Cellulose Solubility, Gelation, and Absorbency Compared with Designed Synthetic Polymers

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Contents

Abstract

Swelling and solubility of polymers, and in particular cellulose, are controlled by interactions, molecular symmetry, chain flexibility, and order/disorder. Theory is used to explain and predict which liquid systems, polymer structures, and chemical modifications form gels and polymer solutions. Extension of these principles leads to super-absorbent polymers. Cellulose is not water soluble, though some water systems can dissolve cellulose, particularly alkaline or strongly hydrogen-bonding solutions. Less hydrophilic derivatives such as methyl cellulose dissolve in water; while with increasing substitution with methyl groups, cellulose becomes soluble in organic solvents such as dichloromethane. Sometimes temperature can enhance solubility or gelation; alternatively adjusting chemistry through functional group modification to reach an optimum between

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intermolecular versus solvation interactions will create exceptional changes in absorbency. The solvation power can be increased by adding strongly ionic, hydrogen bonding or acid–base solutes such as lithium chloride, urea, or sodium hydroxide. Synthetic polymers have been designed and commercialized with specific solubility, solution rheology, gelation, and absorbency for many applications. Synthetic water-absorptive polymers begin with the choice of monomer(s), molar mass, and chain architecture. Cellulose is separated with exact structure that can be derivatized, grafted, or modified to change its native resistance to super-absorbency, gelation, or dissolving in water. Molecular modeling and simulation are used to evaluate parameters that will describe super-absorbent character. This review explores and evaluates the chemistry and structural symmetry of celluloses and synthetic polymers, leading to solubility, and gelation leading to super-absorbency. Cellulose is emphasized and compared with synthetic polymers where chemistries are designed and created at all levels of structure.

Keywords

Cellulose · Solubility · Absorbent · Gel · Super-hydrophilic · Super-absorbent · Solubility parameter · Interaction parameter · Critical solution temperature

1 Introduction

Super-absorbent polymers must have strong affinity for a solvent or swelling liquid, typically water. The affinity for the liquid must exceed the polymer–polymer affinity. The polymer likely to contain functional groups that interact with the liquid, and they will interact similarly with the polymer either intermolecularly or intramolecularly. A tetramer segment of cellulose is shown in Fig. 1 as a stereo-structure and as a molecular model with charge density surface superimposed and a molecular model with hydrogen bonding highlighted. The latter model illustrates that the surface of cellulose is abundant in hydrogen bond donors and receptors for interaction with other cellulose molecules in crystals and with absorbed water. Intermolecular polymer interactions create parallel sheet-like structures such as found in native (type I) and textile cellulose (type II) [1]. Intramolecular polymer interactions form helical structures, such as exhibited by starch and some proteins. Introduction of chemical irregularities into a structure can limit polymer–polymer interactions and favor interactions with a swelling or dissolving liquid. A divide between dissolving and swelling can be made by crosslinking the polymer, whereby solvent can be absorbed until chains and crosslinks become saturated and at thermodynamic equilibrium. An equilibrium swollen polymer or gel is formed when the solvation force is equal to the force for formation of polymer random coils.

Super-absorbent polymers are exceedingly hydrophilic polymers, which form molecular networks that allow exceptional swelling but prevent dissolving. They may be able to absorb 1000 times their mass of water. Natural substances such as carbohydrates, proteins, and their derivatives feature in this class of material because

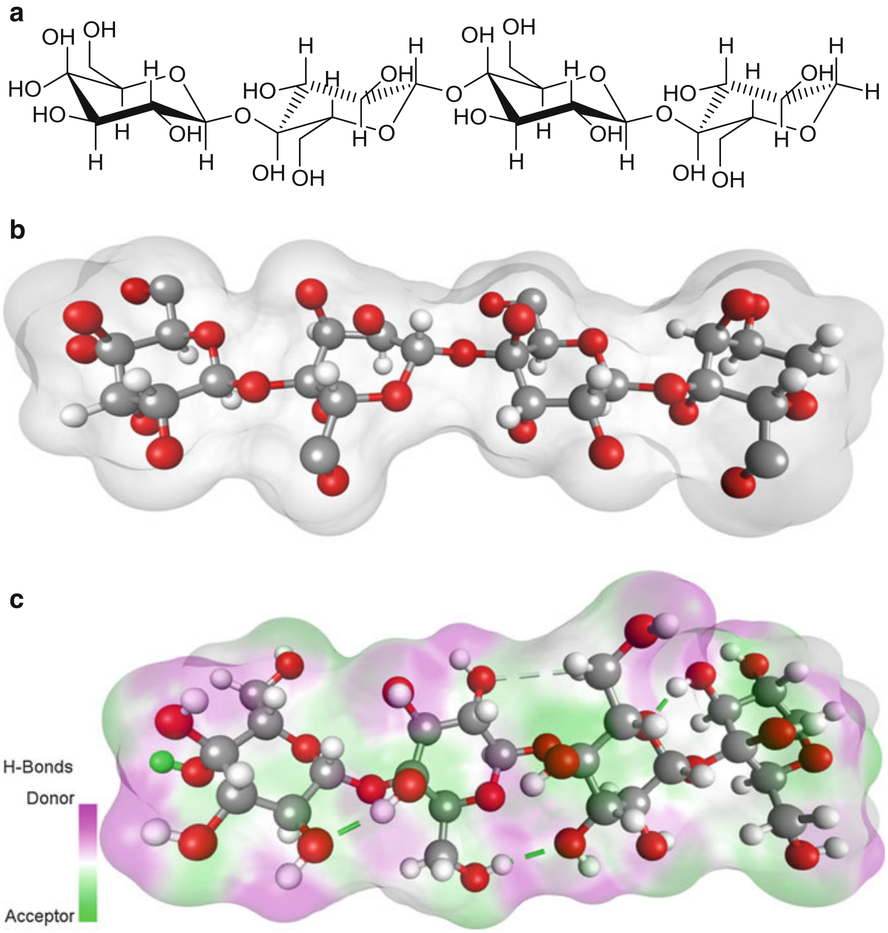
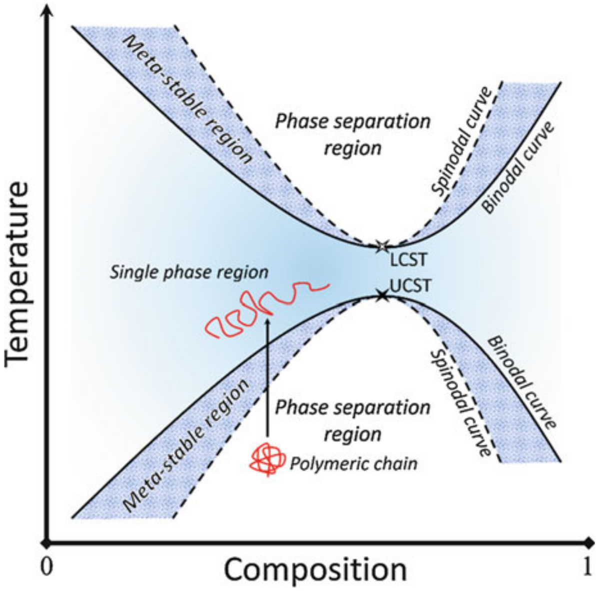


Fig. 1 Molecular structure of cellulose chain segments: (**a**) structure drawing, (**b**) molecular model with total charge density surface, (**c**) molecular model with hydrogen bonding highlighted

most natural species have high water content; water is a necessity for life. There are many synthetic super-hydrophilic polymers that may be based on bio-systems (biomimetic) or principles derived from biomaterials. Solvation principles based on ionic, dipolar, or hydrogen-bonded interactions have been established as an integral part of molecular science. When macromolecules are involved, conformation, packing of chain segments, chain branching, crosslinks, and hydrodynamic volume are additional concepts for solvation. Thermodynamics and kinetics are important for absorption capacity, while absorption rate, desorption rate or hysteresis, gel strength, wicking mechanisms, pH, and ionic sensitivity are additional characteristics. Synthesis and evaluation factors, classified as internal and external factors, of natural and synthetic super-absorbent polymers have been reviewed by Zohuriaan-Mehr and Kabiri [2].

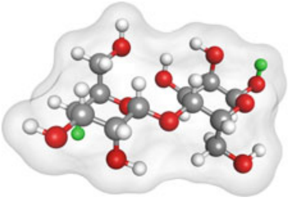
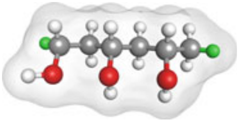
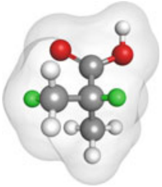
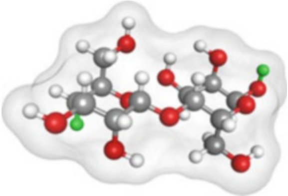
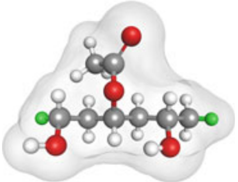
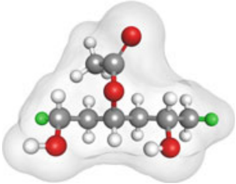
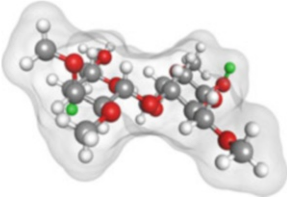
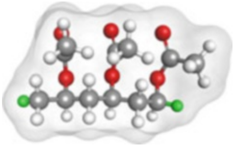
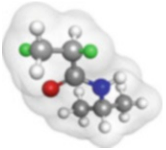
Fig. 2 Schematics of LCST and UCST phase diagram for polymer solutions and blends, showing changes in polymer conformation in one- and two-phase regions



The forces between polymer–polymer, polymer–liquid, and liquid–liquid will all be diminished by increase of thermal energy, or more specifically temperature. Those interactions that decrease most with temperature will determine the nature of the gel or solution. If polymer–polymer interactions decrease most, solvation will increase with temperature, and a lower critical solution temperature (LCST) phase diagram will result (Fig. 2). Solvation and gel formation will increase with temperature. If polymer–liquid interactions decrease most, solvation will be decreased, and polymer solvation and gel formation will reverse upon heating, resulting in an upper critical solution temperature (UCST) phase diagram (Fig. 2). The phase diagram usually shows two boundaries between the separated (two-phase) and solution (one-phase) regions, a coexistence curve (bimodal) for equilibrium phase separation and a stability curve (spinodal) for spontaneous phase separation. The LCST and UCST are the critical points for maximum or minimum temperatures at critical concentrations. Some phase diagrams can combine LCST and UCST behavior when there is an intermediate temperature range within which solubility is favorable.

Other than by thermal changes, polymer–polymer interactions are reduced by decreasing interactive functional groups and/or chain symmetry/regularity. Cellulose is insoluble in water, but monomethyl cellulose is soluble in water and used as a thickening agent, structures shown in Table 1. Replacing some hydroxyl groups with non-hydrogen-bonding methoxy groups reduces inter-cellulose interactions more than it reduced interactions with water, thus allowing water solubility. A synthetic polymer example is poly(vinyl alcohol) (PVAlc). PVAlc is prepared from poly(vinyl acetate) (PVAc), since its virtual monomer, vinyl alcohol, is not stable. PVAc is then hydrolyzed to convert acetate groups to hydroxyl groups. When completely

Table 1 Structures for water-absorptive and water-soluble polymers

Celluloses (monomers)	Poly(vinyl alcohol)	Poly((meth)acrylic)s
 Cellulose	 Poly(vinyl alcohol)	 Poly(methacrylic acid)
 Methyl cellulose	 Poly(vinyl alcohol-co-acetate)	 Poly(hydroxyethyl methacrylate)
 Trimethyl cellulose	 Poly(vinyl acetate)	 Poly(isopropylacrylamide)

hydrolyzed, the pure PVAlc is insoluble because it crystallizes due to symmetry and strong intermolecular hydrogen bonding. When partially hydrolyzed and about 87% hydrolysis seems to be an optimum, with 13% acetate groups remaining, water solubility is optimized. Returning to methyl cellulose, when completed methylated to give trimethyl cellulose, it is water insoluble, but it can be dissolved in polar organic solvents such as dichloromethane. Poly(hydroxyethyl methacrylate) (HEMA) and poly(*N*-isopropylacrylamide) (NIPAM) are much studied polymers with complex interactions with water forming interesting gels, solutions, and phase diagrams.

Another way to increase solubility of polymers is to increase the solvent power. Adding a strong hydrogen-bonding agent to water increased it solvent power. Water–urea mixtures can dissolve cellulose. Acid–base reaction can for salts that are more water soluble so that cellulose is soluble in sodium hydroxide solution. Salt that forms ions in solution increases the solvent power of water, such as lithium chloride solutions that are stronger solvents for highly polar polymers. Sodium chloride and calcium chloride are confirmed to modify water absorption to tapioca starch and contribute anti-plasticization by competing for water with the starch [3].

The consideration of solvation discussed above is about interactions or enthalpy as quantified with solubility parameters, or cohesive energy density, which in a particular polymer–liquid system are equated to the interaction parameter. Entropy is the other thermodynamic parameter that determines solubility or swelling. A swollen or solution polymer becomes less ordered than in the solid and thus gains entropy. The liquid or solvent is even more controlled by entropy because many small liquid molecules that are randomized in the liquid phase lose randomness when they are absorbed into a polymer gel or solvating a polymer in solution. The entropy and interaction parameter concepts are typified by the Flory–Huggins equation (Eq. 1) and the thermodynamic equation defining free energy from enthalpy and entropy (Eq. 2):

$$\frac{\Delta G}{RT} = \frac{\theta_p}{n_p} ln\theta_p + \frac{\theta_s}{n_s} ln\theta_s + \chi\theta_p\theta_s \tag{1}$$

$$\Delta Gm = \Delta Hm - T\Delta Sm \tag{2}$$

where ΔG is the free energy change that must be negative for a spontaneous process such as solubility, χ is the interaction parameter that is a measure on secondary bonding and favors solubility when negative, θ is the volume fraction and n the number of moles of polymer (p) and solvent (s), T is temperature, and R is the gas constant. The entropy (ΔS) is determined by mole fraction and molar volume, the two logarithmic terms in the Flory–Huggins equation. The enthalpy (ΔH) term is a function of interaction parameter and mole fractions of polymer and solvent, the last term in the Flory–Huggins equation. The Flory–Huggins equation is an expanded version of Eq. 2.

This review aims to expand upon these introductory concepts by exploring polymer interactions, solutions, and gels, with emphasis of cellulose and the structures and interactions that lead beyond to super-absorbency. Objectives are to evaluate structure interaction character of synthetic polymers that have been researched or commercialized as super-absorbent materials or solution viscosity modifiers, illustrated in Fig. 3. Molecular modeling and simulation will be applied to evaluate structural, kinetic, and thermodynamic parameters that will typify polymer properties leading to super-absorbent characteristics.

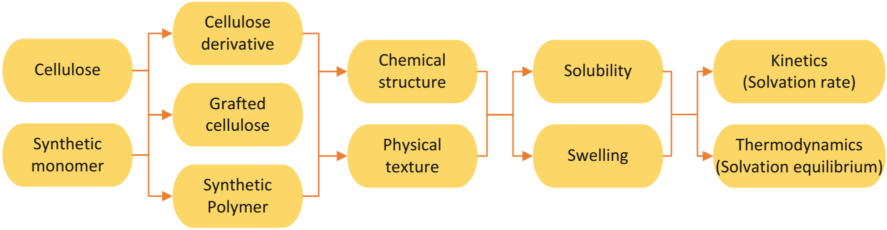


Fig. 3 Review outline, concept, and structure

2 Absorbency, Solubility, and Gelation

Polar polymers absorb and approach equilibrium with atmospheric moisture, that is, humidity. Cellulose and starch typically contain 8–10% water at average humidity of about 50%·RH. Polyamide 6,6 averages 1–2% moisture, and in fiber or thin films, it equilibrates rapidly. The water in polar polymers is a plasticizer. Cellulose fibers become brittle when dried so part of their properties when used as reinforcement in another matrix polymer depends upon their water content, so drying the fibers prior to processing deteriorates composite properties. Starch films are brittle even with equilibrium water content, so they require additional plasticizers such as glycerol, alkyl polyols, poly(vinyl alcohol), and related water-soluble polymers. Water absorption can be increased by destructuring native cellulose and starch with treatments that separate molecules from other components of the natural materials and crystal melting. Melting of these biopolymers means disrupting crystal structure to give an amorphous material, rather than melting in the sense of creating a flowable liquid.

Water absorption causes swelling of polymers in the first instance. Swelling proceeds until polymer–polymer interactions resist further separation of the polymer segments. An extreme of polymer–polymer interactions is chemical bonds or crosslinking where swelling is restricted by the crosslink density. Thermodynamically there are polymer–solvent (water) forces causing absorption, swelling, and potentially dissolving, counteracted by polymer–polymer forces and solvent–solvent forces, combined with loss of entropy or degrees of freedom by the solvating solvent molecules. Poly(2-hydroxyethyl methacrylate) swells to about 36%·w/w of water to form a equilibrium gel that does not proceed further toward dissolving.

Diffusion of liquids and gases through or into polymers displays the same phenomena, though diffusion is typically considered as transport through polymers. Diffusion is the product of solubility and permeability. The diffusing liquid or gas must be soluble in the polymer; this means that the liquid or gas dissolves in the solid to give a solid solution. Additionally, permeability is the transport of liquid or gas across the polymer due to a concentration gradient. Transport through a polymer must be through amorphous regions because any crystalline structures are regular and close-packed, without spaces for foreign molecules. Amorphous regions contain free volume that increases with temperature and expands rapidly at the glass transition temperature (Tg). Permeating molecules must pass through a tortuous path that forms by linking of free volumes. Above Tg rapid segmental motions create rapidly changing free volume array allowing diffusing molecules to move as free volumes open along their path. Below Tg segmental motions are restricted by lack of activation energy, and free volumes become static, preventing diffusing molecules from finding new free volumes for movement. The concentration gradient restricts reverse motion, so the molecules are forced onward. Permeability combined with solubility gives diffusion.

When the polymer–solvent interactions dominate, swelling continues until polymer molecules break from the swollen gel and disperse into a true solution. The separated dissolved polymer molecules adopt a random coil conformation. In a poor solvent, the random coils will be relatively compact because polymer–solvent

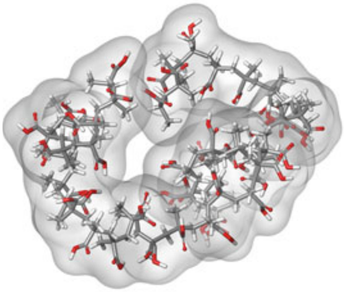
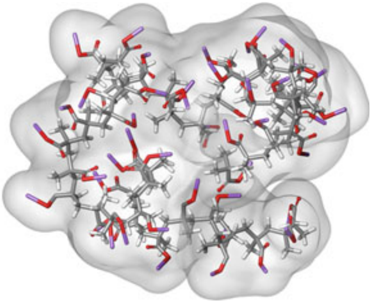
Poly(acrylic acid)		**Sodium poly(acrylate)**	
			
Connolly Surface		*Connolly Surface*	
Occupied Volume	4279.11 Å^3	Occupied Volume:	5539.94 Å^3
Free Volume:	2157.26 Å^3	Free Volume:	2539.02 Å^3
Surface Area:	1861.88 Å^2	Surface Area:	2179.34 Å^2
Smoothed Solvent Surface		*Smoothed Solvent Surface*	
Occupied Volume:	5760.08 Å^3	Occupied Volume:	7333.26 Å^3
Free Volume:	676.29 Å^3	Free Volume:	745.71 Å^3
Surface Area:	1096.56 Å^2	Surface Area:	1354.94 Å^2
Smoothed Accessible Solvent Surface		*Smoothed Accessible Solvent Surface*	
Occupied Volume:	5760.32 Å^3	Occupied Volume:	7334.42 Å^3
Free Volume:	676.06 Å^3	Free Volume:	744.54 Å^3
Surface Area:	1094.84 Å^2	Surface Area:	1345.50 Å^2

Fig. 4 Random coil comparison of poly(acrylic acid) and sodium polyacrylate

interactions are just sufficient to dissolve the polymer. In a good solvent, the random coils in solution are increasingly expanded. If the polymer chains contain charged groups such as carboxylate anions, repulsions between the charges expand and elongate the random coils. Figure 4 illustrates expansion of random coils by interactions or repulsions according to three different surface criteria calculations based on Connolly surface, smooth solvent surface, and smoothed accessible solvent surface. Sodium poly(acrylate) is shown to expand more than poly(acrylic acid). Poly(acrylic acid) can form intramolecular hydrogen bonds that contract the random coils, while sodium poly(acrylate) has carboxylate anions along the chain that repel and expand the random coils.

Stronger polymer–solvent interactions and more expanded random coils increase solution viscosity. The nature of the polymer is important since apart from the relative interactions, the size of random coils is dependent on molar mass. Branching contributes in that a branched polymer, compared with the same molar mass of linear polymer, will have more compact molecules and hence lower viscosity. An extreme of branching is hyperbranched or dendritic polymers, where the radius of the random coils does not increase as rapidly as the molar mass. With these latter polymers, solution viscosity can decrease with molar mass increase at high molar mass has a reverse effect because molar volume grows more slowly.

Rheology is shear rate-dependent viscosity. If the polymer random coils are separated in solution, they move independently, and viscosity increases linearly (Newtonian) with shear rate. If there are interactions between the random coils, then increasing shear rate is likely to disrupt the interactions, and the viscosity will decrease (shear thinning) with increasing shear rate. If the random coils become elongated at higher shear rates, then the elongated coils exhibit increased interactions thus increasing viscosity (shear thickening) with increasing shear rate. Time delay in returning to equilibrium slow shear rate or static viscosity may be experienced after shear thinning or shear thickening; these delays are thixotropy and rheopectic behaviors, respectively.

Gelation is a discontinuity in the rheology where the substance ceases to flow. There are several definitions depending on the context. With oscillatory rheological measurements performed with a sinusoidal shear frequency in the linear viscoelastic region, gelation is where the elastic response (G′) and the viscous response (G″) are equal. The curves of G′ and G″ cross at gelation because the elastic- or solid-like response becomes greater than the viscous- or liquid-like response. The crossover of the curves may occur with increasing frequency, a time-base response, or with decreasing temperature. Gelation in this context is a result of viscosity reaching a value where the substance is in practice a solid, due to intermolecular interactions. When a substance is undergoing a crosslinking reaction, then gelation is defined by the crosslinks as when crosslinked species extend across the system. Figure 5 illustrates the crossing of G′ and G″ curves that indicates a gel point. The curves

Maxwell model	**Four-element model (Maxwell-Voigt or Burgers)**
$G'(\omega) = G_0 \dfrac{\omega^2\lambda^2}{1 + \omega^2\lambda^2}$ $G''(\omega) = G_0 \dfrac{\omega\lambda}{1 + \omega^2\lambda^2}$	$G'(\omega) = G_2 + G_1 \dfrac{\omega^2{\lambda_1}^2}{1 + \omega^2{\lambda_1}^2}$ $G''(\omega) = G_2\lambda_2\omega + G_1 \dfrac{\omega\lambda_1}{1 + \omega^2{\lambda_1}^2}$

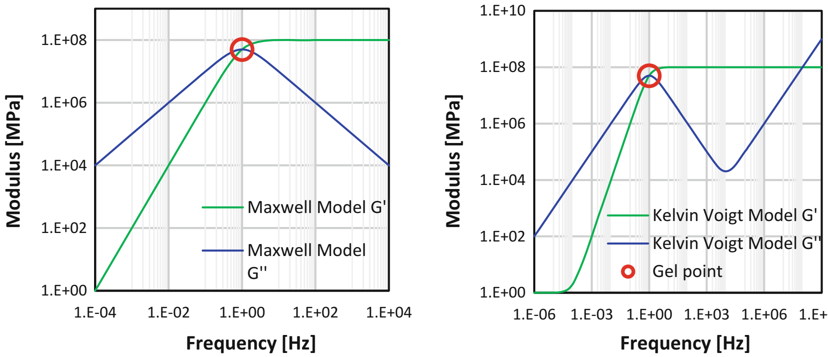


Fig. 5 Complex rheology shear rate curve showing G′, G″ and gel point

were calculated using the Maxwell model and four-element Maxwell–Voigt or Burghers model. A distinction between liquid and solid according to these theories is the relaxation time of the molecules relative to the rate of perturbation.

3 Solubility of Cellulose

Cellulose is not water soluble. As the structural material of plants, it has a configuration enhancing cellulose–cellulose interactions by hydrogen bonding to give two main crystalline forms: native or type I and textile or type II, though other forms are known. Starch has the same chemical structure but opposite configuration about the repeat unit links making it soluble as required for ready metabolism as an energy source. Starch has the linear structure, amylose, like cellulose but with inverted chirality links and a branched structure, amylopectin.

The importance of processing cellulose [4] has resulted in techniques for dissolving it so that regenerated fibers and films can be made. The first technique was complexation with alkaline tetra-ammonia-copper(II), and the cellulose is regenerated by precipitation in acid, such as dilute sulphuric acid. Another route is derivatization using alkaline carbon disulfide to form a soluble sodium xanthate derivative, and the cellulose is again regenerated by precipitation with dilute acid. Cellulose derivatives, crosslinking strategies, and their biodegradability have been reviewed [5], and their response to external physiological stimuli and biodegradability were considered with their use as scaffolding biomaterials, as tissue structures, and in regenerative medicine.

Direct dissolving of cellulose, though not in water, is available using ionic solvents, such as *N*-methyl morpholine *N*-oxide (NMMO). Precipitation of cellulose from NMMO is by extruding the solution into water; after separation of the cellulose, NMMO is recovered for reuse by evaporation of the water due to the high boiling temperature of NMMO. NMMO is used commercially to produce cellulose fibers called Lyocell and Tencel. Other ionic solvents, such as 1-butyl-3-methylimidazolium acetate, have been used to dissolve cellulose. NMMO and ionic solvents have been termed green solvents because they can be purified, dried by evaporating any water, and reused for a new cellulose solution process. Cellulose is regenerated from solution by precipitation into water [6].

Figure 6 shows interactions and phase diagrams for cellulose–water and cellulose–NMMO. The molecular structures reveal hydrogen bond donors and acceptors for the interactions, illustrating the intensity of hydrogen bonds between the species in each case. Calculation indicates a maximum in the free energy of mixing cellulose–water at various temperatures and the energy with molar composition. Cellulose–NMMO exhibits an unexpected minimum in the free energy of mixing with this calculation, which may be indicated by the lower intensity of donor–acceptor sites on the molecular model.

As described above, the configuration of cellulose enhances cellulose–cellulose hydrogen bonding and limits cellulose–water interactions enough to prevent dissolving. The hydroxyl groups on cellulose, particularly the 2-hydroxy, are more

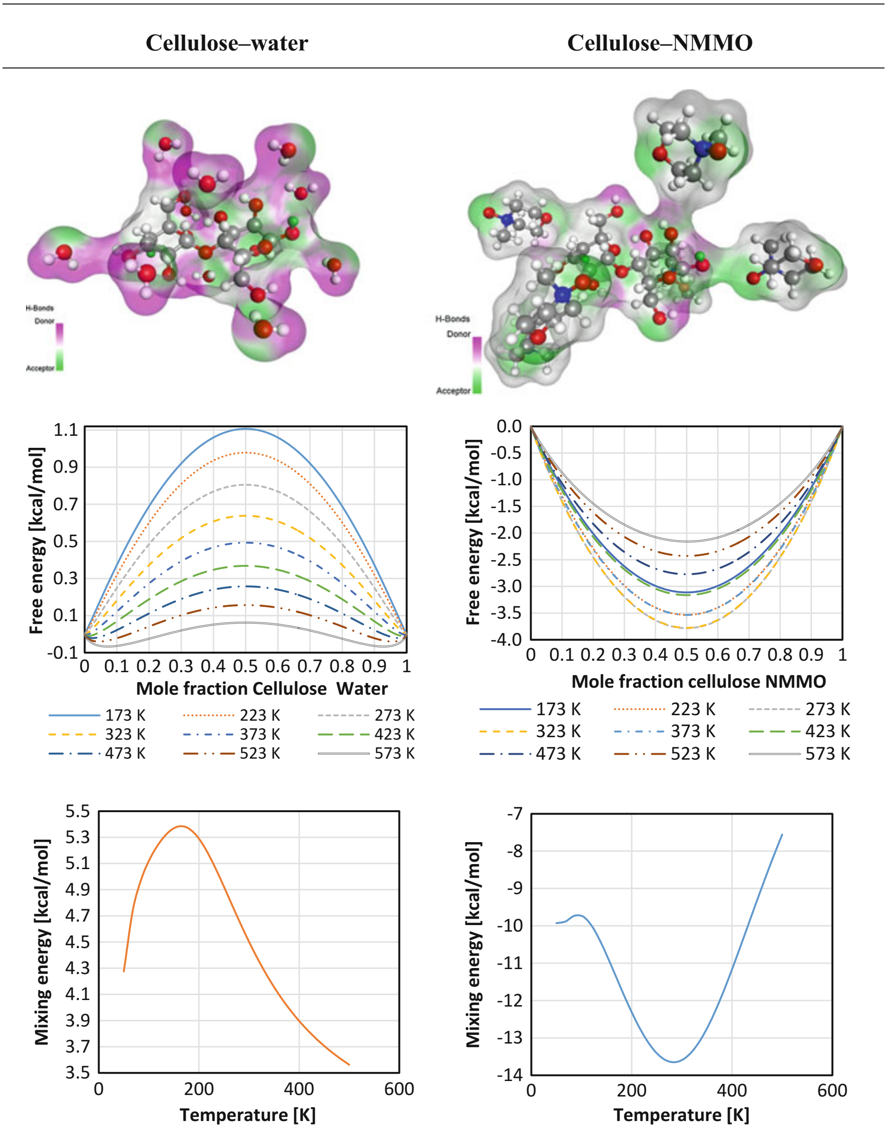


Fig. 6 Cellulose molecular models showing hydrogen-bonding donor and receptors with water (left) and NMMO (right), cellulose solubility predictions in water with UCST, and NMMO with LCST phase diagrams at temperature increments of 50 K from 173 to 573 K; lower curves show the respective mixing energies

acidic than the hydroxyl of a typical alcohol. In sodium hydroxide solution, some sodium salts of cellulose are formed. The sodium salts can accelerate nucleophilic reactions of cellulose, such as formation of methyl, hydroxylalkyl, or carboxymethyl derivatives (see later details of these reactions). The salts facilitate dissolving of cellulose. Since a lower critical solution temperature (LCST) is involved when dissolving cellulose in sodium hydroxide solution, a suspension of cellulose in sodium hydroxide solution must be cooled. The process involves freeze–thaw cycling, and with each cycle, a small increment of cellulose dissolves. Dissolving cellulose is enhanced with added urea, a strongly hydrogen-bonding agent. Sulphite pulp process-separated cellulose has been dissolved in sodium hydroxide and urea at a low temperature [7]. Hydrogels were prepared from cellulose using water with sodium hydroxide–urea and crosslinking with epichlorohydrin, dissolving the cellulose via heating and freezing cycles [8]. Hydrogels from heating showed macroporous inner structure, while fibrous structures were formed in hydrogels prepared from freezing. Transparency and equilibrium swelling decreased, while re-swelling increased, with cellulose content. Cellulose can be dissolved in aqueous sodium hydroxide–urea, sodium hydroxide–thiourea, and lithium hydroxide–urea at low temperatures and the solutions used to prepare cellulose-based functional materials, such as fibers, films, membranes, microspheres, hydrogels, and cellulose derivatives [9].

4 Super-Hydrophilic Synthetic Polymers

Water-soluble synthetic polymers can serve as a guide for solubility of cellulose and its derivatives. Poly(vinyl alcohol) (PVA) has many –OH group pendant from the chain backbone. The –OH groups can hydrogen bond with water facilitating solubility; however they can hydrogen bond with other PVA segments or molecules detracting from solubility. Pure PVA is semicrystalline due to its symmetric molecules and PVA–PVA hydrogen bonds. If there are some acetate groups remaining from PVA synthesis, then the acetate groups occurring randomly restrict crystallinity and decrease hydrogen bonding, making this type of PVA that has increased water solubility. This occurs with about 10–15% acetate groups. With more acetate groups, solubility decreases and pure poly(vinyl acetate) is completely insoluble in water. The PVA case is analogous to cellulose where –OH groups need to be derivatized to facilitate water solubility.

Poly(acrylic acid) (PAA) is water soluble because of its many –COOH groups that hydrogen bond with water. However, in alkaline (e.g., NaOH) solution, the carboxylate groups become ionized $–COO^{-}\ Na^{+}$, and the anions are more strongly interacted with water. The –COO- groups along the polymer chain repel resulting in uncoiling and hence elongation of the PAA chain, allowing more access for water molecule solvation and much increased viscosity. This is analogous to cellulose methylene carboxylate that is strongly water absorbing and readily water soluble and with high viscosity. Poly(methacrylic acid) (PMAA) is similar to PAA, except that the pendant methyl groups add some hydrophobicity and reduce chain flexibility. PMAA–water interactions are reduced upon heating more than PMAA–PMAA interactions, so heating does not increase solubility; on the contrary, cooling increases solubility. PMAA in water exhibits a LCST, though, while cooling increases solubility, it decreases the rate of solubility. Analogous to cellulose in

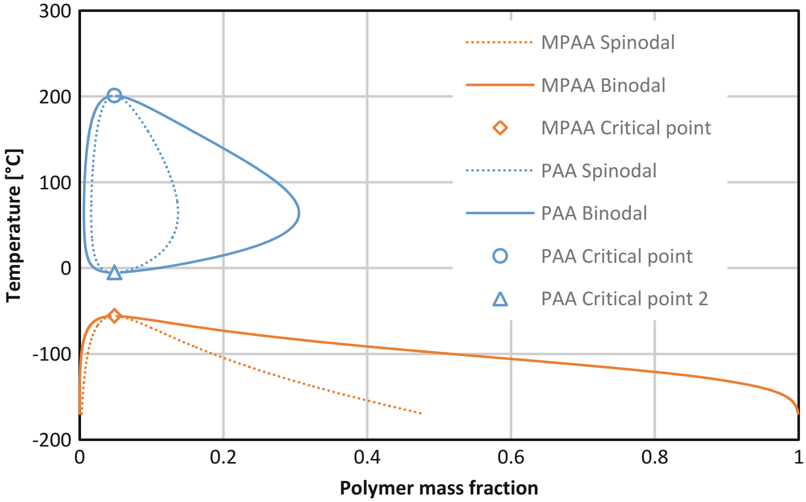


Fig. 7 Composition–temperature phase diagram for poly(acrylic acid) in water

alkaline solutions, PMAA in water is dissolved by freeze–thaw (cool–warm) cycles. A calculated concentration–temperature phase diagram is shown in Fig. 7 including LCST and UCST critical points and binodal and spinodal phase boundaries.

Polyacrylamide (PAM) is a water-soluble polymer or in crosslinked form is used as PAM gels for electrophoresis. PAM gels provide a fixed water phase that allows analyte molecules as large as proteins to migrate under an electrical field. PAM differs from PAA or PMAA in that the polar amide group responsible for solubility can be modified with N-alkyl groups. As the size of the alkyl groups increases, PAM polarity and hence solubility decrease. A critical alkyl group is *N*-isopropyl, *N*-isopropylacrylamide (NIPAM), that exhibits a LCST of 32 °C where the linear polymer becomes insoluble or crosslinked gels shrink considerably. Below LCST hydrogen bonding with water predominates and NIPAM becomes soluble. Concepts relating to NIPAM solubility with its enthalpy of interactions and entropy of movement of water molecules are applicable to cellulose alkyl derivatives.

Polyurethane elastomers are phase-separated materials where the continuous soft phase can be hydrophilic/hydrophobic, depending on structure such as a polyether or polysiloxanediol, and able to expand with water absorption. The urethane segments for a dispersed hard phase function as physical crosslinks and restrains soft phase expansion and hence ultimately solubility [10].

Surfactants display LCST, known as a cloud point. Surfactants are like many water-absorbing or water-dispersible polymers in that they are bipolar with hydrophilic and hydrophobic groups within their molecules. The hydrophobic molecular regions migrate to surfaces, and when all surfaces are saturated, at the critical micelle concentration, they form micelles. When thermal energy disrupts surfactant polar interactions with water, phase separation occurs, and the dispersion becomes cloudy. The cloud point reflects a lower critical solution temperature. Sensitivity of water–polymer interactions to temperature is an important characteristic of water-absorbing cellulose derivatives, especially as to whether LCST or UCST behavior exists. Enhancement or reversal of water absorbance with temperature can be part of the design of material and products to regulate water content relative to ambient temperatures.

5 Super-Hydrophilic Plants

Super-hydrophilic structures are characterized by their physical surfaces that are in some ways analogous to super-hydrophobic surfaces. Water absorption is facilitated by a low contact angle, typically $<10°$. A smooth surface can have increased hydrophilicity if water-absorbing substances are secreted by the plant. Another way is to have high surface porosity giving a larger area over which to absorb water. While convex surface features give high apparent contact angle as in the lotus effect, concave surface features give a low apparent contact angle. Water-absorbing protrusions such as hairs, aerial roots, or sponge-like features are more complex surfaces that increase water absorption rate or create permanent wetness [11]. Super-absorption plant surfaces enhance water and nutrient uptake. Examples are under-water plants and desert plants, the former taking advantage of the environment and the latter surviving in a hostile environment. This description of super-hydrophilic plants concentrates on the surface morphologies that enhance water absorption and retention, as opposed to the chemical structures that attract water.

6 Super-Hydrophilic Cellulose

Cellulose solubility in water is facilitated by reducing hydrogen-bonding groups. This may seem contrary to expectation; however alkylation, particularly methylation, reduces cellulose–cellulose hydrogen bonding, and the alkyl substituent reduces cellulose regularity and ability to pack into crystals. Monomethyl cellulose is water soluble, forming highly viscose solutions. It is used as a thickening agent in many water-based consumer products. Adding further methyl groups reduces hydrogen-bonding capacity further and prevents water solubility. Trimethyl cellulose becomes soluble in polar organic solvents such as dichloromethane. The water solubility of monomethyl cellulose provides a guide for other derivatives to give water solubility.

Reduction of cellulose chain regularity and hence cellulose–cellulose hydrogen bonding can be achieved by using hydrogen-bonding alkyl derivatives. Reaction with propane-1,2-oxide gives hydroxypropyl cellulose with substitution mainly on the more nucleophilic 2-hydroxy position. Hydroxyethyl cellulose can be prepared by reaction with ethylene oxide, though this reaction is less convenient because ethylene oxide is a gas. Structures for hydroxyethyl and hydroxypropyl cellulose are shown in Fig. 8. These cellulose derivatives, together with carboxymethyl cellulose form the basis of cellulose hydrogels, in conjunction with blends with synthetic

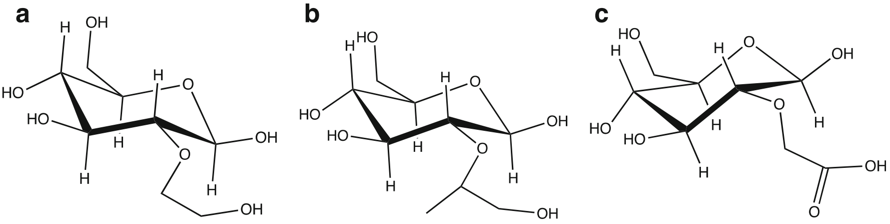


Fig. 8 Water-absorptive and water-soluble cellulose derivatives: (**a**) hydroxyethyl cellulose and (**b**) hydroxypropyl cellulose, (**c**) carboxymethyl cellulose

polymers and polyelectrolyte complexes. Cellulose–inorganic hybrid hydrogels are prepared by dispersing inorganic nanoparticles in a cellulose matrix [12].

Substitution with chloroacetic acid is a nucleophilic reaction that forms the acidic derivative carboxymethyl cellulose (CMC), structure shown in Fig. 8. CMC is soluble in water. In alkaline solution of sodium hydroxide, the sodium salt is formed. Sodium cellulose methylene carboxylate has a negative charge on each substitution. The negative charges reduced cellulose–cellulose interactions by mutual repulsions while increasing interactions with water. Sodium salts are known to be soluble in water, and CMC is no exception; however the repulsions between cellulose chains extend random coils imbibing more water and causing extremely high viscosity to the point of gelation.

Carboxymethyl cellulose has been crosslinked to cellulose using epichlorohydrin in a water solution containing sodium hydroxide and urea [13]. Urea is a hydrogen-bonding additive to assist dissolving cellulose in water, while sodium hydroxide is a base catalyst for the nucleophilic reaction with epichlorohydrin. CMC provided the water affinity and porosity, while cellulose provided structure and strength to the water-swollen gels. Swelling was dependent on CMC content, and swelling diminished with salt concentration in the water.

An extension of cellulose derivatization is formation of graft copolymers between cellulose and another synthetic polymer. With a grafted polymer, the substituent becomes a polymer rather than a single organic group. Grafting is classified as grafting to or grafting from depending on whether the initiating site is on cellulose or the monomer/polymer graft. An example of chain growth grafting from cellulose is the ring-opening reaction with caprolactone. Base catalysis creates an initiating alkoxide from a hydroxyl on cellulose, predominantly the more acidic 2-hydroxy. The alkoxide initiates a nucleophilic ring opening of caprolactone that proceeds with other caprolactone monomers. Radical initiation is induced by redox catalysts such as cerium and peroxide. An oxy-radical is formed that propagates polymerization of styrene, acrylonitrile, and (meth)acrylates including esters or carboxylic acids. The latter carboxylic acids lead to increased water absorbance, while other monomers increase water resistance of cellulose. Cellulose sourced from wheat straw has been grafted with acrylic acid or acrylamide using redox initiation in water with N,N′-methylenebisacrylamide as crosslinker, to obtain materials with up to 134%·w/w water absorbency and 44%·w/w water absorbency in 0.9%·w/w

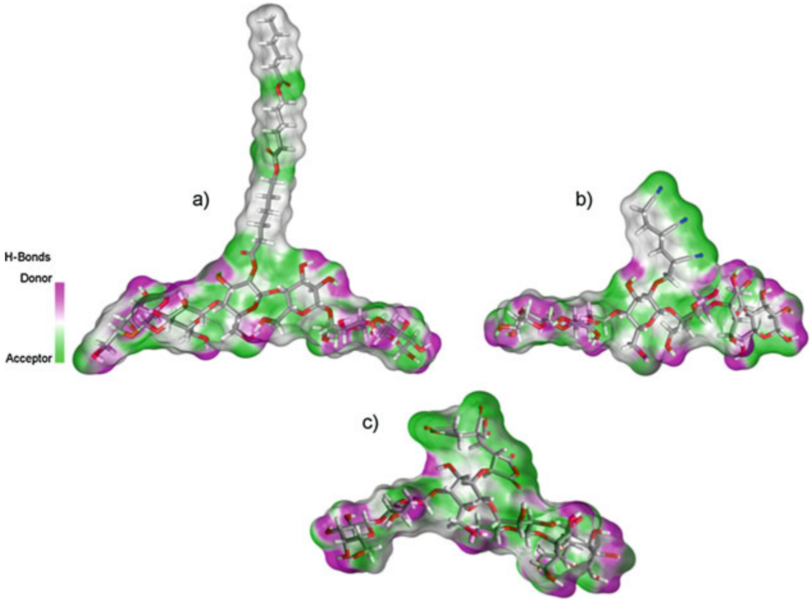


Fig. 9 Grafted cellulose structures with (**a**) caprolactone, (**b**) acrylonitrile, and (**c**) maleic anhydride

sodium chloride solution [14]. Nanocomposite hydrogels have been prepared from carboxymethyl cellulose grafted and crosslinked with methacrylic acid to enhance permeability and drug release. Composition was optimized for swelling and gel strength [15].

Step growth grafting from cellulose can proceed from esterification using maleic anhydride, succinic anhydride, or alkyl succinic anhydrides, linking with diols, glycerol, or formation of some crosslinks within/between cellulose. Cotton cellulose was grafted with succinic anhydride using 4-dimethylaminopyridine as catalyst in solution with lithium chloride and *N*-methyl-2-pyrrolidinone or tetra-butylammonium fluoride and dimethyl sulfoxide. The hydrogels absorbed 400 times by mass of water and functioned adequately in water containing sodium chloride, and they were biodegradable [16].

Figure 9 shows some molecular models of cellulose grafted with caprolactone, acrylonitrile [17], and maleic anhydride. The grafted species may form as compatibilizers for blended polymers or form dispersed phase morphologies within the starch; their resistance to separation is assured by the linking chemical grafts.

Grafting to cellulose can be via the epoxy reaction with cellulose hydroxyls. Typical epoxy resins can be used or copolymer containing epoxide such as poly (ethylene-*co*-glycidyl methacrylate). Another facile grafting to or from reaction is the urethane reaction. An isocyanate-terminated polymer can react with cellulose hydroxyl to form a linking urethane group. Hydroxyl groups undergo many reactions, and those of cellulose being more acidic than typical alcohol hydroxyls are able to participate with advantage in these reactions. A practical problem with

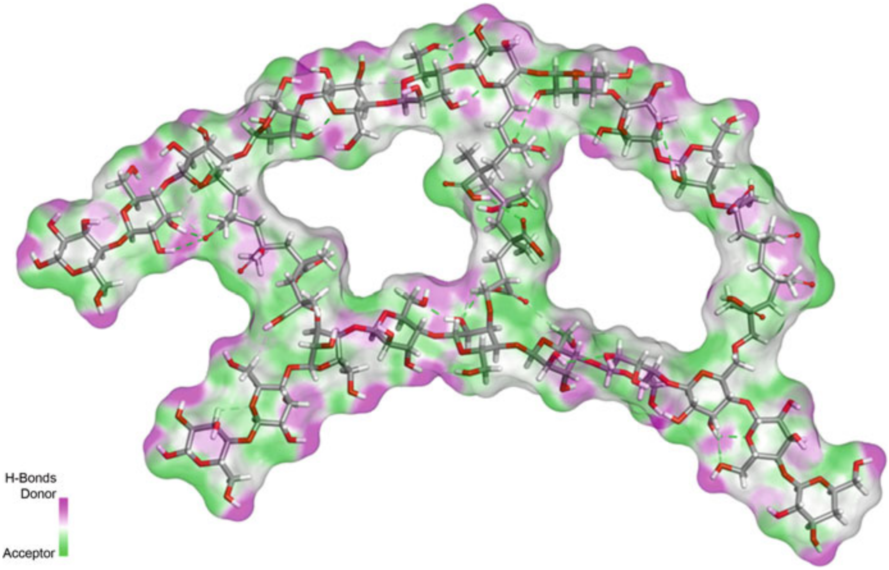


Fig. 10 Grafting and/or crosslinking via epoxy or urethane reactions

performing graft-to reactions is the mutual miscibility or solubility in a mutual solvent since reactions are inefficient when the two reactants are immiscible or incompatible. Some reactions can be performed via reactive extrusion, such as between cellulose dispersed in poly(ethylene-*co*-glycidyl methacrylate) or polypropylene-*graft*-maleic anhydride. Figure 10 shows some schematics of cellulose together with grafted species that may found intermingled or laminar supramolecular structures.

This comparison section is concluded with starch, another hydrophilic natural polymer. Starch differs from cellulose in two structural features. The main distinction is linking of glucose units via alpha-1,4-acetals in starch instead of beta-1,4-acetals in cellulose. This single change in stereochemistry is amplified by the repeating links that may typically be 3000 in cellulose. The alpha links form a helical structure instead of the planar structure that allows close stacking in cellulose. The alpha links create a dihedral bend at each link forming a coil over several links. Thus starch forms an open helical structure that can accommodate absorbed molecules within helices or between helices. Because of this stereochemical difference, starch is more water absorptive and soluble compared with cellulose. Starch with alpha-1,4- links is amylose, a linear molecule similar to cellulose. Another form of starch, amylopectin, contains a small proportion of 1,6-links, where each of these links forms a chain branch. Amylopectin has many branches in each of its very large molecules.

Figure 11 shows amylose and amylopectin chain segments that have partially coiled with energy minimization and molecular dynamics. The bond structure is surrounded by an electron density surface to portray the shape of the molecule. Both

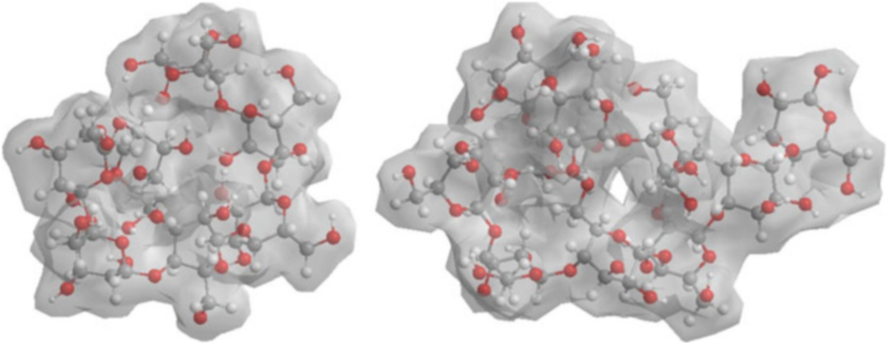


Fig. 11 Starch molecular model showing linear (left), branched (right), and coiling (both)

molecules show an initial inner channel formed by the helical molecules, which for longer chain segments can entrain other molecules such as iodine and stearic acid. Calculation of the electron density surfaces reveals capability as hydrogen bond donors or acceptors in amylose and amylopectin. The electron density surfaces illustrate the ability of starch to absorb and interact with water and other highly polar substances, such as glycerol. Starch interactions with hydrophilic plasticizers such as glycerol and xylitol, in conjunction with water, were shown to limit retrogradation and decrease the glass transition temperature [18]. An anti-plasticizer action was observed for each plasticizer over concentration ranges, which was due to plasticizer–water interactions replacing interactions of both with starch. Xanthan gum and other carbohydrates are strongly water absorptive and may dissolve in water to give highly viscous solutions. Crosslinked gums plasticized with sugars, glycerol, or glycols can be combined with starch to give flexible films with large elongation at break and high water content [19].

Chitosan is closely related to cellulose with the 2-hydroxyl on each glucose monomer unit replaced by an amino group. Chitosan-*g*-poly(acrylic acid)–montmorillonite has been prepared as a super-absorbent nanocomposite, with pH-dependent response [20].

Comparison with synthetic segmented polymers, and trends in behavior described in polymer science theory, is the observation and prediction that branched polymers tend to be less crystalline because branches are an irregularity that inhibits crystallinity and that branched polymers tend to be more soluble than linear polymers of the same chemical structure. Native starches reverse this concept because the branched amylopectin is crystalline while the linear amylose is amorphous. When added to water, it is the linear amylose that is more soluble than the branched amylopectin. Natural polymers or biopolymers and synthetic polymers are sourced or synthesized differently, yet all polymers must conform to the same structure–property relationships that have been established as the basis of polymer science. Fortunately, this chapter is about cellulose, so I can leave it to the reader to consider this contradiction between amylose, amylopectin, and other linear and branched polymers.

7 Comparison Polymers–Super-Absorbent Polymer (SAP) Gel Particles

Poly(hydroxymethyl acrylate) (HEMA) is a water-absorbing polymer used in soft contact lenses. Figure 12 shows polyHEMA segments with associated water molecules and a self-replicating cell containing several polyHEMA chains and absorbed water molecules. It forms a gel upon absorbing about 36%·w/w water; at this water concentration, it reaches equilibrium giving suitable softness, strength, and water content for oxygen transmission for comfort and eye health. From HEMA structure, it could be thought that it should be soluble in water; however water is absorbed, and the HEMA swells until the equilibrium water concentration when polymer–polymer interactions, hydrogen bonds, limit further swelling. Another factor in the equilibrium is the water–HEMA interactions, and the negative contribution of decreased water entropy as bound water has less degrees of freedom than free water. Another possibility is that there is some transesterification in HEMA leading to formation of some ethylene dimethacrylate and methacrylic acid, where the former is a tetrafunctional crosslinking monomer.

Crosslinked poly(acrylic acid) and polyacrylamide have structures where random sequences of the two monomers decrease regularity for polymer–polymer and more water came be absorbed without dissolving the polymer because it is slightly crosslinked. Crosslinking density must be lost to just prevent dissolving while allowing extensive swelling. This copolymer is a typical super-absorptive example that can absorb many times its own mass of water. Increasing pH to form carboxylate salts of the poly(acrylic acid) units further increases water absorption by increased water interactions and expanding the swelling by negative charge repulsions along the macromolecules.

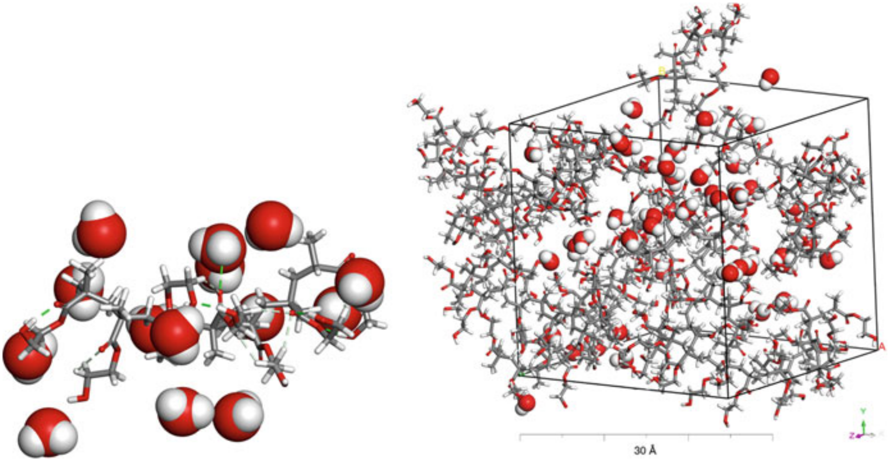


Fig. 12 Molecular model of hydrated poly(hydroxyethyl methacrylate), left, chain segments with absorbed water molecules showing hydrogen bonds; right, a cell containing multiple polyHEMA chains with absorbed water molecules

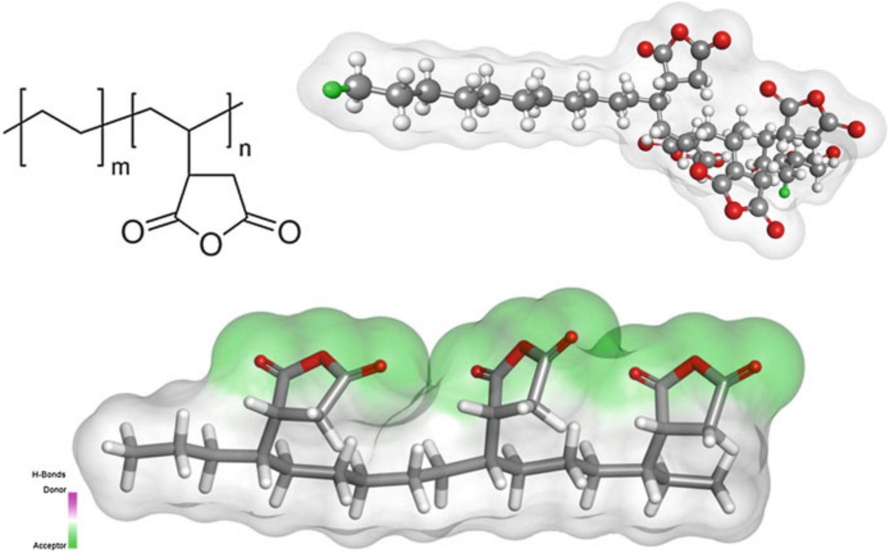


Fig. 13 Molecular structure and models of poly(ethylene-g-maleic anhydride) segment, top, structure and model; lower, model with hydrogen-bonding donors shown

Poly(ethylene-*co*-maleic anhydride) (Fig. 13) is contrasted to the former copolymer in that the ethylene units are hydrophobic while the maleic anhydride units, which are converted into two carboxylic acids when in water, have double carboxylic acid functionality. The reactivity of maleic anhydride, a 1,2-disubstituted alkene, is such that it will not homopolymerize, so each maleic anhydride chain unit will be preceded and followed by an ethylene. While the ethylene units are hydrophobic, they give weak polymer–polymer interactions and reduced regularity within polymer chains allowing random coils to readily swell with absorbed water clustered about the maleate units. When pH is increased and the maleate units, such as dicarboxylates, become salts, water is strongly attracted. This balance of water attraction and polymer–polymer repulsions from the anions and assisted by weak easily disrupted interactions from the ethylene hydrophobic groups is favorable for both sides of the equilibrium equation, resulting in a water super-absorptive polymer.

Sodium acrylic acid-vinyl alcohol copolymer has both monomers with polarity and hydrogen-bonding capacity. Hydrogen bonding within the copolymer chains should cause tight random coils. Water absorption and solubility are likely to occur with this copolymer. Crosslinking should be included to prevent solubility, using a small amount of a diacrylate ester. The pH can be increased to introduce carboxylate anions, again causing ionic repulsions within the polymer and expanding random coils while water will be strongly absorbed forming a super-absorptive gel.

Cationic polymers can be super-absorbents, as well as the more prevalent anionic polymers. Copolymerization of *N*,*N*-diallyl or *N*,*N*-dimethyl ammonium chloride with *N*-vinyl 2-pyrrolidone in the presence of *N*,*N*,*N*′,*N*′-tetraallyl piperazinium dichloride as crosslinker has been used to prepare cationic water absorbents with the cationic monomers being separated by N-vinyl 2-pyrrolidone units [21]. Typically, 0.5% crosslinking gave the highest swelling ratio of 360 times the mass of water when only the cationic monomer was present. Cationic quaternary ammonium polymers have an advantage of being antibacterial. As for anionic water absorbents, the cationic types are susceptible to ionic strength in absorbing water.

Cationic nano-fibrillated cellulose was prepared by etherification with quaternary ammonium compounds, and they exhibited broad-spectrum antimicrobial activity that was proportional to the extent of etherification. Cationized nano-fibrillated cellulose showed cytotoxicity with human cells, enabling the manufacture of safe, insoluble, and permanently antimicrobial materials by an aqueous synthesis [22].

The examples discussed of polyelectrolyte gels demonstrate the principles for achieving facile swelling with strong attraction and hence absorption of water. The anionic carboxylate gels can be extended to zwitterionic gels provided that regularity is disturbed so that positive and negative species do not associate but are open to hydrogen bonding with water, hence facilitating water absorption.

Combinations of natural polymers with synthetic polymer grafts have been discussed. To conclude this section, a further example of graft-polymerizing acrylamide (AM) onto potato starch is presented. Starch is not sufficiently water attractive or soluble to form a super-absorptive polymer alone. When acrylamide is grafted from starch and some bis-acrylamide monomer is added for crosslinking, then water absorption can be adjusted by composition to give water super-absorption; similarly with grafts of acrylic acid and methacrylic acid. These three monomers are water soluble so grafting can be performed in a water solution of starch and a monomer together with a redox initiator. Functional group reactions with isocyanate have been used to form starch–polyurethane grafted hybrids that decrease solubility of films prepared from the starch [23].

8 Kinetics and Equilibria

Water absorption with swelling occurs until there is a balance of free energy due to interactions between each of the components and entropy of the system. This is a thermodynamic equilibrium that is described by the Flory–Huggins equation (Eq. 1) through temperature, molar volumes, and the interaction parameter. Flory–Huggins is much cited because it presents a high-level, lattice-confined overview of the complex and diverse interactions between polymers and liquids. Atomistic molecular models use the Flory–Huggins concepts with constraint of a lattice and with a temperature-dependent interaction parameter based upon all interactions quantified by a validated force field. The equilibrium state of a hydrated polymer gel does not consider time, that is, the kinetics of absorption and desorption (Fig. 14).

Kinetics is the temperature-dependent rate of absorption of water; in addition to solubility is diffusion rate that is often described by the Fick Law. It is likely that the absorption rate will differ from the desorption rate giving a sorption hysteresis. It might be desirable to have rapid absorption of water so that a swollen gel would form

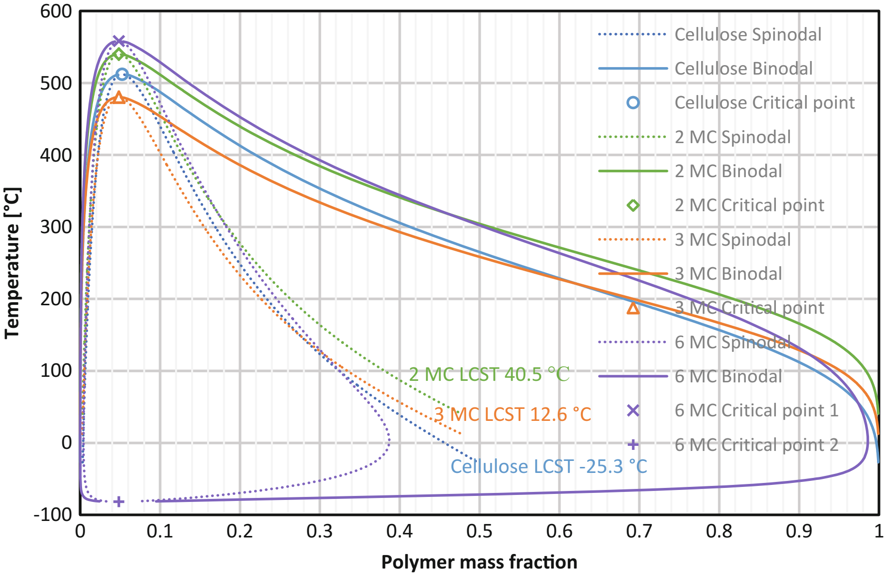


Fig. 14 Molecular model simulated temperature–composition phase diagram for polymer water

rapidly or if a product was designed to contain water spillages that rapid absorption would be preferred. Water-release processes of pre-wetted super-absorbent polymer particles can be slow, so that entrained water would be slowly released, such as over a week, while the water was being released to soil for plants to be grown under constant hydration.

Super-absorptive polymers solvate and bind with water strongly. Water desorption will be resisted both kinetically as observed as hysteresis and thermodynamically since the binding free energy must be overcome by more favorable state for the water. Desorption will be kinetically favored by a low concentration of water, dry conditions, external to the super-absorption polymer gel environment.

9 Applications

Slow release of water to soil for plant growth between watering cycles is important for agriculture and horticulture applications, as mentioned in the previous example. Super-hydrophilic polymers are used in agriculture for water retention on rocky slopes, eco-engineering, soil's water-holding capability, seed germination rate, plant survival, and soil erosion containment [24].

Medical and physiological applications are for wound dressing with included antibacterial agent, especially in the case of burns where an artificial skin is required, controlled release gels, and hot and cold therapy packs. Hydroxyethyl methyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose are used in eye drops, artificial tears, contact lens fluid, cosmetics, adhesives, and excipient/tableting ingredient. Polysaccharide nanoparticle gels for vaccine delivery and treatment of viral or bacterial infections have been described [25]. Tocopheryl acetate has been released from maize starch granules and structural properties; particularly free volume of the macromolecular network was related to release kinetics [26].

Super-absorptive polymers are coated onto or extruded into fibers, yarns, and textiles. These products are used for water blocking, filtration, hygiene, apparel, cable, and related products. Examples include Ultrabloc for dry blocking cables requiring water blocking for fiber optic cables, copper cables, and high-voltage energy cables. Ultrabloc is a spun super-absorbent polymer yarn with a polyester wrap. Another water-blocking and absorbing yarn is Swellcoat. Technical Absorbents manufacture a super-absorbent water-blocking yarn that can be incorporated into cables; it will rapidly absorb liquid from a damaged region and swell to form a gel, blocking any further water ingress. Technical Absorbents can be used for moisture management in garments to transport moisture away from the skin to the garment. Several fabrics for disposable and washable apparel are based on evaporative cooling and wicking. These fabrics create optimum conditions to increase wearer comfort next to the skin and over outer clothing. Star Materials supply fast water-absorbing and high tensile strength yarn, used in communication and optical, power, or marine cables for binding, tightening, and prevention of water penetration.

Swelling controlled by changes in environment, such as acid/base, electrical field, termed smart swelling, can be used for controllable delivery and food packaging. As thickeners and emulsifiers, methyl cellulose will set while hot and liquefy while cold; carboxymethyl cellulose, often as the sodium salt, is used in foods, paint and adhesives as a thickener, in ice-cream to prevent water–ice crystallization, and as an emulsion stabilizer for foods and toothpaste.

Fig. 15 shows the expansion of crosslinked super-absorbent polymers from particles to spheres to enlarged spheres. Expansion occurs until the extended chain segments between crosslinks reach equilibrium with the solvation force of the absorbing water. Pure water typically gives optimal expansion compared with water containing dissolved salts. The water may contain other substances such as nutrients for release to plants or pharmaceuticals for release to assist adjacent tissue healing.

These applications are selected examples since controlling the properties, storage, and delivery of water is a diverse field that includes many materials, with polymers and particularly super-absorptive polymers being substantial contributors.

10 Conclusions

Polymer regularity, polymer–polymer interactions, polymer–liquid interactions, and system entropy have been demonstrated to determine liquid absorbance and solubility. When a polymer is crosslinked, either through chemical bonds or physical interactions, then solubility is prevented, and water absorption is limited by the crosslink density. Super-hydrophilic polymers must be strongly water absorbing

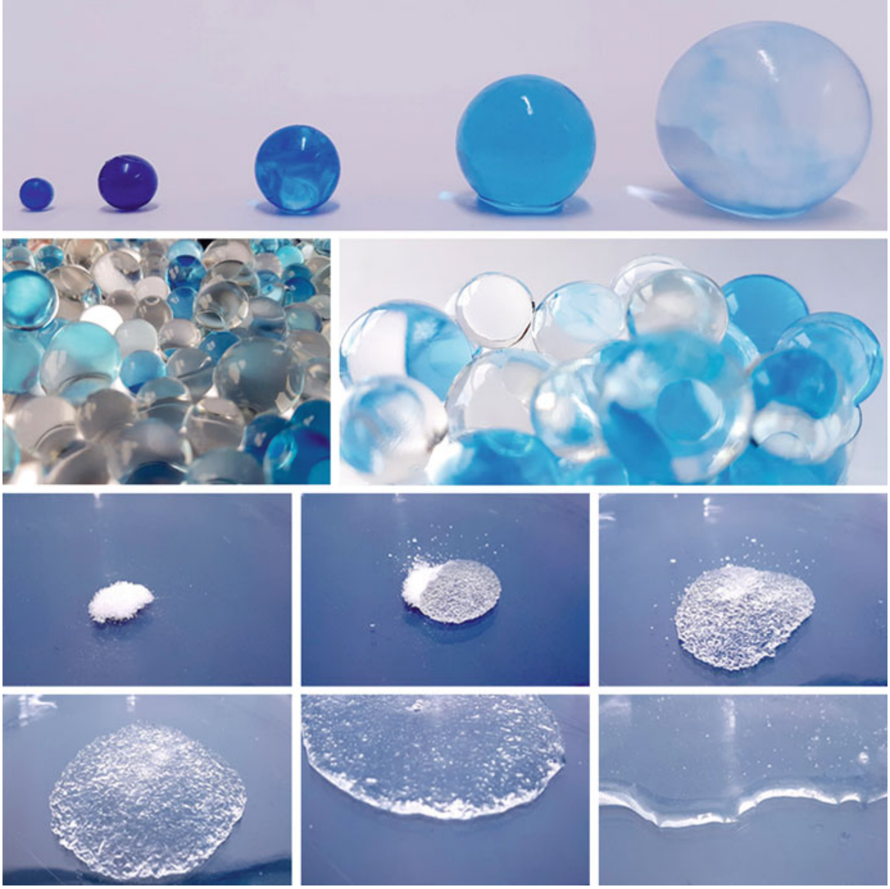


Fig. 15 Images of products using super-absorptive polymers: (top) swelling of polymer beads, (middle) swollen polymer beads, and (lower) swollen polymer particles, white granules, progressively forming a gel as water is added

such that they would dissolve were it not for crosslinks. The interactions thermodynamically contribute to the enthalpy of solvation. Another important thermodynamic factor is the entropy of solvation that is significantly caused by constraints on degrees of freedom of strongly absorbed, hydrogen-bonded water molecules. Enthalpy and entropy combine to give the free energy of solvation that must be negative for spontaneous water absorption. The kinetics of water absorption and any absorption–desorption hysteresis contributes to applications of super-absorbing polymers. Even though a large fraction of water can be absorbed, the time to reach equilibrium must be suitable. Rapid absorption kinetics are favored by surface wetting and porosity, to facilitate diffusion. Cellulose is not sufficiently polar and too regular to be a super-absorbent polymer. Functionalization to form carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and methyl cellulose increases polarity and decreases packing ability of cellulose. Other grafting monomers such as acrylic acid, methacrylic acid, acrylamide, and maleic anhydride increase polarity, and as polymeric grafts, they prevent ordered cellulose structures. Applications of super-hydrophilic cellulose derivatives include water absorption in sanitary products, water and nutrient release in agriculture, and antiseptic hydration materials for wounds and physiological treatments. Since these hydrated materials contain extremely large proportions of water, they can be considered as a means of storing and delivering quantities of solid water.

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