Enhanced Absorbent Products Incorporating Cellulose and Its Derivatives: A Review

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Cellulose and some cellulose derivatives can play vital roles in the enhancement of the performance of absorbent products. Cellulose itself, in the form of cellulosic fibers or nano-fibers, can provide structure, bulk, water-holding capacity, and channeling of fluids over a wide dimensional range. Likewise, cellulose derivatives such as carboxymethylcellulose (CMC) have been widely studied as components in superabsorbent polymer (SAP) formulations. The present review focuses on strategies and mechanisms in which inclusion of cellulose – in its various forms – can enhance either the capacity or the rate of aqueous fluid absorption in various potential applications.

Keywords: Absorbency; Cellulosic materials; Fluff pulp; Superabsorbents; Hydrogels; Carboxymethylcellulose (CMC); Disposable; Rate of absorption; Life cycle analysis

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INTRODUCTION

Cellulose-based products have been used for the absorption of water and other aqueous fluids throughout recent history (Buchholz and Peppas 1994; Chatterjee and Gupta 2002). Among such products, paper towels and tissue papers are some of the most widely used absorbents (Gigac and Fiserova 2008; Beuther *et al.* 2010). Fluff pulps, which are generally based on kraft pulping and optimized for high bulk and absorbency products, are in widespread use, especially for product niches such as disposable diapers (Lund *et al.* 2012). In recent decades the amount of cellulosic fiber employed in making an average disposable diaper, as well as in related products such as incontinence products and feminine hygiene products, has declined; this trend has been attributed to increased use of superabsorbent polymer (SAP) products (Nagorski 1994; Buchholz and Graham 2005; Lund *et al.* 2012). Thus, the goal of this review is to highlight published literature regarding enhanced absorbent materials and products that incorporate various forms of cellulose or its derivatives. Main sections are shown in the following table of contents:

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Although SAPs have a much greater ability to absorb fluids in comparison to cellulosic fibers alone, they have not displaced cellulose completely, nor is such a complete displacement expected. Cellulose, in its various forms, can contribute many positive attributes to absorbent products, including enhancement of SAP performance. Also, there is a widespread perspective that cellulose-based products are beneficial in terms of the environment and personal health.

Some Definitions

Certain terms will be used repeatedly in this article, *e.g.* hydrogel and superabsorbent. The term "absorbent" will be defined here by the phrase "capable of imbibing and holding onto aqueous fluids". "Hydrogel" will be defined as a hydrophilic polymer structure capable of absorbing a lot of water or saline solution. According to Kabiri *et al.* (2011), an ordinary absorbent hydrogel is able to absorb as much as 10 g of pure water per gram of dry-based material. Hydrogels that can accommodate more water than 10 g/g are called superabsorbents. As will become clear from tabulated information in this review, absorbency levels in the thousands of grams of water per gram of SAP have been frequently reported. Laftah *et al.* (2011) suggested a possible further distinction between hydrogels and ordinary absorbents such as paper towels: only the hydrogel-based sorbents are able to provide significant resistance to the release of fluid due to squeezing. To paraphrase Lund *et al.* (2011), hydrogel-based absorbents "swell and restrain" liquids to a remarkable extent. The amount of aqueous fluid held within a gel at equilibrium will be governed by a balance between osmotic pressure, the restraining pressure exerted by the material itself, and any externally applied pressure. The term "osmotic pressure" can be defined as a chemically-induced pressure differential between the inside and the outside of a hydrogel in the presence of a liquid phase. An additional aspect of the definition of a superabsorbent hydrogel is that it needs to be sufficiently crosslinked so that it does not dissolve in the fluid that it is intended to absorb (Zohuriaan-Mehr and Kabiri 2008).

Motivations to Incorporate Cellulose-Based Materials

The most widely used SAP products, to be described in greater detail later in this document, are not readily biodegradable (Dutkiewics 2002; Sannino and Nicolais 2005). Additionally, they are primarily derived from non-renewable resources including petroleum-derived acrylamide (AAm) and acrylic acid (AA) monomers, together with crosslinking agents, most of which can be classified as non-renewable resources (Buchholz and Graham 2005). By contrast, the renewable and biodegradable nature of cellulose is well known (Cooke 1990). Certain derivatives of cellulose such as carboxymethylcellulose (CMC) and hydroxypropyl cellulose (HPC) not only are highly biodegradable, but also, as will be discussed in this article, can form the basis for production of high-performing superabsorbent hydrogels. Various cellulose-based SAPs have been intentionally designed or tested to achieve a suitable degree of biodegradability (Wach *et al.* 2001; Lionetto *et al.* 2003; Sahoo *et al.* 2005; Yoshimura *et al.* 2005, 2006, 2009; Wang *et al.* 2008; Sannino *et al.* 2009; Feng *et al.* 2010a; Kono and Fujita 2012). Kosemund *et al.* (2009) emphasized safety and health issues, which are additional factors supporting the use of cellulose-based polymers rather than the use of petroleum-based SAPs.

Costs of materials have been mentioned as a key factor governing the types and compositions of available absorbent products. For instance, Kabiri *et al.* (2011) reviewed various research studies showing that hybrid superabsorbent structures incorporating montmorillonite "nano-clays" or cellulose-based nanomaterials sometimes achieve superior mechanical properties and can be manufactured at lower costs relative to conventional acrylic-based SAPs. Kono and Fujita (2012) expressed a different view and proposed that a relatively high cost of superabsorbents based on CMC have constituted a key barrier to their widespread use. However, viewed from another perspective, Liang *et al.* (2009) suggest that the relatively high cost of even the acrylic-based SAPs, in addition to their lack of biodegradability, offers motivation for further development of high-performing cellulose-based SAPs, as well as hybrid products that combine favorable aspects of cellulose and acrylamide-based chemistry.

Since the perspective of the present review article is specialized – focusing on the incorporation of cellulose-based materials in absorbent products – readers are encouraged also to refer to related review articles emphasizing various different aspects of absorbency and absorbents. Information related to absorbent products in general has been amply discussed (Buchholz and Peppas 1994; Chatterjee and Gupta 2002; Buchholz and Graham 2005). Likewise, the somewhat narrower topic of superabsorbents also has been well reviewed (Matushek 2008; Zohuriaan-Mehr and Kabiri 2008; Kabiri *et al.* 2011; Laftah *et al.* 2011). The topic of porous hydrogels also has been reviewed (Omidian *et al.* 2005; Lu *et al.* 2007).

Regarding the absorbency of products made mainly from cellulosic fibers, Parham and Hergert (1980) provide a review of fluff pulp, including the history of its development. Gupta (1988) reviewed structural factors affecting the performance of nonwoven absorbents. Fink *et al.* (2001) reviewed the absorbent qualities of certain regenerated cellulose products.

Regarding gel materials, cellulose-based hydrogels have been reviewed by Sannino *et al.* (2009) and by Chang and Zhang (2011), who emphasized non-superabsorbent materials. Athawale and Lele (2001) reviewed starch-based SAPs. Chitosan, which has a molecular structure that is analogous to that of cellulose, has been reviewed in the context of superabsorbent products (Dutkiewicz 2002). Medical applications of superabsorbent materials have been described and reviewed (Wichterle and Lim 1960; Bourges *et al.* 2002). Agricultural applications of hydrogels have been reviewed (Kazanskii and Dubrovskii 1992). Theories to account for the capacities and rates of water absorption into hydrogels have also been reviewed (Scallan 1983; Brannon-Peppas and Peppas 1990; Schuchardt and Berg 1991; Wiryana and Berg 1991; Kazanskii and Dubrovskii 1992; Ganji *et al.* 2010; Zohariaan-Mehr *et al.* 2010).

Sustainability Aspects

The present review article is motivated in part by issues of sustainability, considering factors that may contribute to the minimization of adverse environmental impacts. In principle, resource sustainability is advanced when renewable, bio-based materials are employed in the manufacture of a product; thus the next section of this article will consider a variety of different absorbent products that have been reported to contain cellulose or its derivatives. Product sustainability is often improved when product goals are achieved with a reduction in material requirements. Thus, separate sections of the article will examine chemical and structural effects on the performance of cellulose-based materials that have been used in absorbent products. Aspects related to the composition of the liquid to be absorbed will also be considered. Theoretical aspects will be considered in sections related to absorption capacity and the corresponding rates of absorption. Finally, the life cycle of absorbent products will be considered, asking such questions as "Why can't a highly absorbent product be designed so that it empties itself upon immersion in hot water, allowing it to be easily laundered and dried"? Alternatively, one might ask, "Will the next generation of renewable and biodegradable superabsorbents based on cellulose eventually compete successfully with and displace acrylamide-based SAPs?"

CLASSIFICATION OF ABSORBENTS INCORPORATING CELLULOSE

Tabulation

Since the same set of tabulated data will need to be referenced throughout the article, key information is given in Table A, which due to its length is placed in the appendix. The main categories are organized by absorbent class, fiber, hydrogel, "other," fluid update, "key findings", and a final column for the literature reference in abbreviated form. Within the "fiber" category, separate columns are provided to show the main fibrous components described in a given cited article and any chemical treatments of that fiber. Within the "Hydrogel" category, there are separate columns for the main chemical components of the hydrogel(s) described in a given article, the method of forming the hydrogels, and the type of crosslinking system employed. Under "Fluid uptake" there are two columns corresponding, respectively, to uptake of pure water and uptake of saline solution roughly corresponding to the ionic concentration of bodily fluids. Such concentrations, *e.g.* 0.9% NaCl, are often studied due to the widespread availability of physiological saline solutions.

Cellulose-based Materials and Aqueous Absorbency

Mechanically pulped wood

Among wood-based materials, one of the least expensive that could be considered for application as an absorbent would be mechanical pulp, a material derived by the compression and shearing of wood chips in the water-filled gap between the rotor and stator of a refiner. Eriksson *et al.* (1991) showed that such material can absorb approximately an equal mass of water, even without any specialized treatment. However, the same study revealed a key problem associated with such pulp: The rigid nature of the lignin in mechanically pulped wood resists the swelling of such fibers. One way to overcome such rigidity was demonstrated by removing up to 60% of the lignin. Following such treatment the material was able to take up two to four grams of water per dry gram of fiber. Water uptake also was increased if the temperature of the water was raised above about 70 ^{o}C, which is above the softening point of lignin under water-saturated conditions (Back and Salmén 1982).

Chemically pulped wood

According to Beuther *et al.* (2010), typical paper towels and tissue products that are composed primarily of bleached kraft fibers are capable of absorbing between five and ten times their mass of water without dripping. It was noted that the relative void volume fraction in such paper products can be greater than 0.9 in typical cases. Zohuriaan-Mehr and Kabiri (2008) reported the following values for the absorbency of water by lignin-free products: 1.8 g/g for filter paper; 4 g/g for facial tissue; 12 g/g for bleached kraft fluff pulp; and 19 g/g for cotton balls. The absorptive nature of kraft fibers can be attributed in part to the removal of the more hydrophobic lignin component of the fibers. In addition, the pores left behind by the breakdown and dissolution of lignin during pulping and bleaching gives rise to extensive porosity, though some of the pores close irreversibly when the fibers are dried (Stone and Scallan 1966, 1968; Berthold and Salmén 1997).

Despite their substantially greater absorbency in comparison to mechanical pulp fibers, kraft fibers tend to suffer from one key deficiency: Compared to the mechanically pulped fibers, the wet kraft fibers are not as capable of maintaining a bulky structure, especially when pressure is being applied. Lund *et al.* (2011) showed that such a deficiency can be overcome by crosslinking kraft fibers with a di-epoxide; the treatment makes the fibers remain stiffer when wet, such that greater bulk is achieved in the paper.

Another approach to enhancing the absorptive ability of kraft fibers has been through the use of rewetting agents (Shepherd and Xiao 1999). The surfactants employed significantly reduced the time required to take up a given amount of water. In addition to enhancing fiber wettability, the treatment often increased the size of inter-fiber pores formed by the structure of the paper. Ström and Carlsson (1992) took a different approach, making the kraft fibers more wettable by oxygen plasma treatment; it was found that such treatment could completely overcome the adverse effect of wood extractives, which otherwise tended to decrease the ability of the fibers to take up water.

Regenerated cellulose

Schuster *et al.* (2006) reviewed the water-absorbing properties of regenerated cellulose materials. Lyocell fibers, which are formed from a solution of α-cellulose in *N*-methylmorpholine *N*-oxide (NMMO), were reported to absorb about 5 g/g water. The absorptive ability was attributed to fine-scale porosity, which was extensively documented by means of scanning electron micrographs. The absorption behavior of regenerated cellulose products has been quantified in various studies (Fink *et al.* 2001; Cai and Zhang 2006; Schuster *et al.* 2006). Cellulose regeneration from solvent also can be used as a starting point for preparation of hydrogels (Nishio and Manley 1988; Lim *et al.* 2001, 2003; Saito *et al.* 2003; Chen *et al.* 2008; Chang *et al.* 2010; Lin *et al.* 2010; Chang and Zhang 2011; Kono and Fujita 2012; Kono *et al.* 2013). This topic will be addressed in later sections

New insights regarding the wettability of regenerated cellulose fibers were reported by Yamane *et al.* (2006). These authors showed that the wettability of the resulting fibers was greatly affected by the liquid medium present during regeneration. Also, the wettability could be affected, to some extent, by post-equilibration of cellulose films with either a nonpolar solvent, or a polar liquid such as ammonia or hot glycerol. Such effects were attributed to preferential exposure of different crystal faces of cellulose at the surface. Based on molecular simulation, it was predicted that the equatorial *vs.* the axial sides of glucopyranose rings in cellulose crystallites should exhibit hydrophilic *vs.* hydrophobic character, respectively. In agreement with the work cited above, Quddus *et al.* (2012) carried out molecular simulations of the spreading of pure water onto three crystal planes of cellulose; significant differences in contact angle were predicted based on the analysis.

Aerogels and Foams Prepared from Cellulose

Porous superabsorbent materials, *i.e.* foams, have emerged as an important category of SAPs due to their faster sorption in comparison to conventional SAPs

(Yoshinobu *et al.* 1992; Kabra *et al.* 1998; Omidian *et al.* 2005; Lu *et al.* 2007; Chang *et al.* 2009a; Zamani *et al.* 2010; Salam *et al.* 2011a). However, even without employing SAP technologies (see later), it has been shown that substantial absorbency can be achieved by suitable preparation of highly porous cellulose or its chemical derivatives. Brodin *et al.* (2012) showed that TEMPO oxidation of kraft pulp followed by freeze drying yielded porous foams that absorbed 21 to 65 g/g of water. Other authors (Pääkkö *et al.* 2008; Sehaqui *et al.* 2010, 2011; Theliander *et al.* 2011) showed that highly porous aerogels could be formed by freeze-drying of nanofibrillated cellulose.

Chemically derivatized fibers

Slight derivatization or grafting of the surface of cellulose is a known approach to changing the wettability and other attributes of cellulosic fibers. For instance, oxidation of fibers by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) has been found to increase the water uptake of kraft pulp (Brodin and Theliander 2012; Brodin *et al.* 2012). The effect was attributed to the generation of new carboxylate and aldehyde groups.

More profound effects have been achieved by grafting of polymeric chains by various means onto cellulosic fibers. For instance, improved absorption has been achieved by treating cellulose fiber surfaces with acrylic monomers (Lepoutre *et al.* 1973; Vitta *et al.* 1986; Deo and Gotmare 1999; Gürdağ *et al.* 2001; Sahoo *et al.* 2005; Aliouche *et al.* 2006; Jain *et al.* 2007; Jain and Ni 2008). Warner and Rezai (1997) showed that such treatments can be expected to change the composition throughout the fiber structure, not just at its surface.

In cases where a similar grafting approach is carried out more extensively, rather than ending up mainly with surface-derivatized fibers, the cellulose material becomes extensively transformed (Fanta *et al.* 1987). As shown by Goetz *et al.* (2009, 2011), such an approach can lead to absorbencies in the range of 30 to 200 g/g, especially if a cross-linking agent is employed. Such results show that it is possible to blur the distinction between what is a surface-modified fiber and what is a true hydrogel. Indeed, a unique class of highly absorbent materials has been achieved by basically skipping the conversion of cellulose to CMC, *etc.*, and just grafting cellulose directly, often in combination with crosslinking (Fanta *et al.* 1987; Yoshinobu *et al.* 1992; Gürdağ *et al.* 2001; Farag and Al-Afaleq 2002; Ibrahim and El-Zawawy 2004; Kim and Mun 2009; Yoshimura *et al.* 2006; Liu *et al.* 2009, 2011; Feng *et al.* 2010a; Zhang *et al.* 2010; Goetz *et al.* 2011; Shu *et al.* 2011; Kono and Fujita 2012; Pan and Ragauskas 2012; Wu *et al.* 2012; Xie *et al.* 2012; Kono *et al.* 2013). Thus, hydrogels will be discussed next.

Hydrogel Formation

As mentioned in the Introduction, an absorbent hydrogel can be defined by its ability to hold a relatively large amount of water (up to 10 g/g for ordinary absorbent hydrogels, or more in the case of superabsorbents), by its resistance to the release of aqueous fluids, depending on the applied pressure, and by its resistance to substantial dissolution, despite being chemically compatible with the fluid being absorbed. Absorbent hydrogels are most often prepared from hydrophilic polymers of relatively high molecular mass (Sannino *et al.* 2009; Chang and Zhang 2011). A key step in the formation of any hydrogel is “gelation,” which can be interpreted as the inter-connecting of the macromolecular chains in some manner, such that essentially the whole structure becomes linked together. Many different means of gelation have been demonstrated. For instance, one or more types of polymer chains may be precipitated from a suitable solvent by changing the conditions to reduce the solubility (Nishio and Manley 1988; Tang *et al.* 2010). In some cases progressive gelation can be induced by subjecting a polymer solution to freezing and thawing (El Salmawi 2007). Alternatively, the polymer can be precipitated from the solution by changing the temperature (Joshi *et al.* 2008). This gelation can be attributed to coalescence of polymeric chains due to thermal break-down of the organized cage-like structure of water surrounding each segment of a molecular chain as the temperature is raised through a critical range (Joshi *et al.* 2008). In other cases gelation may develop gradually by means of self-segregation of parts of adjacent chains that have differing hydrophobic or hydrophilic tendency (Sammon *et al.* 2006; Silva *et al.* 2008). Such a mechanism was supported by shifts in the infrared absorption spectra at the temperatures corresponding to gelation (Sammon *et al.* 2006). Further support for the coalescence of polysaccharide chain segments is provided by results of X-ray analysis, which revealed considerable crystalline character in certain hydrogels prepared from hemicellulose mixtures with chitosan (Gabrielli *et al.* 2000).

More aggressive gelation can be achieved by the addition of a suitable agent to form linkages among the chains. One of the simplest approaches, most suitable for the highly soluble polyacrylates and related copolymers, involves the addition of a well-chosen amount of multivalent cation (Kulicke and Nottelmann 1989; Yoshimura *et al.* 2009). Weerawarna and Su (2010) patented a system in which a mixture of kraft fiber and CMC was treated with aluminum sulfate to precipitate the CMC onto the fiber surface; the inventors characterized this approach as a form of crosslinking. In the present context, however, addition of multivalent cations, *e.g.* acidic aluminum compounds, is typically considered undesirable due to a strong suppression of swelling (Kulicke and Nottelmann 1989; Feng *et al.* 2010a).

Covalent crosslinking has emerged as the preferred means of converting suitable hydrophilic polymers into absorbent hydrogels, and many variants of this approach have shown excellent potential for the preparation of superabsorbents (Kabra *et al.* 1998; Liu *et al.* 2002; Sannino *et al.* 2003; Buchholz and Graham 2005; Chang *et al.* 2008; Zohuriaan-Mehr and Kabiri 2008; Laftah *et al.* 2011; Pohjanlehto *et al.* 2011; Kono and Fujita 2012). Notably, the highest levels of swelling are often detected when the extent of crosslinking is just sufficient to cause phase separation (Wach *et al.* 2001). Optimization of the crosslinking thus involves a balance between achieving high absorbency while also achieving suitable mechanical strength and minimizing the amount of material that dissolves into the bulk of the liquid when a highly absorbent hydrogel is in use (Wach *et al.* 2001; Guilherme *et al.* 2005).

Types of Superabsorbent Hydrogels

Acrylic-based hydrogels

To help understand the context of superabsorbent hydrogels that contain cellulosic components, it should be noted that the commercially dominant SAPs do not contain cellulose-based polymers. Acrylic-based and synthetic hydrogels are by far the dominant products manufactured and sold (Askari *et al.* 1993; Buchholz and Peppas 1994; Matushek 2008; Zohuriaan-Mehr and Kabiri 2008; Laftah *et al.* 2011). In general terms, acrylic-based SAPs are most often prepared from aqueous solutions containing acrylic acid (AA) and acrylamide (Am) monomers. These are typically crosslinked with *N,N'*-methylenebisacryamide (MBA) or divinylsulfone (DVS).

Carboxymethylcellulose (CMC)-based hydrogels

Among cellulose-derived materials used in SAPs, CMC holds a lead position (Oppermann 1995; Barbucci *et al.* 2000; Bin *et al.* 2000; Fei *et al.* 2000; Wach *et al.* 2001; Liu *et al.* 2002; 2005a; Bao *et al.* 2012). Crosslinking of the homopolymer can be achieved by gamma irradiation (Bin *et al.* 2000; Fei *et al.* 2000; Wach *et al.* 2001; Liu *et al.* 2002, 2005a), by chloromethylene iodide (Barbucci *et al.* 2000), or by polyvalent carboxylic acids such as citric acid (Demitri *et al.* 2008). Hydrogels formed by mutual gelation or covalent crosslinking of CMC and other water-soluble polymers have been studied (El Salmawi 2007). For instance, superabsorbents have been prepared with combinations of CMC and polyvinyl alcohol (El Salmawi 2007). Alternatively, CMC-based hydrogels have been prepared with the use of highly platy montmorillonite clay ("nanoclay") to achieve a crosslinking effect (El Salmawi and Ibrahim 2011).

Hydroxyethylcellulose (HEC) and other cellulose-derivative-based hydrogels

In an analogous manner to CMC, other cellulose ethers or esters have been used as a basis for forming hydrogels, either alone or in combination with other polymers (Harsh and Gehrke 1991; Oppermann 1995; Kabra *et al.* 1998; Bourges *et al.* 2002; Wach *et al.* 2002; Lionetto *et al.* 2003; Demitri *et al.* 2008; Joshi *et al.* 2008; Dai and Kadla 2009; Bao *et al.* 2012). Bao *et al.* (2012) observed higher absorbency in superabsorbents made from graft copolymers of CMC, in comparison with graft copolymers from hydroxypropyl methyl cellulose, methyl cellulose, and hydroxyethyl cellulose. Like CMC, other derivatives of cellulose and the hydrogels produced from them have been shown to be biodegradable (Lionetto *et al.* 2003).

Copolymers of CMC by reaction with monomers

Considerable research has been devoted to the development of copolymers in which CMC is reacted with acrylic monomers and various crosslinking agents to form SAPs (Kuwabara and Kubota 1996; Pourjavadi and Mahdavinia 2005; Pourjavadi and Ghasemzadeh 2006; Abd El-Mohdy 2007; Ibrahim *et al.* 2007; Pourjavadi *et al.* 2007a-b, 2008, 2009, 2010; Suo *et al.* 2007; Ali *et al.* 2008; Chen *et al.* 2008; Yang *et al.* 2009; El-Din *et al.* 2010; Feng *et al.* 2010a; Lin *et al.* 2010; Wang and Wang 2010; Bao *et al.* 2011; Eldin *et al.* 2011; Huang *et al.* 2011; Liu *et al.* 2011; Shu *et al.* 2011; Varaprasad *et al.* 2011; Wang *et al.* 2011c). Water absorbency values generally in the range of 40 to 1400 g/g have been reported in such studies, with the highest value reported by Pourjavadi *et al.* (2008). Copolymers incorporating CMC have also been prepared with polyvinyl alcohol (El Salmawi 2007), hydroxyethyl cellulose (Oppermann 1995; Lionetto *et al.* 2003; Sannino and Nicolais 2005; Demitri *et al.* 2008; Dai and Kadla 2009), and with hydroxypropylethyl cellulose (Faroongwarng and Sukonrat 2008).

Cellulose-synthetic graft copolymer hydrogels

Although underivatized cellulose is not nearly as hydrophilic as CMC, several investigators have prepared hydrogels by extensive grafting of other monomers onto cellulose, generally employing suitable organic solvent systems (Yoshinobu *et al.* 1992; Wu *et al.* 2008; Chang *et al.* 2009b; Kim and Mun 2009; Buyanov *et al.* 2010; Feng and *et al.* 2010a; Anirudhan *et al.* 2011; Shu and Zhao 2011; Wu *et al.* 2012). Generally, water absorbency values in the range of 60 to 1800 have been reported for such hydrogels, though Kim and Mun (2009) reported a high value of 2500 g/g. As an alternative approach, Kono and Fujita (2012) showed that it is possible to form a hydrogel from a solution of native cellulose in an ionic liquid, employing a widely used crosslinking agent.

Hydrogels based on cellulose with other natural-based polymers

As one might expect based on environmental concerns, many researchers have investigated the preparation of "all-natural-based" hydrogels incorporating cellulose or its derivatives (Harsh and Gehrke 1991; Barbucci *et al.* 2000; Bin *et al.* 2000; Fei *et al.* 2000; Wach *et al.* 2001, 2002; Hirsh and Spontak 2002; Liu *et al.* 2002, 2005a; Rodriguez *et al.* 2003; Sannino *et al.* 2003, 2004a,b; Sannino and Nicolais 2005; Yoshimura *et al.* 2006; Demitri *et al.* 2008; Faroongwang and Sukonrat 2008; Pourjavadi *et al.* 2008, 2010; Chang *et al.* 2009, 2010; Dai and Kadla 2009; El Salmawi and Ibrahim 2011; Salam *et al.* 2011a,b; Wang *et al.* 2011b; Kono and Fujita 2012; Pan and Ragauskas 2012; Kono *et al.* 2013). For instance, a hydrogel based on a combination of cellulose and CMC can be prepared from a solution of the ingredients in a NaOH/urea solvent system (Chang *et al.* 2010).

Major Covalent Crosslinking Agents

Superabsorbent hydrogels that incorporate cellulose-based components, such as CMC, require crosslinking, and many of the crosslinking agents are the same as those used in SAPs not containing any cellulose-based component. Table 1 provides an overview of the most important cross-linking systems that have been employed in studies of superabsorbent hydrogels that have incorporated cellulose-based compounds.

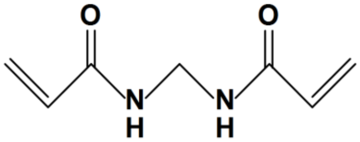
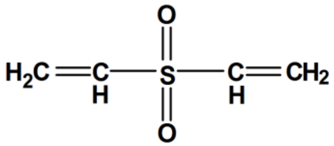
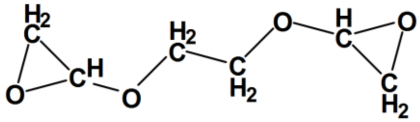
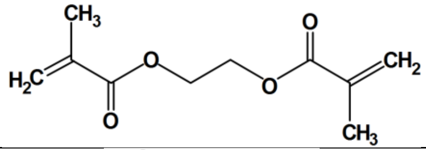
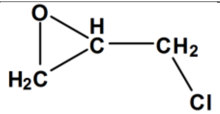
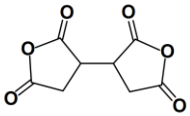
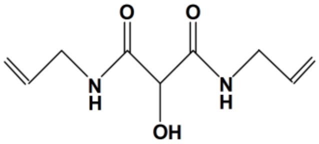
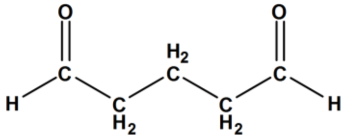
In addition to the agents listed in Table 1, crosslinking also can be achieved by use of dialdehyde cellulose (Han *et al.* 2010), making it possible to achieve crosslinking with multifunctional amines on lyocel fabric. Swelling was decreased by such treatment, which had utility for imparting crease resistance to clothing.

Interpenetrating

One type of hydrogel that merits special mention employs pairs of non-reacting polymer networks, *i.e.* interpenetrating networks. In such systems each network relies on a different crosslinking mechanism, and the resulting hydrogels are formed *in-situ* in such a way that, at least in principle, the two networks can remain intensively entangled. Several reported examples have exhibited high absorption capacity for water (Myung *et al.* 2008; Chang *et al.* 2009b; Chang and Zhang 2011; Varaprasad *et al.* 2011; Liu *et al.* 2013).

There is reason to doubt, however, that an interpenetrating structure is essential in achieving the improved performances reported for such systems. None of the cited articles provides a convincing explanation of why interpenetrating networks would be expected to absorb more fluid. Logic would suggest that such complex, entangled structures would result in more resistance to swelling in comparison to having just one network, in which the crosslinking degree and molecular mass had been suitably optimized. It seems likely that the cellulose-based components of such systems may act as "spacers", partly suppressing the crosslinking within the acrylamide-based component. Further research is also needed to find out whether both networks are truly continuous in such systems.

Table 1. Major Crosslinking Agents Used in Studies of SAP Preparation

Crosslinking agent	**Chemical structure**	**Selected citations**
N,*N*-methylene-bis-acrylamide (MBA)		Gürdağ *et al.* 2001; Kim & Mun 2009; Feng *et al.* 2010a; Bao *et al.* 2011; Pourjavadi *et al.* 2009
Divinylsulfone (DVS)		Lionetto *et al.* 2003; Sannino *et al.* 2004a; Sannino & Nicolais 2005; Dai & Kadla 2009
Ethyleneglycol di-methyl ether (EGDE)		Rodriguez *et al.* 2003;
Ethyleneglycol di-methacrylate (EGDMA)		Vitta *et al.* 1986; Askari *et al.* 1993
Epichlorohydrin (ECH)		Chang *et al.* 2008, 2009a,b; 2010
1,2,3,4-butanetetra-carboxylic dianhydride (BCTA)		Kono & Fujita 2012; Kono *et al.* 2013
Diallyltartardiamide (DATDA)		Pohjanlehto *et al.* 2011
Glutaraldehyde (GA)		Shang *et al.* 2008; Zamani *et al.* 2010

Polyelectrolyte complexes

A unique type of hydrogel can be formed through the use of pairs of oppositely charged polyelectrolytes via the formation of polyelectrolyte complexes (PECs). At least one of the polyelectrolytes could be a cellulosic material such as carboxymethyl cellulose (CMC) (Feng *et al.* 2006; Feng and Pelton 2007) or hemicellulose (Salam *et al.* 2011b). Though PECs generally do not show promise for the absorption of large amounts of pure water, various studies have shown favorable results for the absorption of saline solutions, possibly representing urine (Paula *et al.* 2002; Feng *et al.* 2006; Feng and Pelton 2007). Despite the fact that under many circumstances the ionic interactions are sufficient to maintain the integrity of such gels, some researchers have reported enhancement of hydrogel capabilities when covalent crosslinkers have been applied in the preparation of such PEC hydrogels (Chen and Tan 2006; Shang *et al.* 2008; Salam *et al.* 2011b). As will be discussed in more detail later, the ability of some such hydrogels to increase their absorbency with increasing salinity can be attributed to a salt-induced weakening of the ionic pair-wise interactions that hold PECs together.

Products Combining Cellulosic Fibers with SAPs

A cursory inspection of currently available disposable absorbent products reveals a combination of cellulosic fibers and superabsorbent hydrogel materials, along with various barrier layers, permeable layers, elastic elements, and closures (Nagorski 1994). Within such products, conventional cellulosic fibers, *i.e.* the fluff pulp, play a variety of roles. Though, as mentioned earlier, bleached kraft fibers can absorb about 12 g water per g or solid (Zohuriaan-Mehr and Kabiri 2008), this is not enough to compete with the much higher water-holding capacity of the SAPs. Rather, the fluff pulp is used primarily to provide structure and wicking (Schuchardt and Berg 1991). In particular, the addition the fluff pulp can prevent gel blocking, which is the blocking of liquids by a complete wall of saturated SAP particles that are not separated sufficiently by the fibers. Masoodi *et al.* (2012) carried out studies directed at examining the combined effects of cellulose fiber and CMC hydrogel powder with respect to the wicking and uptake of water. Numerical simulation was used to model the phenomenon observed in the experiment. Though conventional assumptions of flow through capillary structures appear to be valid, the permeability was found to decrease with time (Schuchardt and Berg 1991; Wiryana and Berg 1991; Mosoodi *et al.* 2012). It was proposed in the cited studies that swelling of the hydrogel particles tended to seal off channels within the composite structure.

Weerawarna and Bing (2006) claimed a process in which superabsorbent gels were chemically attached to suitable fibers. Schuchardt and Berg (1991) describe various practical ways in which SAPs have been incorporated into cellulosic pad structures, including the various shapes and sizes of hydrogel particles. The distribution of SAPs within the structure is clearly an important consideration that will merit further study.

Integration of Cellulosic Solids into SAPs

An alternative way in which cellulose can be incorporated into highly absorbent products is by including solid cellulose in the mixture during gelation of the SAP. This approach has been applied by Larsson *et al.* (2010, 2011), with a focus on nanocellulose product applications. These authors observed that the effects of adding nanocellulose, in terms of both swelling and mechanical properties, was approximately the same as the addition of the same mass of conventional crosslinking agent. This suggests that the cellulosic fibrils, by being relatively long, tended to act as reinforcement, forming a nanocomposite structure (Hubbe *et al.* 2008; Pandey *et al.* 2013).

The effects of adding nanocellulose during the preparation of SAPs, as just described, are strikingly in contrast to various results that have been obtained when alkali montmorillonite, *i.e.* “nanoclay”, or other finely divided minerals have been added to the formulation during the preparation of SAPs (Pourjavadi and Ghasemzadeh 2006; Pourjavadi *et al.* 2008; Dai and Kadla 2009; Zhang *et al.* 2008b; 2009; Wang and Wang 2010; Wang *et al.* 2010, 2011a,b,d; Anirudhan *et al.* 2011; Bao *et al.* 2011; Chang and Zhang 2011; El Salmawi and Ibrahim 2011; Kabiri *et al.* 2011). In some cases the inclusion of nano-sized mineral particles during hydrogel preparation yielded a substantial increase in water absorption capacity (Pourjavadi *et al.* 2008; Zhang *et al.* 2008b; 2009; Wang and Wang 2010; Wang *et al.* 2010, 2011a,b,d; El Salmawi and Ibrahim 2011), whereas in some other cases the nanominerals tended to suppress absorbency (Pourjavadi and Ghasemzadeh 2006; Dai and Kadla 2009). A possible mechanism to account for the enhancement of absorption, in the cases indicated, could be a debonding effect, allowing pools of fluid to occupy openings that are made available by poor bonding of the adjacent SAP material to a suitably sized mineral surface. In addition, progressive exfoliation of montmorillonite may provide additional capacity for the holding of fluid (Knudson 1993). Alternatively, in cases where the minerals happen to be better bonded to the matrix, they could be expected to restrain swelling and imbibition.

CHEMICAL EFFECTS

Various published studies have addressed the question, “In what ways can the chemical composition of absorbent material affect its absorbency?” This section first considers publications dealing with the absorbency of cellulose and related biomaterials, followed by various copolymer derivatives, hydrogels, and combined structures.

Cellulose as an Absorbent Material

The chemistry of cellulose itself clearly can contribute to absorbency on account of the numerous hydrophilic –OH groups throughout its structure. The most widely used tissue and towel products are typically made from delignified wood fibers; in other words they are mainly comprised of cellulose and hemicellulose (Gigac and Fiserova 2008). As documented in Table A, the absorbency of ordinary delignified cellulosic fibers often lies in the range between 2 and 10 g/g, based on tests with pure water (Shepherd and Xaio 1999; Gigac and Fiserova 2008; Zhang *et al.* 2008a; Beuther *et al.* 2010). Mechanical pulp fibers, which contain essentially all of the relatively hydrophobic and rigid lignin that was originally present in the wood, tend to absorb less water in comparison to kraft or sulfite (delignified) fibers (Eriksson *et al.* 1991). Breier (1997) reported corresponding values of 0.5 g/g for cotton fiber and 0.6 to 1 g/g for various regenerated cellulose products.

The somewhat higher reported performance of wood-derived fibers, especially after delignification, probably can be attributed to their mesoporous nature and/or internal delamination as a result of mechanical treatments. Also, as will be discussed in detail later in this article, drying of cellulosic material can make a great difference in terms of its pore structure and capacity to absorb water.

Cellulose crystallinity

Though the outermost surfaces of cellulose crystalline regions are able to interact with water, the crystalline domains within the cellulosic material are not expected to imbibe any water molecules (Bergenstrahle *et al.* 2008). Rather, it is the amorphous regions of cellulose, along with spaces occupied by the non-crystalline hemicelluloses, that are expected to swell and accommodate water (Heiner and Teleman 1997; Heiner *et al*. 1998; Bergenstrahle *et al.* 2008; Kocherbitov *et al.* 2008). These regions are represented schematically in Fig. 1. In support of this type of simplified model, it has been shown that the treatment of cellulose with $ZnCl_2$ solution is able to disrupt the crystallization to some extent, an effect that can greatly increase the amount of water absorption (Williams and Stannet 1979; Vitta *et al.* 1986).

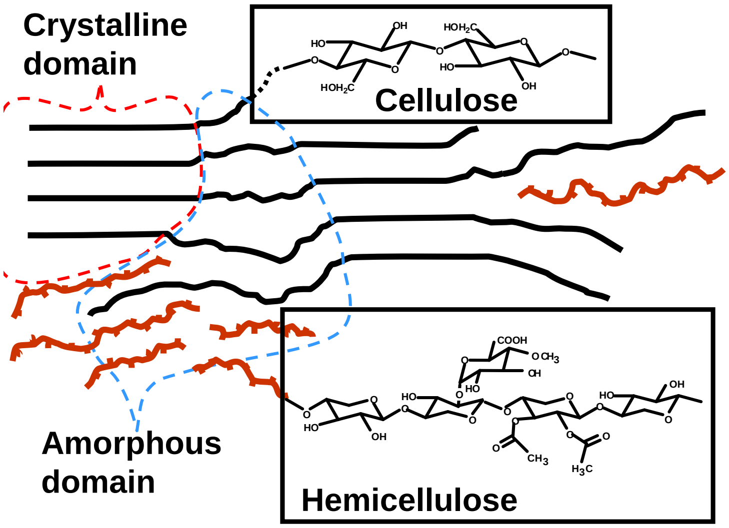


Fig. 1. Representation of crystalline regions and amorphous regions within the nanostructure of delignified fibers from wood

Absorption in the amorphous regions of cellulose, as well as within the domains containing hemicellulose, can be expected to involve strongly bound water, *i.e.* a form of hydration (Joubert *et al.* 1959; Gert 1996). In support of this statement, a strong exotherm has been observed accompanying the first increment of water uptake onto completely dry cellulose (Kocherbitov *et al.* 2008). Water that is strongly bound to cellulose has also been characterized as "hard to remove water" as measured by thermogravimetric analysis or as freezing or non-freezing bound water as measured using differential scanning calorimetry (Park *et al.* 2006, 2007; Sen *et al.* 2012).

In the case of conventional cellulosic fiber materials (not considering hydrogels), a majority of the retained water within a pad or sheet product is likely to reside between fibers rather than within them (Jerkeman 1970). Issues relative to the bulkiness of cellulosic absorbent materials will be discussed in a later section.

Hemicellulose and Absorbency

The swelling of cellulosic fibers has been found to correlate positively with the proportion of hemicellulose (Eriksson *et al.* 1991). The positive contribution of hemicellulose to swelling can be partly attributed to its irregular structure, with branching and side groups (*e.g.* as shown in Fig. 1). The irregularity of hemicellulose tends to discourage its crystallization (Billmeyer 1971; Brydson 1975). Peura *et al.* (2008) observed levels of crystallinity only in the range 16 to 19% in films cast from purified xylan. Likewise, Gabrielii *et al.* (2000) and Gröndahl *et al.* (2004) observed somewhat higher levels of crystallinity in films from aspen wood xylan prepared under conditions optimized to promote crystallization. A second factor that contributes to the hydrophilic nature of hemicelluloses is the content of carboxyl groups, which can dissociate to the carboxylate form at intermediate to high conditions of pH (Lindström and Carlsson 1982). Indeed, Salam *et al.* (2011a) showed that hemicellulose could be rendered even more hydrophilic by derivatizing it to further increase the content of carboxyl groups.

Extraction of hemicellulose from kraft fibers with alkaline solutions has been found to increase the water absorptivity of the fibers (Lund *et al.* 2012). This is somewhat surprising, given the fact that hemicelluloses have a distinctly hydrophilic nature. The explanation appears to lie in the conversion of other ionic forms of the remaining hemicellulose to the sodium form, which is known to enhance swelling (Lindström and Carlsson 1982). The importance of hemicellulose was also shown by Laine and Stenius (1997), who demonstrated a positive relationship between fiber ionic charge and swelling with water. Recently several researchers have attempted to take advantage of the hydrophilic nature of hemicelluloses by using them as a key component of highly absorbent hydrogels (Gabrielli and Gatenholm 1998; Gabrielli *et al.* 2000; Meena *et al.* 2011; Peng *et al.* 2011; Pohjanlehto *et al.* 2011; Salam *et al.* 2011a; Yang *et al.* 2011; Karaaslan *et al.* 2010, 2011, 2012).

Lignin and Absorbency

Compared to the polysaccharides in wood, lignin is more hydrophobic. Obataya *et al.* (2007) found that delignification of wood increased its tendency to swell in water. Likewise, as reported by Parham and Hergert (1980), delignified kraft pulps can be expected to absorb significantly more water than mechanical pulps, in which most of the native lignin still remains after pulping. Further demonstration of the relative hydrophobicity of lignin has been shown by studies in which lignin or its derivatives were precipitated onto cellulose, thus decreasing the substrate's wettability by water (Sipponen *et al.* 2010; Li *et al.* 2011; Payne *et al.* 2012). One way to overcome the adverse effect of lignin on swelling is to heat lignified fibers above approximately 70 ^{o}C (Eriksson *et al.* 1991). Such heating, in the presence of water, was observed to soften lignin sufficiently so that the water uptake was increased.

Extractives and Absorbency

Because the term "extractives" usually implies that a substance can be removed from cellulosic material with an organic solvent (Back and Allen 2000), it follows that most such substances are likely to resist water wetting and penetration. When microfibrillated cellulose materials of different lignin and extractives contents were exposed to an organic solvent to remove any extractives, the water-cellulose interactions as measured by water contact angle all increased, with the largest increases observed for the material with the most extractives initially (Spence *et al.* 2010). However, a search of the literature revealed a paucity of studies attempting to correlate levels of extractives and extents of swelling or absorbency. As already noted, Lund *et al.* (2012) observed an increased swelling of softwood kraft fibers after their extraction with NaOH. Though the authors attributed this effect to the removal of hemicelluloses, it seems likely that at least part of the effect may have been due to removal of certain extractive materials, *e.g.* the salts of fatty and resin acids.

Ström and Carlsson (1992) found that an adverse effect of extractives on the water-wettability of kraft pulps could be overcome by treatment with oxygen plasma. The effect was attributed to oxidation of the exposed lignin. Related results have been published by Uner (2009), who found that corona discharge treatment of paper resulted in increased absorbency. Another way to increase wetting and absorbency involves use of suitable surfactants, *i.e.* rewetting agents (Shepherd and Xiao 1999).

Hydrophilic Substituent Groups and Absorbency

The presence and increasing level of hydrophilic groups in a cellulose-based material can contribute to water uptake in a number of ways, *e.g.* through hydrogen bonding with the water, by electrostatic effects (if the groups are charged), and by somehow interfering with the densified structure of the biomaterial (Lepoutre *et al.* 1973). Effects of several kinds of water-loving ionic groups are considered below.

The relationship between two key types of hydrophilic groups and the transient hydrogen bonds within liquid water is illustrated in Fig. 2. Hydroxyl groups exposed at the surface of an absorbent material can be expected to form hydrogen bonds with adjacent water molecules, as shown in the left frame of the figure. The hydrogen bonding extends, in a continuously changing pattern, throughout the whole liquid phase (Drost-Hansen 1969). The right-hand frame of the figure emphasizes the role of bound ionic groups, which can be expected to have a strong affinity for the polar molecules of water. As shown, the bound negatively charged groups can be expected to interact strongly with the positively charged pole of adjacent water molecules. The water molecules tend to orient themselves in a transient pattern, consistent with their polar nature.

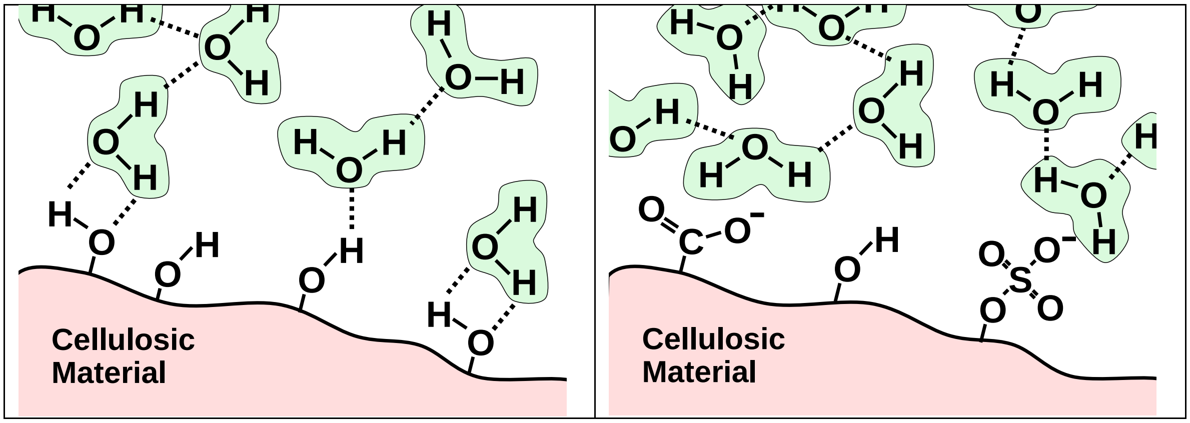


Fig. 2. Representation of hydrogen bonding among the molecules of liquid water and also associated with hydrophilic groups. **Left:** Hydrogen bonding associated with hydroxyl groups bound to a substrate. **Right:** Interaction and orientation of polar H_2O molecules with ionized groups such as carboxylate or sulphonate groups, all associated with the transient hydrogen bonded structure of liquid water

Oxidation

By low levels of oxidative treatment it is possible to increase the proportion of carboxylic acid and/or aldehyde groups on the surfaces of cellulosic fibers. Such oxidative treatment (*e.g.* TEMPO-mediated oxidation) has been shown to greatly increase water absorbency of softwood kraft pulps (Brodin *et al.* 2012; Brodin and Theliander 2012). Periodate oxidation has been shown to offer an alternative means of achieving similar effects (Zhang *et al.* 2008a).

Carboxymethylation and succinylation

Chemical derivatization is another way to increase the number of carboxyl groups on cellulosic surfaces. The idea is to covalently attach groups containing carboxyl functions to the cellulose. In particular, it has been found that carboxymethylation of fibers can greatly increase absorbency even when the treatment level is low enough to avoid solubilization of the source cellulosic material (Schuchardt and Berg 1991). As already noted, however, it is more common to employ extensive carboxymethylation of cellulose, an approach that allows use of fully soluble CMC as a basis for forming superabsorbent hydrogels through crosslinking (Zohuriaan-Mehr and Kabiri 2008;

Sannino *et al.* 2009; Chang and Zhang 2011). Carboxylic acid groups also can be attached to cellulosic fibers by means of reaction with succinic anhydride or maleic anhydride; such treatment likewise has been shown to increase absorbency (Yoshimura *et al.* 2005, 2006).

Sulfonation

Zhang *et al.* (2008a) showed that sulfonate groups can be especially effective to increase the water retention values of bleached hardwood kraft fibers. It was noted that because sulfonic acid is a strong acid, a high proportion of such groups tend to retain their negative charge at any given moment, even when the charge density of a fiber surface is relatively high. The acid groups remain dissociated throughout the pH range where such fibers are likely to be used. Hou *et al.* (2008) also showed that sulfonation improved absorbency.

Sulfonate groups also have been shown to be advantageous in the preparation of high-performing superabsorbent hydrogels. For instance, sulfated starch has been used as a polyelectrolyte component in the preparation of high-performing SAPs (Lim *et al.* 2001). The improved performance, relative to similar hydrogels containing just carboxylate groups, again was attributed to a tendency of the strong acid groups to remain fully dissociated despite the relatively high levels of substitution in the starch-based polyelectrolyte.

Phosphorylation

Saito *et al.* (1994a, 1995) showed improvements in absorbency analogous to those of the sulfate group when using phosphorylated lignocellulosic materials. The phosphate was characterized as “a water-attracting group” (Saito *et al.* 1995). However, in their earlier article the authors had concluded that effects of preparation conditions on surface area and porous structure were more important relative to the content of ionizable groups (Saito *et al.* 1994a). In a third study the same authors attributed the increased absorbency to inter-crystalline swelling (Saito *et al.* 1994b).

Hydrophobic Substituent Groups and Absorbency

Cellulose-based materials are in general hydrophilic, and it has been found that a de-swelling effect can be achieved by derivatization with hydrophobic groups. Such an effect was shown most clearly by Koroskenyi and McCarthy (2001), who used acetylation to systematically decrease the swelling behavior of glucomannan. Obataya *et al.* (2007) showed that acetylation increased the ability of lignin-containing fibers to absorb non-polar solvents. One exception to the rule has been observed when cellulose fibers are derivatized at a low level, *e.g.* 5% substitution of the hydroxyl groups by acetyl groups; in such cases Ehrnrooth *et al.* (1977) reported increased swellability, which was attributed to the reduced crystallinity of the partially substituted cellulose.

Hydrogel Attributes and Absorbency

Considerable attention has been devoted to the absorbency of superabsorbent hydrogels in light of their ability to take up 10 to over 1000 times their mass in water. Various factors involving the structure of hydrogel composition and molecular structure appear to control absorbency. Some of the key factors, as described below, are the molecular mass of the component polymers, the density of crosslinking, and the nature of the chemical species used in the crosslinking. In addition, the presence and density of ionizable groups on polymer chains, which are physically unable to diffuse out of the gel, provide a driving force for osmotic effects, inducing more water to enter the gel.

Molecular mass

High molecular mass has been proposed as being a key requirement of polymers that are intended as the main components of superabsorbent hydrogels (Yoshimura *et al.* 2006). Thus, Kono and Fujita (2012) observed increased absorbency with increasing molecular mass of the cellulose used to prepare a crosslinked CMC hydrogel from an ionic liquid solution. In principle, if the molecular mass is relatively low, then there will be a greater likelihood of dissolution and loss of the polyelectrolyte from the hydrogel during its use. Though a higher degree of crosslinking could be used to overcome such deficiencies, such an approach would not be expected to yield high levels of absorbency (see next).

Crosslinking

In the absence of any crosslinking, many of the most widely used superabsorbent products would simply dissolve when placed in water. Though the highest swelling performance is often observed at the lowest levels of crosslinking (Bin *et al.* 2000; Wach *et al.* 2001, 2002; Liu *et al.* 2005a; Demitri *et al.* 2008; Han *et al.* 2010; Pourjavadi *et al.* 2010; Kono and Fujita 2012), it is generally observed that higher levels of crosslinking (or other reinforcement) are needed to achieve the needed mechanical resilience and resistance to dissolution of superabsorbent products (Guilherme *et al.* 2005; Myung *et al.* 2008; Tanaka *et al.* 2005; Schexnailder and Schmidt 2009; Zohuriaan-Mehr *et al.* 2010).

Somewhat contrary results were reported by Barbucci *et al.* (2000). Although these authors observed a monotonic decrease in swelling with increase in crosslinking up to a 50% level, they observed a higher swelling at “100% crosslinking”. The anomalous behavior was attributed to disruption of hydrogen bonding by the crosslinking agent. Anomalous increases in swelling with increasing crosslinking also have been observed when the crosslinking agent is much more hydrophilic than the polymer chain. Thus, Oliveira *et al.* (2013) showed that increasing crosslinking of cellulose acetate (a hydrophobic polymer) with a di-anhydride increased water sorption. It was noted that the curing of a dianhydride can form two ester bonds and two free carboxyl groups, the latter of which increase the ionic character of the hydrogel at intermediate pH values (Kono and Zakimi 2013; Oliveira *et al.* 2013).

Numerous studies have addressed the goal of finding an optimum level of crosslinking for various types of superabsorbent gels (Ali *et al.* 2008; Pohjanlehto *et al.* 2011; Kono and Fujita 2012). Kono *et al.* (2013) observed that the balance between simple grafting and crosslinking reactions is sometimes sensitive to the choice of solvent system. As one means to control this balance, Lionetto *et al.* (2005) showed that the degree of crosslinking can be monitored during the process by evaluation of ultrasonic wave propagation.

Chang *et al.* (2008) showed that the type of crosslinking, *i.e.* covalent-type *vs.* physical crosslinking, also can make a big difference relative to results. For the observed system it was found that chemical crosslinking yielded higher absorbency. In the cited case the chemical crosslinking approach made it possible to avoid use of multivalent cationic agents. As will be discussed later, such species generally tend to reduce the swelling of typical hydrogels.

Cross-link length

Several innovative studies have shown that, at least in principle, higher absorbency of hydrogels can be achieved by using longer, flexible crosslinking agents (Xiao and Meshitsuka 2001; Sannino *et al.* 2003; Chang and Zhang 2011; Kabiri *et al.* 2011; Pohjantehto *et al.* 2011). In practice this is achieved by inserting a "spacer" between the two reactive groups of a suitable crosslinking agent (Chang and Zhang 2011). The spacer within the crosslinked structure of a SAP can be expected to allow further expansion and therefore greater uptake of aqueous fluid. It is notable that analogous results were obtained when paper was treated with high- *vs.* low-mass polyvalent carboxylic acid species; the longer molecules gave rise to greater tensile strength and folding endurance (Yang and Xu 1998; Xu and Yang 1999).

There is an interesting parallel between the effects of spacers and the effects of certain very fine mineral products, which were mentioned earlier (Pourjavadi *et al.* 2008; Zhang *et al.* 2008b; 2009; Wang and Wang 2010; Wang *et al.* 2010, 2011a,b,d; El Salmawi and Ibrahim 2011). Such nano-minerals, if poorly adhered to the adjacent polymeric material, can be expected to allow the opening up of fluid-filled spaces within the hydrogel. The presence of void spaces in such nanocomposite structures is supported by observations of relatively high opacity in some cases (Dai and Kadla 2009). It seems likely that some of the high levels of water uptake reported for SAPs based on interpenetrating networks (*e.g.* Çaykara *et al.* 2006; Chang *et al.* 2009b) may be due to one network interfering with the crosslinking of the other network during its preparation.

Ionizable Groups and Absorbency

Hydrogels that contain carboxylic groups generally exhibit increasing absorbency with increasing pH, especially within the pH range of about 3 to 7; the following examples are from studies involving cellulose-based materials in SAPs (Barbucci *et al.* 2000; Harsh and Gehrke 1991; Sannino and Nicolais 2005; Pourjavadi *et al.* 2008; Anirudhan *et al.* 2011; Bao *et al.* 2011; Wang *et al.* 2011a). The effect has been attributed to dissociation of the groups to the carboxylate form (Barbucci *et al.* 2000). As noted by Harsh and Gehrke (1991), such effects of pH are consistent with a principle that absorbency increases with increasing charge density. While most such studies have employed pH as the main independent variable to manipulate the charge density, an alternative approach can be achieved by adjusting the composition of the polyelectrolytes used in forming the hydrogel. Thus, Wu *et al.* (2012) determined that absorbency increases with increasing level of charged monomer groups up to a 70% of acrylic acid in a cellulose graft copolymer hydrogel with acrylamide monomers and a crosslinker. Considering the importance of the topic, more research is recommended.

Particle Size of Hydrogel

Based on limited available data, the size of hydrogel particles can affect the rate of absorption of water, but the effect on absorption capacity appears to be weak (Tanaka and Fillmore 1979). The cited study dealt with acryalamide gels formed at a 5% concentration of polymer in water. The cited authors observed that the rate of swelling was inversely proportional to particle size, as would be expected according to a diffusion-limited process. Bao *et al.* (2011) found only a weak and inconsistent relationship between equilibrium absorption and particle size in the case of superabsorbent hydrogels based on CMC, acrylamide copolymer, and montmorillonite nanoparticles.

STRUCTURAL EFFECTS

In principle, structural aspects of various hydrogels can affect not only the absorption capacity but also the rate of filling. The focus here is on the effects of various cellulosic components on absorbent structure and performance in different situations. One can consider three size ranges in which important effects may be manifested, *i.e.* due to the presence of cellulosic fibers, due to nanocellulose, and due to the inherent differences in stiffness of different types of polymer chains within hydrogels.

Macroscopic Structural Effects

Cellulosic fiber use

Fluff pulp, which is usually provided as bleached softwood kraft fibers, is typically a main component of highly absorbent products (Jerkeman 1970; Parham and Hergert 1980; Nagorski 1994; Buchholz *et al.* 2005; Lund *et al.* 2012). Although, as noted earlier, the fibers themselves can accommodate some liquid (Zohuriaan-Mehr and Kabiri 2008), most of the absorption capacity of such products can be attributed to the inclusion of SAPs (Aliouche *et al.* 2001). The fibers are used in order to provide integrity to the product (Brodin and Theliander 2012) as well as to accommodate more rapid wicking of fluid throughout the absorbent and to prevent blocking (Buchholz *et al.* 2005).

According to Buchholz *et al.* (2005) a network of cellulosic fibers intertwined through a loose matrix of SAPs in an absorbent product can be expected to restrict the swelling of the SAPs. A constraining pressure of about 2 kPa was estimated in the cited work. It follows that the fibers within a SAP structure may decrease the absorption capacity; however, the fibers might be needed to maintain structural integrity and to allow quicker distribution of liquid through the product. A typical composition for a disposable diaper has been cited as 43% fluff pulp, 27% SAP material, and the remainder being various plastic materials and adhesives (Edana 2005).

Refining of fibers and absorbency

Refining refers to the repeated mechanical compression and shearing of a slurry of cellulosic fibers in the gap between the raised bars of a stator and a rotor (Smook 1992). The usual intention of refining is to cause internal delamination of the cell wall structure and thereby to increase the flexibility and conformability of the wet fibers. Refined fibers can be expected to develop a greater relative bonded area, hence achieving higher strength of paper products (Page 1969; Lowe *et al.* 2007). However, when high absorbency is the key goal, studies have shown that the extent of refining should be kept low (Gigac and Fiserova 2008). The cited authors observed that the manner of refining, in addition to the applied energy, can be important; a high specific edge load (generally obtained by using refiner plates with a relatively coarse pattern) resulted in higher absorbency of the resulting tissue paper. These effects can be attributed to a more voluminous packing of fibers that have become bent as result of harsh but limited refining treatment. Due to larger void volumes, more water was able to be absorbed into the tissue paper.

Bulk

Consistent with the preceding discussion, factors that tend to reduce the packing density of a structure can be expected to favor more rapid flow into products made from cellulosic fibers. Though mechanical pulp fibers individually tend to have lower absorbency than bleached kraft fibers, they also tend to be stiffer and less compressible, often yielding a bulkier structure of paper. The relationship between fiber stiffness and the resulting paper's apparent density was demonstrated in a fundamental manner by Steadman and Luner (1985). Accordingly, Brodin *et al.* (2012) observed higher absorbency for pads composed of chemithermomechanical pulp (CTMP) fibers in comparison with kraft fibers. In the case of kraft pulps, Lund *et al.* (2011) showed that increased bulk could be achieved by crosslinking the fibers with a diepoxide. Such treatment would find application in products that need to resist wet compaction, as might happen in the case of a wet diaper holding up the weight of a child.

Another way to increase the bulkiness of a dry paper structure is to treat the fiber suspension with a suitable cationic surfactant before the drying process. Fatehi *et al.* (2010) showed that treatment with such "debonding agents" rendered the resulting tissue paper less dense. Likewise, Shepherd and Xiao (1999) showed that surfactant treatment of wet pulp resulted in an increased effective pore size and hydrophilicity of fibers once the paper had been dried. Cationic surfactants yielded the largest increase in the rate of wetting.

Another factor that is sometimes overlooked when considering the absorption capacity of a cellulose-based product is the swelling of the fibers themselves upon wetting, an effect that can change the dimensions of the structure as a whole. Bristow (1972) introduced this concept as a means of accounting for the absorption capacities of fiberboard products. Factors affecting the swelling of cellulosic fibers have been considered in various studies (Jayme and Büttel 1964, 1968; Scallan and Carles 1972; Gigac and Fiserova 2008; Zhang *et al.* 2008a; Cheng *et al.* 2010; Lund *et al.* 2011).

Channeling

Cellulosic fiber webs, especially if the fibers have a relatively coarse and bulky nature, appear well suited to achieving a relatively rapid uptake of water (Beuther *et al.* 2010). Thus, as noted by Rezai and Warner (1997), combinations of SAPs and cellulosic fibers can be used in an attempt to achieve the best results from each component – relatively rapid wicking by the fibers and high absorbency contributed by the hydrogel. Schuchardt and Berg (1991) showed that, to a first approximation, well-established equations of flow through packed beds can be used to model the flow of aqueous fluids through mixtures of cellulosic fibers and superabsorbent hydrogel particles. However, it was apparent that swelling of the SAPs tended to progressively restrict the flow as a function of time. A correction term, *i.e.* a permeability factor, was defined to account for this effect. To make it less likely that swollen SAP particles can seal the passages adjacent to a cellulosic fiber, one could select fibers having an irregular cross-section (Pramanick and Crouse 1998). For instance, certain viscose fibers have been observed to be multi-lobal in cross-section (Schuster *et al.* 2006). The use of twisted, curly fibers for absorbent products has been patented (Sun and Lindsay 2003; Hu and Ko 2006).

As an alternative strategy to achieve high flow rate within a relatively large volume of superabsorbent material, certain authors have prepared superabsorbent fibers. These fibers tend to pack less densely than the same mass of rounded particles. For example, Feng *et al.* (2010b) spun blends of cross-linked polyacryonitrile and cellulose acetate as a means of producing highly absorbent fibers. Related results were achieved by Goetz *et al.* (2011) by extensive grafting of softwood kraft fibers with poly(methyl vinyl ether-co-maleic acid) and polyethylene glycol. Both studies achieved SAP-like levels of water absorbency, while retaining the bulky bed structure inherent in the use of suitably stiff fibers.

Pore structure

Another way in which to consider aspects related to the bulky structure of cellulose-based sorbents is to examine the effects of pore spaces. Such spaces can vary greatly in size, size distribution, and connectivity. Pores also can be quantified in terms of their net volume relative to the solid content. For instance, Beuther *et al*. (2010) estimated that a typical sheet of tissue paper can have a relative void volume greater than 0.9, consistent with the ability to pick up as much as ten times its mass in aqueous fluids. Brodin *et al.* (2012) used porosimetry to quantify the pore size distribution within an absorbent foam; by this means it was shown that inclusion of relatively stiff CTMP fibers resulted in greater preservation of pore volume when a mixed absorbent structure was compressed. Studies by Sannino *et al.* (2004b, 2005) showed that the porous nature of hydrogel foams could be systematically adjusted by varying the conditions of precipitation and foam formation.

At the nano-scale, as noted already, it has been proposed that a significant amount of water contained in a hydrogel may be present as small “lakes” rather than as chemically bound water (Gelin *et al.* 2007). In other words, the distribution of water may be uneven, when considered on a nano-scale. Hydrogels formed in the presence of nano-sized micelles of surfactant molecules have been shown to have enhanced porosity; such effects have been shown to nearly double the absorption capacity for water in some cases (Shi *et al.* 2013). In the case of chemically pulped fibers, effects related to porosity also extend to the nano-scale. A mesoporous structure within various kinds of cellulose material has been well documented (Stone and Scallan 1968; Schuster *et al.* 2006). Also, it has been proposed that grafting of such fibers with hydrophilic polymer chains may serve to brace adjacent microfibrils apart from each other, thus contributing to the swellability and ultimately to the volume available for sorption of fluids (Lepoutre *et al.* 1973).

At a molecular scale it has been proposed that the inherent stiffness of the cellulose polymer chain can lead to a firm hydrogel structure that is less susceptible to collapse of foam structures (Chang *et al.* 2009a; Zhang *et al.* 2010). As a likely explanation, the apparent stiffness may be due to cellulose’s tendency to self-associate into microfibrils, *i.e.* semi-crystalline domains, during the process of gelation (Chen *et al.* 2006; Kondo *et al.* 2008). A substantial presence of crystalline domains has been detected even in the case of hydrogels based on hemicellulose (Karaaslan *et al.* 2010, 2012). Nishio and Manley (1988) showed that the presence of polyvinyl alcohol tended to suppress the formation of crystallinity in cellulose when it was regenerated from an ionic liquid solution. It is reasonable to expect that such microfibrils and partially crystalline character play a role, especially when hydrogels are prepared from solutions of either cellulose itself or of derivatives such as CMC having a low enough degree of substitution as to still permit local, well-organized self-association of chain segments (Thuresson and Lindman 1999; Saito *et al.* 1994a,b; Bhandari *et al.* 2012). Bhandari *et al.* (2012) found an inverse relationship between the swelling tendency and the degree of crystallinity within cellulose films regenerated from ethanol-water-NaOH solutions.

Nanocellulose and Absorbency

During recent years there has been a high level of research activity devoted to the preparation and characterization of very finely separated cellulosic fibrillar or elongated crystalline particles (Klemm *et al.* 2011). Likewise, there has been related patenting activity (Duran *et al.* 2012; Charreau *et al.* 2013). Cheng *et al.* (2010) showed that certain nanocellulose materials by themselves achieved water retention values in the range of 3.4 to 3.5 g/g. Hua *et al.* (2011) patented a production system for nanocellulose and described their use in absorbent products.

Nanocellulose materials can be formed into highly porous, absorbent structures by freeze-drying of their aqueous suspensions. Thus, Pääkkö *et al.* (2008) showed that native cellulose nanofibrils, obtained by enzymatic and mechanical processing of bleached sulfite softwood fibers, yielded strong and voluminous aerogels upon freeze-drying. Immersion of an aqueous suspension of nanofibrillated cellulose in liquid propane, followed by vacuum pumping, yielded an aerogel structure that shrunk by only 7%. A practical, short-cut method was developed in which aerogels were formed by direct vacuum pumping (and induced freezing) of the initial aqueous suspensions. The latter method caused 20% shrinkage. Brodin *et al.* (2012) explored the use of microfibrillated cellulose in combination with macroscopic cellulose fibers in a freeze-dried structure; absorbencies in the range of 21 to 65 g/g were observed. The composite structure displayed better mechanical stability of its foam structure, as well as higher absorbency. Oxidation was used in the cited work to further increase the absorbency of the fiber component of the structure. Kettunen *et al.* (2001) reported an absorbency of 35 g/g in the case of freeze-dried nanocellulose aerogels.

Nanocellulose also has been incorporated into hydrogel products (Abbas *et al.* 2011; Karaaslan *et al.* 2011; Gane *et al.* 2012). The mechanical integrity of such hydrogels is generally improved by such addition (Karaaslan *et al.* 2011), suggesting that the elongated nanocellulose particles can have a function similar to that of a cross-linking agent, or probably more precisely as nano-reinforcement of the gel structure. A tight, relatively defect-free attachment between cellulose nanofillers and a hydrogel matrix has been demonstrated by a high transparency of such nanocomposite hydrogels (Dai and Kadla 2009). This was in contrast with the effect of nanoclay usage, which resulted in opaque hydrogels.

Maintaining meso-pore structure

Cellulosic nanomaterials as part of a hydrogel structure may help to alter or maintain the structure of pores. Spagnol *et al.* (2012a) found that incorporation of cellulose nano-whiskers (*i.e.* long crystals) tended to increase the pore size of starch-acrylic hydrogels. Relatively low levels of nanocellulose addition tended to create defects in the structure, thus decreasing the elastic modulus. However, amounts greater than 5% yielded a net increase in strength, suggesting the presence of a contiguous network of cellulosic elements within the matrix (Favier *et al.* 1997; Chakroborty *et al.* 2006a,b; Hubbe *et al.* 2008).

Effects on swelling

Effects of the presence of nanocellulose on the swelling of SAP composites has been considered in several studies (Buyanov *et al.* 2010; Larsson *et al.* 2010, 2011; Laftah *et al.* 2011; Spagnol *et al.* 2012a). In the review article by Laftah *et al.* (2011), the findings of such studies were summarized by stating that nanofibers can either increase or decrease absorbency in different cases. The hydrophilic nature of cellulosic fibers contributes to the absorbency of the structure as a whole, yet the more rigid nature of the resulting network structure can contribute to decreased absorbency. This may explain an observed complexity of the relationship between nanocellulose content and absorbency (Larsson *et al.* 2011). Anisotropic swelling was observed by Buyanov *et al.* (2010) in nanocellulose-filled hydrogel structures that had been pre-compressed during their formation. Spagnol *et al.* (2012a) reported that although nanocellulose inclusion at relatively high levels decreased absorbent capacity, it also resulted in greater pore size. The increase in pore size was judged to be an important advantage in terms of the absorption rate and the overall performance of the absorbents. The cited authors found, however, that at a low content of nanocellulose (5 to 10%) the water content was the highest. This trend was confirmed in subsequent work (Spagnol *et al.* 2012b,c).

EFFECTS OF FLUID COMPOSITION ON ABSORBENCY

In addition to the chemical and structural aspects of the sorbent material, as discussed in the previous two sections, the absorbency characteristics of cellulose-based materials can also be profoundly affected by the nature of the aqueous fluid to be absorbed. In addition to providing practical information, the goal of this section is to summarize evidence that can be used to support various theoretical concepts, which are addressed in later sections.

Effects of Salinity

Inspection of the last two data columns in Table A reveals a strong contrast between the amounts of pure water taken up by various cellulose-based absorbents *vs.* the corresponding amounts of saline solution (often evaluated with 0.9% NaCl). In typical cases the latter value is less than half of the absorption capacity in the case of pure water. Especially sharp contrasts in capacity, when comparing deionized *vs.* saline water, have been reported in the case of superabsorbent hydrogels (Lim *et al.* 2001; Suo *et al.* 2007; Zhang *et al.* 2008b, 2009; Kim and Mun 2009; Liang *et al.* 2009; Pourjavadi *et al.* 2008, 2009; Chang *et al.* 2010; Bao *et al.* 2011; Liu *et al.* 2011; Wang *et al.* 2011a,c,d; Wu *et al.* 2012).

For certain end-uses it would be highly desirable to maintain a high level of absorbency even in the presence of intermediate levels of salt ions. A number of authors have reported progress in development of somewhat “salt-tolerant” hydrogels (Kulicke and Nottelmann 1989; Yang *et al.* 2009; Wu *et al.* 2012). Yang *et al.* (2009) attributed the observed salt-tolerance to graft polymerization between CMC and polyacrylamide. Rezai and Warner (1997) reported that even though salt greatly decreased the absorbency of acrylonitrile-grafted wood pulp fibers, such fibers still absorbed three times as much water as their ungrafted counterparts. Also, various hydrogels comprised of hemicellulose in combination with chitosan have shown favorable performance in their relative ability to absorb saline solutions (Salam *et al.* 2011b).

Fält and Wågberg (2003) as well as Li and Dai (2004) observed an interesting effect of salt on the swelling of highly purified cellulosic fibers. The samples had been prepared with the complete exclusion of salt ions. Swelling actually tended to increase with the first added amounts of such salts as Na_2SO_4 and NaCl. The effect was attributed to an increase in effective pH within the mesopore spaces within the fibers. Related mechanisms have been further considered (Hubbe 2006; Hubbe *et al.* 2007a), as a way to account for effects of salt concentrations on the streaming potential of cellulosic fibers.

Effect of pH

Conventional kraft fibers used in papermaking are known to exhibit increased water retention with increasing pH (Jayme and Büttel 1964; Lindström and Carlsson 1982). Such effects have been observed most clearly in the case of relatively high-yield pulps, *i.e.* fibers that contain substantial amounts of hemicellulose and other species bearing carboxylic acid groups (Lindström and Carlsson 1982). In comparison, such effects in the case of bleached kraft pulps tend to be small (Lindström and Carlsson 1982; Hubbe and Panczyk 2007a).

In the case of hydrogels having cellulosic content, numerous studies have reported increased swelling with increasing pH, at least up to the neutral point (Vitta *et al.* 1986; Barbucci *et al.* 2000; Sannino and Nicolais 2005; Chen and Tan 2006; Ali *et al.* 2008; Wang and Wang 2010; Anirudhan *et al.* 2011; Bao *et al.* 2011; Eldin *et al.* 2011; Wang *et al.* 2011b,d). Certain studies (Liu *et al.* 2005a; Ibrahim *et al.* 2007; Pourjavadi *et al.* 2007b; Akar *et al.* 2012; Shi *et al.* 2013; Wang *et al.* 2008, 2013) showed a distinct maximum swelling at neutral pH; a possible explanation for this finding is that increasing amounts of ions must be added to such a system to achieve pH values significantly different from 7; such ions would be expected to have the same effect corresponding to the previous subsection (Effects of Salinity). Odd results, roughly opposite to those just cited, were obtained by Varaprasad *et al.* (2011), though no explanation was given. Wang *et al.* (2010) developed a system based on hydroxyethylcellulose-g-poly(acrylic acid) with very finely divided attapulgite mineral that achieved consistent high swelling within the broad pH range between 4 and 10.

Evidence of an additional contribution to de-swelling has been observed in some hydrogel systems at the low end of the pH range investigated. Barbucci *et al.* (2000) observed a strong contraction of hydrogels at pH values well below the pK_a value of the constituent carboxyl groups. The effect was attributed to the formation of hydrogen bonded pairs between adjacent protonated carboxylic acid groups.

Shang *et al.* (2008) developed a creative system in which the bending of a gel body could be used as an indication of the strength and direction of an imposed electric field. According to the authors, the bending of the gel was attributable to slight pH differences on either side of the hydrogel, resulting from the half-reactions at the electrodes used to generate the electric field.

Effects of Valency and Identity of Positive Ions

Numerous studies have shown greater decreases in swelling with increasing valency at a constant concentration of cations in the aqueous solution to which a hydrogel is exposed (Vitta *et al.* 1986; Kulicke and Nottelmann 1989; Feng and Wang 2010a; Bao *et al.* 2011; Akar *et al.* 2013; Chang *et al.* 2012; Li *et al.* 2012; Raafat *et al.* 2012). The effect has been attributed to reversible complexation between the cationic species and one or more carboxylate groups in the hydrogel (Bao *et al.* 2011; Raafat *et al.* 2012). In addition, multivalent cationic species can be expected to have a relatively large effect in reducing ionic double layer forces of repulsion associated with the bound carboxylate groups of a typical hydrogel (Hiemenz 1977). As noted by Vitta *et al.* (1986), by acting as a bridge between more than one carboxylate group in a hydrogel, a multivalent cation can act as a crosslinking agent, thus decreasing swelling.

Though not as obvious or important as the effect of valency, many studies have detected differences in the effects on swelling between cations of the same valency. Two studies dealing with SAPs showed a greater suppression of swelling in the presence of the divalent magnesium ion, in comparison with the same concentration of calcium ion (Bao *et al.* 2011; Li *et al.* 2012). The same authors showed that monovalent sodium ion generally suppressed swelling to a greater degree than the potassium ion. In the case of acrylic-grafted sulfite fibers, Vitta *et al.* (1986) reported the following sequence of increasing water retention values at a fixed concentration of the following ions:

$$Al^{3+} < Cu^{2+} < Zn^{2+} < Ca^{2+} < Mg^{2+} < H^{+} < Na^{+} < K^{+} < Li^{+}$$

It should be stressed that all of the effects related to different cations of the same valency were small relative to the effect of valency. It is interesting, though, that within the individual studies cited, the results tended to follow regular progressions according to the tabulated size of the respective ionic species.

Surfactants and Absorbency

Surfactants have been shown to affect absorbency in three ways. First, in the case of ordinary paper, addition of various surfactants has been shown to facilitate more rapid wetting in some cases (Hodgson and Berg 1988; Shepherd and Xiao 1999). Such treatments were able to overcome a "wetting delay" phenomenon that is often observed when water is spread onto initially-dry paper. Increased absorbency was observed by Shepherd and Xiao (1999) following treatment of the paper with surfactant.

Second, addition of a cationic surfactant before preparation of paper has been found to yield a bulkier structure (Mann and Leah 1987; Fatehi *et al* 2010). The debonding effect of such treatment resulted in dry-strength decreases in the range of 14 to 19%. Poffenberger *et al.* (2000) showed that, due to the hydrophobic nature of typical cationic surfactants, the net effect of debonding treatment during the production of tissue paper may be a reduction in the uptake of water. However, by the careful selection of debonding agents having a relatively hydrophilic character, such decreases can be avoided.

Third, in the case of SAPs, addition of cationic surfactant has been shown to result in a marked decrease of absorbency (Wang and Wang 2010; Wang *et al.* 2011c). Such an effect is consistent not only with the partially hydrophobic nature of the surfactants employed, but also with the expected electrostatic interactions. Wang and Wang (2010) noted that changes in swelling can be affected by screening of the negative charges within the SAP due to the cationic charge of the surfactants, changes in hydrogen bonding interactions, and a hydrophobic interaction between the alkyl tails of the surfactant molecules. In related work, Gawel *et al.* (2012) showed that the nature of a conventional anionic hydrogel was transformed upon the addition of a cationic polyelectrolyte. The surfactant treatment caused the hydrogel to have absorption behavior similar to that of a polyelectrolyte complex type of hydrogel, as was discussed earlier. In the case of ordinary kraft fibers, Swerin *et al.* (1990) showed that addition of cationic polymers caused a loss of swelling. Effects of cationic polymers on the swelling of cellulosic materials and anionic hydrogels will be considered in a later section dealing with theoretic aspects of swelling capacity.

Adsorbed Polyelectrolytes

The term “adsorption” can be defined as a process by which a chemical species (such as a polyelectrolyte) becomes attached to a surface – either on the apparent external surface of a material or on surfaces within a porous structure. A study by Ström and Kunnas (1991) demonstrated that polyelectrolytes adsorbed onto papermaking fibers can make a significant contribution to their water retention value. Cationic polyelectrolytes of high charge density were shown to decrease the amount of water held within the pulp fibers after their centrifugation to remove free water. The effect was attributed to the ability of highly-charged cationic polymers to accelerate dewatering of paper pulp; this was a surprising finding, since water retention value tests are usually intended to provide information about equilibrium conditions. A related study by Hubbe and Panczyk (2007b) confirmed the effect of low- to moderate-mass, high-charge-density cationic polymers on reducing the water retention of kraft pulps. By contrast, sufficiently high levels of very-high-mass cationic polymers tended to increase water retention. The latter effect was attributed to the water associated with the polyelectrolytes themselves in their adsorbed state.

Temperature

Effects of temperature are of both theoretical and practical interest (Miyamoto *et al.* 1995). Some authors have called thermal changes in absorbency a “smart” feature, since they may allow specialized applications of a thermo-sensitive hydrogel (Pourjavadi *et al.* 2007b; Yang *et al.* 2011). Typical temperature-responsive hydrogels exhibit markedly decreased absorbency with increasing temperature (Harsh and Gehrke 1991; Kuwabara and Kubota 1996; Çaykara *et al* 2006; Chang *et al.* 2009b). Decreases in absorbency as high as a factor of five (Kuwabara and Kubota 1996) or ten (Çaykara *et al* 2006) have been reported when comparing absorbency at about 20 ^{o}C to the correspondding value at about 40 ^{o}C. The strongest thermal effects are for SAPs incorporating relatively high proportions of poly(*N*-isopropylacrylamide); these generally exhibit a strong decrease in absorbency at temperatures near to physiological conditions (Kuwabara and Kubota 1996; Liu *et al.* 2004; Chang *et al.* 2009b; Yang *et al.* 2011). For example, Kuwabara and Kubota (1996) used a two-step procedure to graft a 51/49% acrylic acid/N-isopropylacyrlamide onto CMC at a grafting level of 205%; water absorbency fell from about 14 g/g at 10 ^{o}C to 3 g/g at 50 ^{o}C. Çaykara *et al.* (2006) prepared semi-interpenetrating networks of poly-[(*N-tert*-butylacrylamide)-co-acrylamide] with hydroxypropylcellulose; water sorption was observed to fall from as high as 19 g/g at 5 ^{o}C down to about 2 g/g at 40 ^{o}C and above. Chang *et al.* (2009b) reported a decline in absorbency from 18 g/g to 5 g/g over a temperature rise from 10 ^{o}C to 60 ^{o}C in the case of an interpenetrating network of one part cellulose to three parts of poly-NiPAM. Likewise, in the case of SAPs comprising carboxymethylchitosan and poly-NiPAM, Ma *et al.* (2007) observed a decrease in buffer solution absorption from 19 g/g at 25 ^{o}C to 2 g/g at 35 ^{o}C. An opposite thermal effect, with moderately increased swelling of hydrogels with increasing temperature, has been reported less frequently (Liu *et al.* 2005a; El-Din *et al.* 2010). Hirsh and Spontak (2002) showed that the thermo-responsive characteristics can be attributed to changes in the elastic properties of such hydrogels.

External Pressure and Absorbency

In various applications of absorbent materials it may be important to resist the release of water upon compression. In fact, one of the strategies in the design of highly absorbent products is to employ a relatively stiff fiber matrix such that compressive forces acting on SAPs in the product are minimized (Buchholz *et al.* 2005). According to the same source, as has been noted, the presence of fibers also can restrict swelling. Guilherme *et al.* (2005) evaluated the stress-strain behavior of hydrogels as a function of temperature. It was shown that higher temperatures led to increased stress values in the cases considered. This was associated with the absorption of water, *i.e.* osmotic pressure. Sannino *et al.* (2004b) described the development of a test device capable of comparing the effects of compression on the absorption capacity of SAPs. Based on the results shown, it was clear that even a moderate applied pressure of about 300 kPa was sufficient to reduce the swelling with water by 90% in the case of CMC/HEC hydrogels that had been equilibrated (at different levels of compression) for 24 hours.

ACCOUNTING FOR OBSERVED SORPTION CAPACITIES

As has been shown in previous sections, the amount of aqueous fluid taken up by cellulose-based absorbents can depend strongly on the chemical composition and structure of the absorbent, and also on the characteristics of the liquid. Theoretical explanations that have been proposed to account for absorption capacities will be considered here. Some notable review articles that emphasize theoretical issues relevant to the extent of swelling are available (Scallan 1983; Brannon-Peppas and Peppas 1990; Kazanskii and Dubrovskii 1992; Ganji *et al.* 2010).

Quantification of Sorption Capacities

As a first step in reviewing theories to account for absorption capacities and rates, it is important to consider how absorbency is tested. Some notable advances in measurement procedures have been described, as listed in Table 2.

Table 2. Methods for Quantification of Absorption Capacity or Rate

Item measured	Measurement concept	Literature citations
Absorption capacity of loose fibers (water retention value)	Centrifugation of plug of damp fibers to remove internal water	TAPPI 1981; SCAN 2000; Cheng *et al.* 2010
Fiber saturation point	Quantification of the volume of water not accessible by very-high-mass non-interacting polydextran molecules	Scallan and Carles 1972
Amount and state of absorbed water *vs.* time	Infra-red spectroscopy during thermal gelation	Sammon *et al.* 2006
Characterization of the nature of absorbed water *vs.* time	Dielectric spectroscopy	Gelin *et al.* 2007
Wicking rate in tissue & towel	Radial wicking (mass results compared to X-ray densitometry)	Beuther *et al.* 2010
Absorption time of water into paper	Time required for drop to be absorbed into paper	Ström & Carlsson 1992
Quantification of incontinence release amounts	Mass of urine released to paper towel	Neumann *et al.* 2004
Formation of crosslinked structure within a superabsorbent hydrogel	Ultrasonic wave propagation monitoring	Lionetto *et al.* 2003, 2005

When testing the water sorption capacity of cellulosic fibers, Welo *et al.* (1952) observed that a simple weight-loss method, with free evaporation under ambient conditions, was easy and repeatable. The materials were first fully swollen with an excess of water, then weighed periodically. It was found, for each specimen, that weight loss was linear with temperature up to a critical point, and thereafter slowed down. The critical point was identified with the loss of all external water, leaving behind only water of swelling. The water at that critical point was used as an approximation of the water-holding capacity of the fibers. More recently, a similar concept was developed using isothermal drying in a thermogravimetric analyzer; the non-external water was named hard-to-remove water (Park *et al*. 2006).

The Donnan Equilibrium and Osmotic Pressure

When an absorbent material takes up a liquid, either that liquid needs to displace another fluid (such as air), or the material needs to swell to accommodate the new liquid. This section will consider osmotic pressure and various studies showing how osmotic pressure can account for such swelling, especially when a cellulosic material or a hydrogel is placed in water having few or no salt ions (Grignon and Scallan 1980; Vitta *et al.* 1986; Oppermann 1995; Sannino *et al.* 2003; Buchholz *et al.* 2005; Ganji *et al.* 2010). The same principles also apply to cellulosic fibers, though usually to a lesser extent. Part of the justification for considering cellulosic materials in the context of hydrogels involves the presence of ionizable bound groups, mainly carboxyl groups, within their structure (Herrington and Petzold 1992). Such groups contribute to swelling (Grignon and Scallan 1980; Lindström and Carlsson 1982) and ion exchange phenomena (Rudie *et al.* 2006; Hubbe *et al.* 2011) within cellulosic fibers.

One of the most important principles underlying swelling is that, under equilibrium conditions, there will be a fixed relationship between the concentrations of ions inside and outside of a swellable, gel-like material (Grignon and Scallan 1980). In other words a Donnan equilibrium condition will become established between the ion concentrations inside and outside of the hydrogel. If one assumes, for instance, that an aqueous system containing a suspended anionic hydrogel phase contains the ions OH^-, H_3O^+, Cl^-, and Na^+, then the Donnan equilibrium can be expressed in the form,

$$\lambda = [H_3O^+]_g/[H_3O^+]_s = [Na^+]_g/[Na^+]_s = [OH^-]_s/[OH^-]_g = [Cl^-]_s/[Cl^-]_g \qquad (1)$$

where the subscript “g” indicates location within the gel phase and the subscript “s” indicates location within the solution phase, respectively.

A characteristic feature of a typical hydrogel is that ionizable groups are bound to polymer chains within the gel phase. The first analysis of the relationship between such charged groups and swelling was based on ordinary gelatin and the effects of acidity in a surrounding bulk solution (Proctor 1914). Grignon and Scallan (1980) were the first to extend the same concept to the swelling of pulp fibers; they noted that the amorphous polysaccharide regions within pulp fibers can be regarded as being hydrogels. In either case, the tendency of the solid to swell upon placement in deionized water can be visualized as a process whereby water rushes into the hydrogel zones in order to make the value of λ become closer to one. As water progressively enters the gel phase, the ionic concentration associated with the bound ionizable groups becomes diluted; however, in salt-free systems, such dilution is never enough to eliminate the contrast in ionic strength between the inside and the outside of hydrogel zones.

Once equilibrium has been established, the osmotic pressure tending to swell the hydrogel phases within the mixture can be calculated based on the following equation (Ganji *et al.* 2010),

$$\pi = RT\left[\Phi \sum_i \overline{C}_i - \phi \sum_i C_i\right] \tag{2}$$

where Φ is the osmotic coefficient of the gel phase and ϕ is the corresponding quantity for the external aqueous solution. Likewise, $\overline{C_i}$ is the concentration of the ith species in the gel phase and C_i is the corresponding value in the external solution phase. At equilibrium it is understood that the osmotic pressure will be in balance with elastic forces tending to limit swelling in the material (Grignon and Scallan 1980). The following equation can be used to estimate the osmotic coefficient of the gel phase in Eq. 2 (Ganji *et al.* 2010),

$$\Phi = \left\{\phi_P + \frac{n_p}{n_m \alpha}\right\} / \left\{1 + \frac{n_p}{n_m \alpha}\right\} \tag{3}$$

where n_p is the molarity of the polymer, n_m is the molarity of the monomer, and α is the degree of ionization as a fraction.

Entropy of Mixing

A second key factor accounting for the swelling of a hydrogel with water involves the entropy of mixing (Sannino *et al.* 2003; Ganji *et al.* 2010). Such effects can be understood based on Eq. 4, for which a negative value of the change in Gibbs Free Energy (ΔG) of a system indicates that a process will occur spontaneously:

$$\Delta G = \Delta H - T\,\Delta S \tag{4}$$

In this expression, ΔH is the change in heat energy (enthalpy), T is the absolute temperature, and ΔS is the change in entropy. The term S is sometimes called a measure of the disorderliness of a system. In principle, energy is required to separate a mixture into pure subphases; by contrast, miscible materials will spontaneously form a single, disorganized phase with the release of energy when placed together.

Entropy can play a significant role in the swelling of hydrogels because a system in which the gel material is infused with water has greater randomness (higher entropy) than the separated (dry) hydrogel and water phases. The contribution to swelling pressure due to the entropy of mixing can be estimated from Eq. 5 (Ganji *et al.* 2010),

$$\pi_{mix} = -\frac{RT}{V_1}\{\ln(1-\upsilon) + \upsilon + \chi\upsilon^2\} \tag{5}$$

where υ is the polymer volume fraction, V_1 is the molar volume of the solvent, and χ is the interaction parameter.

Figure 3 illustrates another way in which changes in entropy tend to contribute to the swelling of a typical hydrogel material when it is placed in water (Khokholv and Nyrkova 1992). Here it is assumed that the gel material contains ionizable acid-type groups, such as $–COO^-$ or $–SO_4^-$, *etc.* The left-hand frame of the figure represents the gel material in its dry form as the sodium salt of the poly-anionic gel. In such form, the component ions have very limited freedom of motion, being bound by their ionic bonds and the contracted, solidified nature of the gel. As illustrated by the right-hand frame of the figure, the addition of water, along with the swelling of the gel, implies more degrees of freedom. For instance, sodium ions may effectively “switch places” as counter-ions for the bound anionic groups. As indicated in the upper right of the figure, such an exchange even can occur with salt ions from the bulk. Further contributions to disorder and freedom of motion within such a system are associated with chain mobility and the relatively long (in atomic terms) average distance between oppositely charged ions in an aqueous system having very low electrical conductivity (Hiemenz 1977).

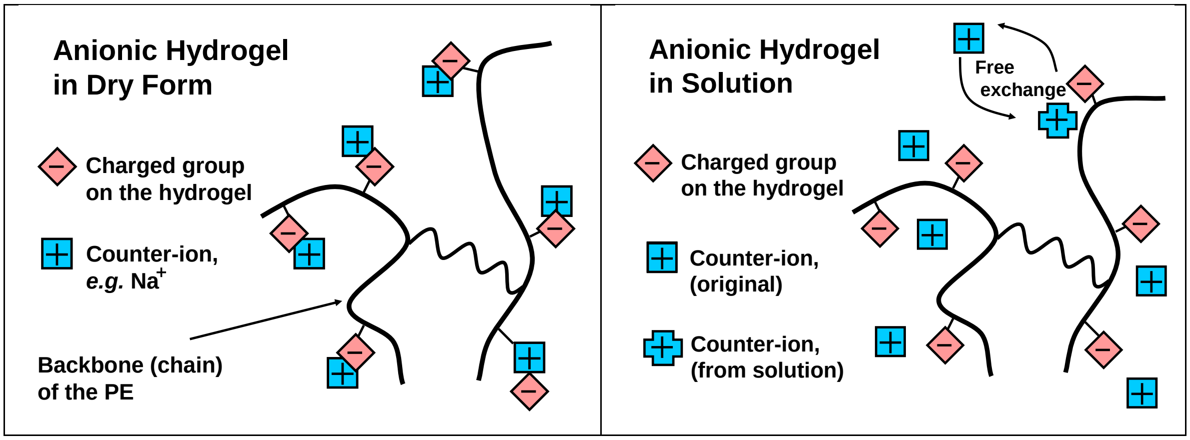


Fig. 3. Illustration of increased disorder and freedom of motion of a counter-ion (*e.g.* sodium) in a typical hydrogel that contains acid groups (*e.g.* carboxylate). **Left:** Dry form as sodium salt of polycarboxylate hydrogel; **Right:** Water-swollen form, in which the counter-ions are free to exchange with each other, to diffuse within the field of electrostatic forces, and also for the polyelectrolyte chain segments to undergo some constrained motion.

Hydration and Hydrogen Bonding Effects

A third key element to account for the swelling of hydrogels, in addition to the osmotic effects and entropy contributions just described, is hydrogen bonding. The relatively strong interactions between water molecules and hydrogel materials promote hydration and ionization, such that the osmotic and entropic effects can operate. The importance of hydrogen bonding relative to hydrogel swelling was perhaps best demonstrated by Koroskenyi and McCarthy (2001), who studied the highly hydrophilic polymer konjac glucomannan. In its native state the gelatinous material absorbed over 105 times its mass of water. By contrast, after full acetylation, removing all of the –OH groups, the same material had a water absorbency of only 1 g/g. Another clue that hydrogen bonding is intimately related to gel behavior comes from infra-red analysis. Sammon *et al.* (2006) detected distinct shifts in the wavelengths of infrared absorbance maxima that were coincident with gelation of hydroxylpropylmethylcellulose (HPMC) as a function of temperature.

Regarding the state of water within a typical hydrogel, various views have been expressed in the literature. According to Karaaslan *et al.* (2012), most of the water within a swollen hydrogel should be regarded as bound water. In other words, its properties can be expected to differ from those of bulk water in terms of such behaviors as freezing tendencies and temperatures. Accordingly, Faroongwarng and Sukonrat (2008) observed that the freezing point of water was depressed within hydrogels. Gelin *et al.* (2007)

estimated that only about 10% of water present in a typical hydrogel acts like bulk water. Their work with measurement of ion diffusion rates, in addition to freeze-fracturing of hydrogels, led to the conclusion that the bulk-like water within hydrogels tended to be confined to isolated "lakes" within the pore structure. This finding suggests that various reported porous hydrogels or "foams" might be expected to contain substantial bulk-like water in addition to chemically bound water (Kabra *et al.* 1998; Omidian *et al.* 2005; Lu *et al.* 2007; Chang *et al.* 2009a,b; Sehaqui *et al.* 2010; Salam *et al.* 2011a). Joshi *et al.* (2008) proposed that the relatively sharp gelation transition that takes place upon heating of methylcellulose solutions can be attributed to a thermal breakdown of the water structure, allowing coalescence of the polymer chains. Venditti and coworkers have demonstrated that freezing and non-freezing bound water and bulk water are present in cellulosic fibers and can be measured with differential scanning calorimetry (Park *et al.* 2007). The heat of vaporization of the bound water can be almost 30% higher than bulk water. For fibers that cannot participate in hydrogen bonding, such as polypropylene, bound water and increased heat of vaporization of waters do not exist (Park *et al.* 2007).

Progress in understanding the nature of water within cellulosic materials has been achieved through advances in spectroscopic methods. Froix and Nelson (1975), using nuclear magnetic resonance relaxation times, concluded that free water, in addition to chemically bound water, existed within cellulosic fibers even in "dry" paper in equilibrium with relative humidity values above 0.1. Using NMR and ESR methods, Capitani *et al.* (1990) came to the conclusion that water domains within cellulose somehow permeate cellulose domains, such that the two kinds of domains interact by hydrogen bonding. Using calorimetric methods, Maloney *et al.* (1998) found evidence that bulk-like water was present within the larger mesopores of never-dried kraft fibers after their placement in water; by contrast, only bound water was present within the cell walls of previously dried cotton. Park *et al.* (2006) showed that such considerations can be used to estimate the dimensions of nano-sized water-filled pores within cellulosic materials.

Elastic Modulus

As proposed by Proctor (1914), the extent of swelling of a typical hydrogel in pure water or various electrolyte conditions can be modeled in terms of a balance between osmotic forces and restraining elastic forces due to the swollen material. Scallan and coworkers extended these concepts to cellulosic fibers (Grignon and Scallan 1980; Scallan and Tigerström 1992). In either case, pure water can be expected to diffuse into a hydrogel until a combination of partial dilution of the effective ionic concentration within the gel, plus elastic stretching of the gel achieves a balance of forces (Vitta *et al.* 1986; Ganji *et al.* 2010). The viscoelastic properties of various hydrogels, sometimes as a function of their state of swelling, have been studied (Guilherme *et al.* 2005; Feng *et al.* 2006; Chang *et al.* 2009a; Dai and Kadla 2009; Larsson *et al.* 2010). Notably, Larsson *et al.* (2011) and Spagnol *et al.* (2012a) showed that the inclusion of microfibrillated cellulose or cellulose nanocrystals within hydrogels had a strong reinforcing effect, essentially increasing the modulus and limiting the amount of swelling. Yoshinobu *et al.* (1992) and Lionetto *et al.* (2003) showed that there was a relationship between the degree of crosslinking and the elastic modulus of various hydrogels. As already noted, Oppermann (1995) proposed that inclusion of cellulose derivatives within a hydrogel can result in stiffening of the gel. Such an effect follows from the inherent stiffness of cellulose, which may be related to local association of cellulose segments.

An elastic contribution to pressure within a hydrogel, resulting from the configurational entropy of polymer chains, can be estimated if one makes various assumptions concerning the nature of the hydrogel. The stretching of polymer segments associated with the swelling of the gel implies a restriction in the number of motions of individual groups and segments along the chain, *i.e.* a loss of configurational entropy when the hydrogel material is stretched. The lead terms in an equation to estimate the resulting contribution to pressure (tending to resist expansion of the gel) are as follows (Ganji *et al.* 2010),

$$\pi_{el} = -v_o RT \left\{ \left(\frac{\upsilon}{\upsilon_o}\right)^{\frac{1}{3}} - \frac{\upsilon}{2\upsilon_o} \right\} - v_o RT \left\{ \frac{3}{5}\left(\frac{\upsilon}{\upsilon_o}\right)^{\frac{1}{3}} \times \frac{1}{n} + \frac{99}{175}\left(\frac{\upsilon}{\upsilon_o}\right) \times \frac{1}{n^2} \quad + \cdots \right\} \quad (6)$$

where v_o is the concentration of the polymer chains at the onset of gel formation.

Network Volume Constraints

Cross-linking effects

As was noted earlier, the highest recorded values of swelling tend to be associated with the lowest practical (and sometimes impractical) extents of crosslinking (Bin *et al.* 2000; Wach *et al.* 2001, 2002; Liu *et al.* 2005a; Demitri *et al.* 2008; Han *et al.* 2010; Pourjavadi *et al.* 2010; Kono and Fujita 2012). The basis for this relationship is illustrated in Fig. 4. As discussed by Ganji *et al.* (2010), it is possible to estimate the maximum extent of swelling of a hydrogel based on the density of crosslinking, and more specifically the lengths of the characteristic polymer segments between adjacent crosslink points. The quantity $\overline{M}_c$, represented by a typical segment in Fig. 4, is defined as the average or typical molecular mass between adjacent crosslink points. The quantity ξ represents the linear correlation distance between the crosslinks. The volume fraction of the polymer in a swollen gel is then given by the following expression,

$$v_{2,s} = V_p / V_g = (1/\rho_2) / [\, (Q_m / \rho_1) + (1/\rho_2) \,] \quad (7)$$

where V_p is the polymer volume within the material, V_g is the volume of the swollen gel phase as a whole, ρ_2 is the density of the polymer, ρ_1 is the density of the solution, and Q_m is the swollen volume on a mass basis. The degree of crosslinking, X, can be defined as

$$X = M_o / (2 \; \overline{M}_c) \quad (8)$$

where M_o is the characteristic molecular mass of the initial polymer chains before crosslinking. In cases where the polymer-solvent interactions have been tabulated, the typical dimensions of spaces between crosslink points can be estimated from (Ganji *et al.* 2010),

$$\xi = v_{2,s}^{-1/3} \, l \left\{ \frac{C_n 2 \overline{M}_c}{M_o} \right\}^{1/2} \quad (9)$$

where l is the bond length between carbon atoms, and C_n is the tabulated ratio for the system, as derived by Flory (1953). It should be noted that while the cited work did not take electrostatic effects into account, such interactions can be expected to profoundly affect polymer conformations (Fleer *et al.* 1993) and hence swelling.

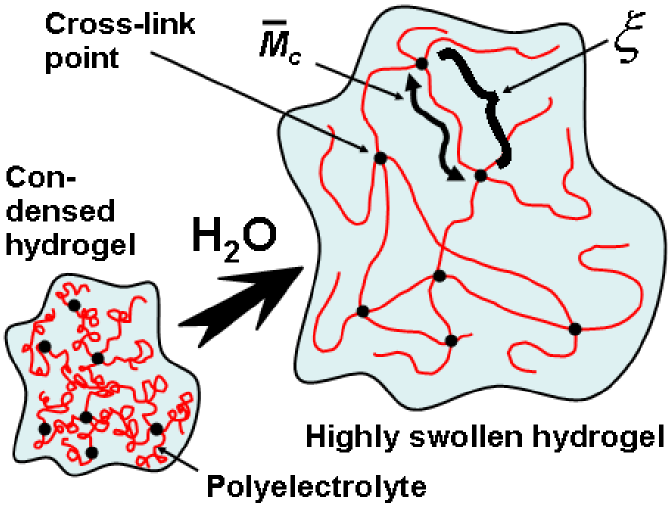


Fig. 4. Representation of a hydrogel in its somewhat condensed (left) and highly swollen (right) states. Solid dots indicate cross-linked points of the polyelectrolyte chains (shown as coiled or wavy lines). The characteristic molecular weight of segments between crosslinks ($\overline{M}_c$) and the correlation distance between crosslink points (ξ) are illustrated by considering one segment.

Cellulosic Fibers and Hydrogel Swelling

Various authors have suggested that a network of cellulosic fibers, *i.e.* a paper-like structure or a loose network of nanofibrillated pulp or fluff pulp fibers filled with hydrogel particles, may play a role in maintaining the structural integrity in a combined absorbent structure that contains SAPs (Buchholz *et al.* 2005; Brodin *et al.* 2012). It follows that such fibers may also restrict the swelling of the SAP material upon introduction of aqueous fluid. The concept is illustrated schematically in Fig. 5.

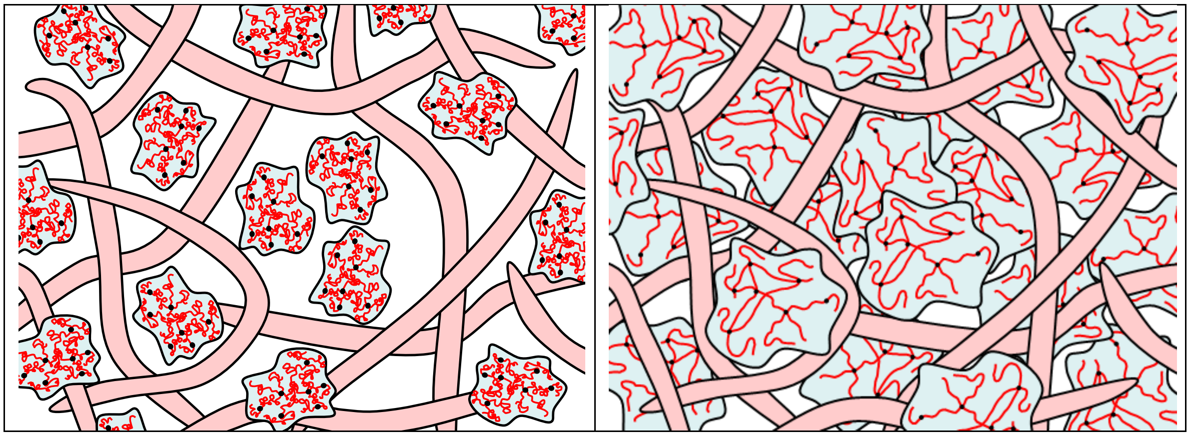


Fig. 5. Illustration of the concept that a network of macroscopic cellulosic fibers in an absorbent product might tend to constrain the swelling of hydrogel particles. **Left:** Representation of dry condition; **Right:** Swollen condition

As was noted earlier, when nanocellulose elements are incorporated into hydrogels, the observed result is generally a marked decrease in absorbency, often accompanied by an increase in the mechanical strength of the gel material (Dai *et al.* 2009; Larsson *et al.* 2010, 2011; Spagnol *et al.* 2012a). In an analogous manner to the mechanism just described to account for the restraining effects of fluff pulp fibers on SAP swelling, some authors have attributed the effects of nanocellulose on SAP absorbency to a "reinforcement" effect (Larsson *et al.* 2011). Indeed, when cellulosic nanofibrils or crystallites have been compounded with various plastics, the resulting "nanocomposites" are typically much stiffer than the matrix plastic material by itself (Azizi Samir *et al.* 2005; Hubbe *et al.* 2008). However, before placing too much weight on any such analogy, it is important to emphasize the huge size difference between a softwood kraft fiber and the smallest classes of cellulosic nanomaterials. Figure 6 provides a schematic comparison. The lengths of the nanocellulose entities, in some cases, may be as much as 10,000 times smaller than a typical fluff pulp fiber. As shown, one of the likely roles of the nanocellulose may be to function as cross-linking points. It is assumed here that polymer segments within the hydrogel may associate locally with the cellulosic surfaces. Such behavior would be consistent with observations that the effects of adding a crosslinking agent or adding nanocellulose are sometimes nearly equivalent (Dai and Kadla 2009; Larsson *et al.* 2010).

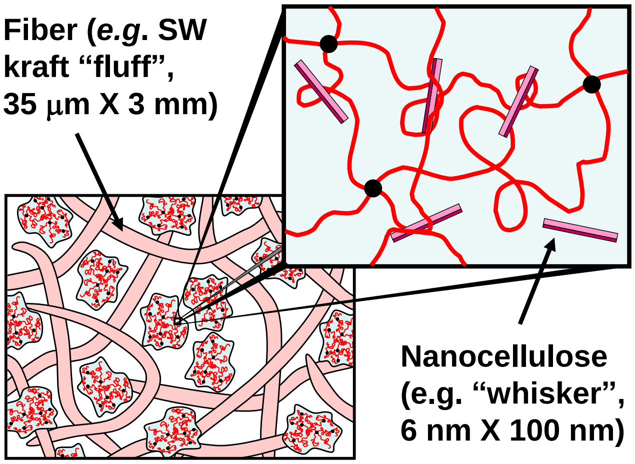


Fig. 6. Illustration emphasizing the great size difference between fluff pulp fibers *vs.* cellulosic nanocrystal, a difference that suggests that their roles with respect to reinforcement, crosslinking, or other effects might also be different

Drying and Absorbency

A profound loss of swelling capacity is known to occur when delignified pulp fibers are dried (Stone and Scallan 1966; Weise and Paulapuro 1999). Loss of fiber absorbency and the relative effects of loss of conformability of the wetted fibers, especially when fibers are dried multiple times, is a major contribution to reduced paper strength when the material is recycled (Weise and Paulapuro 1996; Hubbe *et al.* 2007b).

A unique example of loss of absorbency upon drying was documented by Mizutani *et al.* (1999), who studied the water absorbency of never-dried cotton fibers starting very soon after their biosynthesis in the bowl of the living plant. At the earliest measurable stage, the never-dried cotton fibers were associated with 2.5 times their mass in water. Upon drying of such fibers, they were then only able to absorb water to an extent of about 0.8 times their mass. The effect was attributed to the fact that in the continuously wet condition, while sealed within the fresh cotton bowl, the water present between the adjacent cellulosic microfibrils in the young cotton prevented those fibrils from coming together and hydrogen bonding directly with each other. As shown by Stone and Scallan (1966, 1968), the loss of absorbency upon drying of cellulose fibers generally can be attributed to a partly irreversible closure of submicroscopic pores. Strong capillary forces acting during the drying process (Campbell 1959) can pull the walls of some pores into close contact, and the regularity of the cellulose structure can result in a zipper-like formation of multiple, repeating hydrogen bonds, essentially causing the adjacent surfaces to coalesce into a single cellulosic entity (Hult *et al.* 2001; Pönni *et al.* 2012). Though additional refining has been shown to restore much of the bonding strength that is lost when kraft fibers are dried, the corresponding effects related to restoration of porosity tend to be more limited (Klungness and Caulfield 1982).

Efforts to suppress the loss of absorbency (and other valuable traits such as bonding potential) when kraft fibers are dried have been limited in success (Zhang *et al.* 2002). Early work by Higgins and McKenzie (1963) showed only one kind of treatment – the drying of cellulose fibers in the presence of high concentrations of sugar – that was effective in avoiding the irreversible loss of swelling potential. Work by Lindström and Carlsson (1982) showed that some of the damage could be avoided by drying under neutral to alkaline pH conditions – but only if the pulp *also* had a relatively high level of carboxylate groups, *i.e.* a high hemicellulose content. Subsequent work has confirmed the favorable effects of hemicellulose (Cao *et al.* 1998), which may be attributed not only to its content of carboxyl groups, but also to its somewhat irregular chain structure that tends to resist crystallization. The importance of hemicellulose for swelling of birch kraft pulps was shown dramatically by Moss and Pere (2006). These researchers showed that intentional removal of most of the xylan component from the fibers almost eliminated the ability of such fibers to swell when they were placed back into water.

To avoid the usual deswelling effect of drying, freeze-drying is one strategy that has been successfully employed. Such an approach has been used to prepare cellulose-based “aerogels” that maintain very high porosity, bulk, and absorption capacities (Saito *et al.* 1995; Pääkkö *et al.* 2008; Kettunen *et al.* 2011; Theliander *et al.* 2011; Brodin *et al.* 2012). Another successful approach has been to transfer the swollen cellulosic material to an acetone solution before it is dried in air. Sannino *et al.* (2010) used such an approach to preserve the swollen nature of nanoporous crosslinked cellulose gels when they were dried.

Polyelectrolyte Complexes as a Smart Restraint on Hydrogel Swelling

In view of recent success in achieving highly favorable levels of absorption of saline solution through the use of polyelectrolyte complex hydrogels (Salam *et al.* 2011b), coupled with the tendency of such complexation to restrain the absorption of pure water (Dogu *et al.* 2009), this section will consider theoretical aspects of such absorbency. Wood-derived polysaccharides and their derivatives such as xylans and carboxymethylcellulose (CMC) can be readily incorporated into such systems, in combination with various cationic polymers such as chitosan (Salam *et al.* 2011a,b; Ayoub *et al.* 2013).

The tendency of polyelectrolyte complexes (PECs) to contain relatively little water within their core structure, under conditions where the amounts of oppositely charged bound ionizable groups are in approximate balance, can be understood based on the mechanism shown in Fig. 7. As shown in the figure, there are bound anionic groups on one set of polyelectrolyte chains and bound cationic groups on the other set. In each case the bound charges are balanced by an equal and opposite number of counter-ions. (Note that this is in addition to the various other monomeric ions of each charge in the system. Such ions have to sum up to equal normality of each charge). Upon mixing the two polyelectrolyte solutions, a complex is formed (Michaels 1965). As shown in the figure, the cooperative interactions involved in multiple ionic interactions between the oppositely charged polyelectrolytes tends to drive the complexation to completion. It has been proposed that complexation might occur in a zipper-like fashion or in a disorganized manner (Michaels 1965). In either case, the resulting ion pairs within the PEC can remain stable, such that the charges within the system are essentially self-neutralized. As illustrated in the figure, one of the results, therefore, is that the counter-ions can diffuse away into the bulk of solution. Some authors have credited the resulting increase in entropy as being the most important factor in promoting PEC formation (Michaels *et al.* 1965; Cundall *et al.* 1979; Argüelles-Monal *et al.* 1990; Baker *et al.* 1995).

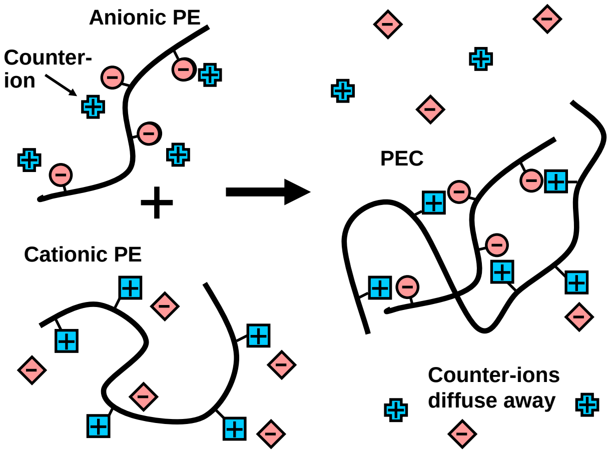


Fig. 7. Mechanism of polyelectrolyte complex (PEC) formation in which ion pairing between bound groups on the respected polyacid and polybase chains make it possible for the monomeric counter-ions to diffuse away, with a large increase in entropy of the system.

Antipolyelectrolyte effect

The tendency of polyelectrolyte complexes and polyampholyte systems to swell with water upon addition of salt has been called the "antipolyelectrolyte effect" (Valencia and Pierola 2007; Dogu *et al.* 2009; Wang *et al.* 2010). Because this effect appears to be consistent with the behaviour of the hemicellulose-based PECs just described, some background will be given here. As an underlying explanation for the effect, it has been shown that the addition of salt tends to weaken the electrostatic interactions within a PEC (Dragan and Cristea 2001). Increased absorbency with increasing salinity of aqueous solutions has been observed in several cases in which oppositely charged polyelectrolytes were employed in the preparation of cellulose- or hemicellulose-based hydrogels (Paula *et al.* 2002; Feng and Pelton 2007; Valencia and Pierola 2007; Wang *et al.* 2010; Shang *et al.* 2008; Salam *et al.* 2011a,b; Gawel *et al.* 2012). Such weakening of the pair-wise associations of ionic groups on the polymer chains allows a partial reversal of the process illustrated in Fig. 7, thus drawing more nomomeric ions, along with some associated water, into the interior of the hydrogel phase.

Fascinating behavior related to the sorption of monovalent salt ions was observed in the course of recent studies with PEC-type hydrogels formed from biopolymers having relatively high charge densities (Ayoub *et al.* 2013). The ability of such hydrogels to remove sodium and chloride ions from solution, beyond what would have been predicted from the concentration of those ions in solution, was attributed to the process described in Eq. 10,

$$\mathrm{RCOO^{-}{-}{-}{-}{}^{+}NH_4R' + NaCl \rightarrow RCOO^{-}\,Na^{+} + R'NH_4{}^{+}\,Cl^{-}} \qquad (10)$$

where the dashed line is used to indicate ion-pair interactions within the hydrogel before introduction of the saline solution. The “R” and “ R’ ” indicate the two respective polyelectrolyte chains. As shown in Eq. 10, addition of NaCl to the material is expected to result in weakening of the complex such that the salt ions behave as counter-ions to the charged polyelectrolyte chains. The effectiveness of the PEC-type hydrogels to enable the removal of NaCl from solution is notable because most reported applications of cellulosic-based materials for ion exchange have involved removal of divalent metal ions (Rudie *et al.* 2006; Hubbe *et al.* 2011; Kumar *et al.* 2011). In such applications it is typical for the divalent ions to displace monovalent ions within the substrate due to their greater binding constants. The process represented by Eq. 10 is unique due to the fact that PEC-based hydrogels can be readily obtained in almost monomer-free condition; upon precipitation of the PEC during its formation, it is possible to decant the salt-containing solution, optionally replacing it with deionized water. Subsequently, upon introduction of a sufficiently concentrated solution of monovalent salt, the PEC interactions becomes weakened to such an extent that Eq. 10 becomes favorable.

ACCOUNTING FOR OBSERVED SORPTION RATES

In addition to the absorption capacity, another main concern of users of absorbent products is the rate of absorption. Several reviews dealing with absorption rates have appeared. In the case of ordinary paper products (not superabsorbent), several key studies have focused on theoretical issues (Bristow 1967; Aspler *et al.* 1987; Schuchardt and Berg 1991). Related numerical simulation work has been reported (Masoodi *et al.* 2012). The following articles have considered rates of absorption in the case of hydrogels (Kabra and Gehrke 1994; Zohariaan-Mehr *et al.* 2010; Wang *et al.* 2011c). Finally, Berg and coauthors have considered the rates of wicking into structures that are contained by fibers and hydrogel materials (Schuchardt and Berg 1991; Wiryana and Berg 1991).

Tests to Measure Absorption Rates

Practical tests of rates of absorbency of cellulose-based materials often involve rapid immersion of material packed into a cage, followed by evaluation of weight gain (Aberson 1969). The cited author noted that the results of such tests can be difficult to interpret. To overcome this problem, a new test was developed in which dry fluff pulp is exposed only on one side (Aberson 1969). As was noted in Table 2 (in previous section), rates of sorption can also be studied by dielectric spectroscopy (Gelin *et al.* 2007), wicking rates (Beuther *et al.* 2010), and the time for a water drop to be absorbed (Ström and Carlsson 1992).

For ordinary paper and paperboard products, various TAPPI methods are available (TAPPI 1996). For instance, TAPPI Method T411 describes the gravimetric Cobb test in which the sample is exposed to the liquid from one side for a set period (*e.g.* 120 s), after which the liquid is poured off and a blotter is used to remove excess liquid. TAPPI Method 491 is a related test in which the whole sample is submerged in the test liquid for a specified period (*e.g.* 10 min), and the sample is blotted with a standard roller before being reweighed. TAPPI Method T432 is intended for highly absorbent paper products such as blotter paper, tissue, and towel. A specified volume of liquid is gently placed on the sample, and one measures the amount of time that passes before the disappearance of specular reflection from the smooth surface of the liquid. TAPPI Method 561 is a dynamic test in which one continuously monitors the mass of liquid remaining in a reservoir attached to a siphon tube in contact with the paper specimen. Related tests have been adopted for evaluation of textiles (ASTM 1983). For instance, test TS-017 is based on the time in second it takes distilled water to climb either 20 mm or 30 mm up a vertical strip of cloth that has been dipped into a beaker. Test TS-018 measures the time for complete sorption and disappearance of a drop of water having a specified size.

For evaluation of events during very short exposure times of paper samples and aqueous solutions, two main procedures have been developed. According to a test developed by Bristow (1967), a narrow strip of paper is mounted on a slowly rotating wheel. A “headbox” with a precisely measured volume of colored fluid and a narrow slit opening at its base is lowered until it touches the sample. The length of the colored streak transferred to the paper can be used to calculate the volumetric uptake per unit of contact time. Related results have been obtained more recently with a device that measures the speed of transmission of ultrasonic vibrations through a water bath as a function of the time after sudden placement of a sheet of paper perpendicular to those waves (Pan *et al.* 1988; Leks-Stepien and Khadzhynova 2005).

Viscous Resistance Limiting Rates of Flow through Porous Material

A key factor that tends to reduce the rate with which an aqueous fluid passes into cellulosic-based materials, including hydrogels, is the fluid’s viscosity. The magnitude of viscous resistance also depends on the sizes and lengths of the passages through which the fluid needs to flow. These relationships have been captured in Darcy’s law and its various refinements by subsequent investigators (Darcy 1856; Masoodi and Pillai 2010). In its simple form, Darcy’s law can be expressed as in Eq. 11,

$$Q = - kA\,(P_b - P_a)\,/\,(\eta\, L) \tag{11}$$

where Q is the flow rate through a porous packed bed of uniform cross-section, k is a permeability constant, A is the cross-sectional area of the bed, P_b is the outlet pressure, P_a is the inlet pressure, η is the fluid’s dynamic viscosity, and L is the linear distance from the inlet to the outlet.

When applying Darcy’s law to predict the rate of wicking in paper, Masoodi and Pillai (2010) noted that the model tended to work best if it was assumed that the material swelled in the course of wetting in order to fully make room for the liquid. The permeability of initially dry paper appears to vary as a function of time during the wicking of aqueous fluid.

Various approaches can be used to estimate the value of the coefficient *k* in the case of paper-like structures (Kozeny 1927; Carman 1938, 1939; Carrier 2002; Chapuis and Auberton 2003; Hubbe and Heitmann 2007). For instance, a simple laminar hydrodynamic model was used to derive the following expression,

$$k = (\gamma / \eta)\,(2/C_{\text{K-C}})\,(1/S_o^2)\,[\,e^3/(1 + e)] \qquad (12)$$

where *k* is the permeability (distance of penetration per unit of time), γ is a unit mass of the fluid, η is the fluid's dynamic viscosity, $C_{\text{K-C}}$ is the Kozeny-Carman coefficient (usually taken to be about 5), S_o is the specific surface area per unit displacement volume of particulate material, and *e* is the fractional void volume (Carrier 2002; Chapuis and Auberton 2003). Ingmanson (1952, 1953) applied similar concepts to the case of cellulosic fibers, taking into consideration the bulky structures formed by fibers, but also considering the compressibility of cellulose. In general, all such models imply that a given applied pressure is likely to result in greater flow with increasing pore size and/or decreasing effective surface area of the packing material. This general prediction has been confirmed, for instance, by studies in which the effective pore size within paper structures was increased by forming the paper in the presence of surfactants (Shepherd and Xiao 1999).

Another approach that has been used to model the kinetics of swelling of hydrogels is based on a visco-elastic model (Omidian *et al.* 1998). Variation of some parameters that can improve the superabsorbent properties can lead to considerable differences in swelling kinetics, which can be fitted to a Voigt-cell (spring and dashpot) model, as

$$S_t = p(1 - \mathrm{e}^{-1/r}) \qquad (13)$$

where S_t is the amount of swelling (g/g) at any moment, *p* is the power parameter (g/g), *t* is time (s), and *r* is the rate parameter. Swelling at different times can be measured in distilled water. Then, the results obtained at equilibrium and the swelling rate of the individual samples can be fitted into the above equation to find the values of the rate and power parameters. Another useful parameter, based on the same model, is the time required to reach 63% of full capacity (Omidian *et al.* 1998).

Capillarity and the Lucas-Washburn Equation

Capillary forces, due to the surface tension of water, are known to play a major role in the absorption of water and other fluids into porous materials (Buchholz *et al.* 2005). Lucas (1918) and Washburn (1921) showed that capillary forces can account for the rise of liquids within straws and related porous systems. It has been suggested that the lumens of cellulosic fibers can play a similar role in the wicking of water (Mizutani *et al.* 1999). Capillary forces also have been credited with explaining the rapid absorption of aqueous fluids into some highly porous hydrogels (Omidian *et al.* 2005). Sannino *et al.* (2003) proposed that capillary forces also can increase the amount of water held within swollen hydrogels. In addition, it is reasonable to expect also that capillary forces are involved in cases where fibers having irregular cross-sections are designed to provide channels for wicking within SAP media (Schuchardt and Berg 1991; Pramanick and Crouse 1998).

Figure 8 illustrates some essential features of the Lucas-Washburn model of capillary absorption. As shown, the capillaries are represented as smooth, cylindrical pores of a selected size. In the simplest case one assumes that the material is comprised of open-cell pores, such that the pressure of "Air" shown in the figure is always equal to the ambient pressure of the bulk liquid. As indicated by Eq. 14, the capillary pressure exerted by the interfacial tension at the meniscus is balanced by a viscous force due to the flow within tight passages as water continues to progress into the pore.

$$\mathrm{d}L\ /\ \mathrm{d}t = \gamma R \cos\theta\ /\ (4\ \eta L) \tag{14}$$

$$L = \{\ \gamma R \cos\theta\ /\ (2\ \eta)\ \}^{1/2}\ t^{1/2} \tag{15}$$

The integrated form of the Lucas-Washburn equation, Eq. 15, indicates that the distance of penetration into the porous material can be expected to be proportional to the square-root of time. Another implication of Eq. 14 is that the rate of absorption is expected to increase with increasing pore size. This prediction is reflected in the more rapid absorption of water into coarse, bulky paper (Aberson 1969).

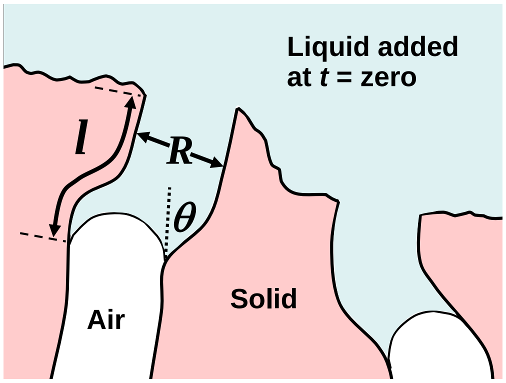


Fig. 8. Idealized representation of porous material having uniform, smooth, cylindrical pores, with a liquid being applied to the outer surface at time equal to zero

Information about contact angles and pore sizes is needed in order to apply the Lucas-Washburn equation to practical systems. The contact angle of water on ordinary kraft pulp fibers has been measured as zero to 52 degrees (Young 1976) or about 56 to 64 degrees (Aberson 1969) in different cases. Since these values are less than 90 degrees, such fibers clearly fall within the category of "wettable" (Adamson and Gast 1997).

The Lucas-Washburn equation has been widely used to fit data related to the absorption of water and other fluids into paper. Two major deviations from the Lucas-Washburn equation were revealed by Bristow (1967), who developed a test method that has since received widespread use by the paper research community (for instance, see Aspler *et al.* 1987). Evidence of each of these deviations can be seen in Fig. 9, which is a replotting of data from Bristow's 1967 publication. The horizontal axis in Fig. 9 is plotted on a "square root of time" axis, matching the form of the Lucas-Washburn equation (Eq. 15). Looking first at the original data (square symbols), it is apparent that about 11 $\mathrm{mL/m^2}$ of water transferred to the paper surface immediately, essentially independent of time. Bristow attributed that feature of the data to the filling of roughness at the paper surface. The other deviation involved an apparent "time delay". For instance, in Fig. 9 a linear rise in transferred liquid *vs.* the square-root of time can be seen following a delay of about 0.2 seconds. Schuchardt and Berg (1991) observed a corresponding wetting delay of about 0.7 seconds in the case of pads made of fluff-grade softwood kraft fiber.

A question that apparently never has been addressed in the literature is whether the original data in Fig. 9 could be made to fit to the Lucas-Washburn equation by subtracting the delay time. To test that idea, Bristow's data has been recalculated after subtracting 0.2 seconds from each of the reported time durations. The diamond-shaped symbols correspond to the adjusted time quantity before calculating the square-roots and replotting the data. As shown, the data remained in reasonable agreement with a straight line. Moreover, the left-hand end of that line corresponding to adjusted zero time was close to the level of the amount of transfer attributed by Bristow (1967) to the volume capacity of the roughness at the paper surface.

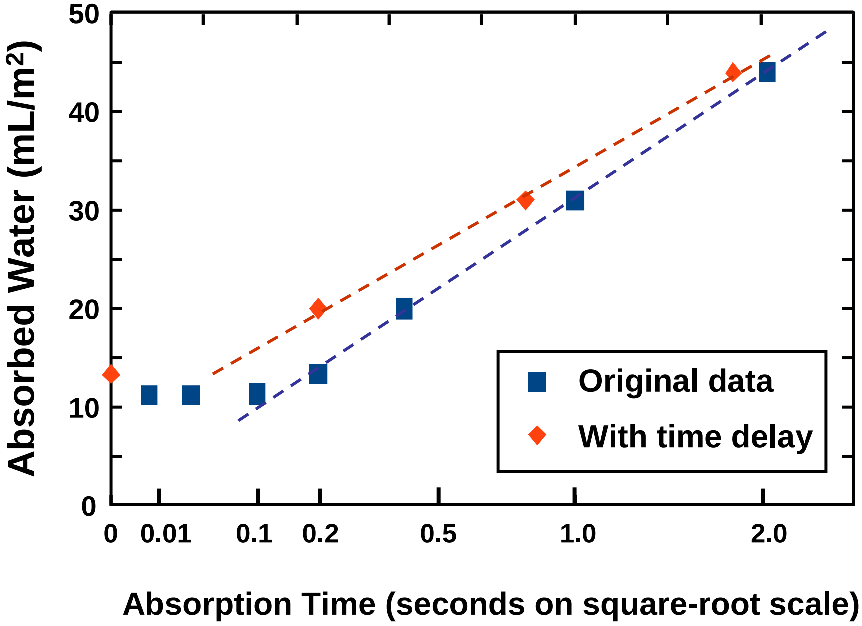


Fig. 9. Data of Bristow (1967) as originally reported and also replotted with a time delay of 0.2 seconds incorporated before the calculation of the square root of time

To explain the existence of a time delay, it has been suggested that humidity adjacent to an advancing droplet of water causes hydration of the cellulosic material and/or reorientation of various chemical groups associated with the cellulosic fibers, extractives, or additives used in papermaking (Lyne and Aspler 1982). Such changes are expected to result in progressive lowering of the contact angle such that the meniscus is then able to advance. It is likely that such effects are compounded by the highly porous nature of paper materials, involving multiple size scale of porosity; therefore it is expected that the effects due to somewhat unfavorable initial contact angles are amplified by the inherent difficulty of spreading a liquid onto a surface that is covered with fine pores (Cassie and Baxter 1944).

Eklund and Salminen (1987) extended Bristow's model to take into account externally applied pressure of the wetting fluid on the rate of absorption into paper. Though this approach was used in an effort to model such processes as the coating of paper, the same principles could well apply to various situations in which absorbent products are used. The cited authors also took into account such effects as air pressure within dead-end pores, vapor-phase transport of moisture, and the swelling for fibers.

Schuchart and Berg (1991) found that the model of Lucas and Washburn fit very well when applied to the absorption of non-swelling liquids such as octane. In the case of water, as mentioned earlier, the permeability of absorbents tended to decrease due to the swelling of superabsorbent hydrogel particles, thus partially blocking flow passages in the material.

Numerical simulation of capillary-induced absorption into paper-like media was carried out by Masoodi *et al.* (2012). Their model included the swelling of the medium as well as the time-varying permeability.

Concepts related to capillarity can be used as a basis for the design of absorbent products. For instance, Aberson (1969) proposed that the pore spaces within a well-designed sorbent material ought to be no larger than the size that will provide enough suction to oppose gravity and hold onto all of the absorbed liquid. Smaller pores, though they would hold onto the fluids even more strongly, would be expected to offer greater resistance to flow, thus probably reducing the initial rate of absorption.

Hodgson and Berg (1988) showed that in some practical cases the rate of wetting of paper products by aqueous liquids could be increased by use of surfactants. It was proposed that the surfactants acted as wetting agents, decreasing the contact angle of water. Note that according to Eq. 14, such an effect would be predicted to enhance the rate of absorbency. On the other hand, surfactants can be expected to decrease the value of the interfacial tension γ in the same equation, which would tend to have the opposite effect. Thus the net effect can be expected to depend on various details, such as the structure of the surfactant and its relative affinity for the aqueous phase *vs.* various interfaces (Simoncic and Roman 2007; Tag *et al.* 2012).

Kettunen *et al.* (2001) demonstrated an innovative system in which a thin, photoactive, temporarily hydrophobic TiO_2 film prevented water from being absorbed into aerogels formed from nanocellulose; upon illumination the materials became fully wettable (very low contact angle) and acquired the ability to take up 16 times their weight in water.

Diffusion as a Rate-Limiting Step in SAP Absorbency

Diffusion is a mass transport phenomenon that involves the movement of individual molecules due to concentration gradients. The driving force behind diffusion is related to the system tending towards a lower Gibbs free energy. Diffusion plays a role in the dissolving of a material, the movement of a liquid through a liquid, of a gas through a liquid, of a gas through a solid, of a gas through a gas, or of a liquid through a solid. As noted by Kabra and Gehrke (1994), in the case of non-porous absorbent hydrogels, diffusion can be expected to constitute the rate-limiting process governing swelling. Thus, the rates of swelling of porous gels can be on the order of one thousand times faster (see also Omidian *et al.* 2005). Also, as noted earlier, Tanaka and Fillmore (1979) found that the rate of swelling of individual gel particles was inversely proportional to the square of their size; this finding is suggestive of a diffusion-controlled mechanism due to the fact that the area of each gel particle is proportional to the square of the diameter.

As an initial approach, diffusion into a hydrogel particle might be modeled in a simple way, assuming isotropic properties and neglecting of any changes in those properties during the process of swelling. Equation 16 (Peppas and Hariharan 1994) represents how the second law of diffusion, according to Fick (1855), could be applied in such a model,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left\{D\frac{\partial C}{\partial x}\right\} - v\frac{\partial C}{\partial x} \tag{16}$$

where C is the concentration of water, t is time, x is the distance of permeation into the material, and v is the convective velocity of the fluid. It should be noted that Eq. 16 applies only in the case of a simple "slab" geometry.

A useful form of the rate equation is obtained when the exponent 0.5, which follows from Fick's derivation, is replaced by an adjustable value n (Ganji *et al.* 2010),

$$Q_t = Q_\infty k\, t^{\mathrm{n}} \tag{17}$$

where Q_t is the mass of fluid absorbed per unit of sorbent mass at time equal to t, and Q_∞ is the value of Q_t after a long time. When using this expression to fit experimental data, the system is considered to be Fickian if the fitted value of n equals 0.5 or is somewhat lower than 0.5 (Ganji *et al.* 2010). Values higher than 0.5 but less than unity indicate anomalous systems in which a combination of mechanisms may govern the rate of absorbency. A value of 1 implies that the rate of fluid uptake is governed only by the rate of relaxation of polymer segments, which is understood to be taking place much more slowly in comparison to the diffusion processes.

Berens and Hopfenberg (1978) noted that although Eq. 17 can be made to fit data corresponding to the initial swelling of hydrogels (up to about 60% of completion), strong deviations tend to be observed at longer times. The following equations were therefore proposed as a more realistic model to fit typical data (Ganji *et al.* 2010),

$$\mathrm{d}Q_t / \mathrm{d}t = k_2 (Q_\infty - Q_t) \tag{18}$$

$$Q_t = Q_\infty (1 - A\, e^{-k_2 t}) \tag{19}$$

where k_2 is the empirically-derived rate constant. The values of the constants A and k_2 are determined from the slope and intercept of a plot of $\ln(1 - Q_t / Q_\infty)$ versus time.

A key problem inherent in using a simple Fickian model to predict absorption rates of hydrogels is that such an approach does not account for major changes that take place in the gel structure and in the polyelectrolyte segment mobility as a result of the swelling process (Peppas and Sahlin 1989; Singh and Weber 1996; Afif and Grme 2002; Rajagopa 2003; Liu *et al.* 2005b). To overcome this deficiency, Peppas and Hariharan (1994) proposed non-Fickian diffusion models in which an outer, swollen layer of each hydrogel particle was presumed to gradually progress inward toward the center of the hydrogel.

A cylindrical model, as shown in Fig. 10, was used to represent the situation in an ideal case. The rate of diffusion of water within the swollen layer was presumed to be much higher than the same value within the non-swollen core of each gel. The model depicted in Fig. 10 is consistent with a “slow reorientation of polymer chains”, as proposed by Ganji *et al.* 2010.

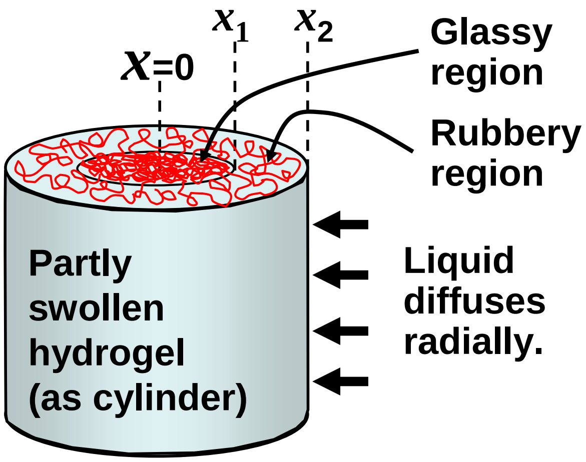


Fig. 10. Model of partly swollen hydrogel as a segment of an infinite cylinder, to enable derivation of a non-Fickian diffusion-based rate of absorbency. The model is based on an assumed much greater diffusion rate within a rubbery (already swollen) layer.

Peppas and Sahlin (1989) developed the following equation to account for such systems:

$$Q_t = Q_\infty (k_1 t + k_2 t^{0.5}) \tag{20}$$

More complex systems have been considered by invoking second-order diffusion kinetics (Yin *et al.* 2002). Li and Tanaka (1990) developed an approach taking account of gradients of stress within the hydrogel. Refinements related to effects of such details as variable surface concentrations, history-dependent diffusion rates, stresses between different parts of a gel, and relaxation of polymer segments have been further discussed by Ganji *et al.* (2010).

LIFE CYCLE AND PRODUCT DEVELOPMENT ISSUES

In view of the high volume of current usage of absorbent products, compounded by the waste inherent in the one-time usage and the non-renewable nature of their petroleum-based components, it is important to consider approaches that can be used to improve the environmental compatibility of absorbent products in future years. Some key elements that have been considered, in this regard, involve biodegradability of SAPs, life cycle analysis, and product development strategies.

Within this section, a life cycle perspective will be used to identify key areas where cellulose-based super absorbents could potentially reduce environmental impacts of absorbent products. Additionally, key areas of uncertainty surrounding environmental impacts will be discussed. A brief discussion of the basics of life cycle assessment is given below, followed by a discussion related to superabsorbents with or without the inclusion of cellulose-based components.

Life Cycle Assessment Applied to Cellulosic SAPs

Life cycle assessment (LCA) can be defined as a way to assess potential environmental impacts associated with a product, process, or service; this generally entails making an inventory of the relevant inputs of materials and energy, as well as releases to the environment, evaluating various potential environmental impacts associated with items on the inventory, and then weighing the results of the analysis in order to make more appropriate decisions (EPA 2012). The use of LCA provides additional information surrounding all the environmental impacts of a product, process, or service to decision makers. By examining a variety of environmental impacts, burden shifting can be minimized through systems thinking. For example, burden shifting can occur when only greenhouse gases (GHG) or only solid wastes are examined. The technique of LCA can be broken down into four distinct steps, (1) goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation. For more complete LCA guidance, ISO 14044 provides explanations and a more detailed procedure for performing such studies. The EPA also has many helpful documents online on how to perform LCAs (EPA 2012).

In the following discussion, diaper production and use will be considered as an example, as there is a significant body of literature surrounding diapers, and they employ traditional SAPs that could be partially or wholly replaced in some products by cellulose-based SAPs.

Product composition

Diapers have the primary function of relieving the issues of incontinence by absorbing and containing solids and fluids. Diapers were originally made from cotton and were washable and reusable. Over the past 50 years, the use of reusable diapers has been replaced, in part, with disposable diapers (Edana 2005). According to Edana, disposable diapers have several main components that work together to remove liquids from the skin and store them until disposal. In this construction, there is a soft nonwoven surface that facilitates moisture removal and is comfortable to the skin. Under the top layer, there is a distribution layer of material that transfers the liquids to the super-absorbent layer. Within the core of the diaper, the superabsorbents are made of SAPs and cellulose pulp store liquids. The internal materials of the diaper are contained by a breathable but aqueous fluid-resistant polyethylene nonwoven fabric or film to prevent moisture transfer from the diaper to surrounding surfaces. These different components require raw materials that are made from a variety of materials. According to Edana (2005), cellulose fluff pulp is the largest component of diapers at 43%, and super absorbents are the second largest component at 27%, as shown in Fig. 11.

Within this discussion, the superabsorbents making up approximately 27% of a diaper will be considered for substitution with a blend of cellulose- and petroleum-based SAPs. Assuming that half the superabsorbent is cellulose-based, the total renewable material content of the diaper would then increase to 56.5%. Since raw materials can account for 84% of fossil fuel use and 64% of global warming potential of a typical diaper (Weisbrod and Van Hoof 2012), this material substitution may be significant. Additionally, Mirabella *et al*. 2013 found that petroleum-based polymer substitution with biobased polymer (polylactic Acid, PLA) may reduce some environmental impact categories on a cradle-to-gate basis.

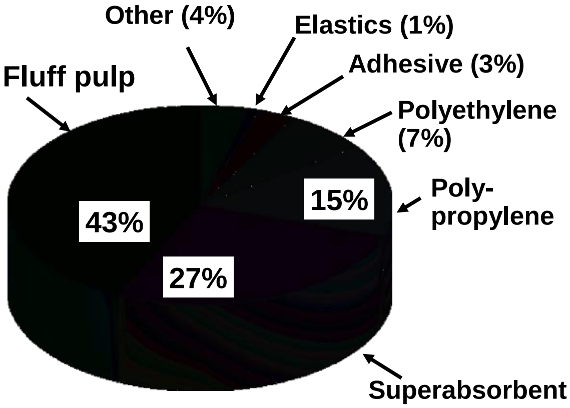


Fig. 11. Average diaper material composition, percentages shown on a per weight basis (based on data from Edana 2005)

Carbon captured in cellulose SAPs

SAPs are traditionally made from petroleum-based polymers, which are a non-renewable resource. Cellulose, when sourced from sustainably managed forests, represents a material that is not only renewable, but also removes CO_2 from the environment through photosynthesis. Incorporating cellulose-based materials into products can achieve significant reductions in GHG emissions due to the carbon removed from the atmosphere contained in the product. Thus, by incorporating cellulose-based SAPs into a diaper, the material would be effectively storing CO_2 that was once in the atmosphere and may be credited for this in an LCA. The cellulose-based SAP does contain carbon sourced from the atmosphere; however, the fossil fuel and chemical use in the production of the cellulose-based SAP will also play a significant role in the overall global warming potential of the diaper (Johnson 1994). Without a full LCA, it is impossible to understand the full implications of this substitution; however, the GHG emissions would likely decrease relative to usage of the current product mix.

Product Use and Reuse

Towards a launderable enhanced sorbent

Based on a consumer survey (Smith and Sheeran 1992) it would appear that there could be strong demand for products that can combine favorable features of current disposable absorbent products together with features of conventional absorbents. In particular, it would be desirable to combine high absorbency levels together with suitability for washing and repeated usage. Up to this point it appears that key challenges facing the development of such products involve suitability for washing and drying.

Beskisiz *et al.* (2009) showed that some textiles comprising superabsorbent fibers can be laundered and even dry-cleaned without excessive loss of their component materials and absorbent nature. The specialized fabric exhibited higher absorbency than conventional fabric; however, it also required a longer drying time after laundering.

The high levels of water held within conventional SAPs after their use, in addition to the gelatinous nature of the swollen material, appear to present a serious challenge in terms of both washing and drying. What is needed, it would appear, is some kind of mechanism by which the swollen nature of the hydrogels can be reversed, such that most of the imbibed liquid can be released during the washing process. In particular, to minimize the time and cost of drying, one would want any SAPs to be in a mostly non-swollen condition before the start of a conventional drying operation. As noted earlier in this article, various researchers have demonstrated thermally-sensitive hydrogels that incorporate a cellulosic component (Harsh and Gehrke 1991; Kuwabara and Kubota 1996; Çaykara *et al* 2006; Chang *et al.* 2009b). Under laboratory conditions many such SAPs have been shown to release 80 to 90% of their water content upon heating to 40 ^{o}C (Kuwabara and Kubota 1996; Çaykara *et al* 2006; Ma *et al.* 2007). It would seem reasonable that such systems could be further developed, along with adjustments in the capabilities of washing machines, such that home laundering of "thermally smart" reusable superabsorbent products could become a practical reality.

Laundering superabsorbents could decrease landfill waste and reduce raw material usage; however, laundering requires large quantities of water and energy (Aumônier and Collins 2005). Many LCA studies have been carried out for disposable and reusable cloth diapers (Aumônier and Collins 2005; Olive 2004). These studies generally indicate that disposable diapers have higher energy use in the production stage, while reusable diapers are most energy-intensive during the use phase when laundering. By introducing a laundering step to a "semi disposable" diaper, the overall energy usage would likely increase. Factors such as number of reuses possible, wash water temperature, water content of diaper entering the drying system, and fluid flow properties from the diaper are critical to understanding the environmental implications of a reusable disposable diaper.

The "thermally smart" superabsorbents could potentially decrease the energy used in laundering and specifically drying. However, significant quantities of energy would be required to heat wash water to 40 ^{o}C or another temperature level required, which may offset the drying benefits of reduced water content entering the dryer. As learned from other textile LCA studies, washing soiled garments in cold water followed by line air-drying can be regarded as the laundering option having the lowest environmental impacts (Levi Strauss & Co. 2009; O'Brien *et al.* 2009). It is unlikely that such a laundering option would be possible with a superabsorbent diaper.

Product End of Life Considerations

Biodegradability of absorbent materials

Several studies have recommended the use of cellulose-based materials in absorbent products in order to achieve suitable biodegradability (Cooke 1990; Lokhande and Gotmare 1999; Fei *et al.* 2000; Dutkiewicz 2002; Lionetto *et al.* 2003, 2005; Chang *et al.* 2008; Demitri *et al.* 2008; Singha and Rana 2011). In particular, various studies have demonstrated biodegradable character of hydrogels that contain a cellulose-derived component (Bin *et al.* 2000; Wach *et al.* 2001, 2002; Lionetto *et al.* 2003; Sahoo *et al.* 2005; Yoshimura *et al.* 2005, 2006; Wang *et al.* 2008; Feng *et al.* 2010a; Kono and Fujita 2012; Xie *et al.* 2012). By contrast, it has long been clear that SAPs based on acrylamide generally have limited biodegradability (Wichterle and Lim 1960). Yoshimura *et al.* (2005, 2006) showed that ester-based cellulosic absorbents, prepared with maleic anhydride, offered particular promise in terms of enhanced biodegradability. On the other hand, Sahoo *et al.* (2005) showed that grafting sometimes can be used as a way to decrease the excessive biodegradability of starch present in the mixture from which SAPs are being prepared.

Despite the demonstrated superior performance of superabsorbent hydrogel materials, it is clear from the product selection available at a typical supermarket that cotton-based products continue to attract substantial customer demand. Some of this demand might be prompted by the fact that typical cotton-based products can be laundered and used multiple times, thus offering a perceived cost savings. In addition, it is likely that customers' environmental concerns contribute to the purchase decision (Smith and Sheeran 1992). For instance, a disposable liner for diaper-type products, composed entirely of "natural materials" has been patented (Flores Gonzales 2010). The core material was comprised of cotton. Macaulay *et al.* (2004) carried out a pilot study evaluating the washing and reuse of absorbent garments for adults with urinary incontinence. Guidelines were given regarding usage of such items. Performance and utility issues were compared relative to disposable incontinence products.

Despite the popular belief that biodegradable materials are inherently better for the environment, there are some situations and limiting factors which complicate this issue. Biodegradable products are often associated with decreased landfill space requirements and material degradation over time. This biodegradation requires oxygen, microbes, and other environmental conditions. When biodegradable products end up in landfills, they generally require as much volume as the non-biodegradable alternative. Additionally, when biodegradable products are buried in oxygen-deprived landfills, they degrade slowly, if at all (EPA 2012). If biodegradation does occur, it will be largely anaerobic, producing methane that is collected or burned in most landfill scenarios in the USA. In some landfills, particularly common in developing countries, methane is not collected, resulting in large contributions to global warming potential, because methane has more than 20 times the global warming effect of CO_2 (Bare 2011). Furthermore, Levis and Barlaz (2011) indicated that biodegradable materials in fact can produce higher end-of-life GHG emissions with similar upstream emissions, resulting in a higher net global warming potential across the product life cycle.

Biodegradable products that are engineered to decompose rapidly often decompose before the methane collection systems used in landfills have been made operational; as a result such products can emit GHGs directly to the environment (Levis and Barlaz 2011). However, when biodegradable diapers are collected and processed in a composting operation, Colón *et al.* (2011) found that 50% of the carbon contained in the diaper was degraded to CO_2.

The effects of biodegradable products on landfill space are controversial as well. Once a landfill is capped, the space required beneath the top cap layer is set. If the internal components of the landfill degrade, the size of the landfill will not necessarily decrease. The contents may become less dense as mass of material is removed as CO_2 and methane; however, the landfill will not likely shrink in size (foot print or height).

On the other hand, one clear benefit of using biodegradable materials does not involve the landfill but rather the inevitability of litter left to decay on the ground. Biodegradable materials left on the surface of the ground degrade at higher levels due to proper moisture content, oxygen levels, and microbial activity. In some applications, biodegradable materials would reduce the quantity of human wastes in the environment; however, one may question this benefit in the case of diapers as they are not traditionally thought to be a litter problem.

Engineering of Sorbent Products for the Application

In general, the design of new highly absorbent products to better meet the needs of consumers must take account of such issues as compact dimensions, dependability of performance, and health effects (Fader *et al*. 2010). As one looks to the future development of sorbent products, typical sorbent performance measurements will remain important. For example, reducing the costs of absorbents will open the use of the materials to wider applications as soil amendments and other high-volume low-value applications. This represents an opportunity for superabsorbents made with natural polymers such as cellulose, starch, and hemicellulose. According to Kono and Fujita (2012), the projected cost of manufacturing SAPs based on carboxymethylcellulose has tended to discourage implementation of production of superabsorbents based on cellulose. However, high cost was also cited as a key concern for SAP usage in general (Liang *et al*. 2009). Furthermore, functional improvements such as higher density, increased mechanical strength, or great absorbency per unit mass may lead to the use of sorbent in new products or new product forms. While progress along these traditional lines will lead to innovations, it is perhaps more important to consider the role of sorbents in a broader sense and how novel functionality can lead to new engineered products.

A universal absorbent can be defined as a material that can take up a wide variety of liquids. While this class of products is limited in number, some every-day materials such as wood fibers, ground wood pulp, or even bark will act as universal absorbents holding both polar and non-polar liquids within the structure of the materials. It may be possible to engineer universal suber-absorbents that take up both polar and non-polar liquids by constructing a block co-polymer in such a way that there are domains of polar and non-polar material (Loh 2002). These types of materials may or may not have to be crosslinked to prevent solubility and their subsequent functioning as suber-absorbents. A material constructed as in Fig. 12 would have domains that are insoluble in polar liquids and domains that are insoluble in non-polar liquids.

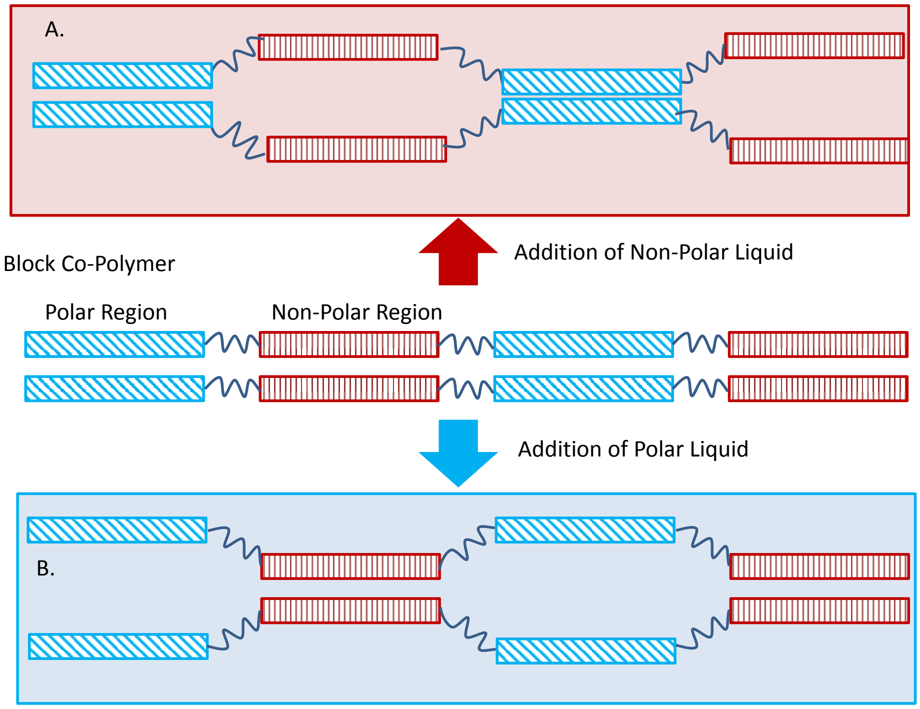


Fig. 12. Block co-polymer containing both polar and non-polar domains. **A:** Immersion of material into non-polar solvent causes the non-polar regions to swell and absorb liquid, while polar regions prevent the dissolution of the polymer. **B:** Immersion of material into polar solvent causes the polar regions to swell and absorb liquid, while non-polar regions prevent the dissolution of the polymer.

The result would be a material that is capable to taking up many different types of liquids. Furthermore, if a material such as this is not crosslinked, then it could potentially provide a "smart" functionality. For instance, it could be optimized to absorb a polar liquid, then when having a non-polar liquid added, to dissolve and release the polar liquid. This could prove useful in many fields including the oil and gas industry.

The ability of materials to respond to environmental stimuli is also of high potential value. Previously in this review it was shown that absorbency is affected by a number of factors including temperature, pH, salinity, and pressure. While for current commercial absorbents the change in the absorptive properties might be relatively small, these responses could be enhanced through the addition of crosslinkers consisting of polymers that are highly responsive of various stimuli. Interestingly, when absorbents take up liquids, they are nearly always accompanied by an associated change in physical dimensions. This allows for one to create products that can respond physically to a chemical or chemi-physical interaction between the absorbent and a liquid. Thus, one may engineer these materials for micro and nanotechnology where movement is needed to be generated in response to a stimulus. In the literature, many examples exist of polymers that can respond to various stimuli by changing conformation (Schmaljohann 2006; Jeong and Gutpwska 2002). This change in conformation can be taken advantage of to create smart absorbents.

Figure 13 shows a schematic example of the effect of a stimuli-responsive polymer acting as a crosslinker in a superabsorbent material. As shown, such as stimuli-responsive material can act to increase or decrease absorption of liquids depending upon the stimuli. Integration of this functionality into absorbents will open the doors to using these materials for products and purposes never before considered.

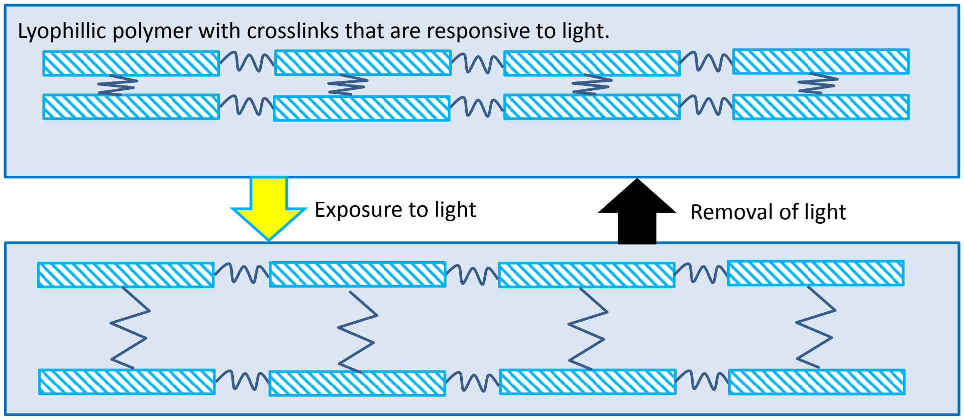


Fig. 13. Schematic view of a lyophilic polymer crosslinked with a light-sensitive polymer. Upon exposure to light, the crosslink polymer conformation changes, allowing for the absorbent to take up a large fraction of liquid. If this is a reversible process, then removing the stimulus could result in the expulsion of the liquid.

Absorbents may also be used to selectively absorb materials from liquids, making them useful for multiple applications. For example, Ayoub *et al.* (2013) demonstrated the use of an absorbent composed of both anionic and cationic polymers for isolating dissolved salt from water. One could also design absorbents that bind or destroy biologically active agents such as viruses or bacteria. This would create an absorbent that not only binds liquids but also disinfects at the same time. The ability to uptake, retain, and disinfect liquids may find uses in a variety of applications and products.

The recyclability of the absorbents is a challenge due to the very nature of absorbents. Absorbents are generally designed to tenaciously retain the liquids they absorb. Thus, subsequently removing those liquids is often energy-intensive or overly time-consuming. The design of an absorbent that could be repeatedly used would potentially be beneficial from both an environmental standpoint and economic standpoint. This may occur by combining together the concept of universal absorbent and or smart absorbents. By creating an absorbent that will release its absorbed liquid upon a stimulus or change in liquid, it is conceivable that absorbent could be easily and conveniently recycled. For example, the conformation of a polymer may be controlled by exposure to certain wavelengths of light. If this polymer is used as a crosslinker in a superabsorbent, then the shrinking and swelling of the polymer could be controlled by the exposure to light. This simple light exposure could be used to expel the retained liquid from the absorbent. This would make recycling of an absorbent as simple as turning on a switch.

Ultimately, absorbents can be used in a wide variety of applications. This utility can be rapidly expanded by integrating novel functionalities into the absorbent. Much of the basic science exists to create these materials. It is simply a matter of economics and desire for such materials to be developed.

CLOSING COMMENTS

As shown by many of the authors cited in this article, the usage of cellulose-based materials in absorbent products represents an intriguing field for academic research and product development. There can be a feeling of magic when one considers the huge ratios that can be achieved between the amounts of aqueous fluid that can be absorbed by much smaller amounts of sorbent material. Several domains of science overlap, including new approaches to synthesis of novel composition and means of crosslinking. The physical chemistry aspects are also fascinating, involving new ways to think about contributions to entropy, Donnan equilibria, the effects of nanostructures on absorption kinetics, and the like. Moreover, absorbent materials are economically important and have large environmental implications. Thus, there is a chance to be a hero – or maybe even to earn some money – if one can come up with an improved practical solution to absorbing fluids in challenging situations.

Although much progress has been achieved in understanding the role of cellulose-based materials and copolymers in the absorption of aqueous fluids, many gaps in knowledge are still waiting to be filled. For example, although it has been claimed that interpenetrating networks of hydrophilic polymers hold promise for superior absorbency (Myung *et al.* 2008), the theoretical basis of such a claim, if valid, would need to be established. Although incorporation of cellulosic components into acrylamide-based absorbent products has potential to make them more biodegradable, it is unclear whether and how quickly such degradation might take place under typical conditions of landfilling. Relatively little has been reported about the effects of squeezing highly absorbent products in an effort to expel the imbibed aqueous fluid. Though resistance to squeezing is sometimes considered to be a characteristic of superabsorbent materials (Laftah 2011), it is clear that application of pressure can at least partly reverse the osmotically-drive effects (Sannino *et al.* 2004b; Li *et al.* 2013). Though the concepts of osmotic pressure and the Donnan equilibrium have provided a basis for understanding absorbency phenomena (Grignon and Scallan 1980), it is unclear how or whether these concepts can be applied to the different kinds of water that are found in practical systems (Maloney *et al.* 1998), *i.e.* non-freezing bound water, bound water having a depressed freezing point, or water within isolated pockets of a hydrogel where the freezing point may be similar to that of bulk water. The contributions of such factors as the entropy of mixing, the entropy due to the freeing up of ions, and the effects of ionic and van der Waals forces within hydrogels during fluid absorption need to be better quantified.

The distance between various simplified theoretical models and the practical realities of commercially viable sorbent products will need to be narrowed (Ganji *et al.* 2010). On the one hand, experiments can be contrived in which independent variables such as the distance between crosslink points are precisely engineered. On the other hand, there is a need for applications of more comprehensive mathematical approaches that incorporate details of the nanostructure of hydrogel materials in a more realistic way.

Various less-glamorous aspects of the usage of highly absorbent materials incorporating cellulosic materials urgently need research attention. Life cycle assessment, if it is to be done well, requires a lot of work to gather high-quality data and to accurately weigh the impact of various aspects of absorbent usage on the environment. Filling the absorbent with fluid appears to have received a disproportionate amount of the attention from academics. More attention needs to be given to what can be done with the absorbent products after they have been used – especially when they are contaminated with bodily fluids and smeared with excrement, *etc.* On May 25, 1961 US president John F. Kennedy challenged scientists and engineers to put a man on the moon and bring him safely back to Earth. A similar challenge could be given at this point for scientists and engineers to design a highly absorbent diaper such that it can be fully laundered, with no significant loss of either its dry mass or absorbency, and requiring little more energy during laundering than is needed for conventional items of reusable clothing.

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APPENDIX

Table A. Tabulation of Research Publications for Enhanced Absorption of Water or Saline Solution by Use of Cellulose-Based Materials or Combinations

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Nano-fibers	Bleached SW kraft	-	Acrylic acid	Cerium	MBA	-	12-25	16		Abbas *et al.* 2011
HGel	-	-	CMC PAM	γ irrad.	Free radical	-	200-700	-	Gelation was suppressed at >70% CMC & > irradiation.	Abd El-Mohdy 2007
Fiber	Unspecified	-	Acrylic acid	Persul-fate	MBA	-	2-5	-		Ahmed *et al.* 2005
HGel	-	-	CMC	Film heated	Fumaric acid	-	0.5 - 3	-	Cured: 60 ^{o}C for 8 hours	Akar *et al.* 2012
HGel	-	-	CMC AcrylicA	γ irrad.	Free radical	-	300-600	200	CMC enhances gelation	Ali *et al.* 2008
HGel	-	-	Cellulose PMAA	Persul-fate	MBA	Bentonite	2400	-	Swelling increased with pH up to 5	Anirudhan *et al.* 2011
HGel	-	-	Acrylic	Inverse polym.	EG-DMA	-	580-930	200		Askari *et al.* 1993
HGel	-	-	CMC AMPS	60-70 C heat	MBA	-	680	20-110	Specific ion effects; highest swelling at pH 5 to 9	Bao *et al.* 2011
HGel	-	-	CMC	DMF soln.	CMPJ	-	4000-17000	-	Effects of crosslinking, pH, and charge density	Barbucci *et al.* 2000
Fiber	SW kraft fiber	-	AA Itaconate	Heat	Free radical	-	40-125	-		Barcus & Bjork-quist 1997
Towel	Kraft fiber	-	-	-	-	-	5-10	-	Test procedure demonstrated.	Beuther *et al.* 2010

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGEL	-	-	CMC	Radiation	Yes	-	40-180	20-80	Swelling decreased with radiation dose.	Bin *et al.* 2000
HGel	-	-	Si-HPM cellulose	Heptane	-	-	-	-	Decreasing pH leads to self-hardening of the gel.	Bourges *et al.* 2002
Fibers	Cotton Lyocell Viscose	- - -	-	-	-	-	0.5 0.6 0.9-1	- - -	Untreated cellulose fiber materials	Breier 1997
Foam	SW kraft	TEMPO Ox	-	-	-	MFC	21-65	-	Freeze drying yielded a high absorption capacity.	Brodin *et al.* 2012
Foam	SW kraft	TEMPO Ox	-	-	-	MFC	-	-		Brodin & T. 2012
Composite	Fluff pulp		SAPs			-	-	12-26	Sorbents are 15% less effective when collecting 100% of spill.	Buchholz *et al.* 2005
-	(Bacterial cell.)	-	Cellulose PAA	-	-	-	-	-		Buyanov *et al.* 2010
	-	-	HP Cell. PNBAm	-	-	-	-	-	Temperature sensitivity	Çaykara *et al.* 2006
HGel	-	-	Cellulose PVOH	Phys & chem xl	Freez-thaw, ECH	-	15-68	-	Chemical crossinking yielded greater swelling	Chang *et al.* 2008
Por. HGel	-	-	Cellulose alginate	NaOH urea	ECH	-	38-254	-	The cellulose provides structure and constraint to the gel.	Chang *et al.* 2009a
	-	-	Cellulose PNIPAM	Inter-penetrate	ECH	-	4-60	-	Heating from 20 to 60C led to major loss of swelling.	Chang *et al.* 2009b

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Por. HGel	-	-	Cellulose CMC	Urea soln	ECH	-	1000	30-200	Cellulose provides structure and constraint to the gel.	Chang *et al.* 2010
Por. HGel	-	-	CMC graft AA	Solvent APS	MBA	-	520	-	Grafting of acrylate on CMC greatly increased sorption rate.	Chen *et al.* 2008
HGel	-	-	CM.chito gr. PAA	Free radical	Acryl PEC	-	200-800	-	Sorption highest pH 4 to 10.	Chen & Tan 2006
MCC MFC	MCC MFC	Homog-enized	-	-	-	-	110;350	-	Water retention measured.	Cheng *et al.* 2010
HGel	-	-	CMC HEC	Alkaline	DVS	CNC, bent.	100-400	-	Nanocellulose decreased swelling.	Dai & Kadla 2009
HGel	-	-	CMC HEC	80 ^{o}C heat	Citric acid	-	400-960	-	Components evaluated separately & as mixture.	Demitri *et al.* 2008
Fibers	Cotton	g-acrylo nitrile	-	-	Free radical	-	26-62	13-35	Saponification yielded super-absorbency.	Deo & Gotmare 1999
HGel	-	-	Cellulose	DMAc-LiCl	-	-	-	-	Kicked out of solution with methanol or isopropanol.	De Oliveira & Glasser 1996
HGel	-	-	CMC acrylamid	γ irrad.	Acryl-amide	-	-	-		El-Din *et al.* 2010
HGel	-	-	CMC PAM	graft	Elec-beam	-	80-140	20-35	Combination electron beam & freeze-thaw worked best.	Eldin *et al.* 2011
HGel	-	-	CMC PAM	graft	Free radical	-	158	-		Eldin *et al.* 2013
HGel	-	-	CMC	-	Freez thaw	Bent-onite	36	-	Salt decreased swelling; clay increased strength	El Salmawi & Ibrahim 2011
Fiber	Spruce TMP	Lignin soften.	-	-	-	-	2-4	-	Delignification 0 to 60% -> sorption from 1 to 2-4 g/g	Eriksson *et al.* 1991

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Fiber	Delignif. cellulose	Acrylo-nitile	-	-	Free radical	-	350-423	72-210	Extensive graft polymerization greatly increased swelling.	Farag & Al-Afaleq 2002
HGels *etc.*	-	-	HPMC, CMC etc.	-	-	-	-	-	Thermal effects, freezable water	Faroongwarng & S 2008
HGel	-	-	CMC	Irrad	Yes	-	40-180	20-80		Fei *et al.* 2000
HGel	(Flax shive)	-	Cellulose ac acrylic	KPS	MBA	-	1000	56-800	Good biodegradability shown.	Feng *et al.* 2010a
HGel	-	-	CMC PVAm	PEC	Stir, dry	-	2-10	2-4	NaCl had mixed effects on swelling.	Feng Pelton 2007
Films	-	-	CMC PVAm	-	-	-	-	-	Swollen gels in water subject to ionic bonding	Feng *et al.* 2006
-		-	Cell acet PAN	Chlor-ate init.	HQ	-	-	-	Crosslinking, Saponification yielded water absorbency.	Feng *et al.* 2010b
Regen	Cellulose	NMMO regen.	-	-	-	-	0.65-1.2	-	Regenerated cellulose properties depend on forming.	Fink *et al.* 2001
Fiber	Bacterial cellulose	-	-	-	-	-	100-124	-	Bulk-like water exists in “lakes” in the gels.	Gelin *et al.* 2007
Tissue	Var. kraft & sulfite	Refining	-	-	-	-	2.0 - 2.9	-	Hardwood kraft pulps gave high absorbency; WRV decreased with refiing.	Gigac & F. 2008
Fiber	Birch kraft	Cross-linking	(MVEMA or PEG)	-	Therm µwave	-	30-37	-		Goetz *et al.* 2009
Fiber	SW kraft	Acidic, drying	(MVEMA or PEG)	-	-	-	96-198	-	Microwave gave higher swelling than thermal curing.	Goetz *et al.* 2011

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	-	-	CGMA AAm	Per-sulfate	Free radical	-	160-400	-	Crosslinking rendered the gels tougher.	Guilherme *et al.* 2005
Anal. solid	Cellulose	grafting	(AA, AASA)	CAN	MBA	-	5-7	-	Up to 19% grafting yielded little increase in swelling.	Gürdağ *et al.* 2001
Lyocel fiber	Oxidized cellulose	XL with amines	-	-	-	-	0.37-0.70	-	Crosslinking decreased absorption.	Han *et al.* 2010
-		-	HPC, MC, HPMC	-	-	-	-	-	Temperature sensitivity	Harsh & Gehrke 1991
HGel	-	-	HPC	NaOH	DVS	-	15-52	-	Crosslinking yields micro-porosity, > swelling.	Hirsh & Spontak 2002
Fiber netwk	Cotton, SW TMP	Kraft, sulfite	-	-	-	-	-	-	Surfactants adsorption & diffusion affect wicking.	Hodgson & Berg 1988
Fiber	Bl. SW kraft	Per-iodate, sulfite	-	-	-	-	1-2.7	-	Sulfonation improved absorbancy.	Hou *et al.* 2008
HGel	-	-	CMC AA plasma	-	Free radical	-	509	-	Grafting conditions were optimized.	Huang *et al.* 2011
Blend	Banana pulp	Bleach, MAH	-	-	-	-	-	-	Esterification was confirmed & increased absorbency.	Ibrahim & El-Zawawy 2004
HGel	-	-	CMC AAm	Electr-beam	Free radical	-	-	-		Ibrahim *et al.* 2007
Fibers	Cellulose	MMA graft	-	-	-	-	20-80	-		Jain & Ni 2008
Fibers	Sulfite	MMA graft	-	-	-	-	22-91	-	Hydrolysis after graft yielded major increase in swelling.	Jain *et al.* 2007

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Gel	-	-	Methyl cellulose	Cool from 95	Phys-ical	-	-	-	Effects of time and temperature on gelation	Joshi *et al.* 2008
Foam gel	-	-	-	-	-	-	-	-	Porous hydrogel sorbed fluid much more quickly.	Kabra & Gehrke 1994
HGel	-	-	HPC	Heat > LCST	DVS	-	-	-	Extensive characterization of pore structure.	Kabra *et al.* 1998
Aero-gel	Nanocr-yst. cell.	Freeze drying	-	-	-	-	35	-	Vapor deposition of TiO_2 film resists sorption until UV illum.	Kettunen *et al.* 2011
HGel	“Wood pulp”	-	Cellulose AM	Cerium hydrol	MBA	-	2500	50	Cerium oxidation enhanced grafting effect.	Kim & Mun 2009
Cellu-lose	-	Perio-date	-	-	-	-	-	-		Kim & Kuga 2002
HGel	(Cotton cellulose)	-	Cellulose	LiCl NMP	BTCA		720		Biodegradability was established.	Kono & Fujita 2012
HGl	-	-	Cellulose chitin	LiCl NMP	BCTA	-	329	150	Biodegradability by both cellulase & chitinase	Kono & Zakimi 2013
HGel	(Cotton cellulose)	-	Cellulose	3 solv-ents	BTCA	-	10-987	-	Electronegativity of solvent anions affected results	Kono *et al.* 2013
HGels	- - -	- - -	Various synthetic Semi-synthetic Fully natural	Var.	Var.	- - -	20-1000 8-300 18-60	20 20 2-3	Higher valent cations suppressed absorbency more. High-levels of cross-linking agent reduce hydrophilicity.	Kulicke & Nottelmann 1989
HGel	-	-	CMC AA NIPAM	H_2O_2 H_2SO_4	MBA	-	2-1150	-	Decreasing absorbency with increasing temperature	Kuwabara & Kubota 1996

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	MFC	-	PAA	KPS	MBA	MFC	10-30	-	Microfibrillated cellulose could add to function of crosslinker	Larsson *et al.* 2010
HGel	MFC	Struct. charge	PAA	Var-ious	Var-ious	-	22-10000	-	Review: reinforcing effects of all MFCs were observed.	Larsson *et al.* 2011
Fiber	SW kraft	g – PAN hydrol.	-	-	Free radical	-	1.5-55	-	Grafted acrylate greatly increased water retention.	Lepoutre *et al.* 1973
Straw graft	Wheat straw	graft	AA,Am, DADMAc	-	Free radical	-	134	34	Ion effects compared.	Li *et al.* 2012
HGel	-	-	Acrylate, Cellulose acetate	APS	Free radical	Carbon part.	208-226	-	Addition of carbon particles increased swelling pressures and flux.	Li *et al.* 2013
Straw graft	Wheat straw	g-AA	Straw AA	APS	MBA	-	470-850	30-66	Effect of valency	Liang *et al.* 2009
HGel	Sugar bagasse	Milling	AA	APS	Free radical	-	800-1300	100	Milling of the bagasse before derivatization greatly increased the absorbency.	Liang *et al.* 2013
HGel	-	-	Starch-SO_4 PAN	DMAc LiCl	-	-	1510	126	Sulfate has inherently higher dissociation.	Lim *et al.* 2001
Regen	Lyocell	-	Starch-g-PAN	NMMO soln.	Spin-ning	-	4-8	-	HSPAN itself had an absorbed 325 g/g water.	Lim *et al.* 2003
Cellu-lose	Cellulose	graft	(AA)	µwave	-	-	-	-	Removal of heavy metals.	Lin *et al.* 2010
HGel	-	-	CMC HEC	KOH	DVS	-	-	-	Hydrogels were found to be biodegradable.	Lionetto *et al.* 2003
HGel	-	-	CMC	γ irrad.	-	-	200-580	60	Became soluble at 70 °C +. Swelling maximum at pH=7	Liu *et al.* 2005a

	Fiber		Hydrogel			Other	Fluid uptake		Notes	Citation
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	-	-	CMC	γ irrad.	-	-	470	100	Calium ion decreased swelling markedly.	Liu *et al.* 2002
HGel	Cellulose	graft	AA, Am, BMA	-	MBA	-	770	86		Liu *et al.* 2011
HGel	-	-	MethCell. NIPAM	-	-	-	-	-	Temperature-sensitive gel	Liu *et al.* 2004
Mix	Straw powder	ground	AA	NaOH ClAcet.	APS MBA	-	220-430	23-43		Liu *et al.* 2009
HGel	Wheat straw	Ground, graft	Acrylate PVA	Inter-penetr.	Free radical	-	100-260	16-30	Claims interpenetrating networks sorb more fluid.	Liu *et al.* 2013
HGel	Cotton & starch	graft	PAN	Radical Hydrol	Acryl	-	148	63		Lokhande & Gotmare 1999
Fiber	Cotton	graft	PAN	Cerium	Free radical	-	2.2-2.8	-	Reversibility demonstrated.	Lokhande & V. 1993
Micro-fibers	Micro-fibers	graft	PAA	Silane, KPS	Free radical	-	4-13	-	Grafting greatly increased water retention.	Loria-B. *et al.* 2002
Fiber	SW kraft pulp	9 cross-link	-	-	BDDE	-	-	-	Wet-bulk was increased.	Lund *et al.* 2011
Fiber	SW kraft pulp	Alkali extrac.	-	-	-	-	0.9-1.6	-	Enhanced water holding ability under pressure	Lund *et al.* 2012
HGel	-	-	Cellulose	TiO_2 photo	DVS	-	-	-	A photocatalytic process was used to reduce DVS pollution.	Marci *et al.* 2006
Fiber	Not-dried cotton	During ripening	-	-	-	-	27-73	-	Presence of water inhibits tight hydrogen bonding in cotton.	Mizutani *et al.* 1999

	Fiber		Hydrogel			Other	Fluid uptake		Notes	Citation
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Paper towel	-	-	-	-	-	-	-	-	Practical test to detect urine loss due to incontinences	Neumann *et al.* 2004
HGel	-	-	Cellulose PVOH	DMAc LiCl	-	-	-	-	Hydrogen bonding found.	Nishio & Manley 1988
HGel	-	-	CMC HEC	-	-	-	-	-	Swelling and elasticity were related to theory.	Oppermann 1995
Aerogels	Nanofiber	-	Cellulose	-	None	-	-	-	The aerogels resist collapse even without crosslinking.	Pääkkö *et al.* 2008
HGel	SW kraft	-	Cellulose	130 C cure	PVM-EMA	-	100-190	-	Ester crosslinked fibers have good water sorption ability.	Pan & Ragauskas 2012
Fiber fluff	SW kraft	-	-	-	-	-	10-13	-		Parham & Hergert 1980
HGel	-	-	Chitosan Nut gum	-	PEC	-	14-44	12-15	Highest sorption at either high or low pH, due to PEC effect.	Paula *et al.* 2002
HGel	-	-	Xylan HP *etc*.	UV radical	DAT-DA	-	100-350	-	Crosslinking had minor effect on absorbency.	Pohjanlehto *et al.* 2011
HGel	-	-	CMC PAA	APS	MBA	celite	310	-		Pourjavadi *et al.* 2007a
HGel	-	-	CMC AAm/PS	70 C APS	MBA	-	1000-1400	70	Di- & tri-valent cations greatly decreased swelling.	Pourjavadi *et al.* 2009
HGel	-	-	CMC	APS	MBA	SiO_2 gel	400-4000	110	pH 8-9 gave highest swelling.	Pourjavadi *et al.* 2008
HGel	-	-	CMC	-	MBA	celite	-	86		Pourjavadi *et al.* 2010

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	-	-	CMC PAN	CAN hydrol	Radical	-	180-680	20-60	Results of pH variations.	Pourjavadi *et al.* 2007b
HGel	-	-	CMC PVP	Radiation	PEC	-	47-145	24-40	Slow release of agricultural urea.	Raafat *et al.* 2012
Fibers	Wood fibers	Graft	(Acrylic)	Cerium base	Free radical	-	40	15-20	WRV of untreated fibers ~2g/g	Rezai & Warner 1997
HGel	-	-	Cat.HEC	NaOH	EGDE	-	30-90	-		Rodriguez *et al.* 2003
HGel	-	-	CMC PVP	Heat treatmt	Agar gelling	-	13-16	-	Medical applications	Roy *et al.* 2010
HGel	-	-	Cellulose	DMSO PF	Coag. regen	-	8	-	Transparent gels from LiCl/DMAc, PF/DMSO, etc.	Saito *et al.* 2003
HGel	-	-	Cellulose	Phosporylatn	Soln., drying	-	-	-		Saito *et al.* 1995
Foam HGel	-	-	Hemicell. Chitosan	XL PEC	Citrate anhyd	-	32	35	Minor antipolyelectrolyte effect observed.	Salam *et al.* 2011a,b
HGel	-	-	Carragnn Acrylate	APS	MBA	-	60-136	28-52	Evaluated in methanol-water mixtures	Salimi *et al.* 2010
Por. HGel	-	-	CMC HEC	KOH Hyalur.	PEG-DVS	-	100-1300	-	Higher length of cross-linker gave higher sorption.	Sannino *et al.* 2003
Por. HGel	-	-	CMC HEC	KOH Hyalur.	DVS	-	60-180	35-100	Dessication in acetone have higher swelling & porosity.	Sannino *et al.* 2004a
HGel	-	-	Cellulose derivativ	KOH	DVS	-	360	-	Pressure (4000 kPa) reduced swelling from 360 to ~0.	Sannino *et al.* 2004b
HGel	-	-	CMC HEC	KOH	DVS	-	47-183	32-110	Ionic strength and pH effects	Sannino & Nicolais 2005

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Fiber	-	-	-	-	-	-	-	-	Water retention value and fiber saturation point	Scallan & Carles 1972
Composite	Whatman TMP	Caboxy methyl	(CMC fibers)	-	-	-	4-5	-	Untreated cellulose exhibited only 22% swelling in water.	Schuchardt & Berg 1991
Fiber	Tencel	Regenerated	-	-	-	-	5	-	Said to be more accessible than other synth celluloses.	Schuster *et al.* 2006
Foam	Cellulose chitin NF	Freeze drying	-	-	-	-	-	-	Attention to mechanical & morpholobical issues.	Sehaqui *et al.* 2010
Aerogels	NFC	Freeze drying	-	-	-	-	-	-	Freeze-drying from tertbutanol	Sehaqui *et al.* 2011
HGel film	-	-	CMC Chitosan	PEC	Glutaraldeh	-	1-8	-	Bending angle evaluated due to electrokinetic effects.	Shang *et al.* 2008
Paper	Bl HW, SW kraft	Surfactants	-	-	-	-	3.0-3.3	-	Surfactants promote wetting	Shepherd & Xiao 1999
Fiber	Sulfonat cellulose	-	-	-	-	-	8+	-	Swellable but insoluble	Shet & Wallajapet 1997
HGel	-	-	Cellulose AA AM	graft	MBA	-	1400	-	Microwave	Shu *et al.* 2011
HGel	-	-	HPC	Heat gelat.	Physical	-	-	-	Hydrophobic interactions govern onset of gelation.	Silva *et al.* 2008
Fiber	*Cannabis indica*	graft	(AA)	Ceric	Free radical	-	-	-		Singha & Rana 2011
Nanocompos	CNW	graft	(starch-AA)	KPS	MBA	CNW	305-481	-	Nanocellulose increased water uptake.	Spagnol *et al.* 2012a
Fiber	Kraft pulps	Delign. Oxygen	-	-	-	-	-	-	Oxygen plasma increased hydrophilicity	Ström & Carlsson 1992

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	-	-	CMC AA_AAm	NaOH	MBA	-	920	85	Optimization	Suo *et al.* 2007
HGel pore	-	-	MC Chitosan	Heat to 37 °C	-	-	-	-	Salts affect gelation	Tang *et al.* 2010
Foam	MFC	Freeze-drying	-	-	-	-	-	-		Theliander *et al.* 2011
HGel	-	-	CMC PAAPS	APS	MBA	-	25-65	-	Semi-interpenetrating nework was optimized at pH≠7.	Varaprasad *et al.* 2011
Fiber	SW sulfite	graft	(AA, MA, *etc.*)	Ceric	EG-DMA	-	48	2-10	Drying did not hurt absorbency.	Vitta *et al.* 1986
HGel	-	-	CMC	Radia-tion	-	-	800	-	Biodegradable by cellulose; high swelling when just gelled	Wach *et al.* 2001
HGel	-	-	HPC	Radia-tion	-	-	150-310	-	Irradiation progressively decreased swelling to ~10.	Wach *et al.* 2002
Corn, cotton, wheat	-	-	Ag fiber AA	graft	-	-	930	-		Wang *et al.* 2007
HGel	-	-	CMC AA MAETAC	Suspen polym	PEC	-	400-2200	-	Absorbency increases with ionic strength; Biodegradable	Wang *et al.* 2008
HGel	-	-	HEC AA	APS 60 C	MBA	Atta-pulgite	330-500	75-300	The mineral could increase absorbency and rate	Wang *et al.* 2010
HGel	-	-	HEC AA	Radical APS	MBA	Vermi-culite	350-950	68	Highest swelling at pH 6-10.	Wang *et al.* 2011a
HGel	-	-	CMC AA	APS	MBA	Atta-pulgite	40-630	-	CTAB treatment yielded great pH sensitivity	Wang & Wang 2010

	Fiber		Hydrogel			Other	Fluid uptake		Notes	Citation
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
HGel	-	-	HEC	APS	MBA	Medic. stone	162-352	48-82		Wang *et al.* 2011b
HGel	-	-	CMC AA PVP	APS	MBA	-	630-742	62-70	CTAB treatment yielded great pH sensitivity	Wang *et al.* 2011c
HGel	-	-	CMC AA	APS	MBA	Medic. stone	317-634	41-58		Wang *et al.* 2011d
HGel	-	-	CMC AA co-AMPS	APS	Free radical	-	400-500	55-70	Optimized XL, CMC content, acrylic monomer ratio; intermediate pH best	Wang *et al.* 2013
Fiber	SW kraft	graft	-	-	-	-	-	-	Homogeneous through the fiber	Warner & Rezai 1997
Fiber	SW kraft fluff pulp	-	CMC	-	Alum. sulfate	-	40-60	20-30		Weerawarna & Su 2010
Fibers		graft	-	-	-	-	30	-	Post-decrystallization; most emphasis on relative humidity	Williams & Stannet 1979
HGel	-	-	Cellulose AA-AAm	APS	MBA	-	875	90		Wu *et al.* 2012
HGel	SW kraft	-	Cellulose AA	-	Free radical	-	239	-		Wu *et al.* 2008
HGel	-	-	CMC PVOH	Freeze thaw	Tangled	-	6-14	-	Swelling favored by higher CMC content & neutral pH.	Xiao & Gao 2008
Fiber	(Bl kraft)	(CMC'd)	CMC	55-65 ^{o}C	PEG-DGE	-	500	-	Longer links gave higher absorbency.	Xiao & Meshitsuka 2001
Fiber	Wheat straw	-	Straw AA AMPS HMAm	APS	Free radical	-	140-360	-	For controlled release of urea as fertilizer; biodegradable	Xie *et al.* 2012

	Fiber		**Hydrogel**			**Other**	**Fluid uptake**		**Notes**	**Citation**
Sorbent Class	Components	Treatment	Components	Forming method	Cross-linking type		Water g/g	Saline g/g	Key Findings	Author (year)
Kraft paper		Poly-COOH	-	-	-	-	-	-	Emphasis on physical properties, not sorption.	Xu and Yang 1999
Fiber	Cotton	Liquid NH_3	-	-	-	-			Treated cotton fabrics showed increased absorbency.	Yanai *et al.* 2006
Fiber	Kraft fiber	Poly-COOH	-	-	BTCA PMA	-	-	-	Emphasis on physical properties, not absorption	Yang & Xu 1998
HGel	Cotton balls	-	Cellulose Succinic anhydrid	Amino pyridin LiClMP	-	-	-	-	Biodegradability shown, salt tolerance	Yoshimura *et al.* 2005
HGel	Cotton balls	-	Cellulose Succinic anhydrid	TBAF DMSO LiClMP	Meth-anol precip	-	20-400	15-100	Biodegradability shown, salt tolerance	Yoshimura *et al.* 2006
Por. HGel	(Bl. SW kraft)	-	Cellulose AAm	Ceric	MBA	-	45-1773	-	Crosslinker level affected results.	Yoshinubu *et al.* 1992
HGel Foam	-	-	CM-chitosan	Pentan	Glutar aldhyd	-	107	37		Zamani *et al.* 2010
Fiber	Bleached HW kraft	Periodat Bisulfate	-	-	-	-	0.4-1.1	-	Oxidation & sulfonation gave higher water retention values.	Zhang *et al.* 2008a
HGel	-	-	Polyacryl ate	KPS	MBA	Hydro talcite	900	140	Hydrotalcite positively affected absorbency at 3% level.	Zhang *et al.* 2008b
HGel	-	-	Polyacryl ate	KPS	MBA	Hydro talcite	1100	145		Zhang *et al.* 2009
Com-posite	-	-	Cellulose PAM	AmPer-sulfate	MBA	-	500	-	Cellulose use made gel mor porous and looser.	Zhang *et al.* 2010

Notes for Table A

Sorbent Classes

HGel = hydrogel
Regen = regenerated cellulose, *e.g.* lyocell

Fibers

CNW = cellulose nanowhiskers
Kraft = kraft pulp fibers

Treatments

MAH = maleic anhydride treatment

Components

AAm = acrylamide
AMPS = acrylic acid (AA)/acrylamide(AM)/e-acrylamido-2-methyl-1-propanesulfonic acid
AAm/PS = copolymerization of acrylamide and 2-acrylamido-2-methylpropan sulfonic acid
BMA = butylmethacrylate
CGMA = methacrylated cashew gum
CMC = carboxymethyl cellulose
CM.chito = carboxymethyl chitosan
g or gr. = graft-
HEC = hydroxyethyl cellulose
HMAm = N-hydroxymethyl acrylamide
HP cell. = hydroxypropyl cellulose
MBAM = N,N-(methylenebisacrylamide)
MAETAC = [2-(methylacryloyloxy)ethyl]trimethylammonium chloride
MethCell = methyl cellulose
PAAPS = poly(acylamide-co-2-acrylamido-2-methy-1-propanesulfonic-acid)
PNBAm = poly(N-tert-butylacrylamide)-co-acrylamide
PNIPAM = poly(*N*-isopropylacrylamide)
PVAm = polyvinyl amine
PVOH = polyvinyl alcohol
PVP = polyvinylpyrrolidone

Forming methods

APS = ammonium persulfate initiator
CAN = cerium ammonium nitrate
Coag = coagulation as a means of gelation of the polymers
DMAc-LiCl = Ionic liquid solvent N,N-dimethylacetamide (DMAc) and lithium chloride
DMSO PF = dimethylsulfoxide paraformaldehyde (solvent system for cellulose)
Interpenet. = Interpentrating network of two polymers constitutes the gel.
KPS = potassium persulfate initiation of free-radical polymerization
LCST = lower critical solution temperature
LiClMP = mixture of lithium chloride and N-methyl-2-pyrrolidinone
LiCl/NMP = dissolution in lithium chloride with N-methyl-2-pyrrolidinone
Regen = regeneration of the cellulose as a means of forming the hydrogel
TiO2 photo = photocatalyzed reaction mediated by titanium dioxide particles

Crosslinkers

CMPJ = chloromethylpyridine iodide
DATDA = *N*,*N*'-diallyltartardiamide
DBBE = 1,4-butanediol diglycidyl ether, a di-epoxide
BTCA = 1,2,3,4-butanetetracarboxylic dianhydride
DVS = divinyl sulfone
ECH = epichlorohydrin
EGDE = ethylenglycol diglycidylether
EGDMA = ethylene glycol dimethacrylate
GA = glutaraldehyde
HQ = hydropropyl acrylate
MBA = *N*,*N*-methylenebisacrylamide
PEGDBE = polyethylene glycol diglycidyl ethers
PVMEMA = poly(vinylmethylether-co-maleic acid)

Other (particles and nanomaterials)

Bentonite = sodium montmorillonite, an exfoliated “nanoclay”
CNC = cellulose nanocrystals