting in the flow disturbance at the entrance. This instability is retained along the capillary and in the extrudate. The instability precludes application of any tension intended to
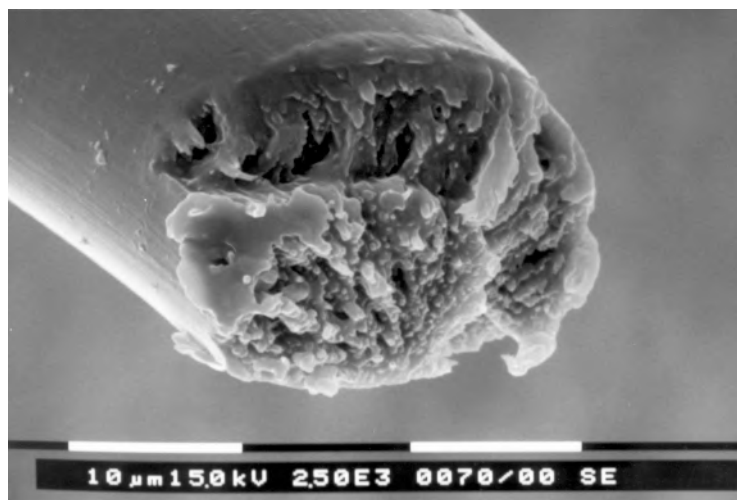
12.6 SEM micrograph of a fiber cross-section exhibiting the defect zone, due to the spinning instability. The fiber was obtained from spinning a 9% (w/w) cellulose solution at 30°C into methanol coagulant bath kept at –4°C with D_r above 1.5. Scale bar equals 10 µm.

induce chain alignment. Therefore, the flow disturbance at the entrance zone of the capillary is the original cause responsible for the poor mechanical properties of the fibers, albeit an anisotropic solution was used for the fiber formation.

The extrudates spun below the critical stress have been shown to have a smooth surface structure without any evidence of instability along its length. In the absence of the instability, extrudate can be drawn to induce chain alignment. This would allow for elongation to take place and thus accommodate chain alignment along the fiber axis. This alignment of the chains would allow for a supporting network that would prevent collapse of the cellulose chains during the removal of the solvent. This is evident from the cross-section of the fiber displayed in Fig. 12.7 by the absence of the spheroid nodules. The cross-section shows elongated fibrils that are aligned along the fiber axis. The ribbon-like fibrils shown in Fig. 12.7 have an average diameter of 0.2 μm.

12.7 SEM micrograph showing the cross-section of fiber exhibiting the elongated fibrils. The fiber was obtained from spinning a 9% (w/w) cellulose solution at 30°C into methanol coagulant bath kept at −4°C with D_r above 2. Scale bar equals 10 μm.

Therefore, two conclusions may be drawn from the instability of the extrudate during spinning. First, the instability of extrudate prevented any drawing or stretching of the extrudate thus eliminating any chance to induce alignment of the chains or anisotropic phase. These chains are then able to support each other to prevent collapsing of the cellulose chains during the removal of solvent. Secondly, the absence of tension along the threadline and hence absence of chain alignment, might also have resulted in the formation

of the spheroid nodules due to the aggregation of the cellulose chains during solvent removal. This sequence of events then contributed to the poor mechanical properties of the fiber.

The general trends of the mechanical properties of the fibers are displayed in Table 12.1. Higher cellulose concentration leads to better mechanical properties. As has been mentioned earlier, the processing conditions for fiber formation, of course, also directly influence the mechanical properties of the fibers. The type of coagulant affects the structural formation of the fibers as well as the properties. The type of appropriate coagulant has been discussed elsewhere [18]. The method of washing of the fiber also directly influences the properties. Washing under tension enhances the properties of the fibers, but reduces elongation. The draw-down ratio, that is, the ratio of the speed of the take-up to that of the extrusion, also influences the properties of the fibers. This ratio affects not only the linear density of the fiber but also the orientation and the crystallinity index. These, then, affect the mechanical properties such as the tenacity and the initial modulus.

The initial modulus of the fiber is a measure of the fiber's stiffness. It is calculated from the slope of the, initial, linear portion of the stress–strain curve. It is related closely to the molecular ordering of the fiber as well as the crystallinity. As shown in Table 12.1 the initial modulus of the fiber is higher for fiber spun from biphasic solutions (12% (w/w) cellulose concentration). This suggests that the pre-ordering in the anisotropic spinning solution contributes importantly to the final molecular ordering in the fiber. The molecular ordering in the solution appears to be retained in the fiber. Similar findings were reported by O'Brien [19] and Kwolek [20] in their spinning of cellulose triacetate and polyamide fibers, respectively. Another way to induce ordering in the fiber is to draw or stretch the fiber. The draw-down ratio, D_r, extant during the spinning process affects the physical properties of the fiber. In general an increase of D_r is accompanied by an increase in tenacity and initial modulus. This is because the drawing or stretching of the extrudate induced molecular alignment or crystallization. This is evidenced by its effect in increasing the crystal orientation factor, f_c.

X-ray diffraction analysis indicates that the cellulose fibers formed from this solvent system exist in the cellulose III polymorph conformation. This polymorph structure is revealed by X-ray diffraction peaks at *circa* 20.8°, which correspond to both the (002) and (101) planes and another at *circa* 12.1° which corresponds to the (10$\underline{1}$) plane. The intensity of these X-ray diffraction peaks of the fiber suggests that it consists of a crystalline structure, in this case cellulose III crystals. As displayed in Table 12.2, the $d_{(002)}$ and $d_{(101)}$ are similar to those of cellulose III. These interplanar spacings are the average distance between the crystalline unit planes, and they are different from one cellulose polymorph to another. This suggests that the CH_2OH moiety of the cellulose polymers are in the 'gg' conformation and are free of

Table 12.1 The mechanical properties of cellulose fibers from NH_3/NH_4SCN solvent system and lyocell

Cellulose concentration (% w/w)	Draw-down ratio	Linear density (denier)	Tenacity (g den^{-1})	Elongation (%)	Initial modulus (g den^{-1})	Second bath	Crystallinity index (%)	Apparent crystal sizes (Å)	Crystal orientation factor (f_C)
8	2.13	3.55	2.87	3.53	169.23	Water	65.49		
9	0.75	10.14	2.09	7.25	73.28	n/a	40.82	9.32	
	0.80	10.40	2.02	7.59	73.93	n/a	39.27	9.71	
	1.01	8.97	2.29	7.32	91.09	n/a	44.62	10.52	
	1.89	3.68	2.67	3.47	108.51	Water	60.72	14.62	0.634
	2.14	3.97	2.65	4.74	125.2	Water	62.03	15.84	0.684
10	2.03	3.62	3.44	5.94	144.22	Water	63.33	13.42	
	2.53	3.27	3.66	5.46	153.13	Water	64.63	13.54	
12	5.77	3.68	3.00	9.60	122.00	n/a	62.32	13.52	0.621
	3.15	4.37	3.77	10.96	138.91	n/a	63.68	15.23	0.672
	3.15	5.45	4.65	4.82	212.12	Water	88.61	19.13	0.826
lyocell		1.50	4.51	12.92	132.27		85.11	20.01	0.756

Table 12.2 The diffraction planes of cellulose polymorphs measured by WAXS

Polymorph	Diffraction angle (2θ;°)			Interplanar spacing (Å)		
	(101)	(101)	(002)	d(101)	d(101)	d(002)
Cellulose I	15.30	16.32	22.76	5.86	5.43	3.90
Cellulose II	12.10	20.45	21.65	7.38	4.35	4.10
Cellulose III	12.18	20.83	20.83	7.00	4.26	4.26
Cellulose fibers from NH$_3$/NH$_4$SCN	12.71	20.91	20.91	7.00	4.24	4.24
Lyocell	12.75	21.00	21.65	6.94	4.23	4.11

the inter- and intramolecular hydrogen-bonding. The structural conformation of lyocell, on the other hand, possesses the cellulose II conformation.

Cellulose fibers with high mechanical properties have been produced from the cellulose/NH$_3$/NH$_4$SCN solvent system. The fiber spun from the biphasic solution has been shown to have superior properties to those from the isotropic solutions. Processing of the solutions is very important in attaining the high mechanical property fibers. Any instability in the extrudate resulted in fibers with low mechanical properties.

The solvent exchange in methanol or ethanol during the coagulation process produced a stretchable gel extrudate which formed fibers with circular cross-section. The stretching or extension of the extrudate was done by setting the speed of the take-up godet higher than that of the extrusion. The velocity ratio of the godet rate to the extrusion rate is known as the draw-down ratio, D$_r$. This ratio controls the linear density of the fiber and hence the morphology and the crystallinity of the fiber. The orientation of the chains and crystalline regions influence the tenacity and the initial modulus.

The method of washing during the solution spinning also affects the mechanical properties of the fibers. The washing (or further solvent removal) of the fiber during the spinning process allowed for washing under tension. The tension on the fibers in the second bath would maintain the molecular orientation attained in the coagulant bath, while removing the remaining solvent. Thus, fibers with high cystallinity index as well as high crystalline orientation factor could be obtained.

The fibers made from this cellulose-solvent system by the above method have tenacity of 4.65 g den^{-1} and initial modulus of 212 g den^{-1}. The tenacity of this cellulose fiber is very similar to that of lyocell, *circa* 4.50 g den^{-1}. The initial modulus of this cellulose fiber is much higher than that of lyocell, *circa* 132 g den^{-1}. The extensional ratio and extrusion speed, however, is lower than that of lyocell.

A cellulose fiber with mechanical properties better than that of lyocell has been made. This cellulose fiber from the NH$_3$/NH$_4$SCN solvent system provides an excellent alternate in producing cellulose fibers simply, quickly and inexpensively as well as attaining high mechanical properties.

12.3   Fibers from chitin and chitosan

Chitin, poly-(1→4)-2-acetamide-2-deoxy-β-D-glucose, is the second most abundant natural polysaccharide and has a molecular structure that is very similar to cellulose, see Fig. 12.1. Chitin can be found in a wide variety of species of lower animals and plants where it is used as cell wall reinforcement. Arthropod shells (exoskeletons) are the most easily accessible sources of chitin; these shells contain 20–50% chitin on a dry weight basis. From a practical viewpoint, shells of crustaceans such as crabs and shrimps are conveniently available as wastes from seafood processing industries, other potential sources for chitin production include krill, crayfish, insects, clams, oysters, jellyfish, algae, and fungi. Squid pens also contain chitin that is classified as β-chitin, this material is distinguished from the ordinary α-chitin in crustacean shells based on the difference in crystalline structure. β-chitin has weaker intermolecular forces and is quite attractive as another form of chitin having some characteristics considerably different from those of α-chitin. The chemistry of β-chitin is rapidly advancing, although this starting material is less abundant and is not yet produced commercially. Chitosan, poly-(1→4)-2-amino-2-deoxy-β-D-glucose, is the deacetylated product of chitin which contains one free amino group for each glucose building unit. However, chitosan is a copolymer composed of the two sugar residues *N*-acetyl-D-glucosamine (GlcNAc) and D-glucosamine (GlcN). Chitosan is one of a few natural cationic polysaccharides that can be derived from crustaceans or various fungi. Practically, however, chitosan is more easily produced from chitin by deacetylation with concentrated alkali solutions at elevated temperatures [21].

Both polymers cannot be melt-processed because extensive hydrogen bonding restricts relaxation of the polymer chains, so that on heating, the polymer decomposes instead of melting. Measurement of water loss for the polymers requires about ten times the amount of energy required to vaporize an equivalent amount of free water, indicating that the water in chitin and chitosan is tightly bonded, hence, dry spinning may not be an option. Therefore, conversion of the polymers to fiber without polymer degradation requires a wet spinning process. Both polymers have attracted much attention due to their unique properties such as biocompatability, biodegradability, and non-toxicity; chitin and chitosan have been utilized in various fields including food science, cosmetics, water engineering, agriculture, medicine, pharmaceutics, textiles, and their applications are still expanding.

12.3.1 Preparation of filament

As mentioned before, it is essential that a stable chitin solution form in order to spin the chitin fibers. There is a long history of attempts to find stable

solvents of chitin, dating back to the work of Von Weimarn in 1926; he reported the first solutions of chitin that could be formed into a 'ropy-plastic' state though no tensile properties were evaluated on these ropy materials [22]. Since then, numerous solvent spin systems have been extensively studied. However, the major difficulty has been to find a stable solvent because of the relatively inert chemical structure of chitin and its rigid crystalline structure. The discovery of various new solvents by Austin and co-workers in the 1970s stimulated new interest in the problem.

Austin suggested organic solvents containing acids such as chloroethanol, sulfuric acid and trichloroacetic acid (TCA) for the direct dissolution of chitin in 1975 [23]. A filament was extruded from the spin solution made with chitin in a mixture of 40% TCA, 40% chloral hydrate, and 20% methylene chloride. The filaments were solidified in the coagulating bath containing acetone, neutralized with potassium hydroxide (KOH) in 2-propanol followed by washing in deionized water, and, then, cold drawn. Other solvent systems for chitin have been proposed [24]. However, they require fairly drastic conditions to dissolve chitin and some are very corrosive or expensive. It is hard to maintain the chitin molecule without depolymerization during the dissolution process.

Chitosan, on the other hand, is readily soluble in dilute acid solutions, offering a convenient and relatively inexpensive solvent for fiber production. As early as 1926, Kunike pointed out that chitosan was easily soluble in dilute acids such as dilute aqueous acetic acid [25]. Despite this advantage over chitin, the study of the production of fibers from chitosan has lagged behind that of chitin, the first significant description of chitosan fiber production being as recent as 1981 [26]. Later, Tokura *et al*. reported that chitosan fibers for various degree of deacetylation can be prepared by extruding dopes in 4% aqueous acetic acid into coagulation bath containing $CuSO_4/NH_4OH$ or $CuSO_4/H_2SO_4$. A complex of chitosan fibers and copper were obtained, but the copper can be removed afterwards [27].

Solvent spin systems as mentioned above were too drastic and harmful to apply for biomedical purpose due to toxicity concerns as well as environmental regulations. Therefore, the development of mild spinning solvents as well as coagulating solvents is required for the preparation of chitin and chitosan fibers and their derived fibers. Tokura and coworkers were attracted to a calcium halides/saturated alcohol solvent system as a solvent for chitin [28]. They investigated the solubility of chitin in various metal salts of Group II of the Periodic Table in combination with alcohols such as methanol, ethanol, *n*-propanol, isopropanol, etc., they reported that the calcium chloride dihydrate saturated methanol (saturated $CaCl_2 \cdot 2H_2O/MeOH$) was the most effective system. This may be due to the fact that the 3-d hydrogen bonding involving the amide and hydroxyl groups of chitin is destroyed by this solvent system without disruption of the glycoside linkage. Among other alcohols, methanol was the best solvent for chitin with calcium chloride dihydrate.

In terms of solubility, there is a clear difference between α- and β-chitin. Lower solubility was found for β-chitin in spite of a looser crystalline structure than that of α-chitin. Since the gelation of β-chitin solution started at a lower chitin concentration than that of α-chitin, the gelation mechanism might be related significantly with the dissolution mechanism. They further investigated the dependence of degree of deacetylation on solubility of chitin for the calcium chloride dihydrate saturated methanol solution using various deacetylated chitins with different molecular weights. It turns out that there is a strong dependency of the molecular weight and the molecular conformation of chitin on the solubility. The better solubility is given by the smaller molecular weight fractions at room temperature. This may be due to the fact that chitin is dissolved by an interaction between a calcium ion and an acetamide group. Also, better solubility is given by deacetylated chitin from that of natural chitin even if of similar molecular weight. Since the deacetylated chitin has a less crystalline structure than that of natural chitin, calcium ions would form a complex with chitin molecule much easier [28].

While calcium chloride dihydrate saturated methanol solution was found to be a mild solvent for chitin, chitosan solutions were found to be coagulated by calcium ion [29]. This system would have an advantage for biomedical applications due to such a potentially non-harmful spinning system. Chitosan solution in 10% acetic acid was spun through a spinneret into the first coagulation bath containing calcium chloride or calcium acetate saturated aqueous ethanol. The chitosan filament in the first coagulation bath was solidified through calcium chelation with the amino group of chitosan. Then, from the biomedical point of view, ethanol was applied to the coagulated chitosan filament instead of methanol, washed with distilled water, and dried in air. A post spinning treatment of the filament is required since the filament is water soluble and very weak. The filaments become insoluble under treatment with tetrasodium ethylenediaminetetraacetic acid for 5 hours or sodium hydrogen phosphate for 5 hours, or sodium hydroxide (NaOH) for 48 hours. The results show that the treatment with diluted NaOH aqueous solution improved the mechanical properties by elimination of chelated calcium ion. The tensile strength of filament treated with NaOH in the dry state was 1.33 g den^{-1} compared with untreated original filament (0.44 g den^{-1}). The remarkable improvement of Young's modulus was shown in the filament treated with NaOH (57 g den^{-1}) compared with the untreated original filament (17 g den^{-1}). Hence, the results suggest that elimination of calcium from the filament is essential to improve the fiber mechanical properties [29].

Chitosan has also been used to prepare coated or bicomponent filaments. A chitosan-coated alginate filament was successfully prepared by the addition of a small amount of chitosan to the first coagulation bath containing the calcium chloride dihydrate saturated methanol solution. Touch and feel as well as mechanical properties of the alginate filament were improved by

coating the alginate filament. Additionally, water insolubility of the resultant filament indicates that the free amino group on the glucosamine residues had an ionic interaction with the carboxylate group on alginate [30].

Over the past 7–8 years, Hirano and co-workers have extensively studied a series of novel functional fibers based on chitin and chitosan. Acylation of chitosan with acid anhydrides such as acetic and propionic anhydride as the reactant introduces amido groups at the chitosan nitrogen. Acetic anhydride affords fully acetylated chitosan. Linear aliphatic N-acyl groups above propionic anhydride permits rapid acylation of hydroxyl groups [31]. Chitosan and aldehyde produce N-alkyl chitosan upon hydrogenation of the resulting Schiff base. The presence of the more or less bulky substituent weakens the hydrogen bonds of chitosan. Therefore, N-alkyl chitosan swells in water in spite of the hydrophobicity of the alkyl chains. N-alkylation, N-alkylidene and N-arylidene chitosan fibers were prepared by the post-treatment of chitosan fibers with aldehydes including vanillin [32].

In the case of N-acylchitosan and their cellulosic composite fibers, the spinning dope was prepared by mixing aqueous 14% NaOH solution of sodium N-acetyl chitosan xanthate with sodium cellulose xanthate. The filaments were spun at 45–50°C through a viscose-type spinneret into a coagulating bath containing aqueous 10% H_2SO_4, 32% Na_2SO_4, and 1.3% $ZnSO_4$ and collected on a roller. The wet fiber obtained was treated in boiling water for 10–20 minutes and in aqueous 0.5% NaOH at 60–70°C for a few minutes, washed with deionized water, and pressed for dehydration. The chitin–cellulose fiber has been commercialized in the Japanese textile industry as a natural functional fiber for socks and underwear, under the trade name of Chitopoly™ by the Fujibo Spinning Co. The choice of an economical solution for fiber spinning and coagulating is essential for industrial fiber manufacturing. In addition, biomedical fibers should be free of trace harmful elements including sulfur, copper, and organic solvents. Therefore, it is necessary to develop a method for the preparation of N-acetylchitosan fibers without using the harmful CS_2. An aqueous solution of sodium N-acetylchitosan salt in aqueous 14% NaOH was spun through a spinneret into a coagulating bath containing aqueous 10% H_2SO_4, 32% Na_2SO_4, and 1.3% $ZnSO_4$ [33].

Other researchers in addition to Hirano have extensively studied the production of various chitin, chitosan, their derivatives, and composite fibers with other polymer materials, since 1994. Their spinning solution, coagulating solution, and polymer materials used in the dope are summarized in Table 12.3. Rathke and Hudson's review concerning chitin, chitosan, and their derivatives covers all of the reported information up to 1994 [24].

Table 12.3 Spinning and coagulation solutions of various fibers based on chitin and chitosan

Authors	References	Fibers	Polymer used in the dope	Spinning solution	Coagulation solution
Hirano, et al.	32	Chitosan	Chitosan acetate	aq. 2% acetic acid	aq. 10% NaOH and 30% Na_2SO_4
				aq. 2% acetic acid	aq. 10% NaOH and 40–43% $(NH_4)_2SO_4$
				aq. 2% acetic acid-MeOH	aq. ca. 5% ammonia and 40–43% $(NH_4)_2SO_4$
	32	Chitin	Sodium chitin salt	aq. 14% NaOH	aq. 10% H_2SO_4, 32% Na_2SO_4 and 1.3% $ZnSO_4$ aq. 10% H_2SO_4 and 40–43% $(NH_4)_2SO_4$
			Sodium chitin xanthate	aq. 14% NaOH	aq. 10% H_2SO_4 and 25% Na_2SO_4 aq. 10% H_2SO_4 and 40–43% $(NH_4)_2SO_4$
	32,33, 58, 59	N-acylation*	Chitosan fiber		
	31,32	N-alkylation* N-alkylidene* N-arylidene*	Chitosan fiber		
	60	N-(carboxyacyl)*	Chitosan fiber		
	61	Chitosan-tropocollagen	Chitosan acetate-collagen	aq. 2% acetic acid	aq. 10% NaOH and 40–43% $(NH_4)_2SO_4$
				aq. 2% acetic acid-MeOH	aq. ca. 5% ammonia and 40–43% $(NH_4)_2SO_4$
	61	Chitin-tropocollagen*	Chitosan-tropocollagen fiber		
	62	Chitosan-silk fibroin	Chitosan acetate-silk fibroin	aq. 2% acetic acid	aq. 10% NaOH and 40–43% $(NH_4)_2SO_4$

Table 12.3 Continued

Authors	References	Fibers	Polymer used in the dope	Spinning solution	Coagulation solution
				aq. 2% acetic acid-MeOH	aq. ca. 5% ammonia and 40–43% $(NH_4)_2SO_4$
	62	Chitin-silk fibroin	Sodium chitin xanthate-silk fibroin	aq. 5% NaOH	aq. 10% H_2SO_4 and 40–43% $(NH_4)_2SO_4$
	63	Cellulose-silk fibroin	Sodium cellulose xanthate-silk fibroin	aq. 5% NaOH	aq. 10% H_2SO_4 and 40–43% $(NH_4)_2SO_4$
	32,33,34, 58, 59	N-acylation-cellulose	Sodium N-acetyl xanthate-sodium cellulose xanthate	aq. 5% NaOH	aq. 10% H_2SO_4 and 25% Na_2SO_4
			Sodium N-aceylation salts-sodium cellulose xanthate	aq. 5% NaOH	aq. 10% H_2SO_4 and 25% Na_2SO_4
Nam, *et al.*	64,65	Chitosan derivative-PAN	N-(2-Hydroxy)propyl-3-trimethyl-ammonium chitosan chloride or water soluble chitosan derivative / Polyacrylonitrile	aq. 46% (w/w) NaSCN	aq. 10% NaSCN
Sun, *et al.*	66	Chitosan- PEG	Chitosan-poly (propylene glycol)	aq. 2% CH_3COOH	aq. 2% NaOH
Nousiainen, *et al.*	67	Viscose-chitosan	Microcrystalline chitosan gel/sodium alginate (2:1)-sodium cellulose xanthate		90 g/L H_2SO_4
Zheng, *et al.*	68	Chitosan-PVA	Chitosan-poly(vinyl alcohol)	2 wt % CH_3COOH	aq. NaOH and C_2H_5OH

Table 12.3 Continued

Authors	References	Fibers	Polymer used in the dope	Spinning solution	Coagulation solution
Li, *et al.*	69	Chitosan derivative-Viscose rayon	*N*,O-carboxylated chitosan-Viscose rayon		
Hirano, *et al.*	59	Chitin-cellulose-silk fibroin	Sodium chitin xanthate-sodium cellulose xanthate-silk fibroin	aq. 5% NaOH	aq. 10% H_2SO_4 and 40–43% $(NH_4)_2SO_4$

* Post-chemical modification at the fiber state.

12.3.2 Fiber performance and characterization

Chitin, chitosan, and their derivative fibers of various tensile and mechanical properties such as toughness, flexibility, and tensile strength can be made under a variety of spinning conditions rather than by their chemical nature. Chitin is a highly crystalline polymer because of the ability of the acetamide groups to form hydrogen bonds. The increase of both the dry and wet strengths with the increase in the degree of acetylation is a reflection of the increase in the interchain forces and the increase in the degree of crystallinity. However, chitosan is a more preferred form of the polymer for formation of fiber rather than chitin, although chitosan is difficult to deacetylate fully. The copolymer structure of partially deacetylated chitosan generally lowers the dry/wet strength properties of chitosan fibers. This may be due to the fact that for the partially deacetylated fibers, the polymer structure is a random copolymer consisting of glucosamines and N-acetylglucosamines. The irregular structure inhibits crystallization and reduces the strength of the fiber. As a result, chitosan has enhanced hydrophilicity compared to chitin, which results in a considerable loss of tensile strength when wet [35].

Several approaches have been developed to improve the mechanical properties of chitosan fibers. The first approach is the application of draw to the fibers, which is a physical process. Fibers can have improved tensile and mechanical properties by further processing. The mechanical properties of fibers can be improved by applying a stretch to the yarn in the coagulation step in the wet spinning, or after coagulation while it is still wet and swollen with water, or after it is dried and just prior to being wound up [36]. East and Qin reported the effects on mechanical properties of chitosan fibers by increasing jet stretch ratio in relation to the maximum draw ratio in the wash and draw bath. They demonstrated a decrease in the maximum draw ratio with increasing jet stretch ratio. They also reported the results for mechanical properties of fibers with variations of the jet stretch ratio at a fixed draw ratio and the results of variations of the draw ratio at a fixed jet stretch ratio. The results indicates that a tremendous decline in breaking strength was shown with increasing jet stretch and draw ratios. On the other hand, only minimal changes in modulus were shown [37].

Knaul et al. discussed the improvement of the drying system employed following the coagulation step to remove excess water from the chitosan yarn. The drying step is essential to the spinning process because the filaments are prepared for winding and individual filaments in the wound yarn need to be well separated. Various drying techniques including direct and radiant heat, forced air, and chemical drying agents were considered and the corresponding impact on the mechanical properties of the product chitosan fibers was analyzed. Mechanical properties of methanol-dried chitosan fibers were superior to those properties of fibers dried using forced air, heat, or

other tested drying agents. The elongation at break for these fibers remained constant or decreased in both the dry and wet states. The wet mechanical values were: modulus of 28.2 g den^{-1}; a tenacity of 1.05 g den^{-1}; and an elongation at break of 18.5% in the methanol-dried chitosan fibers [38].

The second approach to improving mechanical properties is the chemical cross-linking of chitosan fibers. Fiber mechanical properties can be altered by reaction with another compound which involves crosslinking the polymer chains. Wei *et al*. cross-linked chitosan fibers using epichlorohydrin [35]. Results demonstrated a significant increase in wet mechanical properties with increasing reaction time, reaction temperature, and concentration of epichlorohydrin. Dry mechanical properties improved only slightly under the same reaction conditions although the tenacity and modulus were decreased in some cases. Elongation at break remained constant or decreased when determined for both the dry and wet fiber. The dry mechanical values exhibited a modulus of 48.1–73.4 g den^{-1}, a tenacity of 1.19–1.46 g den^{-1}, and a elongation at break of 11.2–7.5% [35]. Knaul *et al*. reported on the changes in the mechanical properties of chitosan fibers using buffered solutions based on potassium dihydrogen phosphate and potassium hydrogen phthalate. The variations were pH, immersion time, and temperature [39].

Hudson *et al*. discussed improvements to dry mechanical properties through post-spinning application of glyoxal and glutaraldehyde to chitosan fibers. Fiber samples were wrapped onto bent glass rods and submerged into 100 cm^3 of either aqueous glyoxal or glutaradehyde solution for one hour at 25°C. After removal from the dialdehyde solution, the fiber was rinsed with distilled water and dried in an oven at 50°C for 16 hours. The variance of initial modulus, tenacity, and elongation-at-break, with increasing concentration of dialdehyde was determined. With increasing amount of dialdehyde, the elongation-at-break decreases. On the other hand, the modulus and tenacity increase to a certain point, but then decrease again with increasing amount of dialdehyde. This suggests that the dialdehyde will degrade the molecular structure at relatively high concentrations or cause stress concentrations in the fiber. This result was even more evident in the stress–strain curve, which displayed an increase in the elastic portion and a corresponding decrease in the plastic region with increasing amounts of cross-linking agent. The disappearance of the plastic region with increasing modulus is a characteristic property of a fiber that is becoming increasingly brittle [40]. This phenomenon was reported by Wei *et al*. for increasing cross-linked density with epichlorohydrin [35].

Lee *et al*. reported on the effects of the concentration of cross-linking agent, epichlorohydrin (ECH), in the spinning dope on the mechanical properties of chitosan fiber. Chitosan fibers are prepared with ECH concentrations from 0.5 to 25.0×10^{-2} M. The wet tenacity increases somewhat as the concentration of ECH increases in the spinning dope. However, the

dry tenacity decreases significantly with an increasing concentration of ECH. The elongation decreases with the addition of ECH for the dry fibers. There is no deleterious effect on the wet fiber properties as a result of cross-linking. However, the work of rupture decreases with the addition of ECH. The saturated concentration of ECH is about 5×10^{-2} M [41].

A third approach for improving fiber performance is the use of chitosan as a fiber coating. Ionic interaction is a convenient way to form tight interactions between molecules. Chitosan is a cationic polysaccharide consisting of glucosamine residues. A tight interaction between chitosan and an anionic polymer such as alginate is expected to improve the tensile strength through ionic interaction. Tamura *et al.* proposed to prepare chitosan-coated alginate filaments for application as a wound healing material. The coating of the alginate filament was achieved by addition of a minimal amount of chitosan solution dissolved in acetic acid to the aqueous calcium chloride solution in the coagulation bath. Coagulated filament was wound up by a stretching procedure in the wet state and dried in air following extensive washing with ethanol. A significant increase of the wet/dry ratio of knot strength is observed and this suggests the tight ionic interaction of chitosan to the alginate filament and the improvement of filament flexibility. Although knot strength in the dry state decreased with the increase of chitosan concentration in the coagulation bath, those in the wet state (about 0.57 g den^{-1}) are independent of the chitosan concentration. In general, these filaments are stronger in the dry condition than in the wet condition. However, the present chitosan-coated alginate filament showed higher wet strength, especially in knot strength. There is also a significant molecular weight dependency for the tensile strength of chitosan-coated alginate filament especially when wet. When chitosan of molecular weight 1.6×10^5 g mol^{-1} is added to the coagulation bath, tensile strengths in dry state (1.13–1.81 g den^{-1}) and wet state (0.7–0.9 g den^{-1}) are improved compared with the filaments coated by chitosan of low molecular weight. This suggests the tight interaction of chitosan with alginate filament. In addition, the coagulation effect of calcium chloride might play a role for the improvement of the filament strength [30].

Mechanical properties of chitin, chitosan, and their derivatives are reported up to 1994 in Rathke and Hudson's review paper [24]. Table 12.4 shows the mechanical properties of various fibers based on chitin and chitosan obtained between 1994 and 2004.

12.3.3 Applications of chitin and chitosan fibers

The antimicrobial activity of chitosan against microorganisms of a wide variety of bacteria and fungi has long been recognized [42]. This unique property has led to many potential applications to food science, agriculture, paper, medicine, pharmaceuticals, and textiles. Mechanisms behind the

Table 12.4 Mechanical properties of fibers based on chitin and chitosan

Fibers	Titer (denier)	Tenacity (g den^{-1})	Elongation (%)
Chitin	3.75–7.89	1.15–1.25	3.6–8.4
Chitosan	4.50	1.29	8.2–10.4
N-acetylation	3.08/4.35	1.30/0.87	11.2/6.9
N-alkylidene	6.2	1.41	12.9
N-arylidene			
N-(carboxyacyl)	4.09–5.85	0.37–0.90	7.6–11.7
Chitosan:tropocollagen			
(90:10)	11.3	1.11	14.4
(70:30)	16.3	1.08	15.7
(50:50)	17.7	1.15	10.9
Chitosan:silk fibroin			
(94:6)	3.24	1.05	8.44
(80:17)	9.70	0.67	4.20
(67:33)	18.5	0.10	0.17
Chitin:silk fibroin			
(83:17)	9.70	0.67	4.2
(94:6)	3.24	1.05	8.4
Cellulose:silk fibroin			
(47:53)	19.7	0.15	0.8
(90:10)	9.9	1.08	35.0
(100:0)	4.1	1.27	39.2
N-acylation:cellulose			
(67:33)	5.31	0.18 (dry)	4.8 (dry)
(50:50)	6.96	0.26 (dry)	4.5 (dry)
(33:67)	3.62	0.53 (dry)	19.1 (dry)
Chitosan derivative:PAN			
(1:99)	94	1.05	15.7
(10:90)	83	1.03	8.8
(20:80)	92	1.16	7.9
Viscose-chitosan	4.5	1.4	20
Chitosan:PVA			
(90:10)		1.9/0.82 (dry/wet)	16/27.3 (dry/wet)
(70:30)		1.9/0.82 (dry/wet)	16/30 (dry/wet)
(50:50)		1.65/0.68 (dry/wet)	14.5/24 (dry/wet)
Chitosan:chitosan derivative:viscose rayon (%)			
(0.4:0.1:99.5)		1.64/0.88 (dry/wet)	21.6
(1.6:0.4:98.0)		1.53/0.80 (dry/wet)	19.5
Chitin:cellulose:silk fibroin (%)			
(9:80:11)	5.0	0.93	25.0
(16:41:43)	4.8	0.70	20.6
(77:11:12)	3.9	0.85	28.6

antimicrobial activity of chitosan have been proposed. One of the most plausible mechanisms is that the antimicrobial activity of chitosan originates from the polycationic nature of chitosan that can bind with anionic sites in proteins, hence, resulting in selective antimicrobial activities toward fungi or bacteria. The antimicrobial activities, which are not found in chitin, mainly depend on the type of functional groups in chitosan and the molecular weight of the base chitosan. The antimicrobial activities are generated from the protonated amino groups in chitosan in an aqueous acidic environment. Another mechanism is that the positively charged oligomer chitosan penetrates into the cells of microorganisms and prevents the growth of cells by inhibiting the production of RNA. In this mechanism, chitosan must be hydrolyzed to a low M_W to penetrate into the cell of microorganisms, though this mechanism is controversial.

A large number of fibers has been used or developed for various applications such as wound dressing materials, sutures, scaffolds in tissue engineering, functional textile, and air filters. Over the past several years, the biomedical application interests for chitin and chitosan have drawn much attention. This is due to the fact that chitin and chitosan are biodegradable, biocompatible, and non-toxic.

Wound dressing

As far as chitin and chitosan based commercial wound dressings are concerned, a Japanese manufacturer, Unitika Ltd, is producing a wound dressing from highly purified chitin, which is available in nonwoven, sponge, and fleece forms. Nara *et al.* patented a wound dressing comprising a nonwoven fabric composed of chitin fibers [43]. Another patent from the British Textile Technology Group (BTTG) reported a procedure for making a chitin-based fibrous dressing. They developed a novel method, which uses a non-animal source, microfungal mycelia, as the raw material, and the resulting microfungal fibers are different from the normal spun fibers [44]. Hirano *et al.* introduced a novel chitin-acid glycosaminoglycan fiber for use as a biocompatible dressing material in the veterinary and clinical fields. Though these fibers are unfit for a textile material because of their mechanical weakness, they are usable as a wound-dressing material in the clinical and veterinary fields because of their ease in handling, soft feel, and protective properties [45].

Sutures

Sutures are either monofilament or monofilament threads in surgery for wound closure. Chitin sutures resist attack in bile, urine and pancreatic juice, which are problem areas with other absorbable sutures [46].

Scaffolds in tissue engineering

Iwasaki and co-workers produced an alginate-based chitosan hybrid polymer fiber using the coagulation system containing the calcium chloride dihydrate saturated methanol solution. They suggest that the fiber has considerable potential as a desirable biomaterial for cartilage tissue scaffolds. In order to maintain the number of attached chondrocytes, high cellular adhesivity is a requirement for scaffold materials in cartilage tissue engineering. In their report, the adhesivity of chondrocytes was significantly higher on the alginate-based chitosan hybrid polymer fiber than on the alginate polymer fiber with its anionic nature. This is due to the fact that the cationic chitosan allows for electronic interaction with anionic glycosaminoglycans (GAGs), proteoglycans, and other negatively charged species. In addition, adequate mechanical strength to maintain the initial shape of the implanted scaffold is necessary. In order to achieve this requirement, they have developed a 3D fabricated scaffold using an apparatus formed from the novel fibers [47].

Tuzlakoglu *et al.* developed 3-D chitosan fiber meshes for potential use in tissue engineering applications. Chitosan solution dissolved in aqueous acetic acid was diluted with methanol, injected into a coagulation bath containing a mixture of 30% 0.5 M Na_2SO_4, 10% 1 M NaOH, and 60% distilled water, and washed with distilled water before being suspended in 50% methanol for 1 hour. A subsequent drying treatment with methanol was used to improve the mechanical strength of the fibers so that the fibers had enough tensile strength to be used for scaffolds. Using a short-term MEM extraction test, the fiber was found to be non-cytotoxic to fibroblasts. Furthermore, osteoblasts directly cultured over the chitosan fiber mesh scaffolds. There was no inhibition of cell proliferation [48].

Controlled release of drug

Liu *et al.* prepared chitosan coated cotton fiber by the reaction between aqueous chitosan acetic acid and oxidized cotton fiber. Since the chemical reaction activity of the amino group is greater than the hydroxyl group of cellulose, the fiber has potential for still more chemical modification. They have tried the control release of the herb medicine shikonin and obtained a good result. Potential usefulness of this fiber as a support for the controlled release of drugs is suggested [49].

Functional textiles

Fuji Spinning Co. Ltd have developed and commercialized the hybrid fiber 'Chitopoly' from chitosan. Originally, Chitopoly was developed for use in atheletic socks and hospital gowns to prevent the spread of disease. Nowadays,

Chitopoly has been widely acknowledged as an undergarment for people with symptoms of atopic allergy [50]. Also, a chitin-cellulose blend fiber, named Crabyon, has been commercialized as a functional textile material for underwear, towels, sportswear, and socks [51].

Industrial materials

Hirano and Hayashi have introduced a novel fragrant fiber and yarn based on chitosan. A bundle of two silk fibroin filaments was coated with a layer of *N*-modified chitosan using fragrant aldehydes such as cinnamaldehyde. A portion of chitosan fiber was suspended in methanol and a fragrant aldehyde was added. The mixture was kept at room temperature for 18 hours, washed with methanol, filtered, and air-dried. The fragrant derivatives, fibers, and yarns are suggested to be useful as a novel biomaterials in a wide field of applications, including air-filters, cosmetics, and textiles [52].

12.4   Future trends

Improvements in cellulosic fibers are continuing along several paths. Cellulose is a sustainable resource and widely available worldwide. It has many desirable attributes for use in textile fibers, including ease of dyeing, comfort and biodegradability. The search continues for solvent components which are easier to handle. In the case of the NH_3/NH_4SCN solvent system, it may be possible to substitute the ammonia for a material with a higher boiling point such as hydrazine or ethylene diamine.

Hattori and Cuculo began an investigation of analogs to NH_3 including hydrazine, hydrazine hydrate and ethylene diamine [53–55]. These systems have shown similar behavior to the NH_3/NH_4SCN in early dissolution studies. One of the solvents, the ethylene diamine/salt system, shows promise as a commercially viable solvent for cellulose processing. This solvent system has great flexibility because salt type and concentration can be varied. Also, formation of ultra fine fibers via electrospinning is possible from the ethylene diamine/salt solvent [56].

Chan *et al*. have reported an investigation of cellulose/ethylene diamine/salt solution rheology [57]. Solutions of cellulose in ethylene diamine/KSCN solvents were found to be strongly shear thinning, approaching Bingham plastic behavior. Shear viscosity was found to be highly dependent on both cellulose and salt concentration as seen in Fig. 12.8. Decreases in viscosity with increasing cellulose or salt concentration indicate onset of liquid crystal formation and, at higher concentrations, phase separation into polymer rich and solvent rich phases. At further increased concentrations, stiff clear gels similar to those observed in the cellulose/NH_3/NH_4SCN system form. Preliminary coagulation studies were performed using a dry-jet wet spinning
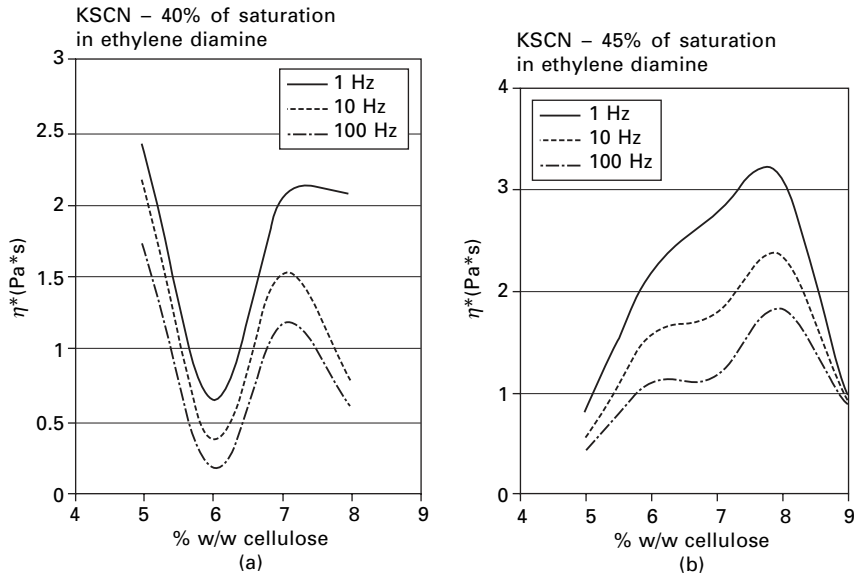
12.8 Effect of cellulose concentration on complex viscosity of samples with KSCN concentration at 40% and 45% of saturation in ethylene diamine [57].

technique. Ethanol and methanol were both found to successfully coagulate fibers. Fiber properties have not yet been optimized.

Chitosan is called the last biomass of the twentieth century, and is a material that waits further development as an extraordinary biomaterial in the twenty-first century. Chitin and chitosan, derived from shellfish waste, continue to be underutilized resources. We believe that to further their development as a resource, that there are needs for products of intermediate value; easy to produce and which capitalize upon the unique features of chitin and chitosan. Fibers and films based on chitin or chitosan have considerable promise for medical textile applications. The commercialization of chitosan-based hemostatic bandages, such as Hemcon™, represents a significant accomplishment in gaining the acceptance of chitosan as a biomaterial.

12.5   Sources of further information

'Solvent Spun Cellulose Fibers', Cuculo, J.A., Aminuddin, N. and Frey, M.W., in *Structure Formation in Polymeric Fibers*, 296–328, D.R. Salem (ed.), Hanser Publishers: Munich (2000).

'Chitin and Chitosan', Jenkins, D. and Hudson, S.M., in *Polymer Encyclopedia of Polymer Science and Technology*, Czekaj, C. (ed.), Wiley Interscience, 3rd edn (2001).

Handbook of Fiber Chemistry, edited by Lewin, Menachem and Pearce, Eli M., International Fiber Science and Technology Series, #15.

12.6   References

1. Swatloski, R.P., Spear, S.K., Holbrey, J.D. and Rogers, R.D., *J. Am. Chem. Soc.*, *124*, 4974, 2002.
2. Scherer, P.C., *J. Am. Chem. Soc.*, 53, 4009, 1931.
3. Cuculo, J.A. and Hudson, S.M., US Patent 4,367,191, 1983.
4. Hudson, S.M. and Cuculo, J.A., *J. Polym. Sci. Polym. Chem. Ed.*, 18, 3469, 1980.
5. Cuculo, J.A., Smith, B., Sangwatanaroj, U., Stejskal, E.O. and Sankar, S.S., *J. Poly. Sci., Part A – Poly. Chem. Ed.*, 32, 241, 1994.
6. Cuculo, J.A., Smith, B., Sangwatanaroj, U., Stejskal, E.O. and Sankar, S.S., *J. Poly. Sci., Part A – Poly. Chem. Ed.*, 32, 229, 1994.
7. DeGroot, A.W., Guinnup, D.E., Theil, M.H. and Cuculo, J.A., *J. Polym. Sci., Polym. Phys. Ed.*, 29, 557–563, 1991.
8. Hudson, S.M. and Cuculo, J.A., *J. Polym. Sci., Polym. Chem. Ed.*, 20, 499, 1982.
9. Cuculo, J.A., Frey, M.W. and Khan, S.A., *J. Polym. Sci., Part B: Polym. Phys. Ed.*, 34, 2060, 1996.
10. Frey, M., Cuculo, J.A. and Spontak, R., *J. Polym. Sci., Part B: Polym. Phys. Ed.*, 34, 2049–2058, 1996.
11. Yang, K.-S., Cuculo, J.A. and Theil, M.H., *J. Polym. Sci., Part B: Polym. Phys*, 30, 315–324, 1992.
12. Frey, M.W., PhD Dissertation, Fiber and Polymer Sciences, North Carolina State University, Raleigh, NC, 1995.
13. Baird, D.G. and Ballman, R.L., *J. Rheol.*, 23(4), 505–524, 1979.
14. Cross, M.M., *J. Coll. Sci.*, 20, 417, 1965.
15. O'Brien, J.P., US Patent 4,501,886, 1985.
16. Navard, P. and Haudin, J.-M., *Br. Polym. J.*, 12(4), 174, 1980.
17. Chanzy, H., Peguy, A., Chaunis, S. and Monzie, P., *J. Polym. Sci., Polym. Phys. Ed.*, 18, 1137, 1980.
18. Liu, C.-K., Cuculo, J.A. and Smith, C.B., *J. Polym. Sci., Part B: Polym. Phys.*, 28, 449–465, 1990.
19. O'Brien, J.P., US Patent 4,464,323, 1984.
20. Kwolek, S.L., US Patent 3,671,542, 1972.
21. 'Chitin and Chitosan', Jenkins, D. and Hudson, S.M., in *Polymer Encyclopedia of Polymer Science and Technology*, Czekaj, C. (ed.), Wiley Interscience, 3rd edn, 2001.
22. Von Weimarn, P.P., *Can. Chem. Metall.*, 10, 227–228, 1926.
23. Austin, P.R., US Patent 3,892,731 1975.
24. Rathke, T.D. and Hudson, S.M., *Rev. Macromol. Chem. Phys.*, C34(3), 375–437, 1994.
25. Kunike, G., 'Chitin und Chitinseide', *Kunstseide (Chemiefasern)*, 8, 182–183, 1926.
26. Mitsubishi Rayon Co. Ltd, Japanese Patent 81,106,901, 1981.
27. Tokura, S., Nishi, N. and Noguchi, J., *Sen-I Gakkaishi*, 43, 288, 1987.
28. Tamura, H., Takeyuki, H., Yukihiko, T., Katsunori, Y., Haruko, K. and Tokura, S., Advances in Chitin Science, 5, 111–114, 2002.
29. Tamura, H., Tsuruta, Y., Itoyama, K., Worakitkanchanakul, W., Rujiravanit, R. and Tokura, S., *Carbohydr. Polyms.*, 56, 205–211, 2004.
30. Tamura, H., Tsuruta, Y. and Tokura, S., *Materials Science and Engineering C 20. Biomemetic and Supramolecular Sys.*, 20, 143–147, Spec. Iss., 2002.
31. Hirano, S., Nagamura, K., Zhang, M., Kim, S.K., Chung, B.G., Yoshikawa, M. and Midorikawa, T., *Carbohydr Polym*, 38, 293–298, 1999.

32. Hirano, S., *Macromol. Symp.*, 168, 21–30, 2001.
33. Hirano, S. and Midorikawa, T., *Biomaterials*, 19, 293–297, 1998.
34. Hirano, S., Zhang, M., Chung, B.G. and Kim, S.K., *Carbohydr. Polym.*, 41, 175–179, 2000.
35. Wei, Y.C., Hudson, S.M., Mayer, J.M. and Kaplan, D.L., *J. Polym. Sci., Polym. Chem. Ed.*, 30, 2187–2193, 1992.
36. Ziabicki, A., *Fundamentals of Fiber Formation*, Wiley: London, 1976.
37. East, G.C. and Qin, Y., *J. Appl. Polym. Sci.*, 50, 1773–1779, 1993.
38. Knaul, J.Z., Hooper, M., Chanyi, C. and Creber, K.A.M., *J. Appl. Polym. Sci.*, 69, 1435–1444, 1998.
39. Knaul, J.Z., Hudson, S.M. and Creber, K.A., *J. Appl. Polym. Sci.*, 72, 1721–1732, 1999.
40. Knaul, J.Z., Hudson, S.M. and Creber, K.A.M., *J. Appl. Polym. Sci., Part B: Poly. Phys.*, 37, 1079–1094, 1999.
41. Lee, S.H., Park, S.Y. and Choi, J.H., *J. Appl. Polym. Sci.*, 92, 2054–2062, 2004.
42. Lim, S.H. and Hudson, S.M., *J. Macromol Sci, Part C, Polym. Rev.*, C43, 2, 223–269, 2003.
43. Nara, K.K., Yamaguchi, Y. and Tanae, H., US Patent 4,651,725, 1987.
44. Sagar, B., Hamlyn, P. and Waler, D., European Patent 460,774, 1991.
45. Hirano, S., Min, Z. and Masuo, N., *Journal of Biomedical Materials Research*, 56 (4), 556–561, 2001.
46. Nakajima, M., Atsumi, K., Kifune, K. and Zikakis, J.P. ed., *Chitin, Chitosan and Related Enzymes*, Harcourt Brace Janovich, New York, 407, 1984.
47. Iwasaki, N., Yamane, S.T., Majima, T., Kasahara, Y., Minami, A., Harada, K., Nonaka, S., Maekawa, N., Tamura, H., Tokura, S., Shiono, M., Monde, K. and Nishimura, S.I., *Biomacromol*, 5, 828–833, 2004.
48. Tuzlakoglu, K., Alves, C.M., Mano, J.F. and Reis, R., *Macromol. Biosci.*, 4, 811–819, 2004.
49. Liu, X.D., Nishi, N., Tokura, S. and Sakari, N., *Carbohydr. Polym.*, 44, 233–238, 2001.
50. Hiroshi, S., Shoji, A., Itoh, Y., Kawamura, M. and Sakagami, Y., 'Antimicrobial Fiber Blended with Chitosan', Karnicki, Z.S., Brzeski, M., Bykowski, P.J. and Wojtasz-Pajak, A., (eds), *Chitin World*, 1994.
51. www.crabyon.it/
52. Hirano, S. and Hayashi, H., *Carbohydr. Polym.*, 54, 131–136, 2003.
53. Hattori, K., Cuculo, J.A. and Hudson, S.M., *J. Polym. Sci., Chem. Ed.*, 40, 601–611, 2002.
54. Hattori, K. and Cuculo, J.A., US Patent Application Serial No. 10/283,505.
55. Hattori, K., Abe, E., Yoshida, T. and Cuculo, J.A., *Polymer Journal*, 36, 123–130, 2004.
56. Frey, M.W., Joo, Y.L. and Kim, C.-W., *New Solvents for Cellulose Electrospinning and Preliminary Nanofiber Spinning Results*, ACS National Meeting, New York City, September, 2003.
57. Chan, H., Carranko, K. and Frey, M.W., *J. Polym. Sci., Part B: Polym. Phys. submitted* 9/2004.
58. Hirano, S. and Usutani, A., *International Journal of Biological Macromolecules*, 20, 245–249, 1997.
59. Hirano, S., Usutani, A., Yoshikawa, M. and Midorikawa, T., *Carbohydr. Polym.*, 37, 311–313, 1998.

60. Hirano, S. and Moriyasu, T., *Carbohydr. Polym.*, 55, 245–248, 2004.
61. Hirano, S., Zhang, M., Nakagawa, M. and Miyata, T., *Biomaterials*, 21, 997–1003, 2000.
62. Hirano, S., Nakahira, T., Nakagawa, M. and Kim, S.K., *Journal of Biotechnology*, 70, 373–377, 1999.
63. Hirano, S., Nakahira, T., Zhang, M., Nakagawa, M., Yoshikawa, M. and Midorikaw, T., *Carbohydr. Polym.*, 47, 121–124, 2002.
64. Nam, C.W., Kim, Y.H. and Ko, S.W., *J. Appl. Polym. Sci.*, 74, 2258–2265, 1999.
65. Nam, C.W., Kim, Y.H. and Ko, S.W., *J. Appl. Polym. Sci.*, 82, 1620–1629, 2001.
66. Sun, S., Wong, W., Yao, K. and Mark, A.F., *J. Appl. Polym. Sci.*, 76, 542–551, 2000.
67. Nousiainen, P., Vehvilainen, M., Struszczyk, H. and Makinen, E., *J. Appl. Polym. Sci.*, 76, 1725–1730, 2000.
68. Zheng, H., Du, Y., Yu, J., Huang, R. and Zhang, L., *J. Appl. Polym. Sci.*, 80, 2558–2565, 2001.
69. Li, Z., Liu, X., Zhuang, X., Guan, Y. and Yao, K., *J. Appl. Polym. Sci.*, 84, 2049–2059, 2002.