THE EFFECT OF POLYMER STRUCTURE AND INTERACTION ON PAPER STRENGTH

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ABSTRACT

Polymers are routinely used in paper making to enhance the strength of paper. The strength enhancing effect of polymers on paper is generally attributed to the increase in the fiber-fiber bond strength. This thesis focuses on the links between the structures and interactions of adsorbed polymers and the resulting strength of fiber-fiber bonds.

Dextran was chosen as the model of strength enhancing polymers in this work. The molecular weight, charge density, and hydrophobicity of the dextrans were varied. Mixtures of dextran and hydrophobically modified dextrans were employed to investigate the role of adsorbed polymer compatibility in fiber-fiber bonding.

Cationic dextran with different charge densities (0.161 - 0.488 meq/g) was prepared. Hydrophobically modified dextran was made by the reaction of dextran with straight chain saturated C3, C4 and C6 fatty acids. The incompatibility of dextran and hydrophobic dextran was evaluated by means of the biphase formation of an aqueous mixture of the two polymers.

The adsorption behavior of dextrans on pulp fiber was measured. It was observed that the maximum amount of adsorption increased with a decrease in the molecular weight and charge density of the dextran.

The strength of paper was evaluated using tensile strength and Scott bond tests. The strength enhancing effect of dextran was given as a function of molecular weight, charge density, hydrophobicity, and incompatibility with hydrophobic dextran. When fiber surface was saturated with dextran, it was found that the tensile strength of paper did not depend on the molecular weight of the dextran in the range investigated (77,000 to 2000,000). The charge density of the dextran affected the strength of paper by changing the maximum amount of dextran adsorbed on fibers. Introducing hydrophobic groups into dextran decreased the strength enhancing ability of dextran. The strength enhancing mechanism of dextran was proposed to be the formation of dextran intermolecular bonds between fibers.

For the first time, the role of polymer incompatibility in determining the strength of paper was demonstrated in this work. It was found that the bond strength between fibers coated with two incompatible polymers was weaker than that obtained from the single polymer coated fibers. The Page equation, along with the model developed in this work, was applied to calculate the bond strength for each type of bonding.

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Chapter 1. Introduction

Paper is made from mechanically or chemically isolated wood fibers, which are suspended in water and filtered off on a wire mesh, pressed and consolidated into a paper sheet. It is a network of wood fibers that are highly bonded to each other. The average fiber in paper is in bonded contact with as many as 20-40 other fibers per millimeter of the fiber's length[1]. The strength of paper is derived from both the fiber strength and the strength of fiber-fiber bonding. In many cases water-soluble polymers are adsorbed onto fibers before the papermaking operation in order to produce stronger fiber-fiber bonds and thus stronger paper. This thesis focuses on the links between the structures and interactions of adsorbed polymers and resulting strength of fiber-fiber bonds.

1.1. The properties of pulp fiber

The major polymeric constituents of wood are cellulose, hemicelluloses and lignin. The wood fibers are themselves a composite material in that they consist of a cellulose microfibrils reinforcing a cementing matrix of hemicelluloses and lignin. The proportions of these polymers are, on average, 45% cellulose, 21% lignin and 34% hemicelluloses in hardwoods, and 42% cellulose, 29% lignin and 28% hemicelluloses in softwoods[2]. In addition, wood contains some low to moderately high molecular weight solvent soluble or water soluble extractives.

They consist of resin, fatty acids and phenolic compounds. It was found some of these extractives impaired the strength of paper[3,4,5,6]

Pulp fibers are produced from wood by mechanical or chemical pulping. Chemical pulping methods rely on the effect of chemicals to separate fibers, whereas mechanical pulping methods rely completely on physical action. The more that chemicals are involved, the lower the yield and lignin content since chemical action degrades and solubilize components of the wood, especially lignin and hemicelluloses. On the other hand, chemical pulping yields individual fibers that are not cut and give strong papers since the lignin, which interferes with hydrogen bonding of fibers, is largely removed[7].

Cellulosic fibers are negatively charged throughout the whole pH-regime. The number of charged groups usually varies between 2 to 30 meq/100g from different types of paper making fibers. The ionizable groups on cellulosic fibers may be carboxyl groups, sulfonic acid groups, or phenolic groups. The carboxyl groups either originate in the non-cellulosic components in the wood itself or are created during the impregnation, pulping or bleaching operations. Sulfonic acid groups are introduced with the sulfite treatment during chemi-(thermo)-mechanical pulping or during sulfite pulping. In native wood most of the carboxyl groups come from the uronic acid residues[8,9]. The charged groups on fibers of both chemical and mechanical pulps have an impact on the swelling properties of the fibers, which are believed to improve the fiber/fiber bonding in a paper sheet[10].

1.2. Surface topography of cellulosic fibers

The nature of fiber-fiber bonding is the adhesion of fiber surfaces. Therefore, the topography of fiber surface is important when considering fiber/fiber bonding. Many external surface models for fiber were, quantitatively or qualitatively, proposed and have been reviewed[11,12,13]. d'A Clark[10,14] proposed that the reducing ends of cellulose chains extend into solution. This model was based on the hypothesis of "partial solution" advanced many years ago (Campbell 1932). Pelton[11] suggested that fiber surface is featured with (a) a layer of water swollen polymer layer; (b) surface roughness, and (c) surface charge groups. The swelling of the fiber surface can be enhanced with beating and refining, which is a mechanical treatment that increases the surface area of fiber and surface fibrils[15,16,17,18]. It is believed that the existence of the swollen layer facilitates the formation of fiber-fiber bonds at molecular level.

The direct evidences of the presence of swollen layer on fiber surface have been observed with Atomic Force Microscopy (AFM) and Surface Force Apparatus. The main findings are:

- AFM images showed the swelling of fiber in water and the subsequent shrinkage when the fibers dry[19].

- The interaction between two cellulose surfaces was dominated by a steric repulsion caused by the dangling tails of cellulose chains[20,21].
- Compared to the adhesion between two dry cellulose surfaces, much stronger adhesion was observed when intermolecular bonds between two cellulose surfaces were developed when they dried from water[21]. The difference between adhesion force was attributed to cellulose chain entanglement and/or chemical adhesion (hydrogen bond) forces which were developed upon drying.

The other important feature of cellulose fiber is its porosity. It is shown that pulp fibers have specific gravity of about two-thirds that of cellulose. The difference caused by the presence of air not only in lumens but also in the many pores of fibers. Attempts have been made to characterize the pore size and size distribution with different techniques[22,23,24].

1.3. The theories of fiber-fiber bonding

1.3.1. The origins of fiber-fiber bonds

Bonding between fibers is the very heart of the strength development for a paper sheet. The following types of bonding are at least theoretically possible and have been proposed based on the experimental evidences from the early work[25].

- Covalent bonding,

- Ionic bonding,
- Hydrogen bonding and van der Waals force,
- Mechanical entanglement of fibers or surface fibrils.

Among these concepts, it is generally accepted that at the molecular level papermaking fibers are held together in the dry or air-dry state by means of hydrogen bonds. The essence of the hydrogen bond in cellulose is that adjacent hydroxyl groups have a strong attraction for each other as water removing during drying[26].

1.3.2. The development of fiber-fiber bonds

Regardless of the nature and extent of the bonds between fibers in paper, the practical interest is the mechanism by which these bonds develop during the papermaking process. Since these bonds are formed at the molecular level, the prerequisite for the formation of bonds is the close contact between fiber surfaces.

Campbell provided the early insight to this question. His theory states that various surface tension effects during the removal of water from a wet fiber mat provides a powerful internal force which pulls adjacent fiber surfaces into very intimate and extended contact. The effect of surface tension depends on the condition that two cellulose surfaces are close together, and have a film of water between them. The tension between two fiber surfaces can be considered with the following equation,

$$F = \frac{2\gamma}{d} \qquad \text{Equation 1.1}$$

where d is the distance between two surfaces, and γ is the surface tension of liquid in between, 72×10^{-3} N/m for water. As evaporation proceeds, the water film draws the flat surfaces together with an increasing pressure. By the time the flat surfaces are 1μm apart, the pressure is calculated to be 144 kPa; at 30Å apart, it is 48,000 kPa[27]. These forces are strong enough to bring fiber surfaces into an intimate contact.

During 1940's to 1960's, people investigated various factors that affected the properties of fiber-fiber bonding, such as the modification on hydroxyl group of cellulose fiber, different solvents medium for papermaking, freeze dried paper, etc. These classical experiments established the information database for understanding the development of fiber-to-fiber bonds[28,29,30,31,32,33,34,35,36,37].

Based on these experimental evidences McKenzie[38] applied diffusion theory, proposed by Voyutskii[39] early in 1963, to the development of fiber-fiber bonding in paper. Instead of the effect surface tension of water during drying of sheet, the theory stresses how molecular segments from opposing surfaces can come sufficiently close to form an adequate hydrogen bonded network. It is believed that water acts as a plasticizer for papermaking fibers and that the water saturated fibers will be plasticized to an extent which is adequate for the development of adhesion. He proposed that the requirements for diffusion controlled adhesion were present under normal papermaking conditions. The evidence such as weak paper obtained from solvent exchange drying or freeze dry provided the proof that the development of the bonds was inhibited if the mobility of the elements within the bonded area was restricted at the fibrillar or molecular level. From the viewpoint of diffusion, the effect of solvent exchange has been understood as that organic solvents are less effective than water in plasticizing cellulosic fibers. Therefore, both fiber conformability and the mobility of individual polysaccharide segments will be reduced as the polarity of the solvent used is reduced. The strength of freeze dried handsheets is significantly lower than that of the corresponding air dried handsheets, because freezing will mechanically hinder the movement of the polysaccharide segments which would otherwise rearrange within the bonded area as part of the process of bond formation by a diffusion mechanism.

According to diffusion theory, the essential steps in papermaking would be (i) consolidation and establishment of areas of interfibre contact under pressure; (ii) intermingling and rearrangement of molecular segments within the bonded region and (iii) formation of intermolecular bonds as the plasticizer is removed.

1.3.3. Fiber properties on the strength properties of paper

Generally, fiber properties affect sheet properties in these aspects[40]:

- Fiber length: This affects sheet formation or uniformity of fiber distribution; the shorter the fibers, the closer and more uniform the sheet formation will be. When two pulps have very different fiber lengths, papers made from the longer fiber will always be stronger in general.
  - Fiber diameter: The effects of fiber diameter, wall thickness, and coarseness on sheet properties is rather complex. These qualities primarily affect fiber flexibility.
  - Fiber strength: The fiber strength is an indication of the maximum strength obtainable from a given pulp. Maximum strength is not achieved in practice owing to the fact that interfiber bond strength is the determining factor. Fiber strength is usually measured by the zero span tensile test.
  - Specific surface and fibrillation: The greater the surface available for bonding, the higher the sheet strength is. However, sheet properties are affected more by the relative bonded area than by the specific surface of the fibers from which the sheet is made.

- Fiber-fiber bonding: The subject of fiber bonding is the fundamental basis of papermaking. In the context of strength properties, it is in practice the limiting factor to determine the strength of paper.

1.4. The structural characteristics of paper and testing methods

Structural characteristics describe how the components are arranged in a sheet of paper. The particular topics of interest are basis weight or grammage, light scattering coefficient, specific volume, formation, smoothness, and porosity. Only the properties that are measured in the following work are briefly reviewed[26, 40, 14, 41].

Basis weight: It is the measure of the weight per unit area of a paper sheet and is determined by measuring its weight and area. Basis weight is affected by the factors such as additional operation that adds something to the sheet, such sizing or coating, conversion processes that apply pigment or functional coating or impregnated the sheet with substances will also contribute to the final basis weight. Moreover, the sheet moisture content also affects basis weight, consequently, it is important that basis weight measurements be made on samples that are in equilibrium with standard relative humidity and temperature.

Light scattering coefficient: The scattering coefficient involves measuring the reflectance of a test sheet backed with a black-velvet-lined cavity, and the reflectance when the sheet is backed with enough of the same or similar colored sheets to make the pile opaque. The importance of this value is that it gives an inverse estimate of the internal bonding of the fibers in a sheet of paper, in which the fraction bonded is called the relative bonded area.

Specific volume: The specific volume, or its inverse, the density, of standard Tappi handsheets gives a good indication of the wet compactability of the wet fibers, the scattering coefficient, the relative bonded area of the fibers. It is obtained by dividing the basis weight with the thickness that is measured with a micrometer, which applies the pressure of 50 ± 2 kPa to the two surfaces of a sheet.

1.5. Strength properties of paper

Depending upon the primary use for which the product is intended, strength properties of paper consist of in-plane tensile strength, toughness, burst strength, folding endurance, internal bond strength, stiffness, tear resistance, and compressibility. While most of these strength properties are increased by the additional bonding between the fibers in a sheet, internal bond strength and resistance to delamination are particularly dependent upon the degree of interfiber bonding. However, properties such as tear resistance and compressibility are impaired with the increased fiber-fiber bonding. In- plane tensile strength, which is referred to the tensile strength in the following, and the internal bond strength, Scott bond strength, are used as the measure of the strength properties of paper in this work.

1.5.1. Scott bond strength

The Scott bond test is an impact test employed for measuring the internal bond strength of paper, more in z-direction[42]. The instrument used in this work is shown in the picture of **Figure 1.1**. The procedure involves laminating a test specimen between a metal block and one leg of a short length of aluminum angle with the aid of a double sided adhesive tape. The block is placed on the frame of an instrument supporting a pendulum, which, upon release, strikes the upper edge of the angle, causing the sheet to split. The Scott bond rupture energy is expressed in energy units for a unit surface produced in the test (J/m^2). This measurement can be used to compare the effects of fiber treatments on bonding if a single type of pulp is used, and the treatments do not change fiber properties[43].

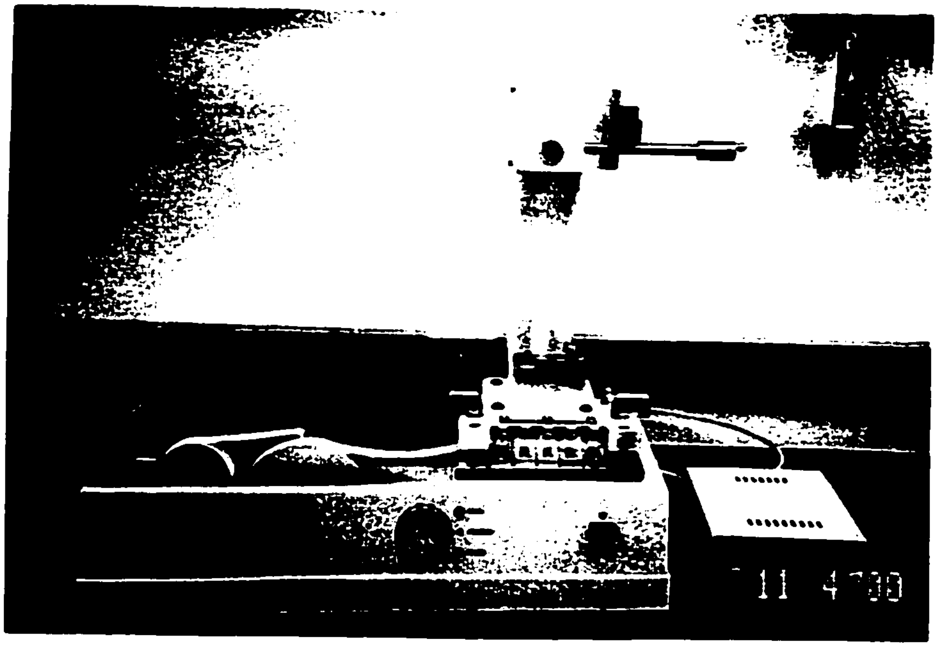

Figure 1.1. Huygen Internal Bond Test, Model 1314 (Labtech)

1.5.2. Tensile strength

Tensile test is made on a strip of 15 mm wide and 100 mm long. The sample is stretched at the constant elongation speed of 25 mm/min. The maximum load divided by the width of sample is the measured tensile strength, in the unit of N/m. In addition, this measurement can also provide the E-modulus, tensile energy adsorption and the strain. The tensile tester used in this work is the horizontal type, as show in **Figure 1.2**.

An often-used parameter is the corrected tensile strength for basis weight, tensile index in the unit of Nm/g, which is calculated by dividing the tensile strength with the basis weight. Breaking length is another parameter used for tensile strength. It is defined as the length of a strip of given paper that will cause it to break under its own weight. The conversion between tensile index and breaking length is

$$T = \frac{T'}{9.8 \times 1000} \qquad \text{Equation 1.2}$$

where T is the breaking length in the unit of kilometer, T' is the tensile index in the unit of Nm/g, 9.8 is the gravitational constant. Both tensile index and breaking length are used in the following chapters.

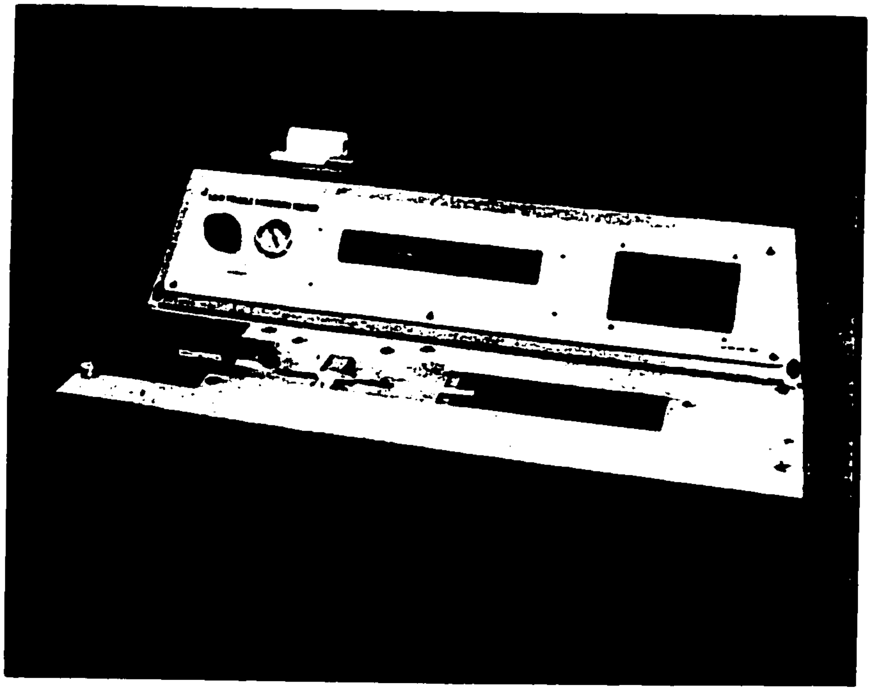

Figure 1.2. L & W Tensile strength tester (From 96 L & W Handbook, Lorentzen & Wettre Paper Testing and Process Optimization, P.125)

1.5.3. Theories of tensile strength

It is well known that paper derives its tensile strength from the tensile strength of individual fibers and the strength of the bonds between the fibers. The relative importance of these two factors depends upon which is the limiting factor under existing circumstances and has been demonstrated in the earlier work[44,45]. Davison[46] demonstrated that, due to creep during tensile elongation, many intact fibers may be extracted from a sheet of paper even though each fiber is bonded many times along its length to adjacent fibers in the web. It is generally agreed that commercial papers can be made stronger by increasing the strength of fiber-fiber bonds.

Many models have been developed to predict the structure and property behavior of paper. In a recent review paper[47], Jayaraman and Kortschot provided comprehensive and critical discussion of all of the important closed-form network models developed in the 1950s, 1960s and 1970s for the tensile strength of paper. They concluded that all the models consider a simplified microstructure, make use of idealized fibers and bonds as basic structural elements and relate the mechanical properties of the network to the characteristics of these elements. Further, they ignore the effect of fiber imperfections like micro-compressions, curl and crimps which have a distinct effect on the stress-strain behavior of the fibers. While each model considers the different variables and sub-processes that result in paper failure, the Page equation is ideal as a simple design tool to relates sheet strength to a variety of sheet structural parameters. The Page equation is used in subsequent chapters to interpret data and is explained below.

The Page equation[48] shows the concept of the interdependent roles played by fiber strength and by bonding strength. It is

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bPL(RBA)} \qquad \text{Equation 1.3}$$

where T is the tensile strength expressed in breaking length; Z is the zero-span tensile strength (a measure of the fiber strength) of the sample expressed as a breaking length; A is the mean fiber cross sectional area; ρ is the density of the fibrous material; g is the acceleration of gravity; b is the shear strength per unit area of the fiber-fiber bonds; P is the perimeter of the average fiber cross section; L is the mean fiber length; RBA is the fraction of fiber surface that is bonded in the sheet. The first term of the right-hand side describes the resistance of fibers to breakage, whereas the second term describes the resistance of fiber-fiber bonds to breakage. Detailed information about Page equation will be discussed in chapter 5.

1.5.4. Strength enhancing polymers

The strength of the fiber network can be increased mechanically by more beating or refining which generates micro-fibrils and promotes the formation of bonds between fibers. However, beating or refining consumes energy and increases paper density which in turn reduces paper porosity, stiffness and tearing resistance. Fines generated by beating slows drainage on the wire and thus papermachine productivity. The use of strength polymer additives may improve paper strength without additional refining.

Dry strength additives, or strength enhancing polymers, are generally water-soluble, hydrophilic polymers, either natural or synthetic. They are routinely added into the pulp fiber to enhance the strength of paper mainly by increasing the fiber-fiber bond strength. The most widely used natural polymers are starch, vegetable gums and cellulose derivatives. Synthetic polymers are mainly polyacrylamide-based. Cationic charged polymers are more often used due to their efficient retention on fiber surfaces than are nonionic and anionic polymers. Theoretically, the dry strength of paper can be enhanced by increasing bonding strength until a state is reached in which the bonds between fibers become stronger than the fibers themselves.

It is believed that the strength of paper is enhanced with strength enhancing polymers by increasing the number of bonds within the bonded area. More detailed work and discussion about the strength additives and their adsorption on fibers[49,50,51,52,53] can be found in several references[54,55,56,57,58,5960,61,62,63,64,65,66.] and the following chapters.

1.6. Objectives and approach of the project

Although strength enhancing polymers have been extensively studied, there is very little knowledge available regarding the relationship of polymer structure and properties to its performance as a strength enhancing polymer. It is, nevertheless, very important information for understanding the strength enhancing mechanism and for designing new strength enhancing polymers.

Therefore, the ultimate objective of this project is defined as:

To establish the linkage between the structure and properties of polymers to the strength enhancing behavior of these polymers in paper.

The approach taken to fulfil the objective is:

1. Choose a family of polymers with well-defined chemical structure and properties as the model of strength enhancing polymers.
2. Chemically modify and characterize the structure and properties of this polymer.
3. Investigate the influence of the various properties of this polymer on the strength of fiber-fiber bonding in paper.

4. Establish the linkage between the structure of strength enhancing polymers and their performance in enhancing the strength of fiber-fiber bonding in paper.

1.7. The outline of the thesis

Dextran was chosen as the model of strength enhancing polymers in this work. The molecular weight, charge density, and hydrophobicity of the dextrans were varied. Mixtures of modified dextrans were employed to investigate the role of adsorbed polymer compatibility on fiber-fiber bonding.

The thesis is divided into seven chapters, consisting of a previously published paper (Chapter 2) and 4 manuscripts which will be submitted in 2000. The final chapter reviews and consolidates the conclusion from this project. A more detailed summary of the chapter contents is now given.

Chapter one. This chapter provides the specific background knowledge about paper and paper properties, summarizes the previous work done in this area, and describes the testing methods used in the following chapters. Finally, the objectives and approach of this project were derived from this chapter.

Chapter two. *Aqueous biphase formation by mixtures of dextran and hydrophobically modified dextran.* A series of hydrophobically modified dextrans was prepared by the condensation of dextran with saturated fatty acids with different chain lengths and their solution properties were investigated. Incompatibility of dextran with hydrophobic dextran was characterized with the biphase formation of the mixture aqueous solution of these two polymers. Phase diagrams were made to evaluate the incompatibility as the function of the degree of substitution, chain length of fatty acids, temperature and molecular weight. This paper has been published on Colloid Polym Sci. 276, 476-482 (1998).

Chapter three. *The effect of molecular weight on paper strength enhancing polymers.* A series of cationic dextrans with different molecular weights, from 77,000 to 2000,000, was prepared. The adsorption of cationic dextran on pulp fiber was studied with the adsorption isotherms and the adsorbed layer thickness. Strength of handsheets was measured with tensile strength and Scott bond energy. The strength enhancing mechanism was discussed, and the effect of dextran on tensile strength and Scott bond strength was further compared. Moreover, the accessible surface areas of fiber to dextrans with different molecular weights were calculated and the fiber surface topography was evaluated with fractal dimension.

Chapter four. *Strength enhancement of dextran-impregnated paper.* The effect of molecular weight of dextran on the strength development of dextran-impregnated paper was investigated in this chapter. The purpose of this work is, firstly, to understand the effect of molecular weight of dextran at larger amounts of addition; secondly, to compare the effect of different adding mode of polymers on the strength development of paper. Furthermore, the polymer distribution within fiber network from the two different adding modes was discussed.

Chapter five. *The effect of charge density and hydrophobic modification on paper strength enhancing polymers.* Cationic dextran with different charge density and positively charged hydrophobic dextran with different degree of hydrophobic substitution were prepared. The adsorption behavior of these dextrans on fiber was investigated. The effect of the charge density and hydrophobicity of dextran on the strength of paper was reported and the strength enhancing mechanism was discussed. Moreover, the interfiber bond strength of paper was correlated to the surface energy of the strength enhancing polymers.

Chapter six. *The role of surface polymer compatibility in the formation of fiber/fiber bonds in paper.* For any polymer materials, the essential concern about the adhesion formed through the diffusion of surface polymers is whether they are compatible. Strong interfacial adhesion can only derive from the compatible surface polymers. The novel idea in this project is to apply the concepts developed in the disciplines of polymer science to understanding the role of polymers in enhancing the strength of paper. For the first time, the attempt was made to provide the direct evidence of the effect of polymer compatibility on fiber/fiber bond strength of paper. This is an interesting question from the viewpoint of both fundamental and practical consideration. Based on McKenzie's diffusion theory, the hypothesis is that incompatible polymers will produce weak bond strength due to their poor inter-diffusion. The incompatible polymer pair, dextran and hydrophobic dextran with different degree of substitution and hydrophobic chain length, has been characterized from the earlier work. Handsheets were made from single dextran coated fiber, single hydrophobic dextran coated fiber and the mixture of these two. The interfiber bond strength of each type of bonding was calculated with Page equation and the model developed in this paper, and effect of polymer compatibility on fiber-fiber bond strength was discussed.

Chapter seven. Overall conclusions of this work with comments and suggestions for the future work is given in this chapter.

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Chapter 2. Aqueous Biphase Formation By Mixtures Of Dextran And Hydrophobically Modified Dextran

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Abstract

A series of modified dextrans was prepared by condensation of straight chain saturated C3, C4 and C6 fatty acids and the phase behavior of aqueous solutions of these materials with unmodified dextran was measured as a function of temperature, concentration and degree of substitution. At a constant degree of substitution the tendency towards aqueous biphase formation increased with the length of the hydrophobic substituent, the temperature and the molecular weight. Fluorescence studies of the modified dextrans with pyrene as a probe indicated the presence of hydrophobic micro-domains. Rheological study showed that there was no large scale association for C3 and C4 substituted dextran, mainly intramolecular association, however some intermolecular association existed for C6 substituted dextran. The results are compared with the behavior of the classical PEG/dextran biphase systems, and mechanisms driving phase separation are discussed.

Keywords: Biaphase formation, hydrophobic modification, dextran

2.1 Introduction

Aqueous mixtures of dextran and polyethylene glycol (PEG) form two dilute aqueous phases, one containing mainly PEG and the other aqueous dextran.[1] These aqueous biphase systems have been extensively studied because of applications in separations of biological materials[2,3]. Dextran also forms aqueous biphases with poly(vinyl alcohol) and with block copolymers of PEG and poly(propylene oxide) (Pluronics). The factors influencing biphase formation which have been reported include the effects of salts, solvents[4,5,6,7,8], temperature[9,10,11,12] and molecular weight distributions[13,14,15].

Thermodynamic predictions of biphase formation have been based on group contribution methods[16] and variations of Flory Huggins theory[17,18,19,20,21]. Wennerström and coworkers state that since there is relatively little entropy cost in de-mixing macromolecules, biphase formation occurs when there are segment-to-segment repulsive interactions between the two types of polymer[17].

In this communication, we report the phase behavior of aqueous mixtures of dextran and hydrophobically modified dextran as functions of the degree and type of modification. This work provides background information for other adhesion studies of the interactions of two surfaces, one bearing dextran and the other bearing modified dextran. The ultimate goal is to link solution phase behavior reported herein with adhesive characteristics; this work is in progress.

The ternary system used in this work is dextran(DEX)/hydrophobically modified dextran(HDEX)/water. Modified dextran was synthesized by esterification of dextran with propionic acid (C3), butyric acid (C4) and hexanoic acid (C6). Using this approach a family of biphase systems was prepared by varying the properties of the hydrophobically modified dextran. This approach allows control of the phase boundary defining the onset biphase formation as well as the solvency properties of the more hydrophobic phase. A couple of related biphase systems have been reported and, where possible, these are compared with the new results from this work. Hydroxypropyl-modified dextran is a biphase system when mixed with aqueous dextran.[2] Lu and coworkers have hydrophobically modified dextran by ester formation with pentanoic acid and have reported the biphase behavior for mixtures with aqueous PEG.[22],[23]

2.2. Experimental

2.2.1 Materials:

Analytical grade solvents were used as received. Millipore water was used for all experimental preparation. Two dextrans (Sigma) were used; the mass average molecular weights, given by the supplier were 74,000 and 167,000 Dalton.

The dextran samples were dried under vacuum at 40 °C for 24 h before use. Formamide, N, N-dimethylformamide was from BDH. 1,3-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (PYP), PYP, DCC, and the carboxylic acids were obtained from Aldrich. Pyrene (Sigma) was recrystallized in ethanol before use.

2.2.2 **Synthesis of modified dextran:**

Hydrophobically modified dextran (HDEX) was prepared by esterification of dextran with carboxylic acids in the mixture of formamide and N, N-dimethylformamide using the procedure reported by Bamford et al.[24](see **Figure 2. 1**). In a typical reaction, dextran was dissolved in a mixture 40/60 (v/v) of DMF and formamide to give an anhydroglucose concentration of 0.65 mol/L. PYP (0.025 mol/L), carboxylic acid (0.25 mol/L) and DCC were added in sequence. The DCC was added as a 50wt% solution in dichloromethane to give a DCC concentration of 0.25 mol/L in the reaction mixture. The molar ratios of anhydroglucose units (MW= 162) to fatty acid in the reactions were 0.1, 1.0 and 1.1. The composition of the resulting HDEX was expressed as a degree of substitution, which was the moles of ester groups divided by the number of moles of anhydroglucose units.

DCC was dissolved in dichloromethane to form 50wt% solution and added dropwise into the flask. The reaction was conducted at 30°C for 16 hrs with stirring, after which the reaction mixture was filtered to remove the dicyclohexylurea, formed by DCC during the reaction. The product was precipitated by acetone and washed four times in acetone to remove unreacted carboxylic acid and solvent. The product was vacuum dried at 40°C and stored at 5 °C.

Six samples of modified dextran were prepared from two dextran and three fatty acids. The compositions are summarized in Table 2. 1.

2.2.3 Characterization of modified dextran:

FTIR was carried out to confirm ester formation after reaction of DEX with fatty acids. Samples of KBr pellet were prepared. Infra-red spectra were recorded on a Bio-Rad FT S-40 FTIR spectrometer from 400-4000 cm^{-1} with a resolution of 8.

A Bruker AC 200 NMR Spectrometer was used to record both ^{13}C and ^{1}H NMR spectra. Degrees of fatty acid substitution on DEX were determined by proton spectra of NMR. ^{1}H chemical shifts were reported relative to the HDO peak at 4.6 ppm.

Molecular weight distributions were obtained by gel permeation chromatography using a Waters 401 Differential Refractive index detector. The column used was TSK gel PW_{XL} 4000 and 3000 with the temperature at 40°C. Water was used as solvent with a flow rate of 0.5 cm^3/min. Calibration curves were obtained from poly(ethylene glycol) and glucose. Mass average molecular weights estimated from the GPC traces were about 2/3 of the LALLs values reported by Sigma. The GPC curves showed no evidence of either scission or crosslinking due to conversion of DEX to HDEX.

The hydrophobic characteristics of the modified dextrans were probed by fluorescence measurements using pyrene as a probe. Samples were prepared using filtered (45 µm Millipore) stock solution of water saturated with pyrene. Steady-state fluorescence spectrums were recorded with an Aminco Luminescence Spectrometer (SLM Instruments Co.) at 23°C and 50°C using an excitation wavelength was 330nm. The excitation slit width is 4 and 1 for excitation and emission respectively. The ratio of the intensities, I1/I3, was used as an indication of the polarity of the environment surrounding the pyrene probes.[25]

A Bohlin VOR Rheometer (Bohlin Instruments) fitted with a C14 concentric cylinder and a 1.6 g cm torsion bar was used to measure viscosity. The experiments were conducted at 25°C at constant shear rate of $20s^{-1}$.

Densities were measured with a DMA 45 (AP PAAR) vibrating U tube densitometer. Temperatures were maintained at 25°C controlled with a water bath (RM6 LAUDA, Brinkmann).

2.2.4 Phase Information

Cloud points were determined by titration of DEX solutions with HDEX until the onset of visible turbidity. Binodal curves were constructed from sets of cloud point data collected as a function of the initial DEX concentration.

Tie lines were determined by mixing polymer solutions in separatory funnels and after 24 hours equilibration, samples from each phase were removed for analysis. Experiments with C6-HDEX were performed at room temperature (~ 23°C) and 50 ±0.5 °C.

NMR was used to determine the molar ratio of two polymers in each phase. The total concentration of carbohydrate in each phase was determined by optical rotation (Perkin-Elmer 241 MC). Calibration curves of rotation versus concentration were made for each polymer. Control experiments confirmed that for mixtures the optical rotation was a linear combination of the contribution of DEX and HDEX. The weight fraction of polymers in each phase was calculated from the feed composition and composition of upper and lower phases.

2.3 Results

A series of hydrophobically modified dextrans (HDEX) was prepared by esterification of dextran (DEX) with propionic acid (C3), butyric acid (C4) or hexanoic acid (C6). The chemistry of the modification is summarized in Figure 2. 1 and the properties of the modified polymers are summarized in Table 2. 1. The esters had characteristic IR adsorption bands at 1735 and 1260 cm^{-1}. The esterification yields, based on fatty acid feed, ranged from 50 to 73 %. The corresponding degrees of substitution (i.e. the number of ester groups per anhydroglucose ring) ranged from 0.1 to 0.6.

^{1}H-NMR was used to measure the composition of purified HDEX polymers. Figure 2. 2 shows spectra for C6-HDEX together with the parent DEX. Peaks centered at 4.8, 3.8, 3.5, 3.4 ppm, were due to anhydroglucose protons and the peak at 4.8 ppm was due to the anomeric proton on C_1[26]. After modification new peaks appeared at 0.7, 1.1, 1.5, and 2.3 ppm for hexanoate modified dextran; the peak assignments are shown in Figure 2. 2[27].

HDEX showed two anomeric proton peaks, one at 4.8 ppm corresponding to DEX and the other at 4.9 ppm. The latter peak was assigned to anomeric protons (C_1) in which the hydroxyl on the neighboring C_2 carbon reacted to form an ester with the fatty acid.[28] The fraction of the total ester groups that were on C_2 was calculated from the total degrees of substitution and relative areas of the 4.8 and 4.9 peak. The results listed in Table 1 indicate that esterification preferentially occurred on C2; this is consistent with published information [12,29].

The solubility of modified dextran in water varied with the degree of fatty acid substitution (DS) and the chain length of substitute. Preliminary work showed that the maximum DS values while maintaining water solubility were 0.26±0.02 for C6 and 0.50±0.02 for C4 modified dextran. These values seem in accord with literature values of 0.81 and 0.69 with ethyl and butyl carbonate substituted dextran[30].

Fluorescence was used to probe hydrophobicity of HDEX. Unmodified dextran is a highly hydrophilic polymer with I1/I3 = 2.3. By contrast, the modified HDEX solutions had I1/I3 values as low as 1.3. For comparison, sodium dodecyl sulfate micelles gave an I1/I3 value of 1.21 in our laboratory. Figure 2. 3 shows results for three types of HDEX with various DS and at various concentrations. When plotted as I1/I3 versus the molar concentration of fatty acid carbons, the C3 and C4 modified dextrans fell on the same curve whereas the C6 solutions gave low I1/I3 values at lower concentrations. The I1/I3 results were not sensitive to temperature. For example, for C6-HDEX the values were 1.47 and 1.45 at 25 and 50 °C respectively.

Hydrophobically modified water-soluble polymers have the potential to form intermolecular aggregates[31-32]. Such behavior is usually evidenced by high viscosities. Reduced viscosities of DEX and HDEX are shown as a function of concentration in Figure 2. 4. The reduced viscosity of C6 modified dextran showed a much stronger dependency on concentration than did DEX, C4-HDEX or C3-HDEX. Results for C3-DEX were slightly above DEX whereas at high concentrations the viscosities of C4-HDEX were slightly less than DEX.

Figure 2. 5 shows part of the binodal phase boundary for two ternary systems both containing water, C6-HDEX and DEX. The two curves correspond to low and high molecular weight dextrans, and the corresponding modified dextrans. In both cases biphase formation occurred at low polymer concentrations. However, the higher molecular polymers phase separated at concentrations a few weight percent lower than the lower molecular weight pair.

Biphase formation was not observed for low degrees of substitution with short chains. For example, with C4-HDEX/ DEX-74/water was one phase for DS values less than 0.32±0.02 for total polymer concentrations less than 35 wt%. Similarly, C3-HDEX/ DEX-74/water formed a single phase up to DS values 0.60±0.02, the highest that we were able to synthesize.

The compatibility of dextran with modified dextran decreased when the degree of hydrophobic modification was increased. The binodal curves for the DEX-176/C6-HDEX-176/water system, shown in Figure 2. 6, illustrate this point. Similarly, the results in Figure 2. 7 show that the two polymers become less compatible when the hydrophobic chain length is increased. For the results in Figure 2. 7 the single phase region for the C6-HDEX is smaller than that of the C4-HDEX even though the C4 containing polymer had nearly twice as many grafted chains (i.e. 0.37 vs 0.23).

The temperature sensitivity of the DEX-74/C6-HDEX/water system was studied and the results are summarized in Figure 2. 8. Comparing 23 °C to 50 °C there was little difference in the position of the binodal curves, however the slopes of the tie lines were greater at high temperature, indicating a greater partitioning of water into the dextran phase. Similar behavior has been reported in the PEG/DEX/water system[11] and the explanation is that water becomes a poorer solvent with increasing temperature for polymers containing small hydrophobic domains such as PEG or HDEX [33, 34].

Some of phase composition and density data are given in Table 2. In the DEX-74/C6-HDEX results, the upper phases were more dilute and DEX rich whereas the lower phase was concentrated and HDEX rich. The density difference between the two phases was in the second decimal place. By contrast, in the

HDEX/C4-HDEX results, the upper phase was HDEX rich, the total concentration was slightly higher than the lower phase, and the density differences were in the third decimal place. It seems reasonable to speculate that the HDEX/C4-HDEX system is near a transition after which no biphase separation occurs and that HDEX/C3-HDEX is beyond the transition and thus does not phase separate.

2.4 Concluding Remarks

The objectives of this work were to prepare a family of polymer pairs in which the compatibly in aqueous solution could be varied in subtle ways. The HDEX/DEX/water systems fulfill these requirements. By varying either the hydrophobic chain or the degree of substitution on HDEX, the compatibility with DEX can be modified. This system is interesting because the chemical structures of DEX and HDEX are so similar. Indeed by employing butyric acid (C4) for the modification, the densities and total concentrations of the equilibrium phases are also nearly equal.

Associative thickener structures such as hydrophobically modified cellulose have been extensively reported in the recent literature. These molecules employ a few (<~ 10 hydrophobes per polymer chain), long (more than 10 aliphatic carbons) hydrophobes [35]. By contrast, the HDEX prepared in this work have about one short (i.e. less than 6 aliphatic carbons) hydrophobic chains for every two anhydroglucose rings. Viscosity and pyrene fluorescence results indicate possible intermolecular association with C6-HDEX, whereas the rheological behavior of C4-HDEX and C3-HDEX were similar to the parent dextran, indicating no intermolecular association. Similarly, the GPC traces of C3 and C4 modified dextran were similar to the parent dextran, indicating that the short hydrophobic chains did not significantly influence the polymer configuration.

The compatibility of HDEX with DEX was characterized in terms of the tendency for aqueous biphase formation. Most of the results were consistent with intuition. Increasing the molecular weight, the hydrophobic chain length or the degree of substitution increased the tendency for biphase formation. The behaviors of HDEX/DEX/water were also consistent with other DEX biphase systems. Figure 2. 9 compares the phase behavior of the present system with two other dextran-based biphase systems taken from the literature. Therefore, it seems reasonable to conclude that the factor governing phase separation in the HDEX/DEX/water are similar to the other biphase systems.

The main conclusions from this work are:

1. The addition of small hydrophobic groups to dextran decreases the affinity of the polymer for water. The modified dextrans become water insoluble when the degree of substitution is around 0.50±0.02 and 0.26±0.02 for C4 and C6

substituted dextran at the molecular weight of 167,000.

2. Pyrene partitions into hydrophobic domains in aqueous solution of HDEX. C3 and C4 modified dextran did not display evidence for intermolecular association whereas C6 modified dextran did.

3. Aqueous mixtures of dextran and hydrophobically modified dextran display aqueous biphase formation at polymer concentrations greater than 5 to 10%. The tendency for phase separation increases with the molecular weight, degree of substitution and the hydrophobic chain length.

4. Increasing temperature from 23 °C to 50 °C drives water from the HDEX-rich phase to the dextran-rich phase.

2.5 Acknowledgments

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Table 2. 1. Properties of modified dextrans.

Sample code	Parent DEX Molecular Weight	Feed Compositio*	% Acid Conversion	Degree of Substitution*	Fraction C2**
C6-HDEX 9-23	74,000	2.8	64	0.23	0.5
C4-HDEX 11-20	74,000	1.8	67	0.37	0.68
C3-HDEX 10-31	74,000	1.2	73	0.61	0.52
C6-HDEX 6-22	167,000	2.6	59	0.23	0.53
C6-HDEX 7-23	167,000	3.2	58	0.18	0.60
C6-HDEX 7-12	167,000	4.2	46	0.11	0.75

*moles of fatty acid/moles of anhydroglucose units.

**fraction of total number of ester groups which are on C2

Table 2. 2. Composition and Density of Upper and Lower Phases

Upper Phase			**Lower Phase**		
HDEX wt %	DEX wt %	Density g/cm^3	HDEX wt %	DEX wt %	Density g/cm^3
C6-HDEX(9-23) and DEX-74 at 23°C					
0.25	11.59	1.0466	18.5	1.32	1.0601
2.52	6.27	1.0296	7.9	2.52	1.0455
1.89	7.57	1.0338	10.66	2.5	1.0413
C6-HDEX(9-23) and DEX-74 at 50°C					
0	11.0	1.0411	22.2	0.92	1.0666
0.3	8.19	1.0306	17.1	1.37	1.0536
0.8	7.20	1.0314	14.8	1.83	1.0484
2.22	5.77	1.0269	9.21	3.25	1.0383
C4-HDEX(11-20) and DEX-74 at 23°C					
11.78	4.16	1.0492	1.55	12.81	1.0519
19.89	1.87	1.0645	1.64	16.84	1.0685
20.44	1.68	1.0743	2.37	19.54	1.0834
12.31	3.78	1.0563	1.53	14.28	1.0587

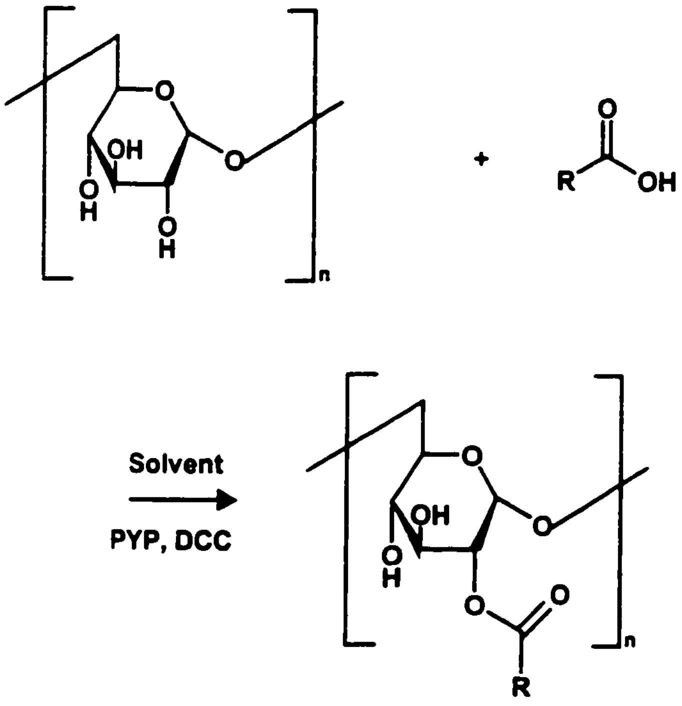

Figure 2. 1 Reaction route for the synthesis of modified dextran. The ester is shown to form on the C2 carbon of the anhydroglucose ring. The R groups are hydrocarbon chains with 2, 3, and 5 carbons.

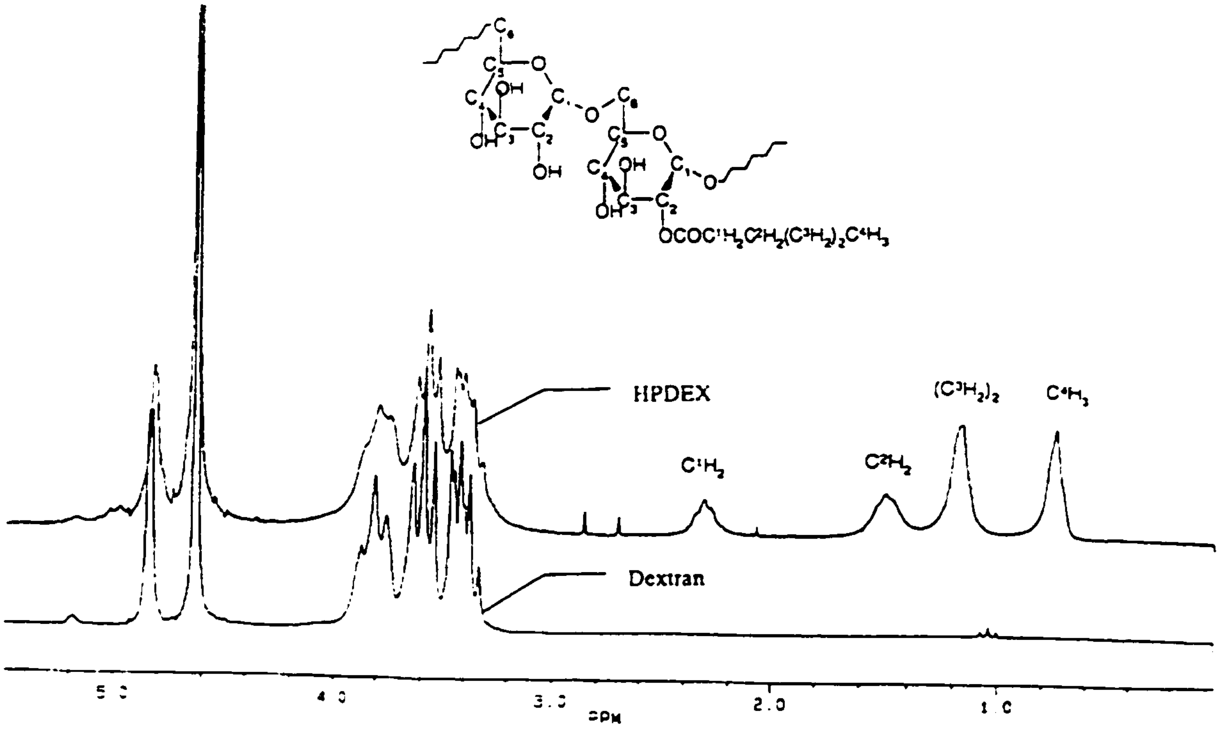

Figure 2. 2 ^{1}H-NMR spectra of C6-HDEX and DEX dissolved in D_2O.

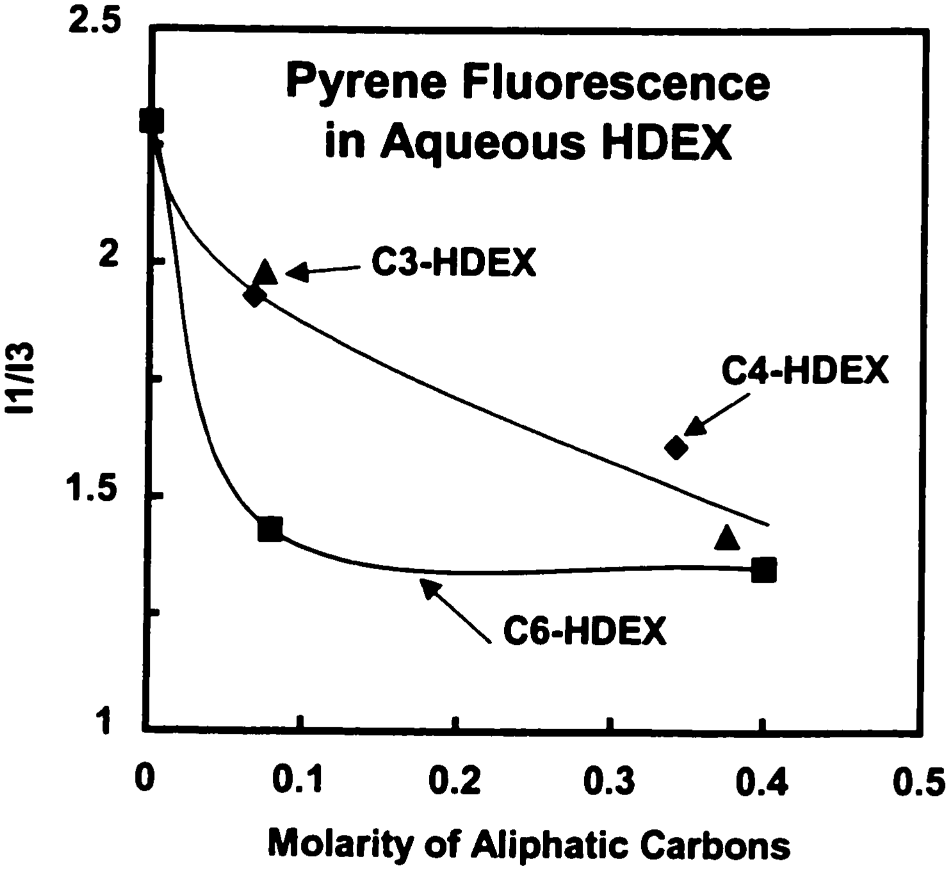

Figure 2. 3 The influence of fatty acid carbon concentration (not including carbonyl carbon) on the I1/I3 value for HDEX. The polymers were 9-23, 11-20 and 10-31; see Table 1 for polymer properties.

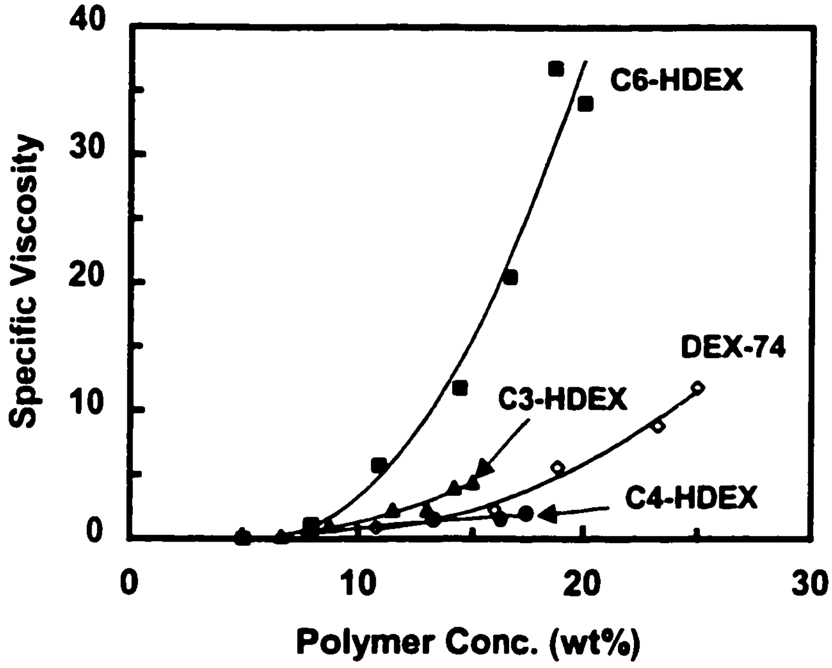

Figure 2. 4 The specific viscosity of aqueous HDEX as functions of concentration at 25 °C with a shear rate of 20 1/s. The polymers were 9-23, 11-20 and 10-31.

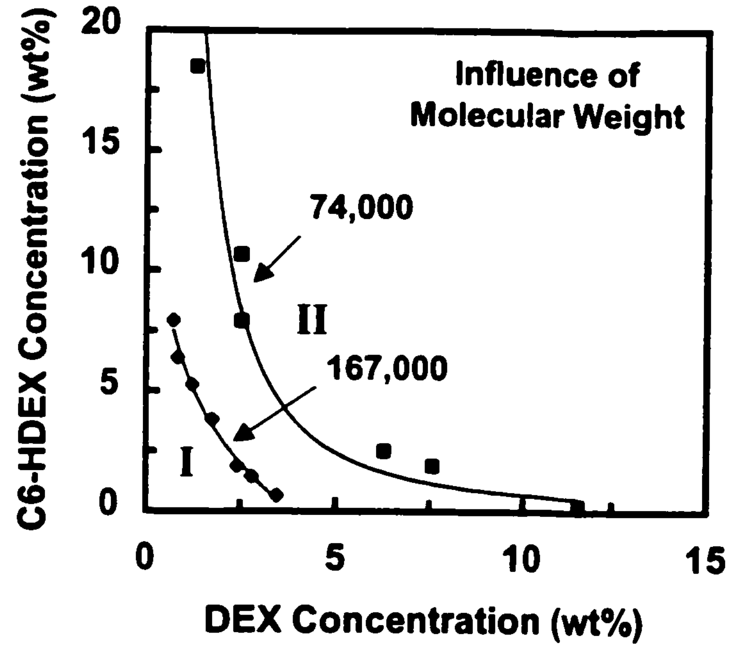

Figure 2. 5 Phase boundaries for C6 modified dextran. For both systems the DS was 0.23 and the temperature was 23 °C. The labels denote the molecular weight of the parent dextrans. The I region corresponds to a I phase region and II the biphase region.

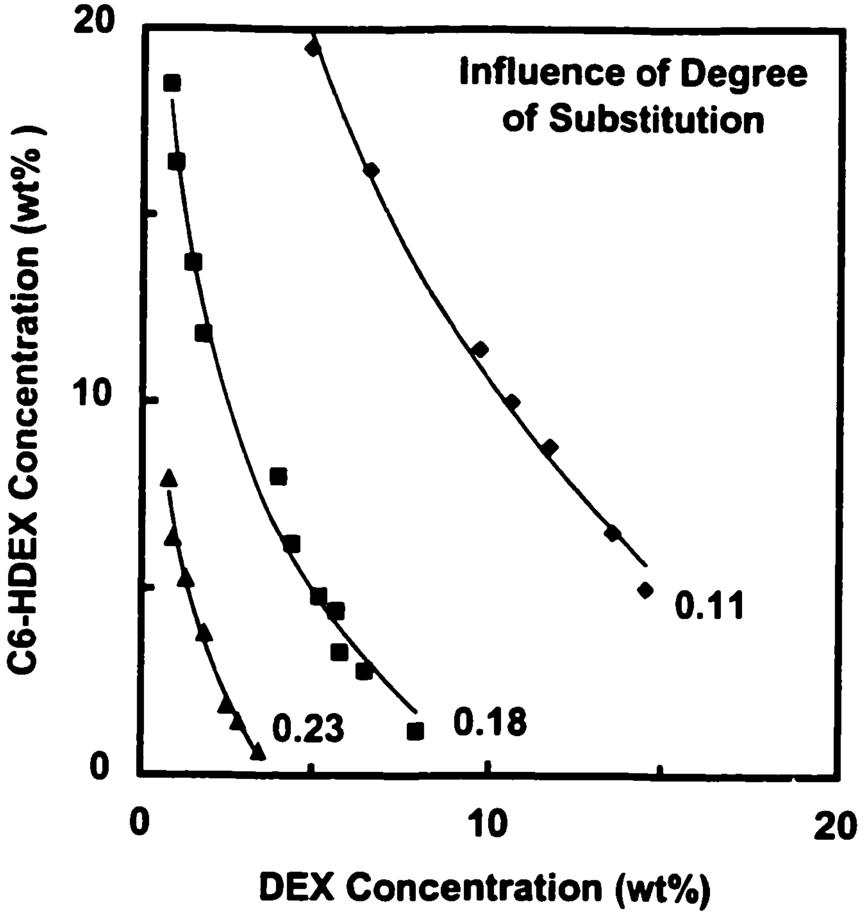

Figure 2. 6 The influence of the degree of hydrophobic modification on the DEX-76 / C6-HDEX / water binodal curves at 23°C.

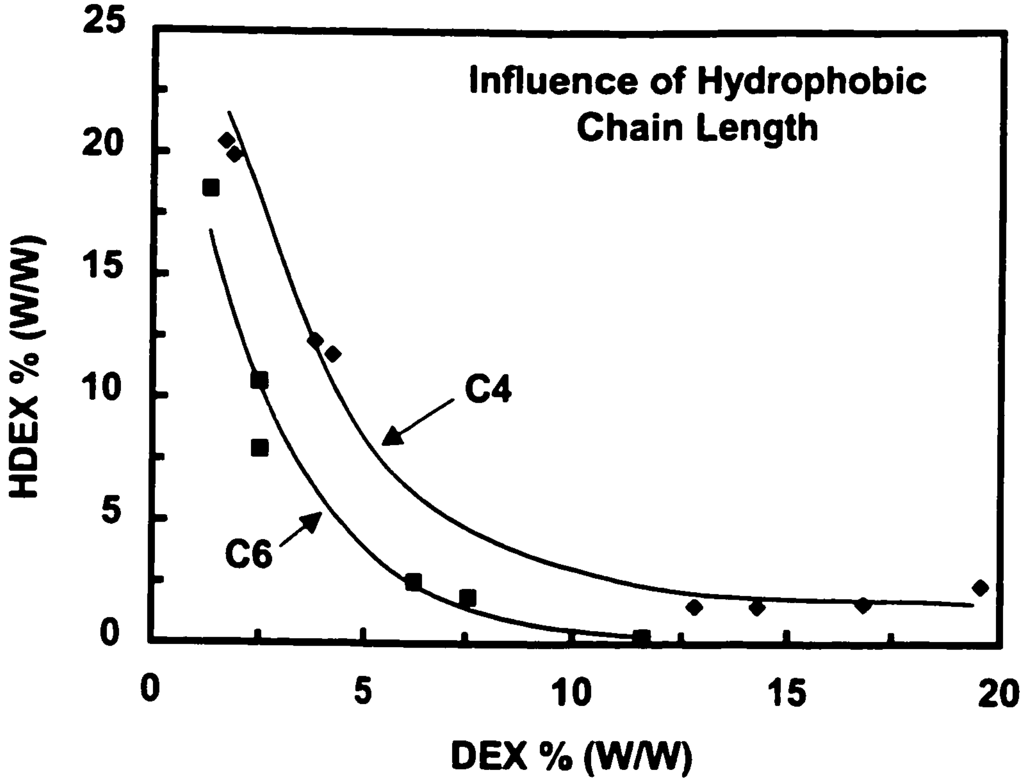

Figure 2. 7 The influence of hydrophobic chain length on phases separation. The systems were aqueous mixtures of DEX-74/C4-HDEX (11-20, DS =0.37) and DEX74-/C6-HDEX (9-23, DS = 0.23) both at room temperature.

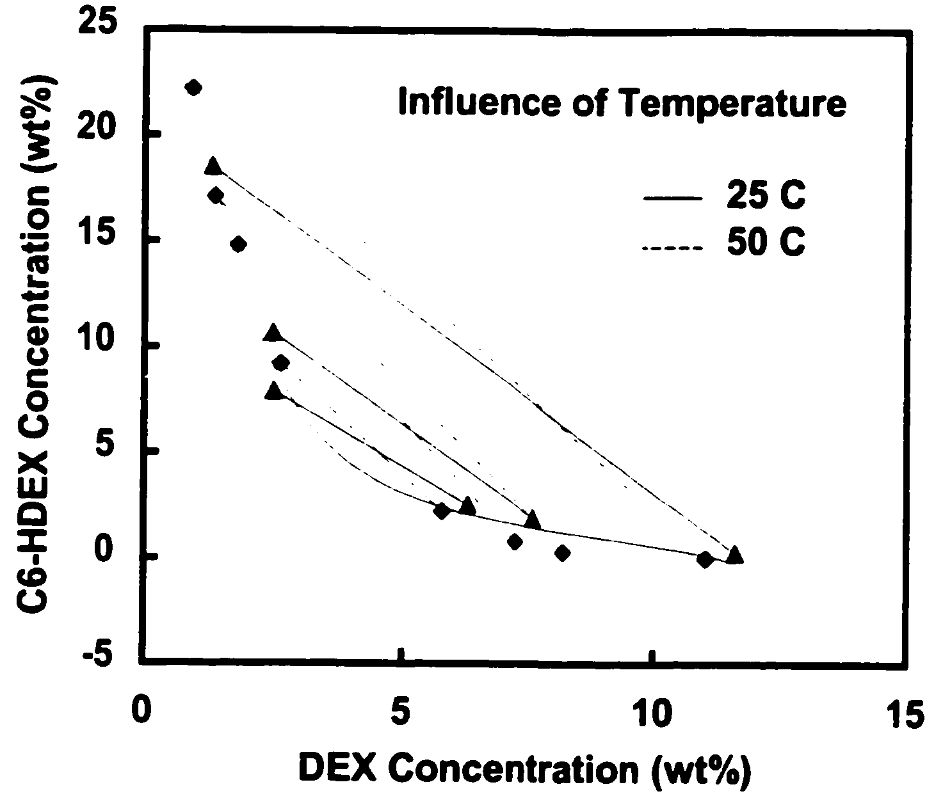

Figure 2. 8 Phase diagrams for DEX-74/C6-HDEX/water at two temperatures. The degree of substitution of C6-HDEX was 0.23.

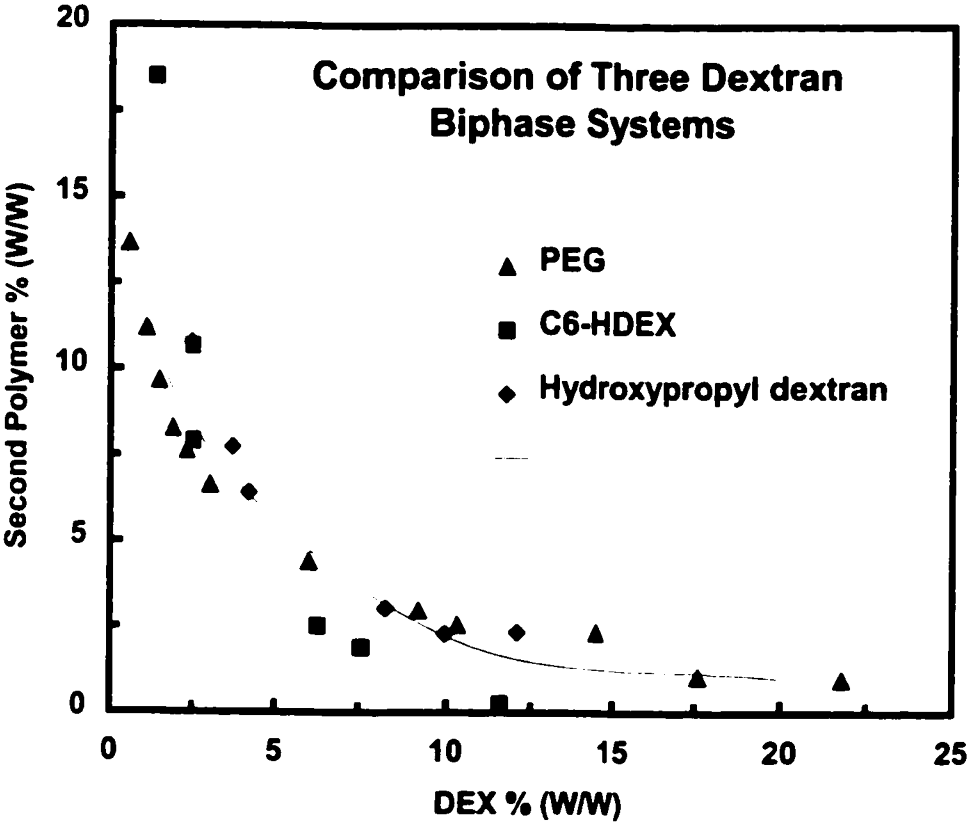

Figure 2. 9 Comparison of phase boundaries of three dextran-based biphase systems. The PEG/DEX and hydroxypropyl-DEX/DEX data were taken from Albertsson [2].

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Chapter 3. The Effect Of Molecular Weight On Paper Strength Enhancing Polymers

Abstract

The influence of dextran molecular weight (77,000 to 2000,000) on the strength of fiber-fiber bonds was investigated. A series of cationic dextrans with different molecular weights, from 77,000 to 2000,000, were prepared and their adsorption behavior on fiber was characterized with the adsorption isotherms and the adsorbed layer thickness. The maximum amount of adsorption of dextran increased with the decrease of molecular weight, while the adsorbed layer thickness increased as the increase of molecular weight. Tensile strength and Scott bond were used to measure the strength enhancing effect of these dextrans on the strength of paper. It was found that the molecular weight of dextran did not affect the tensile strength when the fibers were saturated with dextran. The strength enhancing effect of dextran was attributed to the more intermolecular bonding per relative bonded area between dextran on fiber surfaces. The external surface of fiber accessible to dextran of molecular weight 2,000,000 was estimated as 35 m^2/g. Moreover, the fiber surface topography was evaluated with a fractal dimension of about 2.7-2.9. The effect of dextran on tensile strength and Scott bond strength was further compared.

Key words: strength-enhancing polymer, strength of paper, fiber-fiber bonding, molecular weight, tensile strength, adsorption, surface area, Scott bond, dextran, cationic polymer.

3.1. Introduction

It is generally accepted that the strength of paper depends on the strength of individual fibers, the strength of interfiber bonds, and the distribution of fibers,fillers and fines. Furthermore it is common to express interfiber bond strength as the product of the bonded area (RBA) and the specific bond strength[1]. There has also been considerable debate about the mechanisms of fiber-fiber bonding. Hydrogen bonding between contacting surfaces and the mechanical entanglement of surface fibrils are the most common postulates[2,3], however the interdiffusion of surface water swollen polymers has also been proposed

Polymers are used to increase the dry strength of paper. Davison claims that "The main purpose of a dry strength additive is to improve the degree of bonding between fibers in paper"[2]. The two most widely used strength enhancing polymers are polyacrylamides and starch. Starch is a polysaccharide composed of anhydroglucose units that are joined by 1,4-α-D-glucosidic bonds. Starch chains are either straight (amylose) or branched (amylopectin). The molecular size of starch depends on the sources and can range from hundreds of thousands to as much as a hundred million Daltons. Starch is insoluble in cold water, but it is gelatinized when heated in water, which results in a viscosity increase[4].

Cationic polymers are more effective than anionic or nonionic polymersbecause the cationic polymers readily adsorb onto anionic fiber surfaces.

Cationic starch is produced by condensing on small molecules containing positive charge groups, such as amino, imino, and ammonium groups[5]. The cationic charge content is expressed as the degree of substitution which is the number of substituents per anhydroglucose unit (maximum value is three). Most cationic starch has a cationic DS of 0.02-0.05[4].

Most of the publications dealing with the mechanisms of paper strength enhancing polymers deal with starch; some key results are now summarized. Tensile strength and Scott bond tests are the two most used as the measures of strength properties of paper. It is believed that Scott bond measures the internal bond strength in z-direction[6]. Cationic starch has the greatest influences on the z-direction strength of paper. Gaspar showed that the Scott bond values can be more than doubled with starch dosages below 1%[7,4]. Others have shown that bursting strength and compression resistance were also increased with starch addition[8]. By contrast, the change in tensile strength with starch addition was not as remarkable as Scott bond. It was found that the tensile strength increased with the amount of starch on fiber but it reached an optimal level, where further starch adsorption did not contribute to the strength[9]. Howard and Jowsey[10] found the first 0.5% was most effective in enhancing paper strength. In general, it is believed that cationic starch increase the strength of paper by increasing the bond strength rather than bonded area[7,10,11].

The addition of PAM greatly increased the water retention value of the pulp. Both tensile strength and Scott bond strength were improved[12]. In his discussion of the anionic PAM alum system Linke stated that "It can be seen that a certain molecular weight or size has to be reached before the best dry strength improvement is obtained, but if the molecular weight is increased too far, then the tensile, fold, and burst properties are somewhat diminished." The negative effects of very high molecular weights were attributed to PAM induced fiber flocculation giving poorer formation.[13] There has been recent interest in the use of intermediate MW PAM (25,000 to 250,000 Dalton) as surface strength enhancing polymers for mechanical pulps[14].

Reactive PAM based polymers are used as wet strength agents and it is suggested that the wet strength enhancing effect is mainly due to the covalent bonds between PAM and cellulose fibers[15].

Although the strength enhancement of cationic polymer has been extensively studied, the linkage between the chemical structure and properties of the polymer and the strength enhancing performance of this polymer has not been established. For example, one of the essential properties of a polymer is its molecular weight, but there is very limited data regarding the influence of the molecular weight of strength enhancing polymers on the strength enhancement of paper in the literature. Laleg and Pikulik worked on cationic aldehyde starch, a wet-web strength additive, with molecular weight from 8 million to 127 million[16].

It was found that the influence of starch with considerably different molecular weight was similar at the same addition level. The small difference in tensile strength was attributed to the efficiency of adsorption in the fiber network because their results showed low molecular weight starch adsorbed less than the high molecular weight starch. The other available work was about the effect of polyethyleneimine on tensile strength. It was found that, at the same amount of cationic charge, molecular weight strongly affected tensile strength when it was below 5000, after which it only slightly increased the strength and the mechanism of strength enhancement was attributed to interfiber ionic bond[17].

The objective of this work is to establish the linkages between the structure of strength enhancing polymers to their performance in strengthening paper. Dextran was chosen as the model of strength enhancing polymer due to its well-defined chemical structure and properties. Dextran consists of anhydroglucose repeat units joined by α-acetal linkage through carbons 1 and 6, see Figure 3. 1. It is a relatively linear polymer[18], with 95% of repeat units in the main chain while the remaining linkages account for the branching of dextran. Unlike starch, dextran forms true stable solutions in water with no tendencies towards gelation. Hydrated dextran has a relatively compact coiled conformation in solution[19]. Dextran does not adsorb onto cellulose. Indeed, narrow molecular weight dextrans have been employed as non-adsorbing probes to estimate the pore size distribution in fiber walls[20].

In this work, the strength properties of unbeaten bleached kraft pulp handsheets are reported as functions of the amount and molecular weight of cationic dextran (CADEX) added to the pulp suspension. Adsorption isotherms and measurements of CADEX adsorbed layer thickness on colloidal silica are used to help interpret the paper strength data.

3.2. Experimental

3.2.1. Synthesis of cationic dextran

Five dextrans (Sigma) were used; the mass average molecular weights, given by the supplier were 77 000 (77K), 167 000 (167K), 200 000 (200K), 464 000 (464K) and 2 000 000 (2M). Cationic dextrans with charge density of about 0.25-0.3 meq/g were prepared. Similar chemistry as preparation of cationic starch was used[5]. 2,3-epoxypropyl-trimethylammonium chloride (ETAC) was from Fluka. The chemistry of the reaction is shown in Figure 3. 2. ETAC readily reacts with dextran in NaOH solution[21]. The concentrations of the reagents are listed in Table 3. 1. In a typical reaction 30 gm dextran was added into 140 mL of 5% NaOH solution. After 1.5 hours stirring at room temperature, 3.5 gm of 72% ETAC solution in water was added and the temperature was raised to 40°C. The reaction was allowed to cool after 5-6 hours and the pH was neutralized to 6-7 with hydrochloric acid. The product was dialyzed (3,400-1,400 MW cutoff, supplier) for 10-14 days and then freeze dried. Dried dextrans were stored in a refrigerator set at 4°C.

The charge density, defined as the number of moles of charge per gram of dextran, was determined by polyelectrolytic titration with polyvinyl sulfate potassium[22]. Titration was conducted with titrator Mettler DL25, along with particle charge detector of PCD 03 series, produced by Muetek Analytic Inc.

The GPC measurement on the molecular weights of dextran and CADEX did not evidence any decomposition of dextran under the strong caustic condition.

3.2.2. Adsorption isotherms of dextran on fiber

50g of 0.5% fiber, the same as used for handsheets, suspension with pH adjusted to 8.0 with 0.01mol NaOH was shaken at a constant rate of 240/min for 10 min. 1% CADEX solution was added and the suspension was shaken for another 10 min. It was then filtered on a Buchner Funnel fitted with a weighed filter paper Munktell no. 3. Debo Grave, Sweden. The fiber cake was dried in an oven set at 105°C overnight and weighed. The amount of dextran not adsorbed in the filtrate was determined through polyelectrolyte titration as described above. The amount of dextran adsorbed on fiber was calculated by subtracting the dextran left in the solution from the total dextran added.

3.2.3. CADEX adsorption onto silica microspheres

The adsorbed layer thickness of various cationic dextran was estimated from the difference in hydrodynamic diameter of colloidal silica (150 nm diameter, Bangs Laboratories Inc.) 2 drops of 12% colloidal silica were diluted with 15 mL of distilled, deionized and filtered water, making the concentration of silica microsphere about 0.05%. The suspensions were titrated with 0.3% cationic dextran aqueous solutions until the hydrodynamic diameter was constant,.

Dynamic light scattering measurements were made with a Brookhaven Model BI-9000AT, coupled with 202 channel BI-9000AT digital correlator. The He-Ne laser producer was a Lexel model 95-2, made by Lexel Laser Inc. A thermostated bath control unit maintained the temperature at 25.0 ± 0.1°C. The scattering angle was set at 90°C and the wavelength of laser was 514 nm. A 1st and 2nd order cumulant fit was used to give the hydrodynamic diameter.

3.2.4. Handsheet preparation

A primary objective of this work was to determine the influence of CADEX molecular weight on fiber-fiber bond strength. Therefore, unbeaten, bleached kraft softwood pulp, was used so that sheet strength was low and was sensitive to the degree of interfiber bonding. The pulp was from SCA research AB in Sundsvall, Sweden.

Handsheets for tensile strength test with basis weight 65 g/m^2 were prepared with a handsheet machine constructed especially for making small sheets at SCA research AB in Sundsvall, Sweden. It was made from stainless steel and PMMA and the size of the sheet was reduced to approximately 150x40 mm to decrease the amount of material needed. The SCAN M5:76 procedure was followed as closely as possible in the sheet making. Deionized water was used in handsheet making. The pulp was disintegrated at 3000 rpm for 10 min before used. CADEX was added into 0.5% consistency pulp with pH adjusted to 8 and adsorbed for 10 min under the constant stirring. The excess CADEX was then washed with water (pH 8). All handsheets were prepared with two wet pressing pressures, 800 and 1600 kPa and the tensile index of handsheet at 550 g/m^3 was obtained by linear interpolation. At least three handsheets were made for each molecular weight CADEX at one pressing pressure and one additional level. Polymer-free sheets were prepared at five different pressing pressures (200, 400, 800, 1200, 1600 kPa. and it was found that sheet densities had approximately linear relationship to the pressing pressures (see Figure 3. 3). Handsheets for Scott bond test with basis weight of 65 kg/m^2 were made with tap water using a British sheet machine following Tappi test method T205 sp-95. The light scattering coefficient of the sheet was determined with an Elrepho Reflectometer (Zeiss, Germany) according to standard Scan-C 28:76.

3.2.5. Mechanical properties of paper

Tensile strengths were measured following standard Scan P:67. Two strips were taken from each handsheet giving six measurements for each experimental condition. Tensile measurements were made with a horizontal tensile tester, model TH1made by Lorentzen & Wettre. A Huygen Internal Bond Tester was used to measure the Scott-bond strength. Ten measurements were made for each sample.

3.2.6. Confocal laser scattering microscopy:

A Zeiss LSM 510 confocal laser scanning microscope (Germany) was used to record the cross-sectional image of fiber coated with dextran of molecular weight 77,000 and 2,000,000. The objective lens was 63x. The light source was a 25 mW argon ion laser with an excitation wavelength at 488 nm, BP 505-559 filter was used to cut off the long wavelength emission light. The reflected light fluorescence was HBO 50W Mercury Vapor Short Arc Lamp. The transmitted DIC (Differential Interference Contrast) and laser scanning images were captured simultaneously and overlaid to produce a single image. The fiber was soaked with 0.1% aqueous fluorescence dextran solution for 10 to 20 min. The excess solution was removed by centrifuge and the fiber was air-dried, imbedded in the Epoxy resin, and sectioned into 1.5 μm.

3.3. Results

A series of cationic dextrans (CADEX) with different molecular weights, but similar charge densities, 0.25-0.3 meq/g, were prepared, and their properties are listed in Table 3. 2. The adsorption isotherms on fiber and the effect of CADEX on the strength properties of paper are now presented.

3.3.1. Adsorption isotherms of CADEX on fiber

Adsorption isotherms for CADEX on pulp were measured and shown in Figure 3. 4. The adsorption plateau decreased with increasing molecular weight. The solid lines in the graph are the fitting curves with Langmuir equation, see Appendix 3.1 for details. It appeared that Langmuir equation was fairly good in simulating the adsorption of dextran on fiber in this case. The calculated maximum amounts of adsorption were 116, 86, 60, and 33 mg/g for CADEX3-24(77K), CADEX4-6(200K), CADEX4-3(464K) and CADEX3-49(2000K), respectively.

The adsorbed layer thickness of CADEX on colloidal silica was measured by dynamic light scattering in order to get an indication of the adsorbed layer thickness on pulp fibers before drying.

Figure 3. 5 shows the results as function of CADEX molecular weight. The adsorbed layer thickness of dextran increased from a few nanometers for CADEX3-24 (Mw 77K) to 24 nm for CADEX3-49 (Mw 2M). In the same graph, the radius of gyration of unmodified dextran is plotted as the function of Mw of

dextran[20]. Except for the highest molecular weight, the adsorbed layer thickness greater than the radius of gyration.

3.3.2. Tensile strength index of paper treated with CADEX

All the handsheets were prepared at two different wet pressing pressures, 800 and 1600 kPa, with four different amounts of addition for each CADEX. The tensile data are listed in Table 3. 3, which contains the tensile index, elastic modulus and tensile adsorption energy (TAE). The modulus of the handsheets was approximately independent of molecular weight, indicating that the various treatments on fiber did not change the stress transfer in the sheets. This was suggested to be a prerequisite for using tensile strength as a measure for fiber-fiber bond strength[32].

TAE increased as the density of sheets and the amount of adsorption of CADEX on fiber increased; however, except at the low adsorption level, the molecular weight did not show significant effect on TAE.

All the tensile index results presented in the following graphs are interpolated to a handsheet density of 550 kg/m^3.

Figure 3. 6 shows the change in tensile index as the function of amount of dextran adsorbed on fiber. The error bars on the graph are the standard deviations of the data from 6 measurements. It was found that tensile index kept increasing as the amount of DEX3-24 (77K) increased. However, for CADEX3-49 (2M) treated

pulp, the tensile strength was fully developed at the dextran content of 20 mg/g. Moreover, it was noted that Mw did not make a big difference in enhancing the tensile strength of paper when the fiber surface was fully saturated with dextran. Compared with the polymer-free paper, the ultimate increase in the tensile strength was around 35%, irrespective of molecular weight.

Figure 3. 7 shows more clearly the effect of Mw on tensile strength with fiber surface partially (10 mg/g) and fully covered with dextran. The tensile strength of paper treated with 10 mg/g CADEX increased with dextran molecular weight whereas fully covered fibers did not show a systematic variation in tensile strength with molecular weight.

The light scattering coefficient of paper was measured and plotted against the amount of CADEX adsorbed at the same density of handsheets, 550 kg/m^3 (Figure 3. 8). It was found that scattering coefficient of paper made from CADEX treated fiber was slightly reduced compared to polymer-free paper; it was, however, fairly constant among papers treated with different molecular weights and different amounts of CADEX. The implication is that the bonded area was approximately independent of molecular weight.

3.3.3. Scott bond strength

The results from Scott bond tests shown in Figure 3. 9 were obtained from the handsheets made at the same pressing pressure but not with exactly the same density. The Mw investigated in this work was from 77K to 5-40M and amount of dextran added was 40 mg/g which is below saturation for all but the highest molecular weight CADEX (see Figure 3. 4). The Scott bond strength increased linearly with the logarithm of the molecular weight. It was more Mw dependent than tensile strength. Compared to CADEX3-24 (77K) treated paper, the increase in Scott bond for CADEX3-49 (2000K) treated paper was 47%.

Figure 3. 10 shows the change in Scott bond strength at different amount of CADEX3-24 (77K). It was noted that the Scott bond strength did not change very much over the various amounts of CADEX3-24 added. Unlike tensile strength shown in Figure 3. 7, Scott bond of paper treated with CADEX3-24 (77K) did not reach the same level as that obtained from CADEX3-49 (2M) treated paper, 44 J/m^2, even at very high amount of addition.

3.4. Discussion

3.4.1. Adsorption of CADEX on fiber

CADEX showed classical adsorption behavior for cationic polymers on wood pulp fibers. The adsorption plateau for CADEX on fiber was reduced as the Mw increased. This adsorption pattern has been studied in the early work on polyacrylamide[23,24,25,26,27]. The maximum amount of adsorbed PAM on fiber surface decreased from 50 mg/g to 13 mg/g when the molecular weight increased from 15,000 to 6,500,000. The porous nature of fiber is believed to be the main reason for the increased adsorption of lower molecular weight polymer in fiber. According to Stone and Scallan[20], the higher molecular weight molecules were restricted primarily to the surface and perhaps to the sub-surface lamellae of the fibers while the lower molecular weight ones were distributed throughout much more of the cell wall. It was demonstrated by the solute exclusion technique that dextran with Mw less than 200,000 can more or less pass through fiber wall. Studies of the adsorption of polyethylenimine with different sizes on fiber[28] suggested that larger pores of about 50 nm were present as the openings between macrofibrils. Apparently more adsorption for low molecular weight dextran was attributed to the penetration of dextran molecules into fiber wall.

The fluoresence images provided further direct evidence for the different distributions of dextran inside fiber wall. Since the images were produce from the overlaid laser scanning and transmitted images, in the meantime that the distribution of dextran in fiber can be observed, the region that is not coated with dextran can also be seen. The images shown in Figure 3. 11 suggested that both fiber surfaces and lumens were covered with less dextran in the case of high molecular weight than the low molecular weight.

The adsorption capacities as functions of CADEX molecular weight can be used to estimate the specific surface area of the pulp fibers. Two models were used to calculate the area occupied with one CADEX molecule. In the first, CADEX was assumed to adsorb as a sphere with a radius equal to the radius of gyration (Rg) of the unmodified dextran. In the second it was assumed that the CADEX adsorbed as a disk with the same thickness as measured for CADEX on silica and the disk volume was assumed to be equal to $4/3\pi Rg^3$. The detailed calculation is in Appendix 3.2.

Figure 3. 12 shows the log (n) vs log (r) for the two models, where n is called monolayer value of dextran on fiber which is the number of moles of dextran required to cover per unit mass of fiber, and r is the radius of dextran from sphere and disc models. In both cases the mole number of dextran increased with decreasing Mw which is consistent with the literature. Both models gave a linear correlation, which corresponded to a surface fractal dimension of 3.00 for the sphere model and 2.47 for the disc model. Fractal dimension of the surface measures the geometric characteristics of the surface of an object. For the classical concept of smooth, flat areas, the fractal dimension is around 2. It refers to rough surfaces when the fractal dimension is between 2 and 3 with a fractal theory limit

of 3[29]. The calculated fractal dimensions from both models indicated that fiber surface was quite rough.

The surface area accessible to CADEX3-49, the largest CADEX is considered as an estimate of the external surface area capable of participating in fiber-fiber bonding. Based on the disc model, the distributions of different molecular weight dextrans in the fiber were calculated and the results are listed in Table 3. 4. It was noted that CADEX3-24, the smallest dextran, had about more than 60% of the total amount of adsorption inside fibers. The calculated external surface area was 35 m^2/g. This estimate of external specific surface area is similar to Stone and Scallan's estimate of 24 m^2/g for pore size of 10-100 nm[30] for bleached pine sulphate pulps. Alince and van de Ven's estimated that the specific surface area was 10 to 25 m^2/g for a bleached softwood kraft pulp based on accessibility to PEI molecules of diameter about 25 nm and smaller[28].

Furthermore, the adsorbed layer thickness of CADEX on colloidal silica provides some information on the conformation of the adsorbed CADEX on fiber surfaces[31]. CADEX4-3 (464K) and CADEX4-6 (200K) exhibited more extended conformation than the other two since the adsorbed layer thickness was nearly double the radii of the gyration for these two polymers (see Table 3. 4).

Although CADEX3-49 (2M) was much flatter on silica microsphere, the adsorbed layer thickness was still higher than the rest of the others. The results from the adsorption isotherm of PAM on polystyrene latex suggested that higher molecular weight PAM had slightly longer loops and tails than low molecular weight ones[24].

3.4.2. The influence of molecular weight on interfiber bonding

In every case the tensile strength was increased by CADEX addition. On the other hand, there was little change in the light scattering coefficient (Figure 3. 8) suggesting that the relative bonded area was constant and that the tensile strength increase with CADEX addition was due to an increase in the specific bond strength per optically bonded area.

In order for dextran to enhance interfiber bonding, the polymer must be adsorbed on the exterior fiber surfaces. Thus, at low levels of addition (at or below 40 mg/g), lower molecular weight CADEX are less effective strength enhancing polymer (see Figure 3. 7 for tensile or Figure 3. 9 for Scott bond strength) because much of the polymer is adsorbed onto interior surfaces where it does not affect bonding. Although the fact that low molecular weight polymers can access more surface has been established before, we believe that this the first time that the corresponding effects on paper strength has been reported.

When the fiber surface was saturated with CADEX, tensile index no longer depended on the molecular weight of CADEX. The tensile strength of paper treated with different molecular weight dextran reached the similar ultimate value, of approximately 30 Nm/g. This result seemed to imply that the tensile strength development was governed by the degree of surface coverage with dextrans instead of the molecular weight. This is a remarkable result for one might imagine that interfiber bonds start to form during pressing when the sheet is wet. Under these conditions the ability of adsorbed dextran on one fiber to reach an adjoining fiber should increase with adsorbed layer thickness and thus molecular weight. The Scott Bond experiments were performed at only one polymer loading, 40 mg/g, which was below the dosage required to saturate the exterior fiber surfaces (see Figure 3. 4) for the lower molecular weight dextrans. Nevertheless, the molecular weight dependence of Scott Bond was large: it increased 47% as the molecular weight of CADEX changed from 77K to 2M, whereas the increase in tensile index was only 16% at the same amount added, 40 mg/g. Laleg and Pikulik's work showed that for cationic aldehyde starch with molecular weight from 8 million to over 100 million, the tensile strength increased about 16% whereas the Scott bond strength increased about 24%[16]. Furthermore, as shown in Figure 3. 10, the Scott bond strength of paper treated with CADEX3-24 (77K) did not reach the same strength level obtained from CADEX3-49 (2000K) treated paper even at the amount of addition as high as 140 mg/g. Thus, it seems that Scott bond was indeed molecular weight dependent whereas tensile strength was not. It is known that Scott bond and tensile strength experiments measure different properties. The paper fracture process is not controlled in a Scott bond test, nevertheless Scott bond energies do seem to be correlated to the z-direction interfiber bond strength[32,6] whereas conventional tensile strength is sensitive to the shear bond strength.

The moduli of dextrans with different molecular weight were measured and found very similar (see Chapter 4). There is not enough evidence, however, to determine the influence of polymer modulus on the strength of paper. Although it was suggested that a critical modulus had to be reached for a polymer to enhance the strength of paper[33,34], the relationship between modulus of a strength enhancing polymer and the strength of paper has not been well understood.

3.5. Conclusions

1. Molecular weight of CADEX (cationic dextran), ranging from 77,000 to 2,000,000, did not effect tensile strength of paper if the fiber surface was saturated with CADEX.

2. The Scott bond strength of paper treated with CADEX increased exponentially with the molecular weight ranging from 77,000 to 2,000,000 at the additional level of 40 mg/g.

3. Like the behavior of other linear cationic polymers, the capacity of fibers to adsorb CADEX increased with decreasing molecular weight.

4. The adsorbed layer of thickness of CADEX at the silica water interface increased with polymer molecular weight.

5. Based on simple models for the configuration of adsorbed CADEX, the fractal dimension of the unbeaten kraft pulp fibers was 2.98 and the exterior specific surface area was about 35 m^2/g.

3.6. Acknowledgements

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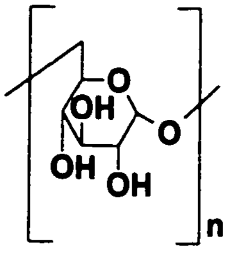


Figure 3. 1 The chemical structure of dextran. The anhydroglucose repeat units joined by α-acetal linkages through carbons 1 and 6.

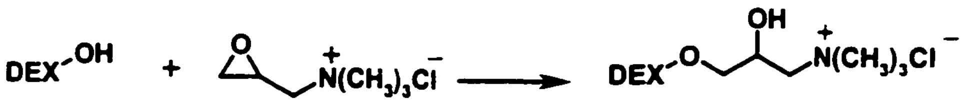


Figure 3. 2 Reaction route for the synthesis of CADEX from dextran.

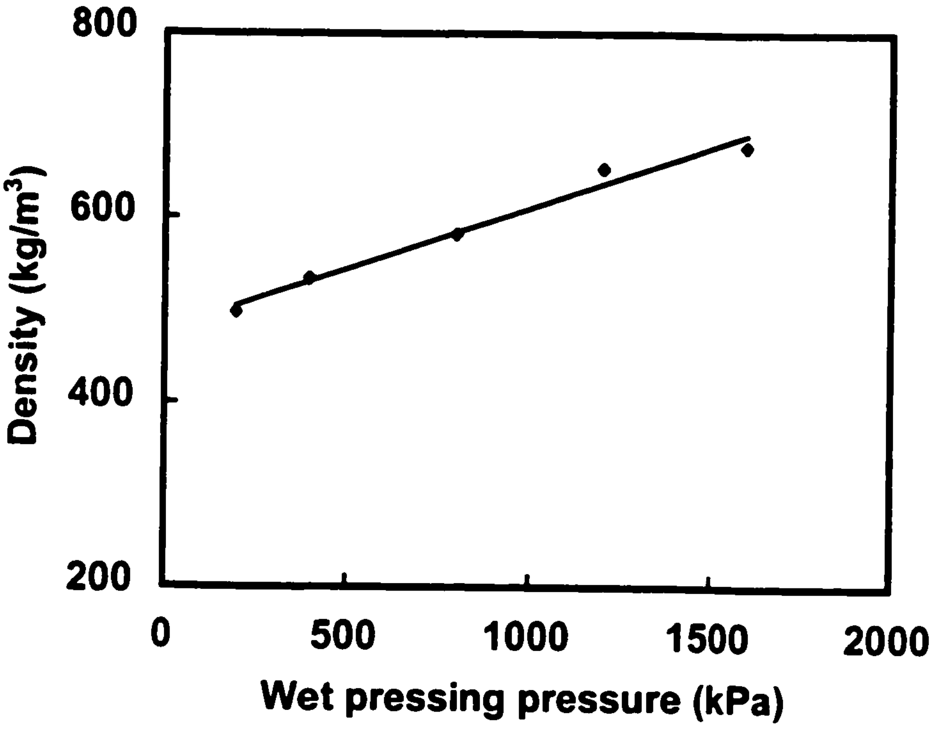


Figure 3. 3 Handsheet apparent densities as a function of wet pressing pressure.

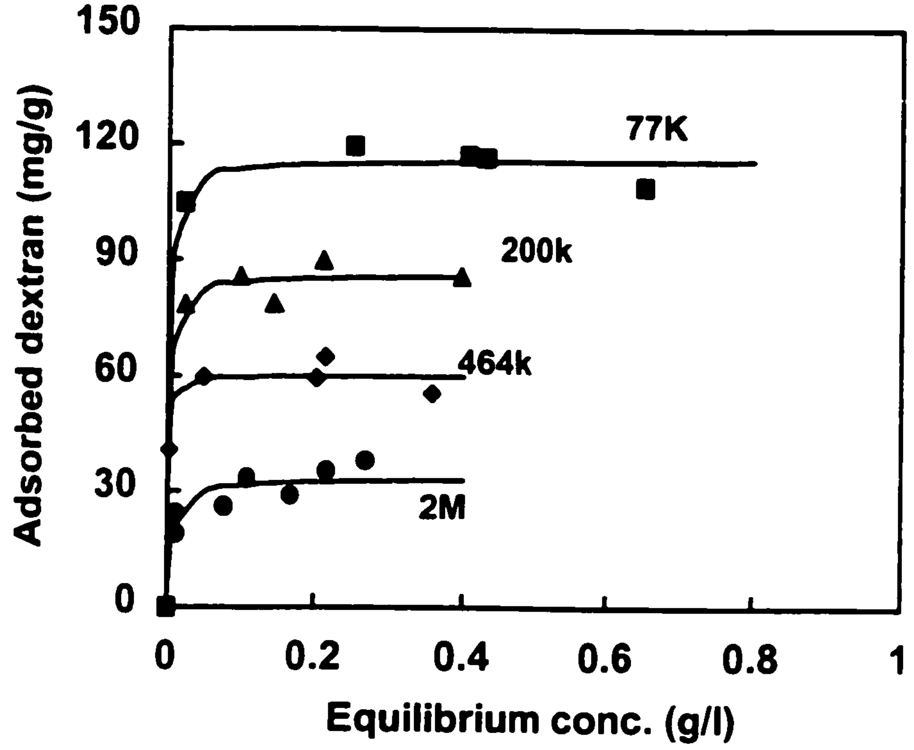


Figure 3. 4 The effect of molecular weight on the adsorption isotherms for cationic dextrans on unbeaten softwood bleached kraft pulp fiber. The pulp consistency was 0.5% and the temperature was 23 °C. The solid lines were the fitting curves of Langmuir equation with the maximum amount of adsorption of 116, 86, 60, and 33 mg/g for molecular weights of 77K, 200K, 464K and 2000K.

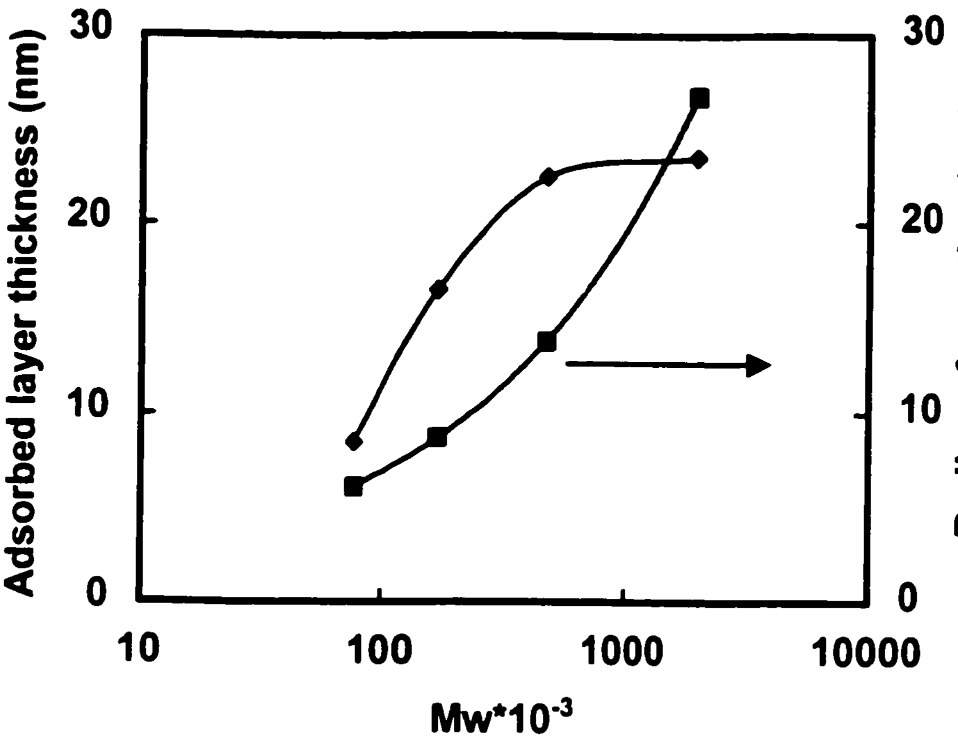


Figure 3. 5 **The affect of molecular weight on the adsorbed layer thickness of CADEX onto aqueous colloidal silica particles.**

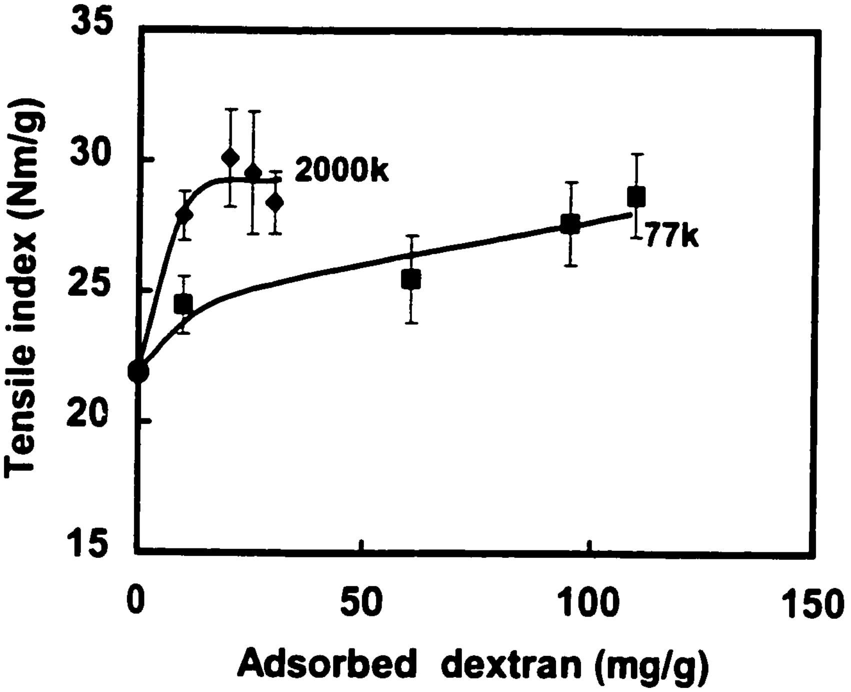


Figure 3. 6 The tensile index of paper as function of amount of dextran adsorbed on fiber. The tensile index values reported in this paper are interpolated to an apparent handsheet density of 550 kg/m^3.

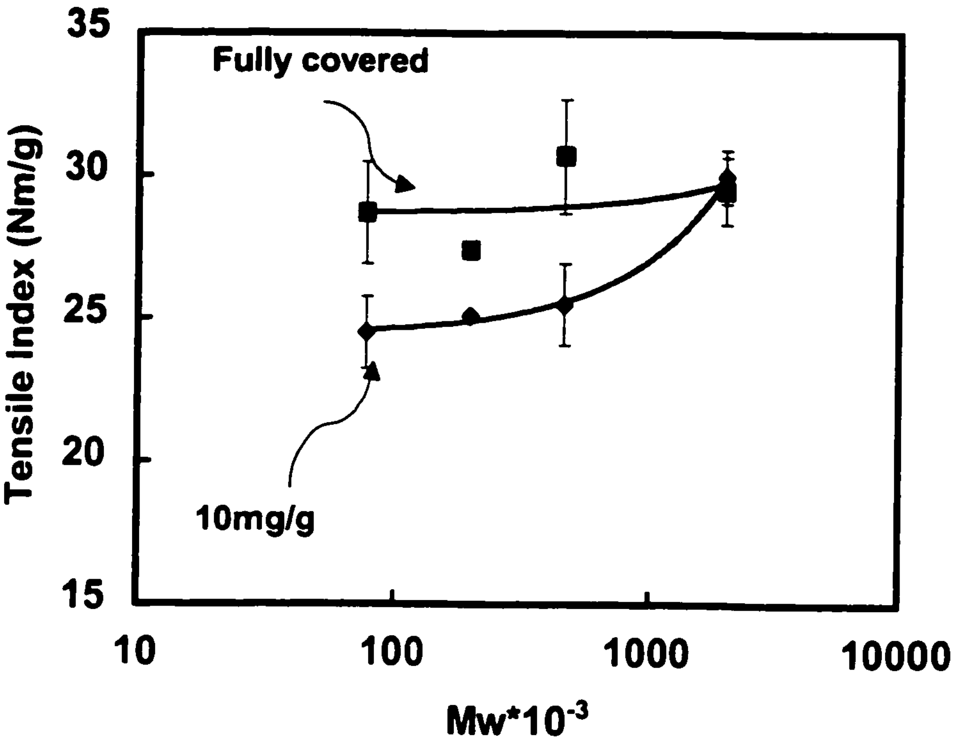


Figure 3. 7 The influence of CADEX molecular weight on tensile index for two surface coverages.

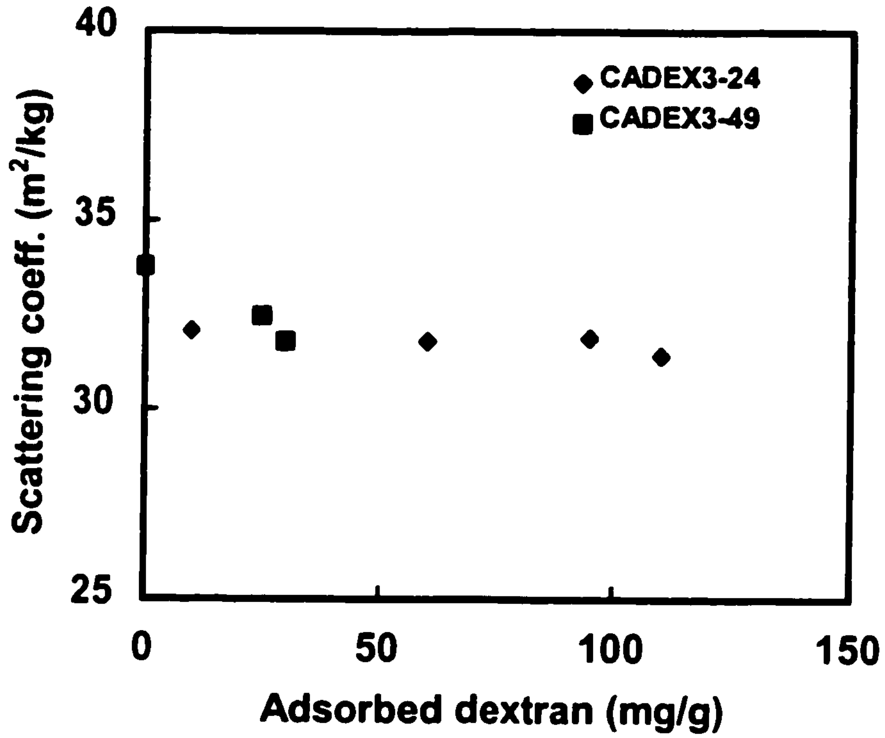


Figure 3. 8 Light scattering coefficient as the function of the amount of CADEX adsorbed on fiber.

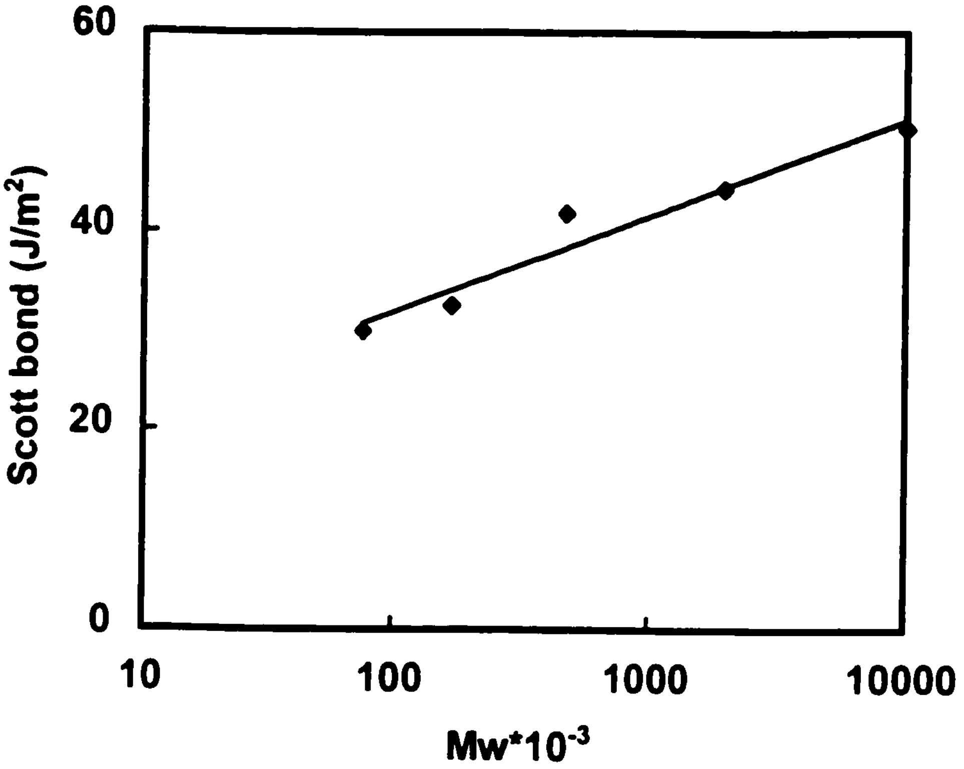


Figure 3. 9 The influence of CADEX molecular weight on Scott bond Strength. The CADEX dosage was 40 mg/g.

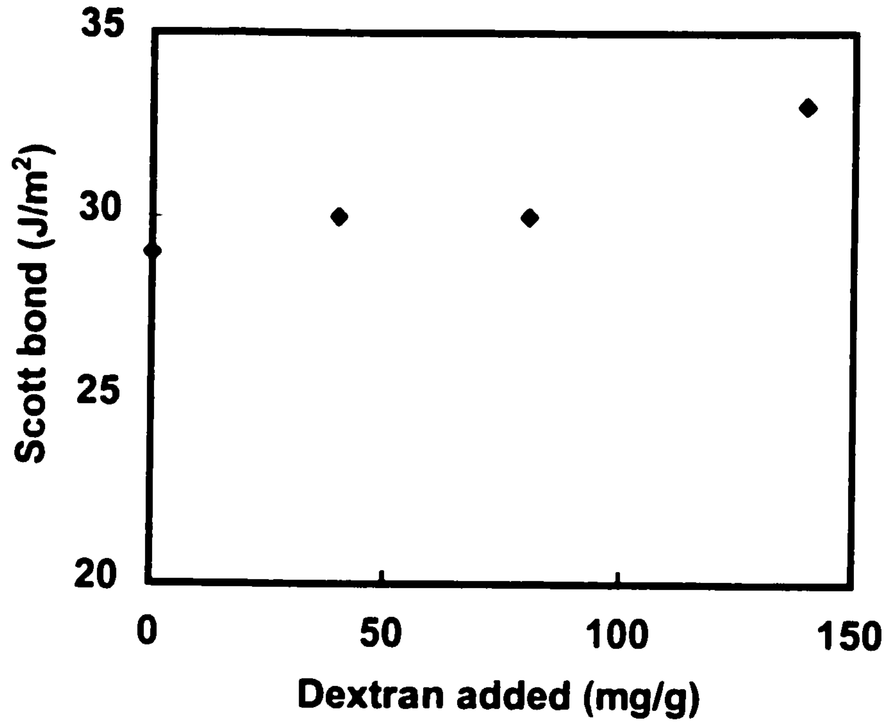


Figure 3. 10 The Scott Bond strength versus the amount of CADEX3-24 (77K) added to the fiber.

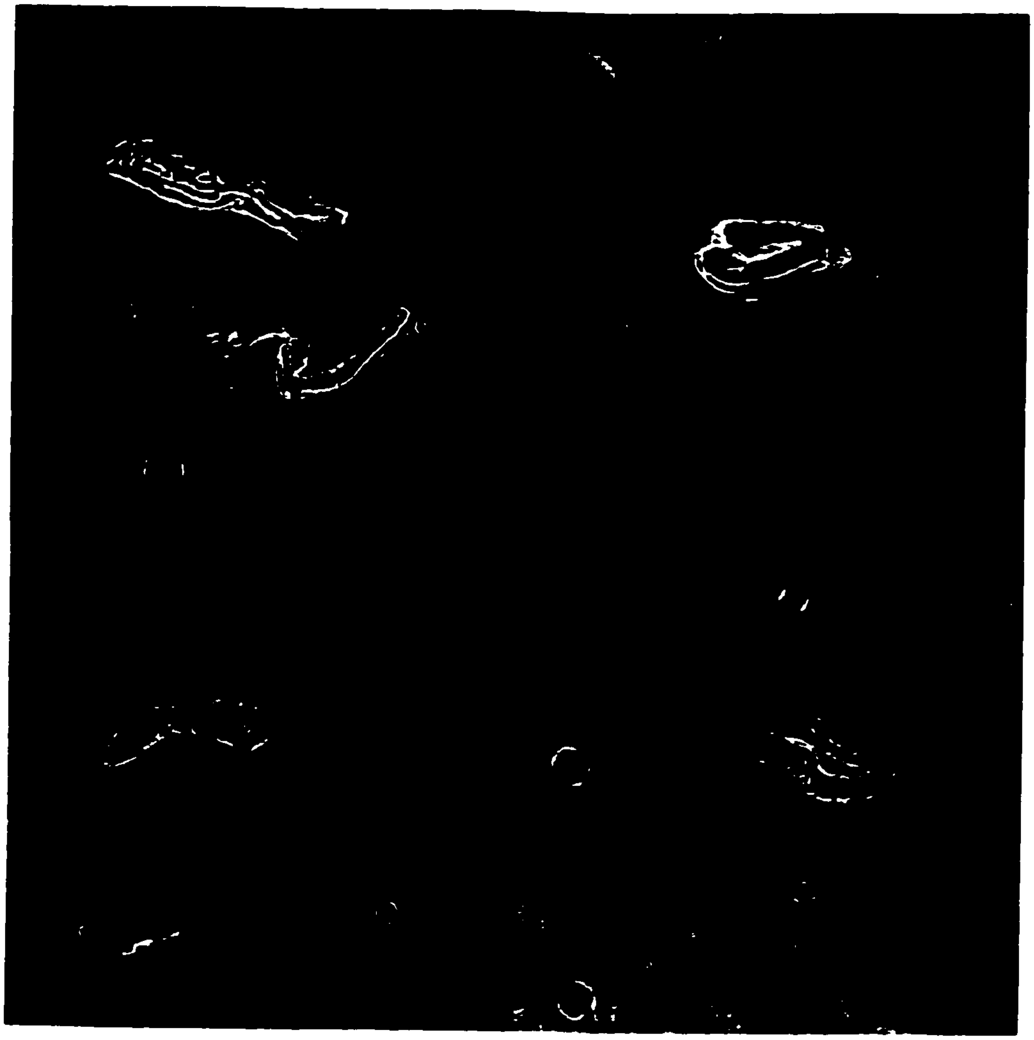


Figure 3. 11 The fluorescence image of cross-section of fiber coated with different molecular weight dextrans. (A) and (B): Mw 77,000; (C) and (D): 2,000,000.

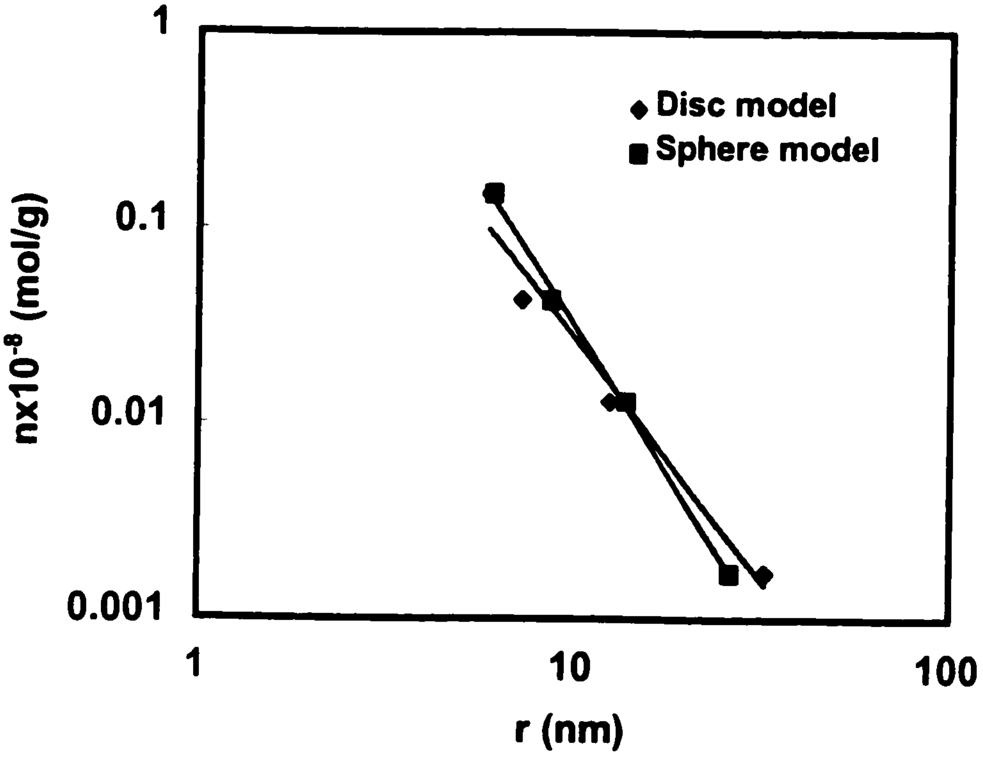


Figure 3. 12 The relation between monolayer value of dextran on fiber and the radius of dextran. The slopes from sphere model and disc model were -3.00 and -2.46, respectively, corresponding to the fractal dimensions of 3.00 and 2.46.

Table 3. 1 **Reaction conditions for the preparation of CADEX from nonionic dextran.**

Code of dextran	**MW*10^{-3}**	**Concentration of 5% NaOH %**	**Weight ratio of dextran to ETAC**
CADEX3-24	77	33	10
CADEX4-6	200	27	9.1
CADEX4-3	464	24	9.2
CADEX3-49	2,000	18	8.6
CADEX3-40	5,000-40,000	14	8.6

Table 3. 2 **The properties of the cationic dextrans used in this work.**

Code of dextran	**Mw of dextran*10^{-3}**	**Radius of gyration (nm)[a]**	**Charge density (meq/g)[b]**
CADEX3-24	77	6.1	0.253
CADEX4-6	200	9.4	0.302
CADEX4-3	464	13.8	0.321
CADEX3-49	2,000	26.8	0.284
CADEX3-40	5,000-40,000	60.4	0.035

[a] Interpolation of the data given by Stone and Scallan for uncharged dextrans[20]

[b] Obtained by polyelectrolyte titration.

Table 3. 3 Tensile data of handsheets at different pressing pressures and different amounts of addition.

CADEX3-24 (Mw. 77k)

Pressing pressure (kPa)	800				1600			
Adsorbed amount (mg/g)	10	60	95	115	10	60	95	115
Density (kg/m^3)	511	478	508	506	597	597	600	604
Scattering coeff. (m^2/kg)	33.5	33.46	33.85	32.61	30.83	30.43	29.55	29.93
Tensile index (Nm/g)	21.9	19.5	25.4	26.7	27.6	29.4	30.3	31.2
E-modulus (GPa)	1.72	1.32	1.81	1.85	2.29	2.41	2.45	2.55
TAE (J/m^2)	20.7	14.4	29.6	29.7	33.1	35.8	37.5	40.8

CADEX4-6 (200k)

Pressing pressure (kPa)	800				1600			
Adsorbed amount(mg/g)	10	33	67	87	10	33	67	87
Density (kg/m^3)	527	518	537	550	605	580	579	607
Tensile index (Nm/g)	23.5	24.4	25.1	27.4	29.0	29.3	31.2	33.8
E-modulus (GPa)	1.73	1.71	1.90	2.04	2.35	2.32	2.35	2.65
TAE (J/m^2)	27.4	27.6	28.5	31.3	37.3	33.6	43.7	48.2

CADEX4-3 (464k)

Pressing pressure (kPa)	800				1600			
Adsorbed amount (mg/g)	9	34	53	60	9	34	53	60
Density (kg/m^3)	527	536	533	527	616	613	607	593
Tensile index (Nm/g)	23.2	24.4	26.6	28.9	32.0	32.3	33.3	34.1
E-modulus (GPa)	1.85	1.93	2.01	2.05	2.70	2.61	2.64	2.65
TAE (J/m^2)	23.1	27.5	29.4	35.3	44.0	42.3	47.5	43.7

CADEX3-49 (2M)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10*	20*	25	30	10	20	25	30
Density (kg/m^3)	588	561	513	526	584	572	596	594
Scattering coeff. (m^2/kg)	32.49	31.91	34.38	32.64	31.45	31.04	30.07	30.21
Tensile index (Nm/g)	27.9	30.2	26.1	25.9	29.0	30.3	33.8	33.0
E-modulus (GPa)	2.14	2.15	1.86	1.88	2.24	2.26	2.34	2.32
TAE (J/m^2)	33.5	30.4	26.3	26.2	32.2	26.8	46.4	46.3

* Wet pressing pressure was 1200 kPa.

Table 3. 4 Distributions of CADEX on fiber. Details of calculation was attached in Appendix-I.

Code of CADEX	Maximum adsorption* mg/g	Amount inside fiber wall (percentage)	Amount on external fiber surface mg/g
CADEX3-24	116	75 (65%)	40
CADEX4-6	86	15 (17%)	70
CADEX4-3	60	4.7 (8%)	55.3
CADEX3-49	33	0 (0)	34

* Calculated from the Langmuir equation.

Appendix 3.1 Applying Langmuir Isotherm to the adsorption data

Sample calculation for the dextran with Mw 77,000

Langmuir equation

$$\theta = \frac{b \cdot c}{1 + b \cdot c}$$

where

b - is constant
c - is equilibrium concentration of dextran in solution,and
θ – is the surface coverage

$$\frac{1}{\theta} = 1 + \frac{1}{b \cdot c} \quad \text{substitute}\,, \theta = \frac{\Gamma}{\Gamma\text{max}} \rightarrow \frac{1}{\Gamma} \cdot \Gamma\text{max} = 1 + \frac{1}{(b \cdot c)}$$

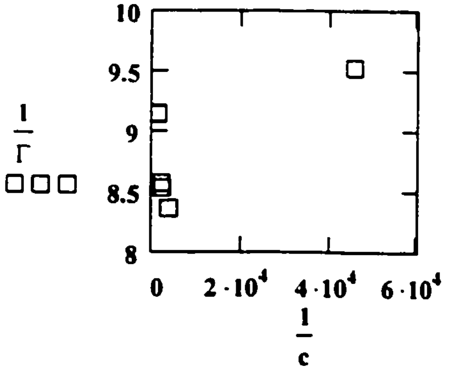
$$\frac{1}{\Gamma} = \frac{1}{\Gamma\text{max}} + \frac{1}{\Gamma\text{max} \cdot b \cdot c}$$

Linearized version of equation

(a) Calculate b and Γmax

The adsorption data of dextran on fiber

$$\Gamma := \begin{pmatrix} 105 \\ 119.6 \\ 117.2 \\ 116.7 \\ 109.3 \end{pmatrix} \cdot \frac{mg}{gm} \qquad c := \begin{pmatrix} 0.022 \\ 0.252 \\ 0.405 \\ 0.429 \\ 0.651 \end{pmatrix} \cdot \frac{mg}{gm}$$



$$\Gamma\text{max} := \frac{1}{\text{intercept}\left(\frac{1}{c}, \frac{1}{\Gamma}\right)}$$

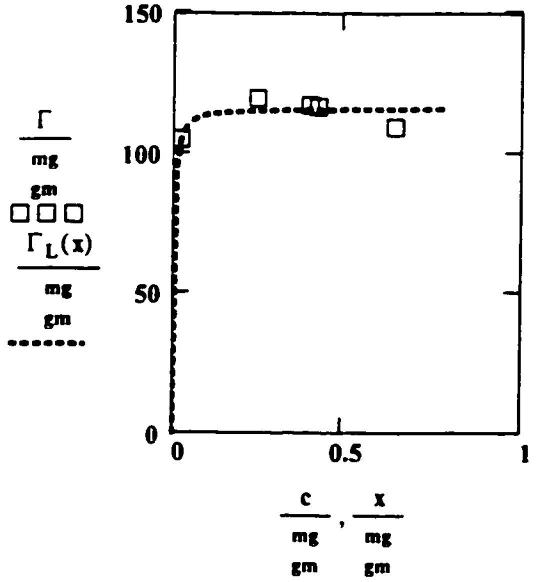
$$\Gamma\text{max} = 116.174 \frac{mg}{gm}$$

$$b := \frac{\dfrac{1}{\text{slope}\left(\dfrac{1}{c}, \dfrac{1}{\Gamma}\right)}}{\Gamma\text{max}} \qquad b = 4.377 \times 10^{5}$$

(b) Comparing experimental and theoretical curve

Defining Langmuir function

$$\Gamma_L(x) := \frac{b \cdot x}{1 + b \cdot x} \cdot \Gamma\text{max} \qquad x := 0 \cdot \frac{mg}{gm}, 0.01 \cdot \frac{mg}{gm} .. 0.8 \cdot \frac{mg}{gm}$$



Appendix 3.2 Calculation of fractal dimension and external surface area of fibers

Two models, sphere model and disc model, were used to calculate the occupied area with a CADEX molecule. The assumptions were:

1. CADEX was assumed to adsorb as a sphere with a radius equal to the radius of gyration (Rg)of the unmodified dextran.

2. CADEX adsorbed as a disk with the same thickness as measured for CADEX on silica and the disk volume was assumed to be equal to $4/3\pi Rg^3$.

Rg: radius of gyration of unmodified dextran, nm.
h: adsorption layer thickness on silica microspheres, nm.
R: radius of the disc, nm.
Ad: maximum adsorption, mg/gm.
n: monolayer value of dextran on fiber which is the mole number of dextran required to cover per unit mass of fiber, mol/gm.
Da: Fractal dimension of fiber surface.

For polymer adsorption on fractal surfaces

$n \alpha R^{-Da}$

If considering the polymer conformation is not significantly different from the solvent conformation

$n \alpha Rg^{-Da}$

(a) Calculate R, the radius of the disc

$$nm := 10^{-9} m \quad Nav := 6.023 \cdot \frac{10^{23}}{mole}$$

$$h := \begin{pmatrix} 8.5 \\ 16.5 \\ 22.5 \\ 23.5 \end{pmatrix} nm \quad Rg := \begin{pmatrix} 6.1 \\ 8.7 \\ 13.8 \\ 26.8 \end{pmatrix} nm \quad Mw := \begin{pmatrix} 77 \\ 200 \\ 464 \\ 2000 \end{pmatrix} \cdot 10^3 \frac{gm}{mole}$$

$$\frac{4}{3} \cdot Rg^3 \cdot \pi = h \cdot \pi \cdot R^2$$

$$R := \overrightarrow{\left(\frac{4}{3}\cdot\frac{Rg^{3}}{h}\right)^{0.5}} \qquad R = \begin{pmatrix} 5.967 \\ 7.295 \\ 12.479 \\ 33.047 \end{pmatrix} \mathrm{nm}$$

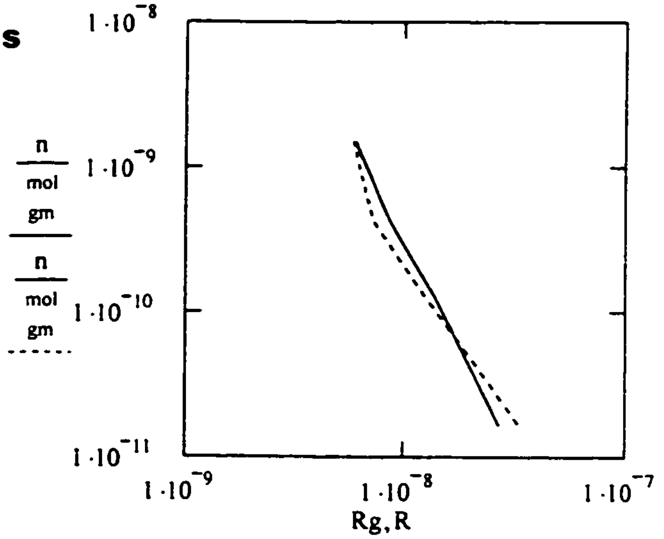
(b) Calculate n

$$Ad := \begin{pmatrix} 116 \\ 86 \\ 60 \\ 33 \end{pmatrix} \frac{\mathrm{mg}}{\mathrm{gm}}$$

maximum adsorption obtained from Langmuir equation

$$n := \overrightarrow{\left(\frac{Ad\cdot 10^{-3}}{Mw}\right)} \qquad n = \begin{pmatrix} 1.506\times10^{-9} \\ 4.3\times10^{-10} \\ 1.293\times10^{-10} \\ 1.65\times10^{-11} \end{pmatrix} \frac{\mathrm{mol}}{\mathrm{gm}}$$

(c) The fractal dimensions



$$vx := \log\left(\frac{Rg}{nm}\right) \qquad vy := \log\left[\frac{n}{\left(\frac{mol}{gm}\right)}\right] \qquad \text{slope}(vx, vy) = -3.003$$

$$vX := \log\left(\frac{R}{nm}\right) \qquad vY := \log\left(\frac{n}{\frac{mol}{gm}}\right) \qquad \text{slope}(vX, vY) = -2.469$$

The fractal dimension for sphere model is about 3, and it is 2.47 for disc model.

(d) The distribution of dextrans with different molecular weight in fibers.

Assuming (1) the area accessible to dextran 2000,000 is the external surface area of fibers; (2) Disc model.

Mole of dextran distributed inside fiber wall, M

$$M := \overrightarrow{\left[\frac{\frac{Ad}{Mw}\cdot R^2 - Ad_3\cdot\frac{(R_3)^2}{Mw_3}}{R^2}\right]} \qquad M = \begin{pmatrix} 1\times 10^{-6} \\ 9.135\times 10^{-8} \\ 1.36\times 10^{-8} \\ 0 \end{pmatrix}\frac{mole}{gm}$$

Mass of dextran distributed inside fiber wall, W

$$W := \overrightarrow{(M\cdot Mw)} \qquad W = \begin{pmatrix} 0.077 \\ 0.018 \\ 6.311\times 10^{-3} \\ 0 \end{pmatrix}\frac{gm}{gm}$$

Accordingly, dextran in the fiber wall is 75, 15 and 4.7 mg per gram of fiber as the Mw changing from 77k to 2000k.

$Wo := Ad - W$ Mass of dextran on the external surface of fibers

$$Wo = \begin{pmatrix} 0.039 \\ 0.068 \\ 0.054 \\ 0.033 \end{pmatrix} \frac{gm}{gm}$$

$$S := \overrightarrow{\left(\frac{Wo}{Mw} \cdot Nav \cdot \pi \cdot R^2\right)}$$

External surface area of fiber

$$S = \begin{pmatrix} 34.097 \\ 34.097 \\ 34.097 \\ 34.097 \end{pmatrix} \frac{m^2}{gm}$$

3.7. References

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Chapter 4. Strength Enhancement Of Dextran-Impregnated Paper

Abstract

Dextran with molecular weights from 77,000 to 2000,000 was used to impregnate handsheets made of unbeaten, bleached, softwood kraft pulp. The effect of molecular weight and the amount of dextran added on the tensile strength of the impregnated paper was investigated. It was found that the tensile strength of treated paper increased with the increase of the molecular weight of dextran. At the same dextran content, the higher the molecular weight dextran used, the stronger was the impregnated paper obtained. The strength enhancing effect of dextran was attributed to the increase in both bonded area and intermolecular bonds of between dextran. In contrast with the wet-end added polymer which is distributed uniformly on fiber surface, it is proposed that impregnation may give a polymer distribution that is more efficient in strengthening the fiber network.

Key words: strength-enhancing polymer, impregnation, strength of paper, fiber-fiber bonding, tensile strength, dextran, molecular weight.

4.1 Introduction

Dry strength aids can be added into a fiber network in different ways depending on the final usage of the paper. Most commercial additives are added internally to the aqueous pulp slurry due to their water-soluble properties, which is referred to wet-end added in this paper. They are also applied to the paper surface to improve the surface strength properties. Impregnation is of interest in the preparation of special grades of paper, and the additive level is often high, 10-50%, based on fiber weight[1].

In earlier work, polymers with a wide range of properties, from glassy to elastomeric, were used to study the mechanical properties of impregnated paper[2]. It was found at moderate levels of polymers, <50%, the fiber-fiber bonds played a dominant role in determining tensile strength and modulus. Among many polymer variables, it was suggested that hardness, defined as the temperature at which shear modulus was about 0.03 GPa, was the most important[2,3,4]. It was found that both the modulus and tensile strength of paper were impaired when soft polymer, modulus less than 0.2 GPa at 20°C, was used. A study[4] on the delamination of paper showed that non film-forming polymer imparted only minor improvements to the delamination resistance. The variables of polymer and the treatment conditions investigated also included particle size of polymer latex, functional group, amount of addition level, plasticizer, heating[5,2-4], etc. It is interesting to note that molecular weight has not been among those that were investigated.

This work is part of our extensive systematic study relating the polymer structure to its performance as a strength enhancing polymer. Dextran (DEX) was chosen as a surface polymer model to elucidate the relationship between properties of a strength enhancing polymer and its performance in strengthening paper. In our previous work cationic dextran (CADEX) was prepared and added into fiber by adsorption. It was found that molecular weight of CADEX, in the range of 77,000 to 2,000,000, did not affect the tensile strength of paper if the fiber surface was saturated with CADEX. However, at the low level of adsorption, because of the different fiber surface coverage with CADEX of different molecular weights, high molecular weight CADEX behaved more efficient than low molecular weight CADEX in strengthening the paper. The strength enhancement of paper was attributed to the improvement of interfiber bond strength that was obtained from the intermolecular bonding of CADEX.

The objective of this work is to understand the relationship between molecular weight of dextran and the strength properties of impregnated paper at the large amount of addition. Unlike wet-end added dextran, which essentially forms an adsorption monolayer on fiber, the amount of dextran added into fiber network can be easily controlled with impregnation. The amount of dextran used in this work varied from 20 mg/g to 180 mg/g. The effect of molecular weight and the amount of addition of DEX on tensile strength of paper was investigated. Moreover, the strength enhancement of treated paper obtained from impregnation and wet-end added was compared.

4.2 Experimental

4.2.1 Preparation of handsheets

Five dextrans (Sigma) were used; the mass average molecular weights, given by the supplier were 77,000, 167,000, 200,000, 464,000 and 2,000,000. Millipore water was used to prepare dextran solution.

Previously dried bleached softwood kraft pulp was obtained from Avenor, Thunder Bay Mill. Standard handsheets were made with tap water using the British sheet machine following Tappi test method except basis weight, which was 68±1 g/m^2 in this work. Concentrations of the dextran aqueous solution used for impregnation were 1%, 2%, 5% and 8%. Dry handsheets were dipped into dextran solution and held until saturated. Impregnated sheets were dried under the restraint over night.

All the testing of the dry sheet properties conformed to Tappi procedures. These tests included basis weight, apparent density, light scattering coefficient, and tensile strength. Eight strips were prepared for one tensile test, and the standard deviation was calculated. The basis weight of impregnated paper was calculated based on the total weight of impregnated paper.

4.2.2 Mechanical properties of dextran

The mechanical testing was performed in a dynamic mechanical analyzer (DMA), Dupont 983 at the constant temperature 25°C and fixed frequency 1Hz. The test was run isothermally for 10 min. Testing samples were prepared by impregnation of inert glass fiber braid with 10% dextran aqueous solutions. The samples were air-dried over night and the dimensions of the samples were measured. Shear storage modulus was calculated with DMA standard data analysis program.

The measurement of viscosity was carried out with the concentric cylinder type rheometer, BohLin Rheometer (VOR) at temperature 22°C with frequency sweep from 0.1 to 20 Hz. The system used was C25 with the torsion element 10.592g cm. The concentration of the DEX was 40%, and the molecular weights used for the measurement were 77,000, 167,000, 464,000 and 2,000,000.

4.3 Results

The relevant properties of dextran with molecular weight from 77,000 to 2,000,000 are listed in Table 4. 1. The radius of gyration was obtained by interpolating the available data[6]. The size of dextran increased as the increase in molecular weight, and the radius of DEX2M was almost twice as the radius of

DEX464K. DMA measurement showed that the moduli of dextrans used in this work were very close.

The densities of impregnated paper with different molecular weight DEX are shown in Figure 4. 1. The density of the original sheet, which is called untreated paper later on in this paper, was about 515 kg/m^3. The densities of the impregnated paper were reduced compared to the untreated one; however, it slightly increased as the molecular weight increased from 490 to 511 kg/m^3 for paper treated with DEX77K and DEX2M respectively. The set of data on the top of the graph is the effect of polymer on the density of impregnated handsheets, assuming there was no swelling during the impregnation. The thickness of the dextran added was calculated based on the data of the density of dextran, 1200 kg/m^3, and the amount of dextran added. Therefore, the thickness of the impregnated paper was taken as the summation of the thickness of dextran added and the thickness of the untreated handsheet. It was noted that if water did not swell the paper, the densities of the impregnated handsheets were higher, about 550 kg/m^3, which was 11% to 7% increase as the molecular weight varied between 77,000 and 2,000,000. Figure 4. 2 shows the effect of dextran content on the densities of impregnated handsheets with DEX464K and DEX2M. The densities of the impregnated paper were slightly lower than the untreated one because of the paper swelling, but they were slowly approaching the original density of the untreated handsheet as the dextran content increased.

Figure 4. 3 to Figure 4. 10 presents the results from tensile strength test, containing the tensile index, elastic modulus and the strain at break.

Figure 4. 3 is the typical stress-strain curve for paper treated and untreated with dextran. Both stress and strain of paper increased in the presence of DEX. The effect of molecular weight on the tensile index of the impregnated paper is shown in Figure 4. 4. The dextran content on paper was about 0.09 ± 0.01 g /g for all testing samples. The second y-axis is the light scattering coefficient. Tensile index increased with the increase in the molecular weight of DEX, slowly at low molecular weight, followed with a sharp increase between DEX464K and DEX2M. The increase percentage was about 27 from DEX77K to DEX464K, while it was 50 from DEX464K to DEX2M. The scattering coefficient was reduced and it fell quickly between molecular weights of 464,000 to 2,000,000, corresponding to the steep increase in the tensile index.

The influence of molecular weight at different additional levels was investigated and the results are shown in Figure 4. 5 and Figure 4. 6. The zero dextran content represents the untreated paper. The tensile index of the paper was linearly proportional to the amount of dextran content in paper. The paper treated with DEX2M was stronger than that treated with DEX464K at any dextran contents, more than 50% when dextran content was about 0.1 g/g. Scattering coefficients decreased as the amount of dextran contents increased as seen in Figure 4. 6. While the scattering coefficients of paper treated with DEX2M were lower than that of untreated paper at any amount of dextran content. for paper treated with DEX464K, at the low dextran content, it was slightly higher than the untreated paper, and it dropped gradually as the dextran content increased. At any dextran content, the scattering coefficients from DEX2M treated paper were lower than that of DEX464K treated paper.

Figure 4. 7 shows the effect of molecular weight on the breaking strain of the impregnated paper. The strain of untreated paper was approximately 0.017. All the treated paper had higher strain than untreated, and the strain increased linearly as the molecular weight in the logarithmic relation. At the same dextran content, as shown in Figure 4. 8 the strain of DEX2M treated paper is always higher than that treated with DEX464K.

It was noted that unlike tensile strength that depended on the molecular weight of DEX, modulus seemed not to change much for the paper treated with different molecular weight (Figure 4. 9), only about 17% from the lowest to the highest molecular weight. The same results were obtained from the paper treated with DEX464K and DEX2M at the different contents shown in Figure 4. 10. The moduli of the two dextran treated papers were very close at dextran contents between 0 to 0.18 g/g; but it increased linearly as a function of dextran content.

4.4 Discussion

4.4.1 Effect of DEX on the interfiber bonding of impregnated paper

Impregnation of paper with water soluble polymer will bring about two changes in the relative bonded area of a fiber network. The first is the enhancing effect of polymer on the interfiber bonding. However, in the meantime, the interfiber bonds are impaired with rewetting due to the swelling of paper. As shown in Figure 4. 4, with the same amount of dextran content in fiber, high molecular weight dextran was more effective in enhancing the interfiber bonding than the lower molecular weight one. This probably was caused by the penetration of low molecular weight dextran into the fiber wall that led to less amount of dextran contributing to the interfiber bonding. In our previous work with cationic dextran, it was estimated that, for dextran of molecular weight 77,000, the amount of dextran penetrated inside fiber wall was about 60% of the total adsorbed dextran.

A consistent observation was also found from the results of density of the impregnated paper. As shown in Figure 4. 1, the difference between the measured density of impregnated paper and the calculated one can be considered as the result of paper swelling. It was noted that the lower the molecular weight, the more influence of paper swelling was observed. For the high molecular weight dextran, such as DEX2M, the influence from the paper swelling was negligible, and there was no significant difference in the density of the paper treated with DEX2M and DEX464M as the dextran contents were above 0.1 g/g.

As shown in Figure 4. 6, the influence from paper swelling occurred prior to the observed effect of polymer enhancement in the case of DEX464K impregnation. As the dextran content increased, a balance existed between these two, and eventually the latter turned into the dominant factor. In the case of DEX2M impregnated paper, however, the light scattering coefficient was nearly decreased linearly as the DEX2M contents increased, which indicated that the relative bonded area was enhanced even at the very low dextran content. The constant falling down of light scattering coefficient indicated that fiber network was still the main structure of the paper to hold the load.

As illustrated in Figure 4. 6, the more bonded area of DEX2M treated paper than DEX464K treated one was probably attributed to the different types of bond formed during the impregnation. Since the radius of gyration of DEX2M is large, twice as much as that of DEX464K, it was possible that most of DEX2M might only fill the gaps between fibers (unbonded area), but hardly pass through the already bonded area due to its large molecular size. This polymer could form additional bonded area at the periphery of the formerly bonded area that is similar to the so called "skirt" effect proposed by Nanko and Ohsawa[7]. The skirt is formed by the adhesion of the S1 layer, which has swollen and separated from the S2 layer of the same fiber, to the surface of the mating fiber. The evidence for the skirt effect was reported from work on the fiber wall damage during bond failure[8]. It is suggested that the skirt effect is particularly effective in enhancing the interfiber bond strength. More important than the additional bond area that the skirts provide is their role in distributing the stress at the periphery of the bond. The stress concentrations that are expected to be large at this area are reduced and redistributed by the skirts, and a higher load can be sustained. On the other hand, the distribution of DEX464K within the fiber network would be more uniform since only part of it contributed to the new bonded area while the others might go through the bonded area and partially replace the fiber-fiber bonding.

It has been known that an increase of liquid viscosity will slow down the rate of penetration into a capillary[9]. Therefore, the distribution of polymer in the fiber network could also be related to the rheological properties of dextrans. We have observed that the viscosity obtained from DEX2M was higher than that of DEX464K at the same solution concentration. To understand the effect of the rheological properties of DEX at the different molecular weight, we measured the dynamic viscosity of concentrated dextran solution, 40%, and the results are shown in Figure 4. 11. The viscosities of the dextran solution increased as the molecular weight increased, and except for DEX2M, they remained constant over the range of shear rate from 0.1 to 20 Hz. The rheological property of DEX2M behaved differently. The reduced viscosity of DEX2M as the shear rate increased indicated the rearrangement and reorientation of entangled molecular chains.

When paper was soaked with dextran solution, the less viscous solution would penetrate more and faster into the capillaries of fiber network, while the more viscous dextran solution would be retained to fill up the void and form additional bonded area at the periphery of the formerly bonded area.

4.4.2 Effect of DEX on tensile strength and modulus

As shown in Figure 4. 4, the strength of paper was enhanced with all the dextrans investigated in this work. It was obvious that, in most of the cases, the stronger paper obtained from the impregnation was attributed to the enhanced bonded area with dextran, as shown both in Figure 4. 4 and in Figure 4. 6. However, it was also found that compared to the untreated paper, higher tensile index was obtained even though the relative bonded area of paper was lower than the untreated paper. This indicated that the intermolecular bond strength of dextran was strong enough to compensate the influence from paper swelling. The stronger intermolecular bond strength of dextran than the interfiber bond strength could be attributed to the more efficient intermolecular diffusion of dextran due to its water soluble properties and flexible molecular segments[10]. It is believed that the formation of entanglements through the intermolecular diffusion is the determining factor for the development of adhesive strength at the interface of polymers[11,12,13,14].

The molecular entanglement of the high molecular weight DEX was also illustrated in the results of strain. The effect of molecular weight on the strain

(Figure 4. 7) suggested that the higher extensibility of paper resulted from higher molecular weight was due to its more entangled molecular conformation because it tended to stretch longer before pulled off.

The moduli of dextrans used in this work were very close, from 550 to 600 MPa for Mw of 77,000 and 2,000,000 respectively. While the tensile index of the treated paper was doubled in comparison with the untreated paper, the moduli of different molecular weight dextran treated paper were very close at the same dextran content as shown in Figure 4. 9 and Figure 4. 10. Neither modulus of strength additives nor modulus of impregnated paper seemed strongly related to tensile strength of impregnated paper. The relation between tensile strength and elastic modulus of paper has been thoroughly studied and reviewed by Page and Seth[15,16,17,18]. The main factors to affect the modulus of paper are the elastic molulus of fibers, the degree of bonding, the presence of curl, kinks, crimps, and microcompressions in the fibers. Ways used to improve tensile strength such as adding strength agent, increasing wet pressing pressure and beating on straight, thin-walled flexible fiber, could keep elastic modulus constant but only changed the end points of stress-strain curves. Our results can be interpreted with this theory since the treatment on handsheets did not change the fiber properties. The slight increase in the modulus of paper with the dextran content was attributed to the increase in the degree of bonding (Figure 4. 10).

4.4.3 Comparison of the different adding modes

The effect of adding mode was compared for dextran with two different molecular weights and at the same amount of adsorption, 25 mg/g. The absolute tensile strength data obtained from these two adding mode were not comparable since different wet pressing pressures were used in making handsheets, however, the comparison can be made between the two adding modes by looking at the percentage increase in tensile strength of treated paper. The results are listed in Table 4. 2. DEX2M and DEX464M were added with impregnation, while CADEX3-49 and CADEX4-3 were wet-end added. The dextran content in all the cases was 25 mg/g. It showed that wet end added polymer was more effective in enhancing paper strength than polymer added with impregnation, especially for low Mw dextran. Compared to untreated paper, the increase in tensile strength of DEX464K treated paper was 8.9%, whereas it was 16.9% for the wet end added. In the case of DEX2M, this increase was 32% for impregnation and 35% for wet-end added. This observation agrees with Stratton[19]. He suggested that supplementing the bonding in the crossover area between the fibers was an important mechanism for strength aids, and internal treatment was more effective.

However, it must be pointed out that the comparison of the tensile strength increase was not made under the same sheet density in case of the impregnation. The less effective strength enhancing effect obtained from impregnation might be due to the paper swelling. If the tensile strength of impregnated paper was compared with the untreated one at the same density, the increase in tensile strength observed from the two adding modes should be much closer, which was illustrated in the case of DEX2M treated paper as shown in Table 4. 2.

The other contrast between the two adding modes is the distribution of polymer within fiber network. When the polymer is wet-end added, it is adsorbed on fiber surface uniformly; whereas in the other case, it distributes unevenly. High molecular weight polymer may prefer to form additional bonded area at the periphery of the formerly bonded area instead of passing through the bonded area due to its large molecular size, while low molecular weight polymer can go through both areas, even the fiber wall. In this sense, impregnation might be more effective in strengthening the paper because it makes more efficient use of polymer to produce more bonded area, especially for high molecular weight polymers. However, as discussed, two factors affect the interfiber bonding simultaneously. Therefore, how to balance these two factors and optimize the strength enhancing effect from the polymer additives is a very interesting question that needs further investigation.

4.5 Conclusions

1. Compared to untreated paper, all the dextrans investigated in this work enhanced the tensile strength of the impregnated paper. At the same dextran content, the higher the molecular weight dextran used, the stronger was the impregnated paper obtained.

2. Tensile strength of the impregnated paper increased as the result of increase in bonded area and intermolecular bonds of dextran.

3. Modulus of impregnated paper did not depend on the molecular weight of dextran; but it slightly increased with dextran content.

4. Wet-end added polymer is adsorbed uniformly on fiber surface; in contrast, polymer added through impregnation ends up with uneven polymer distribution within fiber network.

5. The rheological properties of polymer seemed to effect the bond formation during the impregnation. High viscous polymer tended to form additional bonded area at the periphery of the formerly bonded area, while the less viscous polymer could penetrate into the small capillaries, such as the bonded area or the fiber wall.

4.6 Acknowledgements

The authors thank SCA Research, Sundsvall Sweden for financial support. We thank Pulp and Paper Research Center at University of Toronto for allowing us to use the facilities. We acknowledge Dr. Derek Page for many useful discussions regarding paper testing.

Table 4. 1 **Properties of dextran used in this paper**

Code for dextran	**Mw of dextran 10^{-3}**	**Radius of gyration (Å)***	**Shear storage modulus (MPa)**
DEX77K	77	61.3	550
DEX167K	167	94.5	
DEX464K	464	138.4	
DEX2M	2000	268.3	600

* From reference 6.

Table 4. 2 Comparison of two adding modes. Dextran content in all cases was 25mg/g. CADEX4-3 and CADEX3-49 were wet-end added, where DEX464K and DEX2M were added with impregnation.

Polymer code	Density (kg/m^3)		Tensile index (Nm/g)		Increase in tensile strength %
	Untreated	Treated	Untreated	Treated	
DEX464K	515	484	20.7	22.6	8.9
DEX2M	515	500	20.7	27.4	32.5
CADEX4-3*	550	550	21.9	25.6	16.9
CADEX3-49**	550	550	21.9	29.5	34.8

* Cationic dextran with Mw 464K, wet-end added.

** Cationic dextran with Mw 2 million, wet-end added.

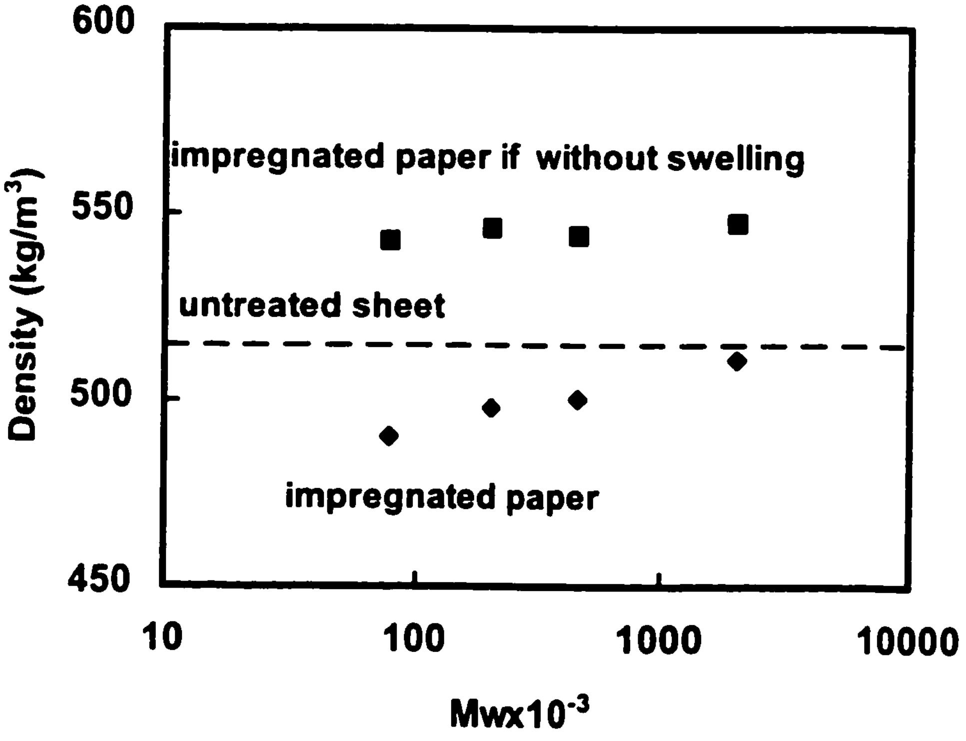

Figure 4. 1 Density of dextran impregnated paper as the function of Mw. The density of untreated paper was 515 kg/m^3.

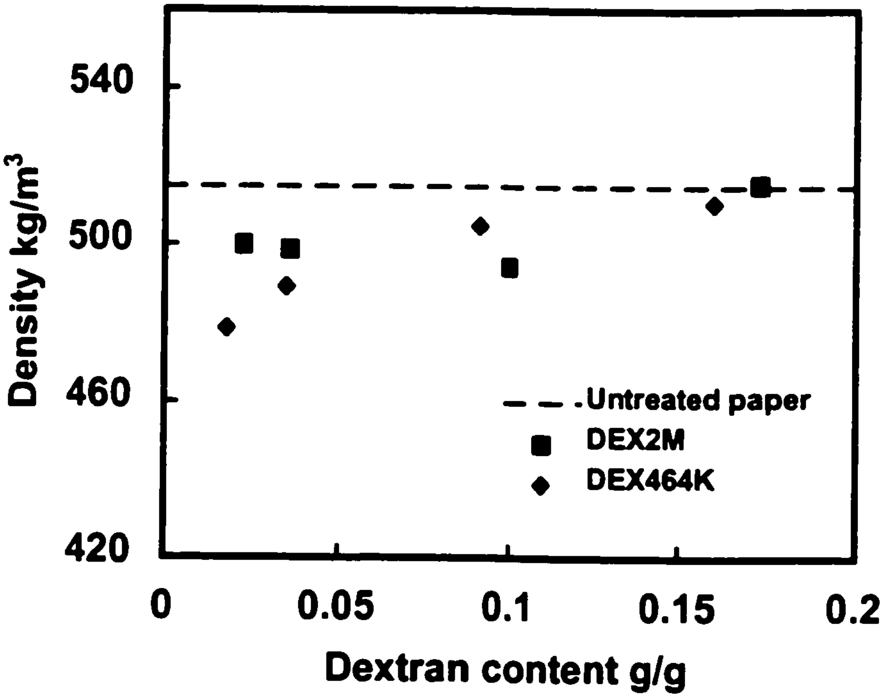

Figure 4. 2 Density of dextran impregnated paper at different dextran contents.

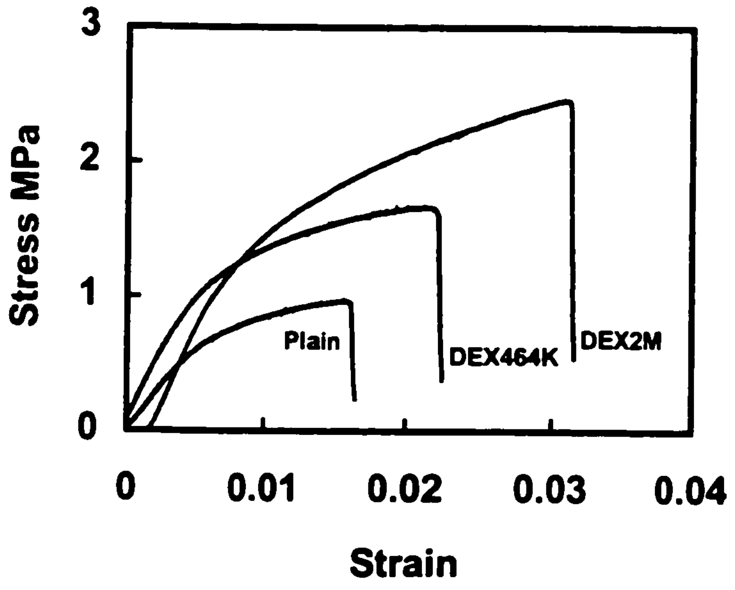

Figure 4. 3 Typical stress-strain curve for paper treated and untreated with dextran.

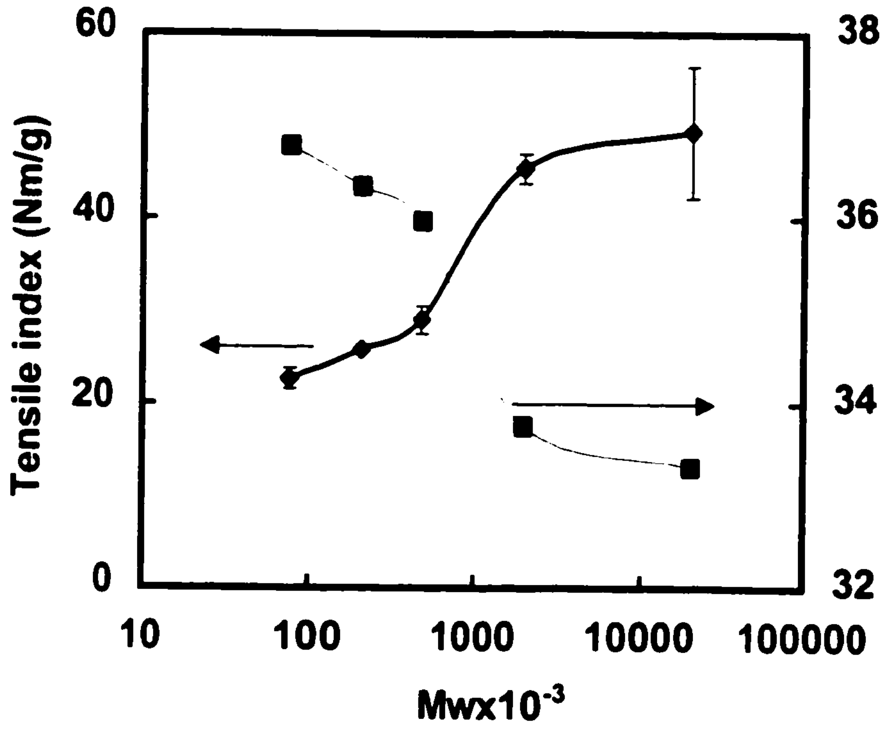

Figure 4. 4 Effect of Mw on the tensile index and light scattering coefficient (second y-axis). Dextran content was almost the same for all testing samples, 0.09 ± 0.01 g per gram of fiber. The tensile index of untreated paper was 20.7 Nm/g, and light scattering coefficient was 34.9 kg/m^2.

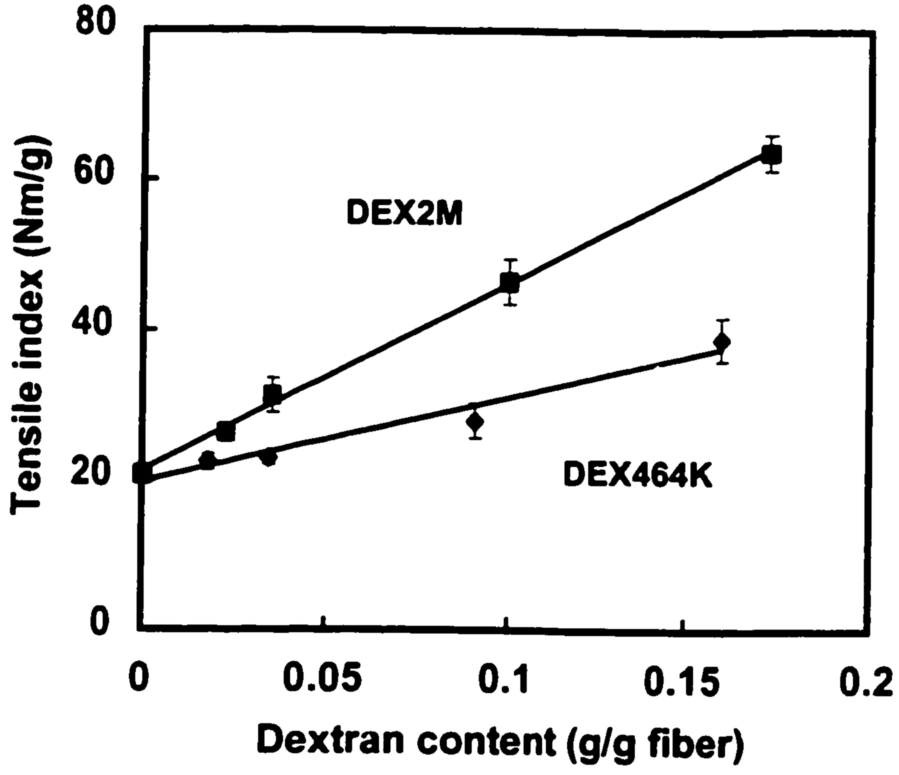

Figure 4. 5 Tensile index of impregnated paper with different dextran contents. The measured handsheets were impregnated with DEX464K and DEX2M.

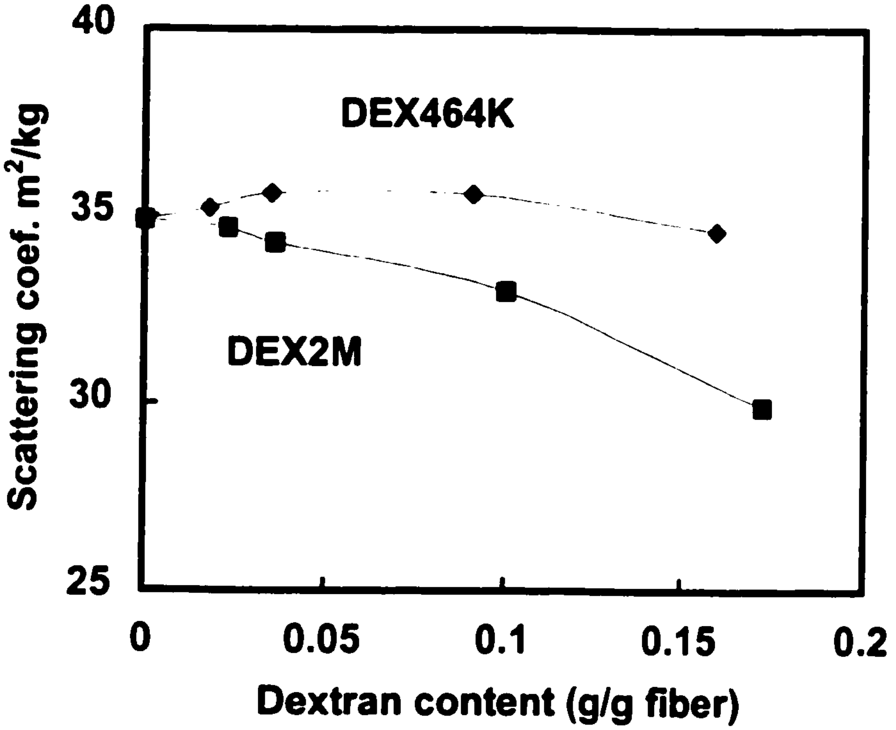

Figure 4. 6 Light scattering coefficient of impregnated paper with different dextran contents. Same sample as used in Figure 4. 5.

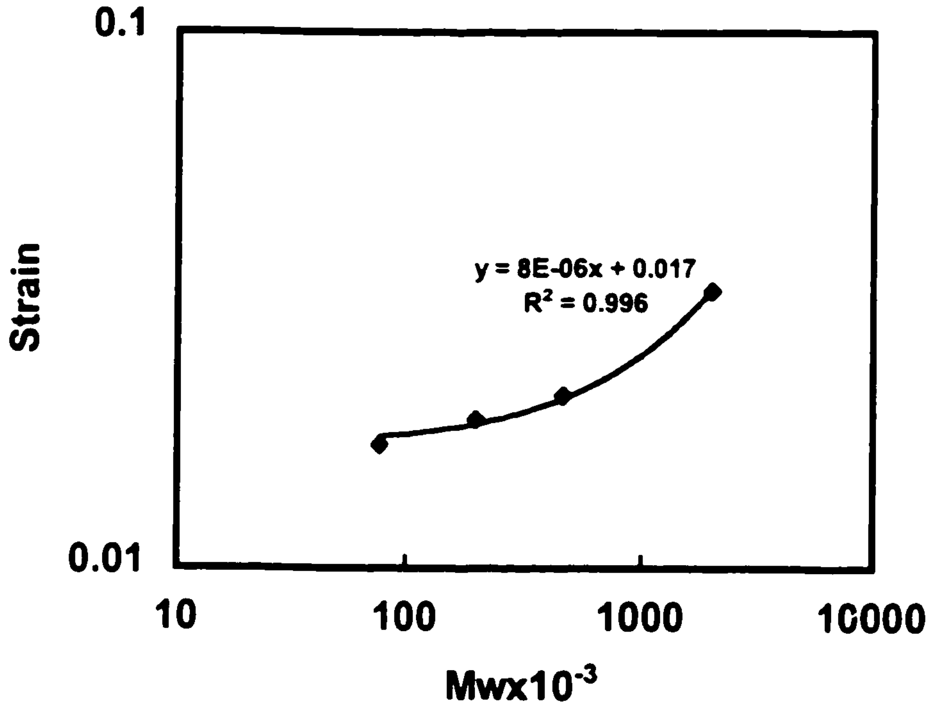

Figure 4. 7 Strain at breaking of impregnated paper with different molecular weight DEX, same sample as used in Figure 4. 4. The strain was linearly proportional to the molecular weight in logarithmic relation.

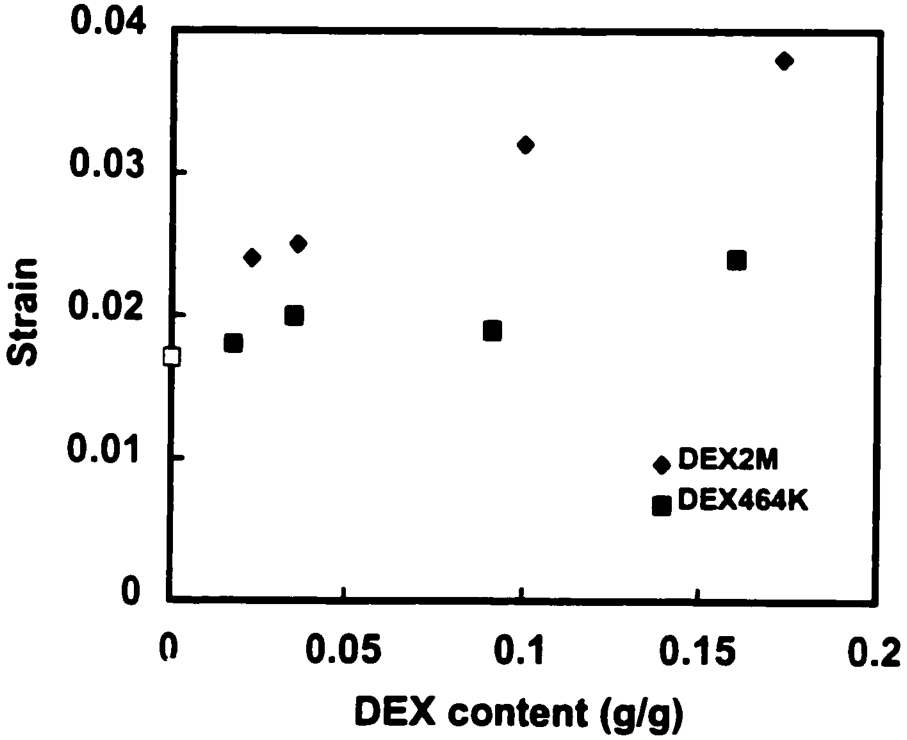

Figure 4. 8 Stain at breaking with different dextran content, same sample as in Figure 4. 5.

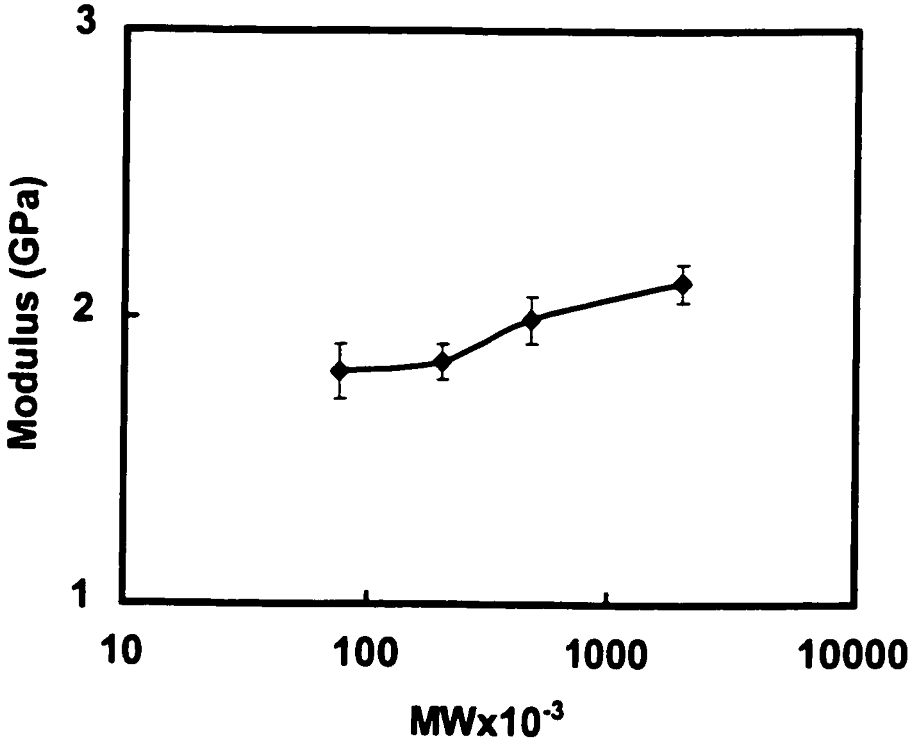

Figure 4. 9 Effect of Mw of dextran on the moduli of dextran impregnated paper. The moduli were calculated as the initial slope of stress-strain curve. Same sample as used in Figure 4. 4.

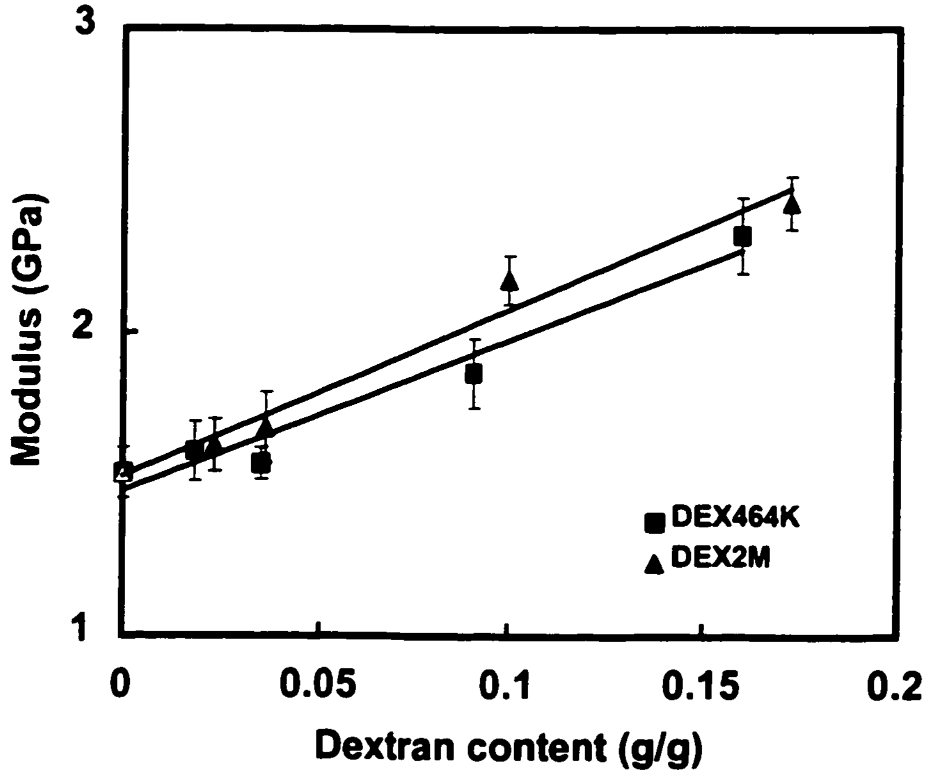

Figure 4. 10 Modulus of dextran impregnated paper at different dextran content. Same sample as used in Figure 4. 5.

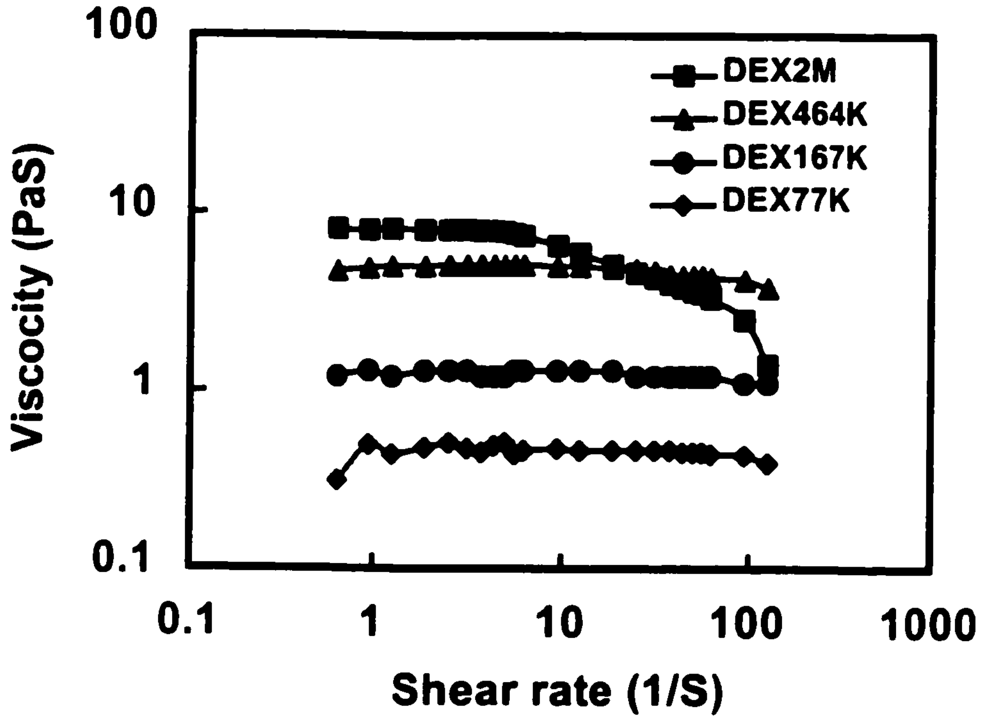

Figure 4. 11 Viscosity of DEX vs. Shear rate. Concentration of DEX is 40%. Measurement was conducted with BohLin Rheometer, shear rate sweep test. Torsion element was 10.592g cm, measuring system was C25.

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Chapter 5. The Effect Of Charge Density And Hydrophobic Modification On Paper Strength Enhancing Polymers

Abstract

Cationic dextrans with and without hydrophobic substituents were prepared and added to paper to give paper strength as functions of charge density and the degree of hydrophobic substitution. The adsorption behavior of these dextrans on fiber was investigated as the function of the charge density and the degree of hydrophobic substitution. It was found that the maximum adsorption of dextran on fiber increased with decreasing charge density. The strength enhancing effect of these dextrans on paper strength was evaluated with tensile strength and Scott bond strength. The charge densities within the investigated range, 0.16-0.49 meq/g, did not participate in the formation of fiber-fiber bonding. Hydrophobic dextran decreased the strength enhancing effect compared with dextran without hydrophobic modification. The surface energy of hydrophobically modified dextran was further correlated to the strength of fiber/fiber bonding, and a linear relationship was found between them.

Key words: Strength enhancing polymer, strength of paper, fiber-fiber bonding, tensile strength, Scott bond, cationic polymer, hydrophobic polymer, diffusion, charge density, adsorption, dextran.

5.1 Introduction

It is known that cationic polymers, such as cationic starch and polyacrylamides, used as the strength enhancing polymers in paper making. They generally increase the internal bond strength, tensile strength and burst strength. The strength enhancing effect is mainly attributed to the increase in interfiber bond strength[1,2,3]. Much work has been devoted to understanding the adsorption of cationic polymers on cellulose fiber. The influence of molecular weight and charge density, two essential parameters, has been thoroughly investigated[4,5,6,7,8]. Besides, electrolyte concentration and pH value of the fiber suspension, the types of pulp and kinetics of adsorption have been well studied[9,10,11,12,13,14].

However, there are very few systematic studies to elucidate the relationship of the structure and properties of strength enhancing polymers to their performance in strengthening the paper.

This paper is part of our extensive systematic study relating the polymer structure to its performance as a strength enhancing polymer. A polymer with well-defined chemical structure and properties was chosen as the model of strength enhancing polymers. Dextran was chosen for this purpose. The properties dextran used varied in molecular weight, charge density, hydrophobicity and compatibility with hydrophobic dextran, and the influence of these properties on the strength of paper was investigated. The present work addressed the influence of charge density and hydrophobic degree of dextran on the strength properties of paper.

Charge density is one of the important parameters for a cationic polymer. Park and Tanaka[15] worked on polyacrylamide with two different charge densities, and found that as a paper strength additive low charge density (0.6 meq/g) polyacrylamide was always more effective than high charge density (2.9 meq/g) one due to the existence of protruding hoops and tails of polymer segments. However, very little literature data is available to quantitatively describe the influence of charge density on the strength of paper.

The effect of hydrophobic components on the properties of paper is important for the reason of a practical concern in papermaking. It has been long known that the strength of paper is impaired in the presence of hydrophobic components, which are originated from wood resins, lignin or the external additives[16,17,18]. In a closed white water system, the concentration of these materials can be accumulated very high. Therefore, a fundamental research to relate the strength properties of paper to the hydrophobic degrees of a polymer is very essential.

In our previous work, cationic dextran (CADEX) was prepared for the adsorption of dextran on fiber surface. The effect of molecular weight of CADEX, from 77,000 to 2,000,000, on the strength of paper was investigated. It was found that the molecular weight of CADEX essentially did not effect the tensile strength of paper when fiber surface was saturated with CADEX. However, it affected the strength development of paper at the low level of adsorption (below 40 mg/g) due to the different fiber surface coverage with different molecular weight CADEX. The higher amount of maximum adsorption for low molecular weight CADEX than high molecular weight one was attributed to the penetration of small molecules inside the fiber wall. It was also proposed that the adsorbed CADEX enhanced the interfiber bonding through the formation of intermolecular bonds.

In the current work, CADEX with low charge densities from 0.16 to 0.49 meq/g were prepared. Hydrophobically modified cationic dextran with the similar charge density and different hydrophobic degrees was made by the reaction of CADEX with butyric or hexanoic acid. The effect of hydrophobic groups on the strength of paper was investigated. Furthermore, the surface energy of fiber was directly correlated to the strength of paper and the strength of interfiber bonding.

5.2 Experimental

5.2.1. Preparation of hydrophobically modified cationic charge dextran

Dextran from Sigma, with mass average molecular weight of 2,000,000 given by the supplier, was used as the starting material in this work. Cationic dextran (CADEX) was prepared by the reaction of dextran with 2,3-epoxypropyl-trimethylammonium chloride (ETAC) from Fluka. Details of this reaction were described elsewhere[19]. Charge density, defined as the mole of cationic charge per gram of dextran, was measured by polyelectrolytic titration with polyvinyl sulfate potassium.

Hydrophobically modified CADEX (C-CADEX) was prepared by the esterification reaction of CADEX with fatty acids, butyric acid (C4) or hexanoic acid (C6) (Aldrich). The reaction was performed in the mixture solvent of formamide and N,N-dimethylformamide (BDH). 1,3-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine (Aldrich) were used as a coupling agent and catalyst. The same chemistry was used as in our previous work[20]. The degree of hydrophobic substitution (DS), defined as the ratio of hydrophobically substituted hydroxyl groups to the total glucose units, was determined with ^1H NMR recorded by a Bruker AC 200 NMR spectrometer. The spectrum is shown in Figure 5. 1. Peaks centered at 4.8, 3.8,3.5, 3.4 ppm were due to anhydroglucose protons and the peak at 4.8 ppm was due to the anomeric proton on C1. After modification new peaks appeared at 2.3, 1.5 and 0.8 ppm for butyrate modified dextran, and the new peak at 3.0-3.1 ppm was assigned to the methyl groups on the quaternary nitrogen. The modified dextrans were stored at 5°C all the time before being used.

5.2.2. Adsorption isotherms and thickness of adsorption layer

Adsorption isotherms of CADEX and C-CADEX were determined with the 0.5% fiber suspension following the same procedure described elsewhere[19].

Silica microspheres bearing the surface charge of carboxylic group were used as the substrates for the measurement of adsorbed layer thickness. The diameter of the particle size was measured with dynamic light scattering. The difference between the radius of bare particles and that of polymer-coated particles was defined as the hydrodynamic layer thickness[19].

5.2.3. Handsheet preparation

Unbeaten, bleached kraft softwood pulp was from SCA research AB in Sundsvall, Sweden.

Handsheets for tensile test with basis weight of 65 g/m^2 were prepared with small handsheet former built up at SCA research AB in Sundsvall, Sweden. At least three handsheets were made for each modified dextran at one pressing pressure. Four levels of addition were chosen for each CADEX, covering from 20 mg/g to the saturated coverage of fiber surfaces. In order to compare the mechanical properties of the handsheets at the same sheet density, 550 g/m^3, all handsheets were prepared with two wet pressing pressures, 800 and 1600kPa. Details for handsheet making were described elsewhere[19].

Handsheets for Scott bond test with basis weight of 65 kg/m^2 were made with tap water using the British sheet machine following Tappi test method. Adsorption of cationic dextran on fiber was performed following the same procedures as used in the handsheet making for tensile test.

5.2.4. Mechanical properties of paper

Tensile strength was measured conforming to standard Scan P:67. Six tests were taken for each sample. The tests were run on horizontal tensile tester, model TH1 made by Lorentzen&Wettre. Huygen Internal Bond Tester was used to measure the Scott-bond strength, 10 measurements at least for each sample.

5.3. Results

A series of CADEX with different charge densities was prepared. CADEX3-49, with charge density of 0.284 meq/g, was used to prepare hydrophobically modified CADEX. Hydrophobic group was butyrate (C4) or hexanoate (C6). The charge densities and degree of hydrophobic substitution of modified dextran used in this work are summarized in Table 5. 1. Charge densities ranged from 0.161 to 0.488 meq/g. Hydrophobically modified CADEX had the similar charge density, 0.21 to 0.28 meq/g, since the same CADEX was taken as the parent dextran for the hydrophobic modification. The charge density of C6-CADEX3-83 was lower than the others probably due to the increase in the mass of repeating units of modified dextran. The degrees of substitution for C4 modified CADEX were 0.42 and 0.66, and it was 0.27 for C6 modified CADEX.

The data obtained from tensile test are summarized in Appendix 3.1, which contains tensile index, elastic modulus and tensile adsorption energy. The results of tensile index presented in the following graphs are based on the same density of handsheets, 550 kg/m^3, which was obtained by interpolating the tensile index data at two different densities.

5.3.1. The influence of charge density

The adsorption isotherms of CADEX are shown in Figure 5. 2. The general trend was that high charge density correlated with lower adsorption plateau. As the charge density increased to 0.488 meq/g, the adsorption of CADEX on fiber was very low, 5 mg/g.

The effect of charge density on tensile index is shown in Figure 5. 3. It has to be pointed out that the x-axis is the amount of dextran added, not the adsorbed. It was observed that there was an optimal additional level for each CADEX to reach its ultimate tensile index. For lower charged CADEX, this additional level was higher, and the ultimate tensile index obtained was higher too, while the ultimate tensile index of paper treated with highly charged CADEX was low and was obtained at low additional level. The ultimate tensile index for

CADEX3-74 (0.161 meq/g) was about 33 Nm/g, whereas it was about 24 Nm/g for CADEX4-7 (0.488 meq/g).

Figure 5. 4 shows the effect of the amount of adsorbed dextran on tensile index. This graph was converted from Figure 5. 3 by changing dextran added into dextran adsorbed on fiber based on the adsorption isotherm. It appeared that the data obtained from the paper treated with dextrans of different charge density lined up on one smooth curve. The tensile index increased at the beginning as the adsorbed dextran going up, then it leveled off at the amount of adsorption of about 25 mg/g. Further adsorbed dextran did not contribute any more to the development of tensile index.

The influence of charge density on the Scott bond strength is shown in Figure 5. 5. CADEX3-49, CADEX3-74 and CADEX3-86, with charge densities of 0.284, 0.161 and 0.377 respectively, were added at the same amount, but not resulted in the same amount of adsorption on fiber. It was found that Scott bond strength nearly kept constant, 46 J/m^2, when the adsorbed amount of CADEX was above 16 mg/g. The Scott bond strength of polymer-free paper was 29 J/m^2.

5.3.2. The influence of hydrophobic groups

Hydrophobic groups affected the adsorption on fiber differently depending on the substituents. As shown in Figure 5. 6, compared to CADEX3-49, which had no hydrophobic substituent, C4 substitution enhanced the adsorbed amount of

CADEX on fiber, whereas C6 slightly reduced it. The maximum adsorption for C4-CADEX3-76 and C6-CADEX3-83 was about 45 mg/g and 30 mg/g, respectively, while it was about 35 mg/g for CADEX3-49.

The adsorbed polymer layer thickness was measured because it can provide the information regarding the configurations of adsorbed polymer on a surface, which is important for understanding the molecular interaction at the interface[21]. The results of adsorbed layer thickness for CADEX and C-CADEX are listed in Table 5. 2. The thickness for CADEX with different charge densities was more or less the same, whereas the adsorbed layers of C-CADEX on silica microspheres were thinner, especially for C6 modified CADEX, only 6 nm.

The influence of hydrophobic degrees on tensile index is shown in Figure 5. 7. Paper treated with C-CADEX was weaker than the paper treated with CADEX. It was noted that the tensile index obtained from C-CADEX was even lower than that of polymer-free paper when the adsorption amount was low. However, as the amount of adsorption increased, C-CADEX turned to enhance the strength of paper. The strength enhancing effect was observed at the amount of adsorption of 17 mg/g for C4-CADEX3-62 (DS, 0.42) and C6-CADEX3-83 (DS, 0.27), while C4-CADEX3-76 (DS, 0.66) impaired the strength of paper until the amount of adsorption was over 40 mg/g.

Figure 5. 8 shows the influence of hydrophobic groups to the Scott bond strength. At the same amount of added C-CADEX, 20 mg/g, Scott bond strength

decreased as more hydroxyl groups substituted. The Scott bond strength obtained from C4-CADEX3-76 with DS of 0.66 was the same as that obtained from polymer-free paper. In this graph, DS of 0.45 was converted from C6-CADEX3-83 with the formula of (DS of C6 x 5)/3. The Scott bond strength was linearly correlated to the DS with C4.

5.4. Discussion

5.4.1. Influence of charge density

As shown in Figure 5. 2, charge density inversely affected the adsorption of DEX on fiber. The extreme case is the adsorption of CADEX4-7. This result agreed with the literature data on cationic polyacrylamide and starch[4,9,6,5,8]. It was found that the equilibrium adsorbed amount for polyacrylamide, molecular weight of 340,000, decreased from 50 mg/g to about 4 mg/g as the charge densities changed from 0.6 to 2.5 meq/g. It was proposed that polymers with high charge density had more extended conformation than that with low charge density, and a stronger electrostatic blocking effect existed between adsorbed polymer and the polymer in solution[14]. For cationic starch with degree of substitution of 0.015-0.050, it was found that the amount of adsorption was restricted by a constant amount of charge, 1.5 μeq starch/g[8]. Dextran used in this work had the charge density from 0.16-0.49 meq/g, which was equivalent to the degree of substitution of 0.026-0.08. It seemed that the amount of adsorbed

CADEX3-49 (0.284 meq/g) and CADEX3-86 (0.377 meq/g) kept a constant amount of charge around 10 μeq CADEX/g of fiber. However, it was not applied to CADEX3-3-74 (0.016 meq/g) and CADEX4-7 (0.488 meq/g).

As shown in Figure 5. 4, it appeared that, irrespective of the charge densities, an optimal adsorbed amount of CADEX existed for paper to reach the ultimate tensile index. Apparently charge density only effected the amount of maximum adsorption of CADEX on fiber which in turn affected the tensile strength, but did not directly effect the tensile strength of paper in the range investigated in this work. This mechanism is completely different from the interfiber ionic bond, which was proposed as the strength development with polyethylenimines[22]. The results from Scott bond (Figure 5. 5) also showed that the Scott bond strength kept constant for the paper treated with CADEX of different charge densities. Addition of CADEX no longer contributed to Scott bond strength when the adsorbed amount reached 20 mg/g.

5.4.2. Influence of hydrophobic substitution

The effect of hydrophobic substitution on the adsorption is shown in Figure 5. 6 The increase in the adsorption of C4-CADEX on fiber may imply the more compact molecular configuration. The thinner adsorption layer (Table 5. 2) also indicated the smaller hydrodynamic size of C4-CADEX compared to CADEX. Our previous work showed that there might be intramolecular association for C4-DEX because its specific viscosity was lower than that of DEX. In contrast to C4-DEX, C6-DEX displayed a bit of intermolecular association[20]. The thinner adsorbed layer of C-CADEX might be the indication of the strong intermolecular interaction and the interaction of polymer molecules with silica surface instead of with water.

Compared to the CADEX, introduction of hydrophobic groups hindered the interfiber bonding as shown in Figure 5. 7. At low amount of adsorption, tensile strength of C-CADEX treated paper was even lower than the polymer free paper. It has been long believed that interfiber hydrogen bonding is the primary source of fiber-fiber bonding in dry paper[23,24]. Therefore, the decrease in tensile strength is supposed to be natural as the results of reducing the sites of interfiber hydrogen bonding due to the replacement of hydroxyl groups with hydrophobic groups. Similar observation was made from the esterified fiber by Higgins and McKenzie [25]. Their work suggested that of the total hydroxyl groups in the cellulose fiber, about one of 10,000 might normally participate in interifber bonding. Deuterium exchange experiments showed that up to 2% hydroxyl groups became bonded during the papermaking process[26].

It is interesting to note that C-CADEX functions as a strength enhancing polymer when the amount of adsorption increases although the strength enhancing effect is not as strong as CADEX. Two points were emphasized here. First the strength enhancing performance of C-CADEX was poorer than CADEX due to the weakening of hydrogen bonding. Secondly, compared to polymer-free paper, paper was strengthened with C-CADEX despite of its hydrophobic properties. This might imply that as the more C-CADEX adsorbed on fiber, interfiber bonding was recovered by the means of the sufficient intermolecular diffusion of the adsorbed polymer layers. Although the intermolecular diffusion also happened to cellulose fiber, CADEX and C-CADEX were more effective for their water-soluble properties and loops and tails formed on fiber surface. As shown in the case of C4-CADEX3-62 and C4-CADEX3-76, the higher the DS of hydrophobic group, the more absorbed amount was required to get adequate hydrogen bonds to strengthen the paper. The tensile strength from C6-CADEX3-83 and C4-CADEX3-62 treated paper followed the similar trend as the function of the amount adsorbed, which indicated that C6 and C4 with the current DS affected the strength of paper equally. It makes sense if the DS of C6-CADEX3-83 is equivalent to the DS of C4-CADEX3-62. They were indeed close. The DS of C6-CADEX3-83 is equal to 0.45 when converted to the DS of C4 substituent, whereas, the DS of C4-CADEX3-62 was 0.42.

It has been identified that the formation of intermolecular entanglements through diffusion is the determining factor for the development of adhesive strength at the interface of polymers[27,28,29,30]. The diffusion theory has been applied to paper making process and used to explain the strength development of paper by McKenzie[31]. He proposed that the requirements for diffusion controlled adhesion were present under normal papermaking conditions. The evidence such as weak paper obtained from solvent exchange drying or freeze dry provided the proof that the development of the bonds was inhibited if the mobility of the elements within the bonded area was restricted at the fibrillar or molecular level. Direct evidence of diffusion between the interface of cellulose films was also found from the surface force measurement[32]. It was claimed that the water swollen cellulose layer has long charged cellulose chains extending about 100 nm from its surface. It was also found that the adhesion force developed upon drying was much larger as compared with the adhesion observed when the cellulose surfaces were brought into contact in dry air. This stronger adhesion force was attributed to the cellulose chain entanglement and the hydrogen bonding force.

The effect of molecular interdiffusion can be further illustrated if we compare the data obtained from McKenzie's work[25] to ours. Figure 5. 9 shows the effect of degree of butyrylation on the tensile index of paper. It has to be clear that the hydrophobic groups were introduced directly on cellulose fiber in McKenzie's work, while in our work it was first grafted onto cationic dextran, and then the hydrophobic dextran was adsorbed on fiber surfaces. It happened that the initial tensile index (DS=0) was similar for these two systems. It was noted that at the same DS, the tensile index obtained from our work was always higher than that obtained from McKenzie's. The lower tensile index obtained from hydrophobically modified fiber might be due to the insufficient molecular diffusion caused by the reduction in the affinity of butyrylated cellulose fiber to water; whereas in our work higher the tensile index was attributed to the better intermolecular diffusion of hydrophobic CADEX due to its water soluble properties.

5.4.3. Surface energy of strength enhancing polymer vs. bond strength of interfiber bonding

Surface energy is a measure of thermodynamic energy of adhesion. For the two identical surfaces, the relationship between the thermodynamic adhesion energy W and surface energy γ is $W = 2 \cdot \gamma$; for two different materials, the relation becomes $W = \gamma 1 + \gamma 2 - \gamma 12$, where $\gamma 1$ and $\gamma 2$ are the surface energy of the two materials, and $\gamma 12$ the interfacial energy. The thermodynamic work W differs remarkably from the apparent work in practice, Wapp, since the Wapp is the combination of the reversible work to create new surface and the irreversible dissipation that lost in deforming the materials surrounding the new surfaces. In general, the irreversible dissipation is much greater than thermodynamic work. However, a relation was suggested between W and dissipation, $Wapp = W \cdot P$, where P is a universal dissipation function. This relation suggests that although the significant difference exists between W and Wapp, thermodynamic work of adhesion plays an important role in determining the adhesion and fracture mechanics[33].

Despite the fact that the surface energy of cellulose fiber or paper has been given lots of attention[34,35,36,37], for the first time, the present work correlated the surface energy of fiber to the strength of interfiber bonding. The surface energy of hydrophobically modified dextran was calculated as the summation of the surface energy of the two components, dextran and propane, based on the fraction of surface area of each component that was calculated with the software Hyper Chem5. One repeating unit of C4 hydrophobically modified dextran with the DS of 1/3 was drawn and the surface area was calculated. The same procedure was followed for dextran. The surface area of the hydrophobic component was obtained by subtracting the surface area of dextran from the surface area of hydrophobically modified dextran. The calculated surface area of dextran and C4 hydrophobic component were 339.4 and 109.3 Å^2 respectively. The area fraction of each component was the ratio of the area of this component to the total area. DS of C6-CADEX3-83 was converted into the equivalent DS of C4, which was 0.45. The surface energy of dextran[38] was taken as 41 mJ/m^2, and surface energy of propane as 15 mJ/m^2, obtained by extrapolating literature data[39]. The detailed calculation was attached in the Appendix 5.2. The surface energy of C4-CADEX3-76 was obtained from contact angle measurement[*] with diiodomethane. The measured surface energy was 38.1 mJ/m^2, which was agreeable to the calculated one, 38.0 mJ/m. In Figure 5. 10 the tensile index of handsheets was plotted against the surface energy of modified dextran calculated at different

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[*] Done by Boxin Zhao in this laboratory.

degrees of substitution. The tensile index used in the graph was the one that was obtained when fiber surface was fully covered with C-CADEX, which corresponding to the plateau value in Figure 5. 7. Bond strength was calculated from the Page equation, which is $B = \frac{1}{\left(\frac{1}{T} - \frac{9}{8 \cdot Z}\right)}$, where T is the breaking length of paper, Z is the zero-span tensile strength, which is 12 km for the fiber used in this work. It showed that both tensile strength and bond strength were linearly related to the surface energy of modified dextran. The similar relation was observed with Scott bond strength as well, which is shown in Figure 5. 11. It is not surprising that the measured bond energy is about a thousand times higher than the surface energy since the dissipation loss and dynamic energy are involved in the practical measurements. What is more important is that thermodynamic energy can reflect the interfiber bond energy to some extent.

5.5. Conclusions

1. Charge density effected the tensile strength by changing the amount of adsorbed dextran on fiber. Nevertheless, it did not directly influence the strength development of interfiber bonding.
2. In agreement with the literature data, the adsorbed amount of dextran on fiber increased as the charge density decreased.
3. The ability of dextran to strengthen paper decreased with the increasing hydrophobic substitution.
4. The interfiber bond strength of paper treated with C4-CADEX was linearly related to the surface energy of C4-CADEX.

5.6. Acknowledges

The authors thank SCA Research, Sundsvall Sweden for financial support. We also thank Raiso Chemicals Canada for providing the Scott bond tester. We acknowledge Dr. Derek Page for many useful discussions regarding paper testing.

Table 5. 1 Characteristics of DEX used in this work.

Code of dextran*	Hydrophobic substituent	Charge density (meq/g)	DS
CADEX3-49	No	0.284	0
CADEX4-7	No	0.488	0
CADEX3-86	No	0.377	0
CADEX3-74	No	0.161	0
C4-CADEX3-62	C4 fatty acid	0.284	0.42
C4-CADEX3-76	C4 fatty acid	0.274	0.66
C6-CADEX3-83	C6 fatty acid	0.214	0.27

*** Mw of parent dextran is 2 million.**

Table 5. 2 **Effect of charge and hydrophobic group on the adsorbed layer thickness on silica particles. The layer thickness was measured with DLS. The concentration of particle dispersion was 0.05%. 3% dextran solution was dropped in and measurement was conducted after 10 minutes**

Code of dextran*	**Charge density (meq/g)**	**DS**	**Adsorption layer thickness on silica particle (nm)**
CADEX3-49	0.284	0	23.5
CADEX3-86	0.377	0	28.5
CADEX3-74	0.161	0	31
C4-CADEX3-62	0.284	0.42	20.5
C4-CADEX3-76	0.274	0.66	16
C6-CADEX3-83	0.214	0.27	6

*** Mw of parent dextran is 2 million.**

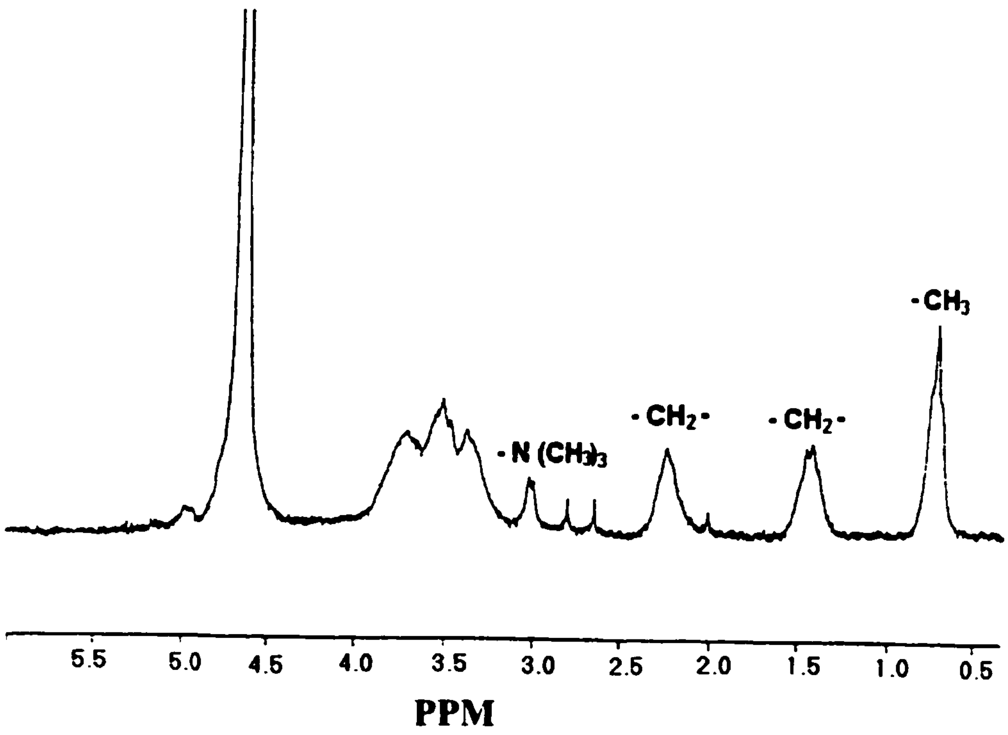

Figure 5. 1 H^1-NMR spectra of cationic charged hydrophobic dextran dissolved in D_2O.

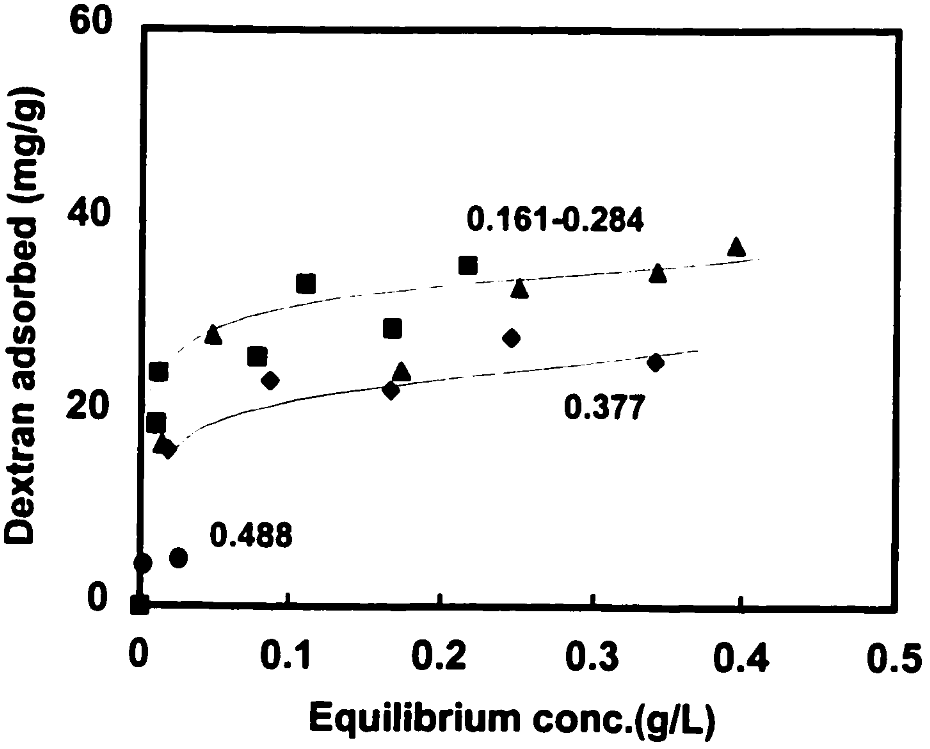

Figure 5. 2 Adsorption isotherm of dextran with different charge density on fiber.

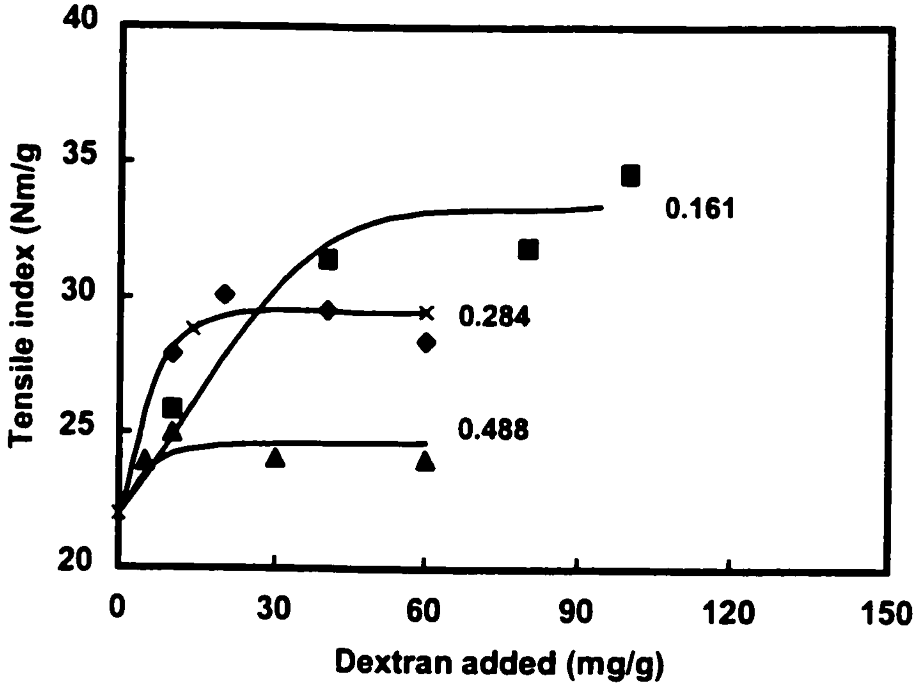

Figure 5. 3 Effect of amount of dextran added on the tensile index. Figures in the graph indicate the values of charge densities of CADEX.

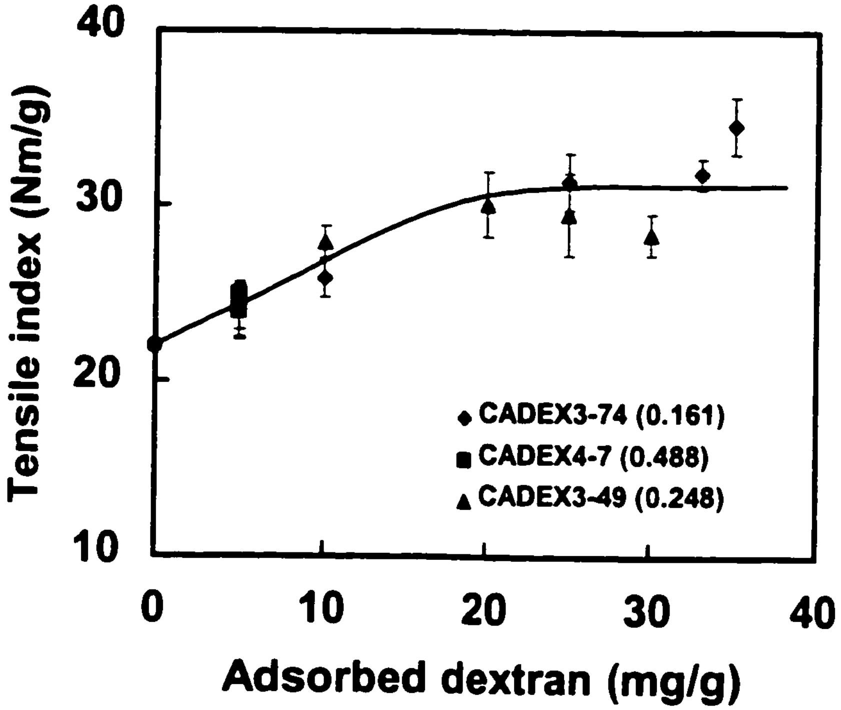

Figure 5. 4 Effect of the charge density on the tensile index of paper. The data were obtained from the paper treated with CADEX of different charge densities. Charge density effected tensile strength by changing the amount of dextran adsorbed on fiber.

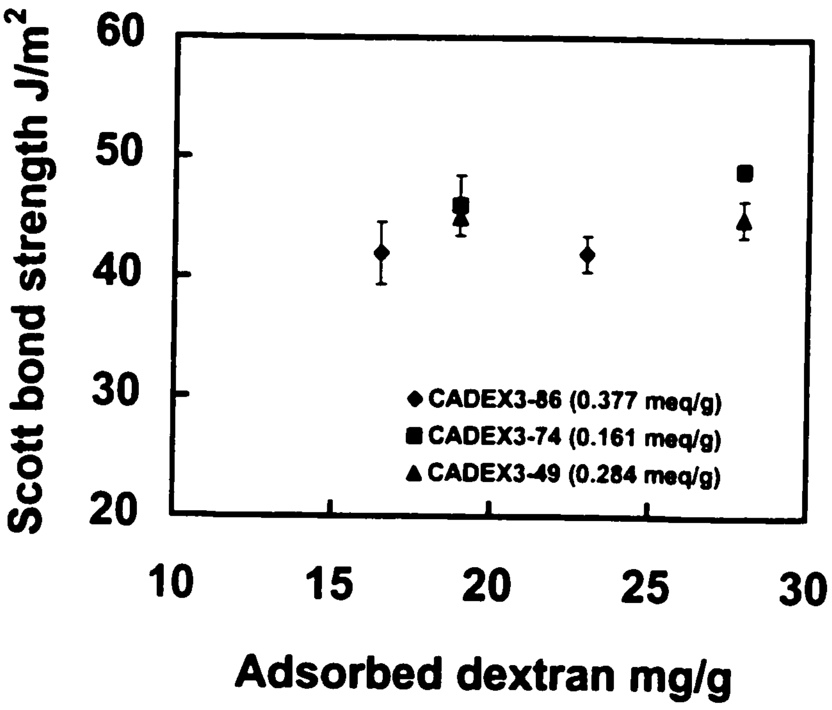

Figure 5. 5 Effect of the charge density on Scott bond strength. The data were obtained from the paper treated with CADEX of different charge densities.

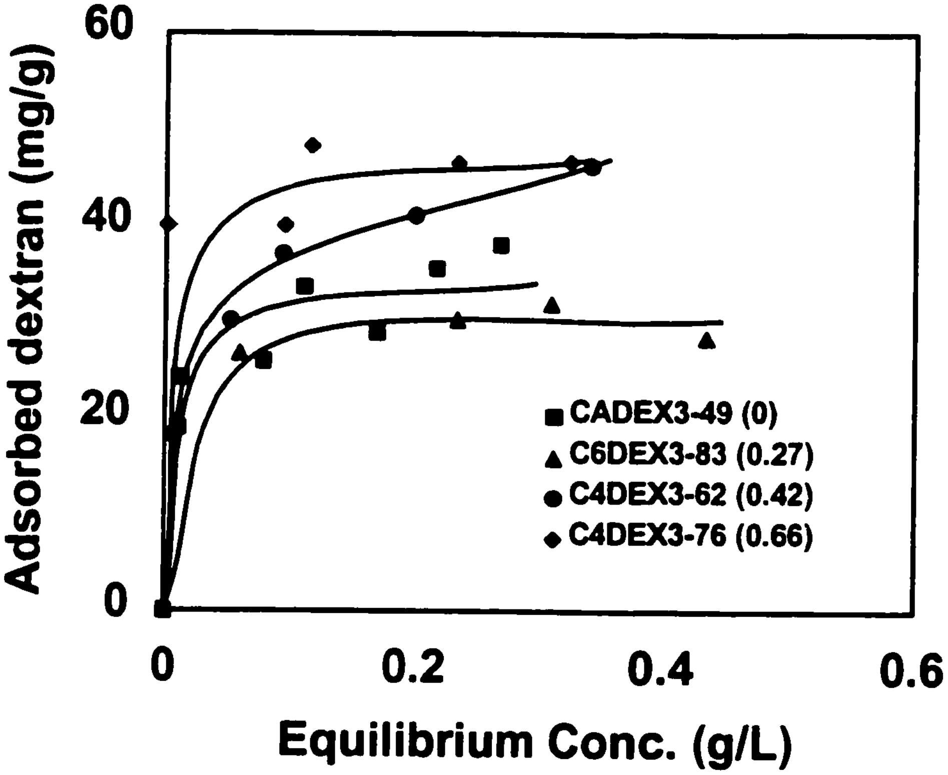

Figure 5. 6 **Adsorption isotherm of CADEX with the different DS of hydrophobic substitution.**

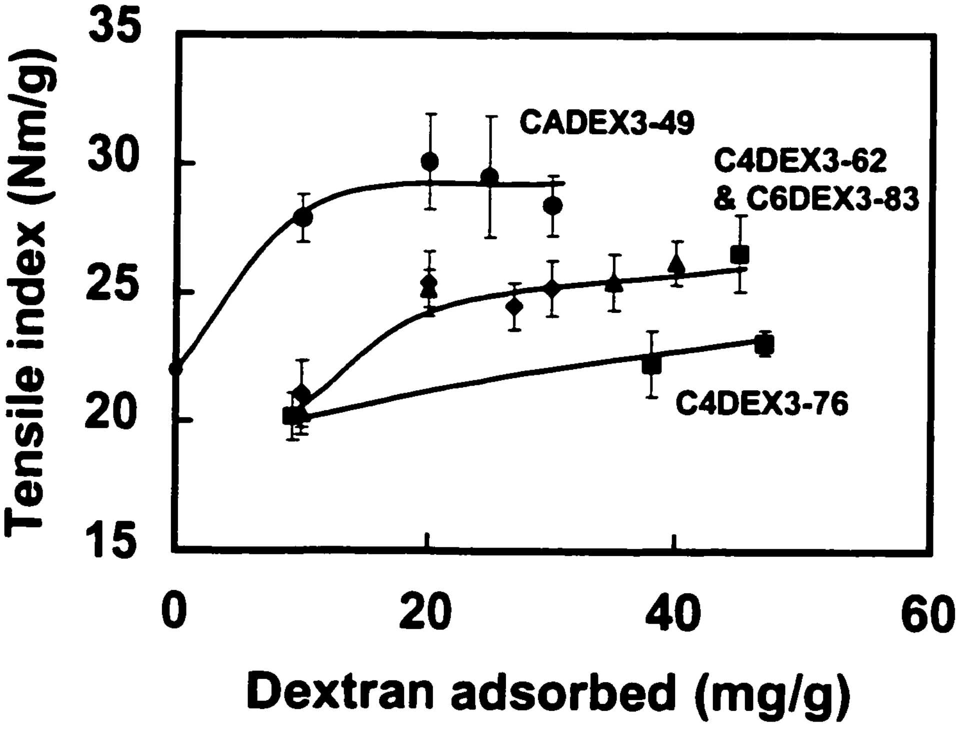

Figure 5. 7 Effect of the DS of C-CADEX on the tensile index of paper.

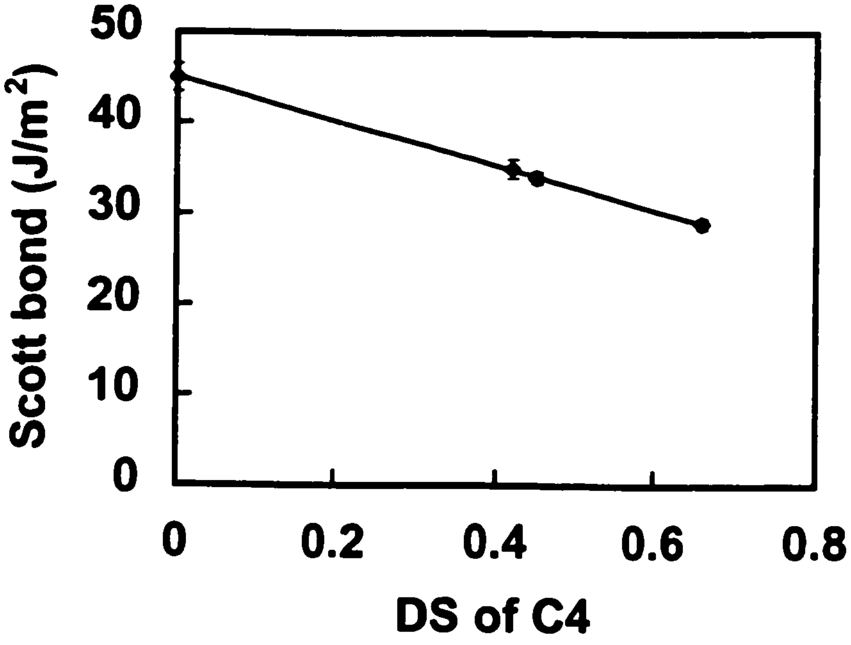

Figure 5. 8 Effect of the DS on Scott bond strength. The amount of dextran added was 20 mg/g. Scott bond linearly decreases with the DS of C4 increases. DS 0.45 was the equivalent DS of C4 converted from the DS of C6-CADEX.

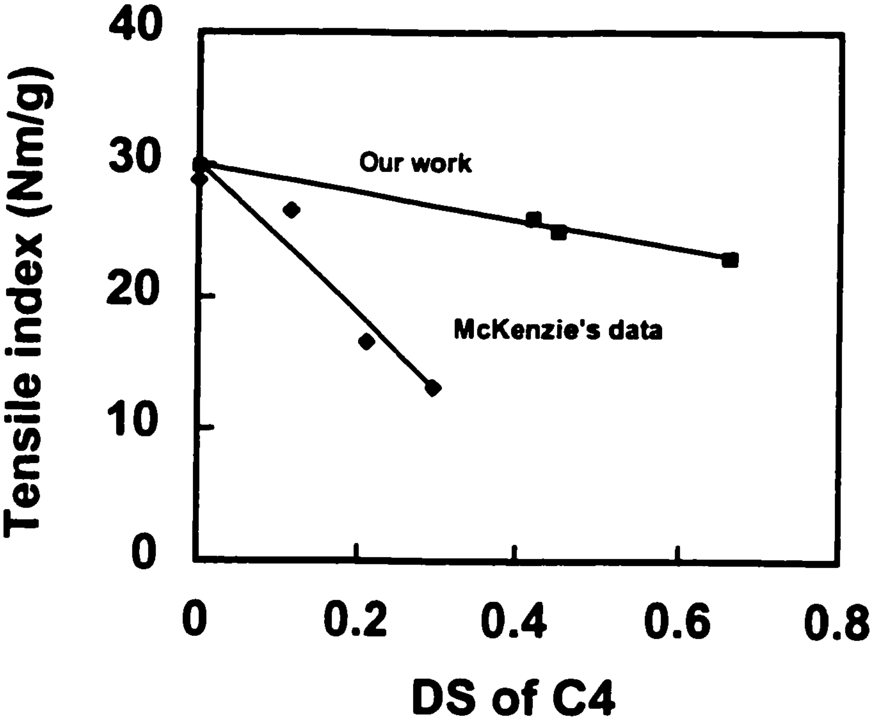

Figure 5. 9 Comparison of the McKenzie's data to the current work.

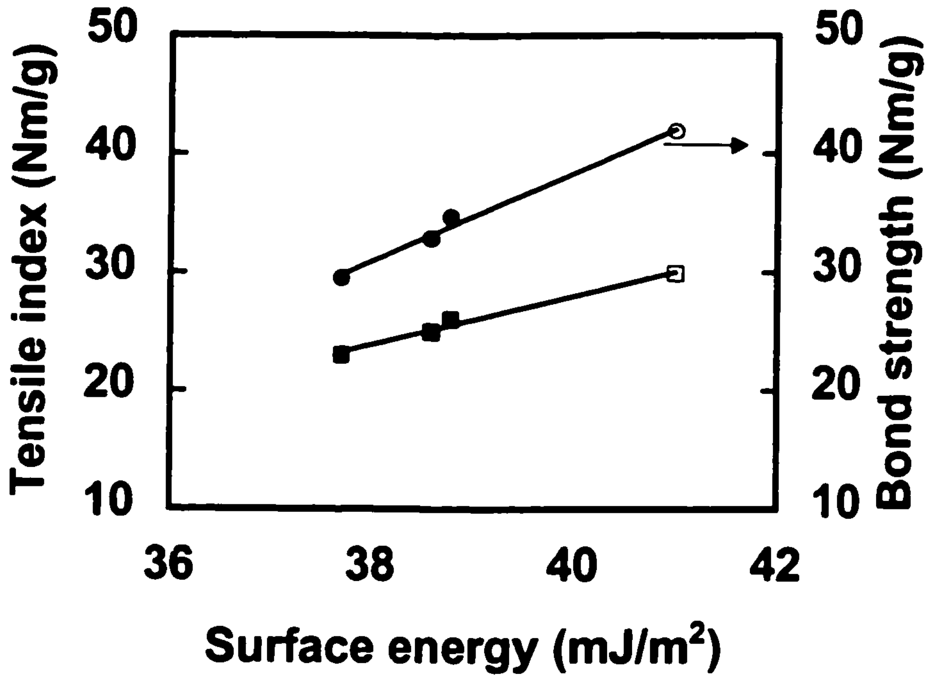

Figure 5. 10 The relationship of tensile index and bond strength of paper as the function of surface energy of CADEX. The tensile index was the one that was obtained when fiber surface was fully covered with C-CADEX. Detailed calculation on the surface energy is in Appendix-II. The opened symbols indicate the CADEX with DS 0.

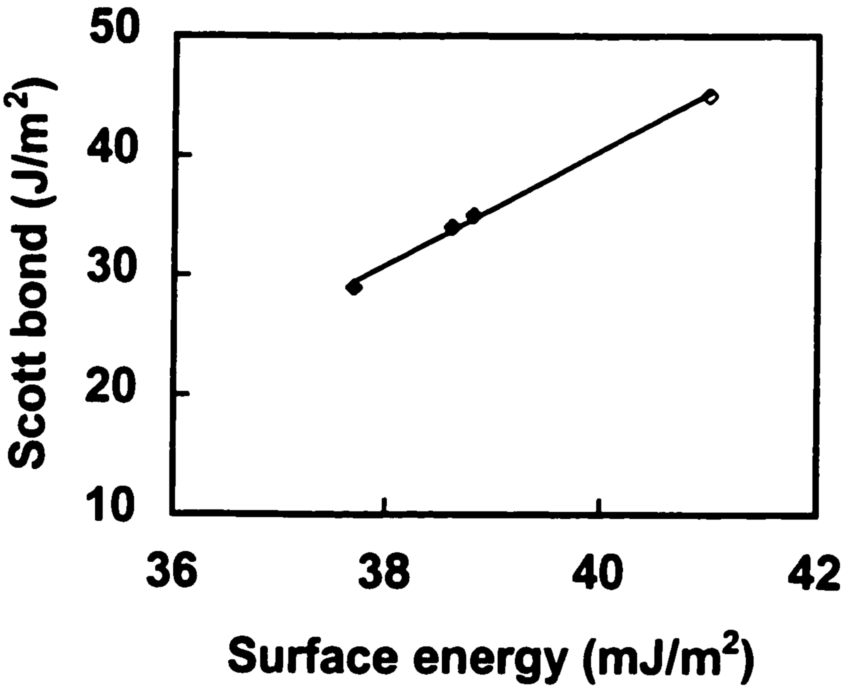

Figure 5. 11 The relationship of Scott bond strength of paper as the function of surface energy of CADEX. The opened symbol is for CADEX with DS 0. The Scott bond strength was the same as used in Figure 5. 8.

Appendix 5.1 The effect of charge density and hydrophobic groups of CADEX on the mechanical properties of handsheets

CADEX3-49 (CD 0.284)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10*	20*	25	30	10	20	25	30
Density (kg/m^3)	588	561	513	526	584	572	596	594
Scattering coeff. (m^2/kg)	32.49	31.91	34.38	32.64	31.45	31.04	30.07	30.21
Tensile index (Nm/g)	27.9	30.2	26.1	25.9	29.0	30.3	33.8	33.0
E-modulus (GPa)	2.14	2.15	1.86	1.88	2.24	2.26	2.34	2.32
TAE (J/m^2)	33.5	30.4	26.3	26.2	32.2	26.8	46.4	46.3

*** The wet pressing pressure was 1200 kPa.**

CADEX4-7 (CD 0.488)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	4.5	5	5	5	4.5	5	5	5
Density (kg/m^3)	517	517	513	519	591	598	571	581
Tensile index (Nm/g)	20.9	22.4	21.2	21.3	27.7	28.8	25.7	26.8
E-modulus (GPa)	1.62	1.68	1.59	1.65	2.26	2.31	2.13	2.16
TAE (J/m^2)	21.2	23.8	22.4	20.6	34.2	41.5	28.6	37.7

CADEX3-74 (CD 0.161)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10	25	30	34	10	25	30	34
Density (kg/m^3)	528	546	554	548	616	606	611	609
Tensile index (Nm/g)	24.1	30.9	32.3	34.4	31.0	38.5	38.4	41.0
E-modulus (GPa)	1.78	2.15	2.20	2.23	2.51	2.67	2.70	2.71
TAE (J/m^2)	30.2	45.1	48.8	57.4	43.2	65.5	64.2	73.9

C4-CADEX3-62 (DS 0.42)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10	19	35	40	10	19	35	40
Density (kg/m^3)	538	509	510	523	596	581	596	570
Tensile index (Nm/g)	19.2	20.9	22.0	22.7	24.7	28.4	29.4	28.8
E-modulus (GPa)	1.65	1.57	1.57	1.67	2.15	2.18	2.17	2.07
TAE (J/m^2)	17.7	20.9	24.9	26.2	27.3	39.1	43.7	36.2

C4-CADEX3-76 (DS 0.66)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10	38	44	46	10	38	44	46
Density (kg/m^3)	508	511	498	518	599	600	559	582
Tensile index (Nm/g)	17.7	19.4	21.2	20.4	23.1	26.0	27.5	25.8
E-modulus (GPa)	1.42	1.36	1.47	1.55	2.05	2.14	2.05	2.06
TAE (J/m^2)	15.4	20.8	24.7	19.8	24.2	31.5	34.0	29.5

C6-CADEX3-83 (DS 0.27)

Pressing pressures (kPa)	800				1600			
Adsorbed amount (mg/g)	10	19	27	30	10	19	27	30
Density (kg/m^3)	525	533	517	530	593	609	614	616
Tensile index (Nm/g)	17.8	24.2	21.0	22.9	26.7	29.5	31.3	32.8
E-modulus (GPa)	1.46	1.75	1.53	1.73	2.29	2.25	2.39	2.62
TAE (J/m^2)	16.1	31.4	25.5	28.3	32.6	45.1	46.2	47.2

Appendix 5.2 Calculation of surface energy of C4 hydrophobically modified dextran

Assumptions: The surface energy of hydrophobically modified dextran is the summation of the surface energy of the two components, dextran and propane based on the fraction of surface area of each component.

DS– is the degree of substitution of C4
S – is the surface area of dextran calculated with software Hyper Chem5
s – is the surface area of propane
γs – is the surace energy of dextran
γl – is the surface energy of propane

$$mJ := 10^{-3}J$$

$$DS := \begin{pmatrix} 0 \\ 0.42 \\ 0.45 \\ 0.66 \end{pmatrix} \qquad S := 339.38A^2 \qquad s := 109.26A^2$$

$$\gamma s := 41\frac{mJ}{m^2} \qquad \gamma l := 15.02\frac{mJ}{m^2}$$

$$f := \frac{S}{S + DS \cdot s}$$ Area fraction of dextran

$$\gamma := \gamma l \cdot (1 - f) + \gamma s \cdot f$$ **Surface energy of C4 hydrophobically modified dextran**

$$\gamma = \begin{pmatrix} 41 \\ 37.906 \\ 37.712 \\ 36.447 \end{pmatrix} \frac{1}{m^2} mJ$$

5.7. References

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Chapter 6. The Role Of Surface Polymer Compatibility In The Formation Of Fiber/Fiber Bonds In Paper

Abstract

For any polymer materials, the essential concern about the adhesion formed through the diffusion of surface polymers is whether they are compatible. Strong interfacial adhesion can only derive from the compatible surface polymers. This work was attempted to provide the direct evidence of the effect of polymer compatibility on fiber/fiber bond strength of paper. The question answered in this chapter is how the incompatible polymers on fiber surfaces will affect the strength of fiber/fiber bonding. An incompatible polymer pair, dextran and hydrophobic dextran, was identified from our earlier work. Handsheets were prepared from dextran coated fiber, hydrophobic dextran coated fiber and mixtures of these two. Tensile strength of the handsheets was measured and the fiber/fiber bond strength, calculated with Page equation, was decomposed to yield the strength of each type bond. The results indicated that among three types of bonding, dextran/dextran, hydrophobic dextran/hydrophobic dextran and hydrophobic dextran/dextran, the bond strength of hydrophobic dextran/dextran was the weakest. Finally, the mechanism for the development of fiber-fiber bonding between the incompatible polymer was prepared.

Key words: strength enhancing polymer, strength of paper, fiber-fiber bonding, compatibility, diffusion, surface properties, tensile strength, Page equation, dextran, hydrophobi polymer

6.1 Introduction

Paper is the network of fiber bonded together by the force of cohesion of fiber surfaces. The nature of the forces has been the core to understand the strength development of a paper sheet. Among many theoretically possible forces[1], there is a general agreement that hydrogen bond is the primary source of interfiber bond strength in a network of cellulose fiber.

A further question about interfiber bonding is how these fibers can get intimate contact to form the molecular level bonds. It has been clear that the surface tension of water plays an important role to pull fiber together during the water removing. While many experimental evidences from the earlier studies[2,3,4] supported the theory, it was also found that strong paper could be obtained from low surface tension solvents, such as acetone, when fiber surface was modified with acetylation[5,6].

The concepts of polymer compatibility, mixing and inter-diffusion have been well developed in the disciplines of polymer solution thermodynamics and in polymer blending. Proposed by Voyutskii[7] early in 1963, the diffusion theory in the adhesion of polymer states that the intrinsic adhesion of high polymers to themselves (autohesion), and to each other, is due to mutual diffusion of polymer molecules across the interface. The occurrence of this process requires that the macromolecules or chain segments of the polymers (adhesive and substrate) possess sufficient mobility and are mutually soluble.

McKenzie applied this theory to the strength development of fiber-fiber bonding. Fiber surface is a water swollen polymer layer that is featured with molecular chains extended into the water and negative charge groups[8,9], as shown schematically in Figure 6. 1. The water swollen polymer layers either originate from wood fiber itself, such as water swollen carbohydrates, lignin, and some charge groups from pulping process, or are introduced by adding functional additives during papermaking, such as strength enhancing polymers, retention aids and sizing agents. These polymers can remain and be carried over the whole process of paper making in the closed water system[10,11,12]. Diffusion theory of fiber-fiber bonding addressed the importance of mobile molecular segments on the fiber surface, and the intermingling and rearrangement of them within the bonded region. McKenzie proposed that the requirements for diffusion controlled adhesion were present under normal papermaking conditions. The evidence such as weak paper obtained from solvent exchange drying or freeze dry provided the proof that the development of the bonds was inhibited if the mobility of the elements within the bonded area was restricted at the fibrillar or molecular level[13].

A fundamental question which should be addressed about any molecular inter-diffusion is whether the components are miscible or not. The adhesion between the phases is believed to play an important role in determining mechanical behavior of these mixtures. For incompatible polymers, the adhesion is not developed across the phases, and as a result, the mechanical stress in one phase cannot be efficiently transferred to the other phase, which may lead to extremely poor mechanical properties[14]. For those situations where it does not exist naturally for lack of chemical affinity, a large body of technology has been developed to reduce it in polymer science.

Although the compatibility of the polymers that exist in papermaking is unknown, it must be remembered that the vast majority of randomly selected polymer pairs are not miscible. One of considerations about the mixture polymers is the effect of their compatibility on fiber-fiber bonding since only compatible polymers will give strong adhesion between two phases. Although this is an important concept in the strength development of interfacial adhesion in polymers, there is no fundamental research done in this area in paper science. The current work is aimed at understanding the effect of polymer compatibility on the strength of fiber-fiber bonding in paper from the viewpoint of the theories developed in polymer science. The hypothesis is that paper made from fibers that bear incompatible polymers is weaker than that made from fiber coated with single type of polymer.

This work is part of our systematic study on the linkage of the structure of strength enhancing polymers and their performance in strengthening paper. In our previous work, dextran was chosen as the model of surface polymer on fiber due to its well-defined chemical structure and water soluble properties. Cationic dextran was prepared for the purpose of adsorption on fiber. The effect of molecular weight, charge density, hydrophobicity of the cationic dextran on the strength of paper has been investigated. As to the influence of hydrophobic groups, it was found that hydrophobic dextran strengthened paper although the strengthening effect was reduced in comparison with that of dextran. It was proposed that the strength enhancement of hydrophobic dextran was due to the more efficient intermolecular bonding of this polymer than cellulose molecules in water.

In the following work, the incompatible polymer pairs were defined and applied to fiber network at different mixing ratios. Tensile strength of paper was measured and the strength of fiber-fiber bonds was calculated with Page equation. The bond strength between single type of fiber-fiber bonding was further calculated with the model developed in this work, and the mechanism for the development of interfiber bonds was discussed.

6.2 Experimental approach

6.2.1 Incompatible polymer pair

The incompatible polymer pair used in this work is dextran and hydrophobically modified dextran with the molecular weight of 2,000,000. Hydrophobically modified dextran was prepared from the condensation reaction of dextran with straight chain saturated C4 and C6 fatty acid[15]. Degree of hydrophobic substitution (DS), defined as the ratio of hydrophobically substituted hydroxyl groups to the total glucose units, was determined with ^1H NMR recorded by a Bruker AC 200 NMR spectrometer. The incompatibility of these two polymers was demonstrated in our previous work with the phase behavior of the mixture aqueous solutions of these two polymers. Phase diagrams were measured as a function of DS, hydrophobic chain length and molecular weight. Figure 6. 2 shows the phase boundary lines of DEX/C-DEX/H_2O system with different hydrophobic chain length; the DS of C4-DEX is 0.37 while it is 0.23 for C6-DEX. Region I indicates the single phase region, and region II the biphase region where the phase separation occurs.

Both dextran and hydrophobically modified dextran used in this work was cationically charged for their adsorption on fibers. Details for making cationic charge dextran (CADEX) and cationic charged hydrophobic dextran (C-CADEX) have been described elsewhere[16]. Charge densities of the cationic dextran used in this work, defined as the mole of cationic charge per gram of dextran, were close, from 0.21 to 0.28 meq/g.

Table 6. 1 lists the relevant properties of all dextrans used in this work. Four types of dextrans used in this work were CADEX3-49, C4-CADEX3-62, C4-CADEX3-76 and C6-CADEX3-83. Three pairs of incompatible polymers employed were CADEX3-49/C4-CADEX3-62, CADEX3-49/C4-CADEX3-76,

and CADEX3-49/C6-CADEX3-83. The DS of hydrophobic substitution for C4-CADEX3-62, C4-CADEX3-76 and C6-CADEX3-83 were 0.42, 0.66 and 0.27 respectively. The degrees of hydrophobic substitution of these polymers were higher than those used in our previous work for the consideration of the increased affinity of polymers for water due to their cationic charges. No phase diagram was prepared for the incompatible pairs used in the current work, however, the incompatibility of them was confirmed with the phase separation observed from the their aqueous mixture solution. The picture shown in Figure 6. 3 is the biphase formed from 10% aqueous solution of CADEX3-49 and C4-CADEX3-76. The similar phase behavior of uncharged dextran was proposed to the charged dextran for that it was reported that the general features of the phase diagram for these two polymers were similar to those of the uncharged polymers[17].

6.2.2 Handsheet preparation and tensile strength measurement

It is important in this work that the initial interfiber bond strength is low so that the effect of polymers on the interfiber bonding can be optimized. For this purpose unbeaten, bleached softwood kraft pulp with zero-span strength of 12 km was used for making handsheets. The pulp fiber was treated with CADEX and C-CADEX separately following the same procedure described elsewhere[18]. Corresponding to the amount of saturated adsorption on fiber[19], the additional amount for all the dextrans was 40 mg/g, except for C4-CADEX3-76, which was 60 mg/g. Handsheets were made from each single type of fiber and the mixture of fiber treated with CADEX and C-CADEX at the different mixing ratio. The mixing ratios were 0:1, 1:2, 1:1, 2:1, and 1:0 based on the weight of dextran fiber to hydrophobic dextran fiber. A small handsheet former build up at SCA research AB was used and the standard SCAN M5:76 was followed. Handsheets were made at two different pressing pressures and the tensile index at the sheet density of 550 kg/m^3, obtained by interpolating the tensile indices at the two densities, was used as the measured results in this paper. Tensile strength test conformed standard Scan P:67.

6.3 Theoretical consideration

6.3.1 Tensile strength and Page equation

Tensile strength test, measuring the breaking force of a paper strip when the fixed elongation rate is applied to the strip, was chosen as the measure for the fiber-fiber bond strength in the current work. It has been well known that tensile strength derives from the tensile strength of individual fibers and the strength of the bonds between the fibers. Many attempts have been made to develop the algebraic expressions for the tensile strength of paper in terms of its structure. A recent review paper by Jayaraman and Kortschot provided comprehensive and critical discussion of all the important closed-form network models for the tensile strength of paper[20].

While all the models consider a simplified microstructure and the idealized fiber and bond properties, which is the major limitations of the network model, the Page equation is ideal as a simple design tool to relate sheet strength to a variety of sheet structural parameters.

The Page equation is developed on a semi-empirical basis. It rationally correlates the tensile strength in terms of the sum of two components: intrinsic fiber strength and a cohesion factor as shown in the following equation.

$$\frac{1}{T}=\frac{1}{F}+\frac{1}{B} \qquad (1)$$

where T is the tensile strength, the first term of the right-hand side is an index that describes only the resistance of fibers to breakage, and the second is an index that describes only the resistance of bonds to breakage. More specifically, it is related to fiber and sheet properties in the following form:

$$\frac{1}{T}=\frac{9}{8\cdot Z}+\frac{12A\rho g}{bPL(RBA)} \qquad (2)$$

where A, P and L are the fiber dimensions of cross-sectional area, perimeter and length, and b, RBA are bond strength per unit area and the relative bonded area[21].

The assumptions in this equation are that (a) fibers are straight and free from crimps and kinks; have a uniform elastic modulus along their lengths; and (b) the sheets have good formation[22]. Under these assumptions, using equation

(2) should be possible to calculate the fiber-fiber bond shear strength, b, if the tensile strength of the sheet and six other variables in the equation are measured. It is noted that Page equation can be only used to calculate the bond strength when the fibers in the fiber network are identical.

However, in practice paper is not always made from a single type of pulp. One of the common cases is the blending of mechanical and kraft pulp in papermaking. Mechanical pulp is widely used in printing paper due to its good printability and low raw material costs. In order to enhance the strength properties and runnability of the wet and dry paper web, chemical softwood pulp is added. It has been well known that the tensile strength of a mixture of different kinds of pulp is often lower than could be expected linearly from the tensile indices of the components[23,24]. In addition to some explanations that have been provided to this phenomenon in the literature[25,23], many researchers have developed theories and models to simulate the effect of mixture pulp on the tensile strength of paper[26,27,28].

In this work, we will deal the same type of fiber with different surface properties, which means that the fiber network is composed of the same fiber but with different types of fiber-fiber bonding. If the presence of the various polymers does not change elastic modulus of fiber and keeps sheet good formation, which is true under the present conditions, Page equation should be able to be applied to calculate the interfiber bond strength in this case. The problem is how to calculate the bond strength for each type of bonding.

6.3.2 Bond strength of the mixture fiber network

Let us start with equation (2). Tensile strength on the left hand side can be measured. On the right hand side, zero-span tensile strength is also measurable. Since the addition of polymers does not affect the fiber strength itself, we can safely use the zero-span strength of untreated fiber as the zero-span strength of the treated fiber in the equation. The second term consists many parameters, among which A, ρ, P, L are constant because they are the intrinsic properties of fiber which are not affected by the addition of polymers. Now the only variable left is the bond strength, which is the product of b, the shear bond strength per unit bonded area, and RBA, the relative bonded area. Therefore, we can just apply the simple form of equation (1) to calculate the second term of the right-hand side, the bond strength index, which is referred to as bond strength in this paper,

$$B = \frac{1}{\frac{1}{T} - \frac{9}{8Z}} \qquad (3)$$

However, the bond strength calculated from the above equation is the apparent bond strength of the mixture types of bonding in the mixture fiber network. Further work is required to calculate the bond strength for each type of fiber-fiber bonding.

Bdd, Bcc and Bdc stand for the bond strength of CADEX/CADEX, C-CADEX/C-CADEX and CADEX/C-CADEX respectively. The bond strength of the mixture pulp can be expressed as the weighed average of bond strength from each type of bonding. Given the fraction of DEX coated pulp in the mixture x, the formula of the weighted average bond strength of the mixture pulp is written as

$$B = x^2 Bdd + (1-x)^2 Bcc + 2x(1-x)Bcd \qquad (4)$$

where the first term of the right-hand side counts for the contribution from the Bdd, the second for the contribution from Bcc and the third one for the contribution from Bcd.

Equation (4) is rearranged as following

$$B = (Bdd + Bcc - Bcd) \cdot x^2 + (2Bcd - 2Bcc) \cdot x + Bdd \qquad (5)$$

In this equation, B, which can be calculated from equation (3) since the tensile strength and the zero-span strength are known, is the binomial function of the fraction of dextran treated pulp x. It happens that the experimental bond strength calculated from equation (3) can be also fitted to a binomial function of x as shown in Figure 6. 5.

$$B = A_2 x^2 + A_1 x + A_0 \qquad (6)$$

where A_0, A_1, and A_2 are the constants from the regression equation. Compare equation (5) and (6), we can set up the following equations:

$$\begin{aligned} Bdd + Bcc - Bcd &= A_2 \\ 2Bcd - 2Bcc &= A_1 \qquad (7) \\ Bdd &= A_0 \end{aligned}$$

where Bdd, Bcc and Bcd are solvable with the above three equations.

6.4 Results

Figure 6. 4 shows the breaking length of paper sheets treated with different incompatible polymer pairs at the different mixing ratios. The breaking length of polymer-free paper was 2.24 km, shown as a circle on the graphs. Both CADEX and C-CADEX enhanced the strength of paper in comparison with the polymer-free paper. For all the incompatible polymer pairs, the tensile strength obtained from the mixture fiber was slightly lower or equal to the tensile strength of C-CADEX treated paper. The same trend was also observed with the E-modulus as shown in Table 6. 4 where the mechanical properties of paper with different densities measured from tensile testing are tabulated.

Based on the above consideration, the fiber-fiber bond strength of paper made with the mixture pulp was calculated with equation (3) and fitted with a binomial function of x.

Figure 6. 5 shows the results of the bond strength at different fraction of dextran treated fiber x and the fitting curves. While the bond strength between C-CADEX was weaker than that between CADEX, it was observed that the bond strength of the mixture pulp was lower than the bond strength of both

CADEX/CADEX and C-CADEX/C-CADEX. Of the three different mixing ratios in the three incompatible polymer pairs, the weakest bond strength was obtained when the fraction of CADEX fiber was 0.33. In all the cases, the results can be regressed precisely with the regression coefficients close to 1.

The bond strength for each type of bonding was calculated with equation (7) and the results are listed in Table 6. 3. It was observed that the Bcd was lower than both Bdd and Bcc in all three incompatible polymer pairs, of which the strength of CADEX3-49/C4-CADEX3-62 bond is the weakest, about 33% lower than the bond strength between C4-CADEX3-62 itself.

6.5 Discussion

The incompatibility of dextran and hydrophobically modified dextran was studied in our previous work. It was found that the phase separation was occurred for the aqueous mixture of dextran and hydrophobically modified dextran at different degrees of substitution corresponding to the different chain length of the substituent groups. For the same length of substitutent, the tendency towards aqueous biphase formation increased with the degree of hydrophobic substitution; whereas at a constant degree of substitution, it increased with chain length of hydrophobic groups[15], as seen in Figure 6. 2.

The effect of incompatible polymers on the formation of fiber-fiber bonding can be illustrated with Figure 6. 6. At the initial stage of the formation of fiber –fiber bonding, because the concentrations of dextran and hydrophobic dextran in water are very low, there are no any interactions between them and the fibers are held together with surface tension of water (Figure 6. 6 (a)). As water is being withdrawn, the fibers are getting closer and starting to bond each other. Some fiber-fiber bonds are formed between two identical polymers, while the others are formed between two different polymers. Since both dextrans are water soluble, in the case of two identical polymers, the molecular chains can diffuse into the opposing surface and generate strong interfacial adhesion (Figure 6. 6(b)). Although the extent of intermolecular diffusion might be the same for dextran and hydrophobic dextran, bond strength between hydrophobic dextran was weaker than that between dextran due to the less sites of hydrogen bonding. The fiber-fiber bond strength was found to be proportional to the degree of hydrophobic substitution, and the weakest bond strength was observed from the dextran with the highest hydrophobic degree[19].

In the case of incompatible polymers, when the concentrations of dextran and hydrophobic dextran reach the critical concentrations for phase separation, the molecules on each fiber surface tend to stay away from another, which results in weak adhesion across the interface of the two fibers (Figure 6. 6(c)). If the fiber-fiber bond strength from the mixture of the two incompatible polymers is a linear combination of the contribution of dextran coated fiber and hydrophobic dextran coated fiber, the difference between this and the measured bond strength can be used to evaluate the intensity of the influence from polymer incompatibility. In all the polymer pairs, the most significant influence was observed when two types of fiber were mixed at half to half. It makes sense since a half of the fiber-fiber bonds is formed between incompatible polymers, while in the other mixing ratios, the amount of bonds between incompatible polymers is less than the sum of the other two types of bonding, see equation (4).

Based on the conclusion obtained from our previous work, the tendency towards the phase separation for CADEX3-49/C4-CADEX3-76 was supposed to be stronger than that for CADEX3-49/C4-CADEX3-62 since the DS of C4-CADEX3-76 (0.66) was larger than the other (0.42). Therefore, it was expected that the weaker bond strength was obtained from the bonding between CADEX3-49 and C4-CADEX3-76. However, the weakest bond strength was obtained from the bonding of CADEX3-49/C4-CADEX3-62 instead, although CADEX3-49/C4-CADEX3-76 is more incompatible. It seemed there was no direct relation between the interfacial adhesion strength of the two polymers and the tendency for their phase separation in the aqueous mixture solution. The followings will provide some explanation to what happened behind the apparent phenomenon of this result.

It is known that the inter-diffusion of polymers determines the strength of interfacial adhesion. For incompatible polymers the inter-diffusion is very poor, it, however, exists to some extent. In the case of the present work, the polymers are physically bonded onto fiber surfaces. There is no interaction between these polymers when the water content of a paper sheet is high, larger than 70%, because fiber is too far to interact each other. The interaction between the surface polymers can only occur in or after the stage of pressing, during which most of water is removed and the water content is reduced to about 60% or lower. Mixing between two dextrans could happen at this stage if their concentrations are still in the single phase region. However, as the concentration of dextrans reaches the critical concentration for phase separation during water being removed, the mixed dextrans will tend to separate and keep themselves on their own surfaces. Since the polymer concentrations of the system keep changing as water is being withdrawn, the polymer composition on each fiber surface keeps changing too. This process will be going on until at certain polymer concentration that the movement of polymer chains is too slow. At this stage the rearrangement of the two dextrans on each fiber surface is complete and ends up with two separated fiber surfaces bearing different dextrans, with only very few dextran inter-diffusing to the opposing fiber surface (Figure 6. 6(c)). Phase separation was a slow process. For dextran, two separated phases could be obtained over night at the concentration about 10%, however, it took a few days to get clearly separated phases. The standard tensile strength testing of the handsheets was performed after 12 to 24 hours drying at 23°C with RH of 50%. Therefore, it is very possible that some mixing between the two incompatible dextrans is remained. The intensity for the separation of two dextrans might depend very much on the paper making process, such as pressing, drying, and even some properties of a paper sheet itself. Although cautions were taken to control these parameters consistently during the handsheet making, any subtle difference might cause the different mixing intensity of the incompatible dextrans, which in turn affects the interfacial adhesion strength of between these two polymers. What might happened is, for some reasons, the system of CADEX3-49/C4-CADEX3-62 reached the more complete phase separation (less diffusion) than CADEX3-49/C4-CADEX3-76 did, which is possible due to the various affecting factors during the handsheet making. This might result in the stronger bond strength from CADEX3-49/C4-CADEX3-76 than from CADEX3-49/C4-CADEX3-62.

The results from the current work provided the direct evidence of the effect of polymer compatibility on the interfiber bond strength, which has never been reported. It clearly demonstrated the fact that although both polymers in the incompatible polymer pairs enhance the strength of paper, strong paper is not necessarily made when the mixture of the two polymers are added into the fiber network. As in any other polymer materials, the effect of surface polymer compatibility is essential to determine the strength development of fiber-fiber bonding for paper. In addition, it provided the direct evidence of polymer diffusion across the interface during the strength development of interfiber bonding, which supported the diffusion theory proposed by McKenzie.

6.6 Conclusions

1. The role of polymer compatibility in the strength development of paper was demonstrated. It was found that the bond strength of the incompatible polymer pair was lower than that obtained from the each single polymer in the pair. In addition, this work provided direct evidence for McKenzie diffusion theory in the development of fiber-fiber bonding.

2. The bond strength of the mixture fiber network could be split into three types of bonding and the contribution from each type of bonding could be calculated.

3. Although bond strength between hydrophobic dextran was inversely proportional to the degree of hydrophobic substitution, no relation was found between the tendency for phase separation of an incompatible polymer pair and the fiber-fiber bond strength developed between the two polymers.

6.7 Acknowledges

The authors thank SCA Research, Sundsvall Sweden for financial support. We acknowledge Dr. Derek Page for many useful discussions regarding paper testing.

Figure 6. 1 The features of pulp fiber surfaces.

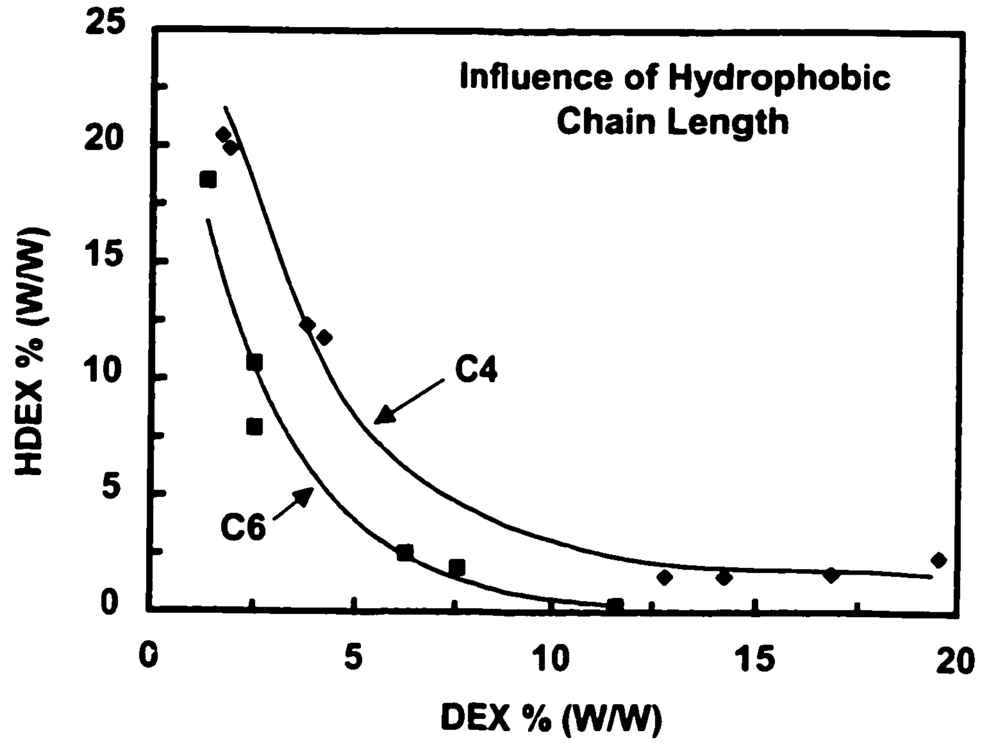


Figure 6. 2 Phase boundaries for C4 and C6 modified dextrans. The DS for C4 modified dextran was 0.37 and it was 0.23 for C6. The molecular weight of dextran was 74,000. The I region corresponds to a single phase region and II the biphase region[15].

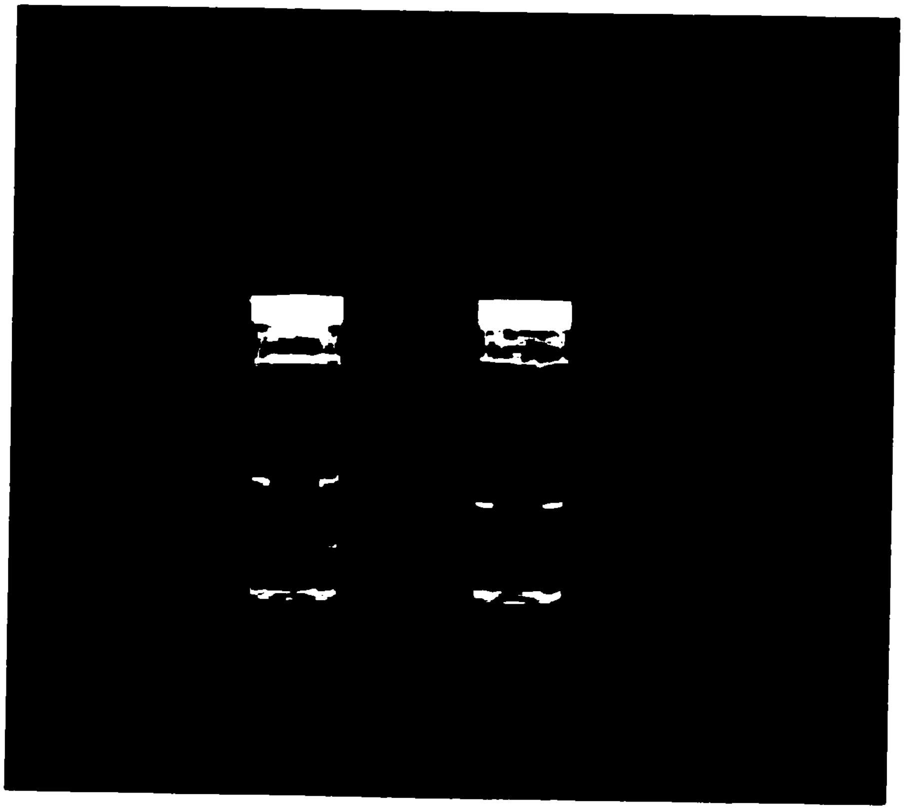
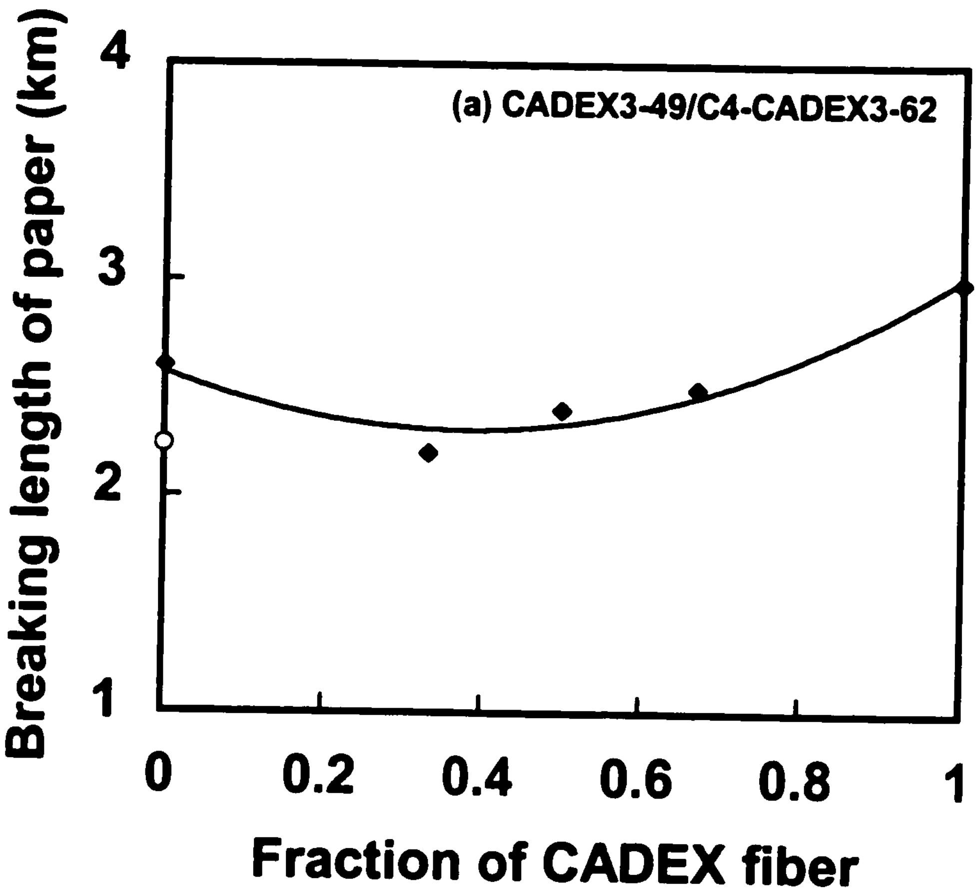
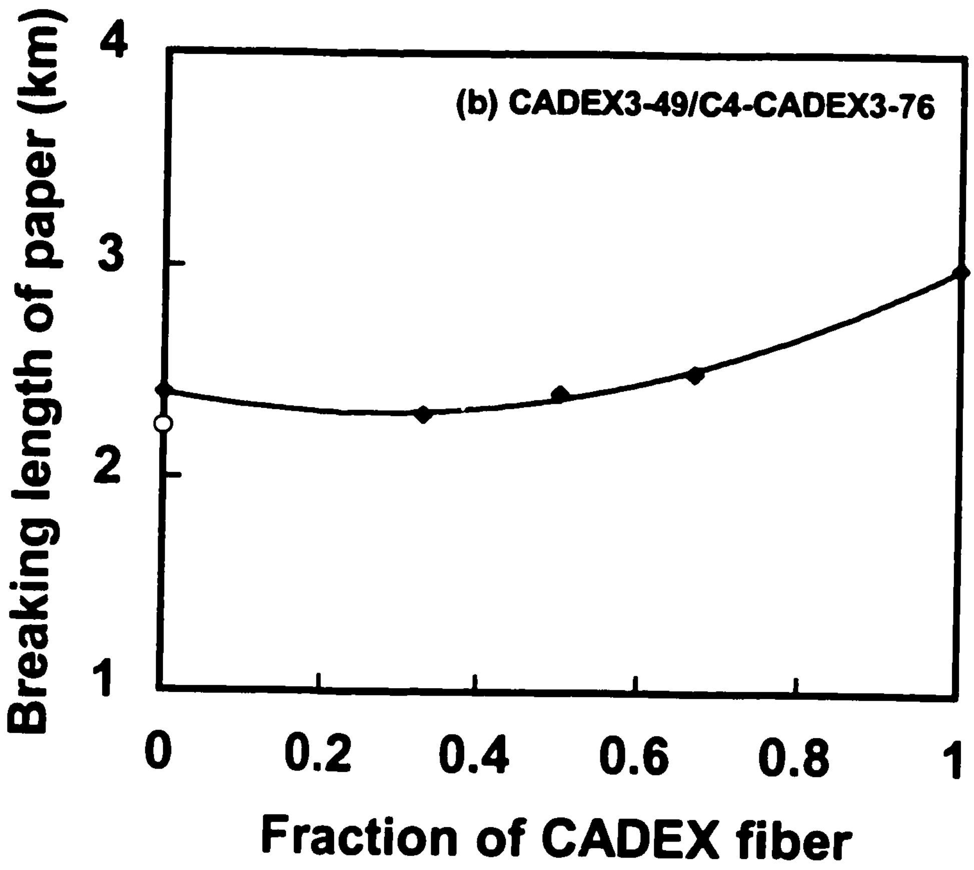


Figure 6. 3 The biphase formation of the mixture aqueous solution of CADEX3-49/C4-CADEX3-76. The concentration of both solutions was 10%.


(a) CADEX3-49/C4-CADEX3-62
Breaking length of paper (km)
1
2
3
4
0
0.2
0.4
0.6
0.8
1
Fraction of CADEX fiber


(b) CADEX3-49/C4-CADEX3-76
Breaking length of paper (km)
4
3
2
1
0
0.2
0.4
0.6
0.8
1
Fraction of CADEX fiber

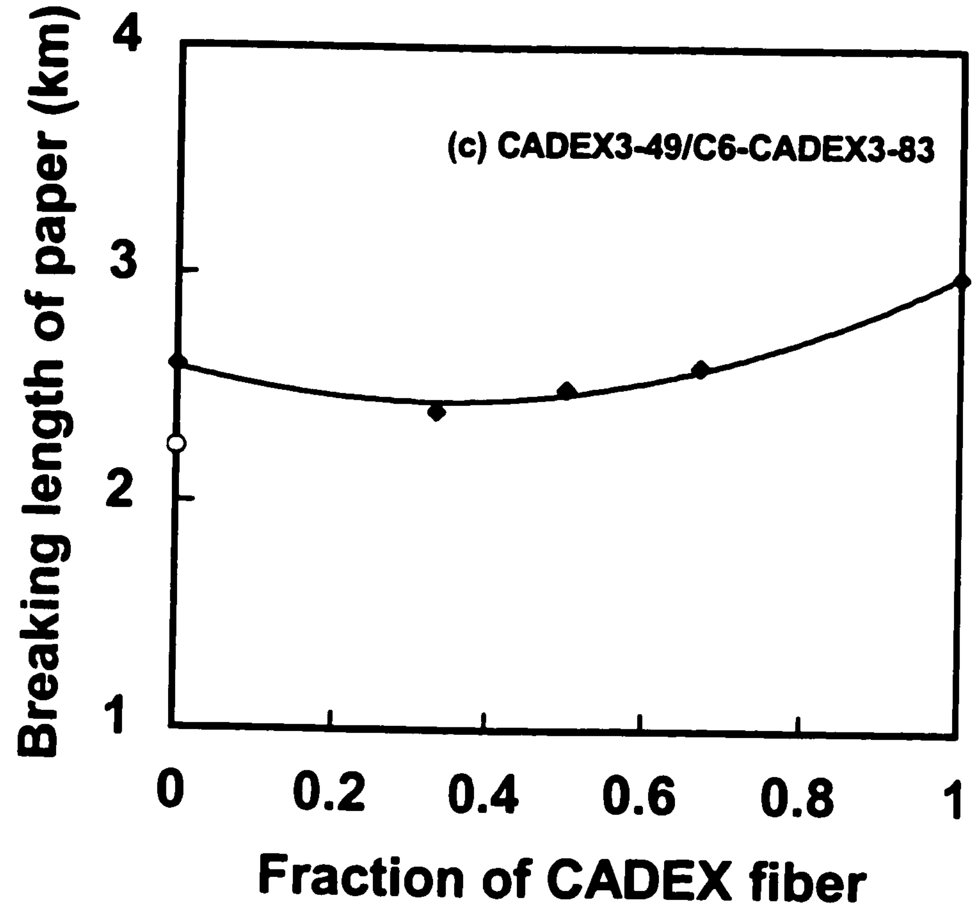
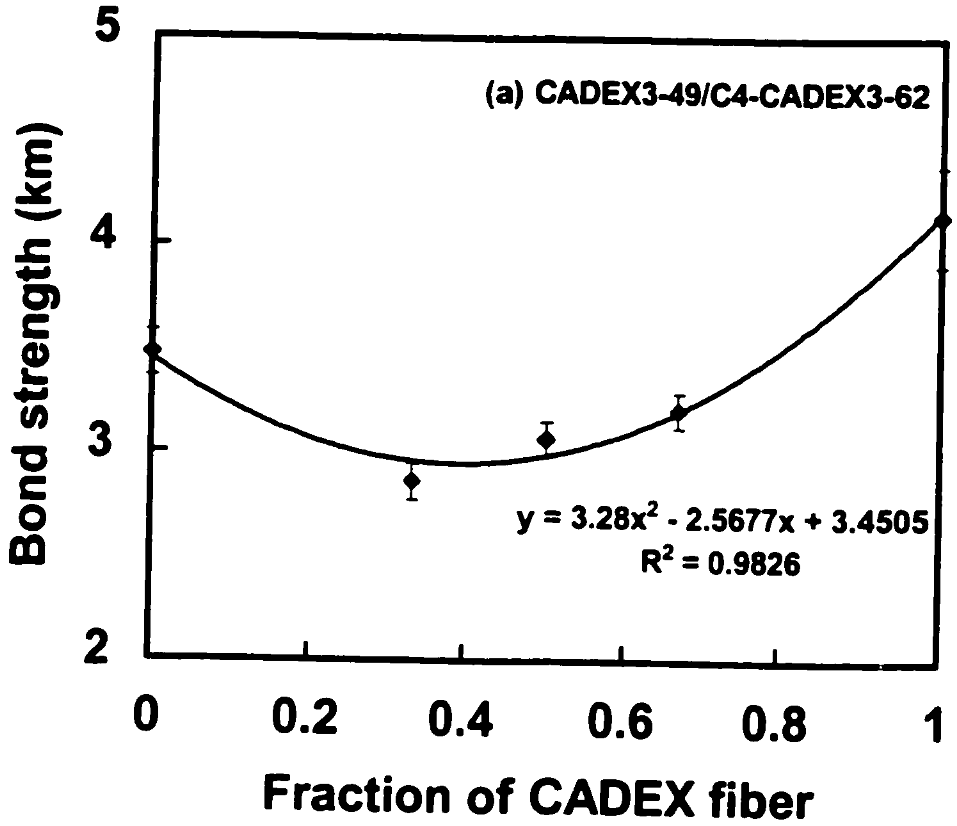


Figure 6. 4 The measured tensile index of paper made from the mixture fiber at different mixing ratios. The incompatible polymer pairs used were CADEX3-49/C4-CADEX3-62 (a), CADEX3-49/C4-CADEX3-76 (b), and CADEX3-49/C6-CADEX3-83(c).


(a) CADEX3-49/C4-CADEX3-62
y = 3.28x^2 - 2.5677x + 3.4505
R^2 = 0.9826
Bond strength (km)
Fraction of CADEX fiber
5
4
3
2
0
0.2
0.4
0.6
0.8
1

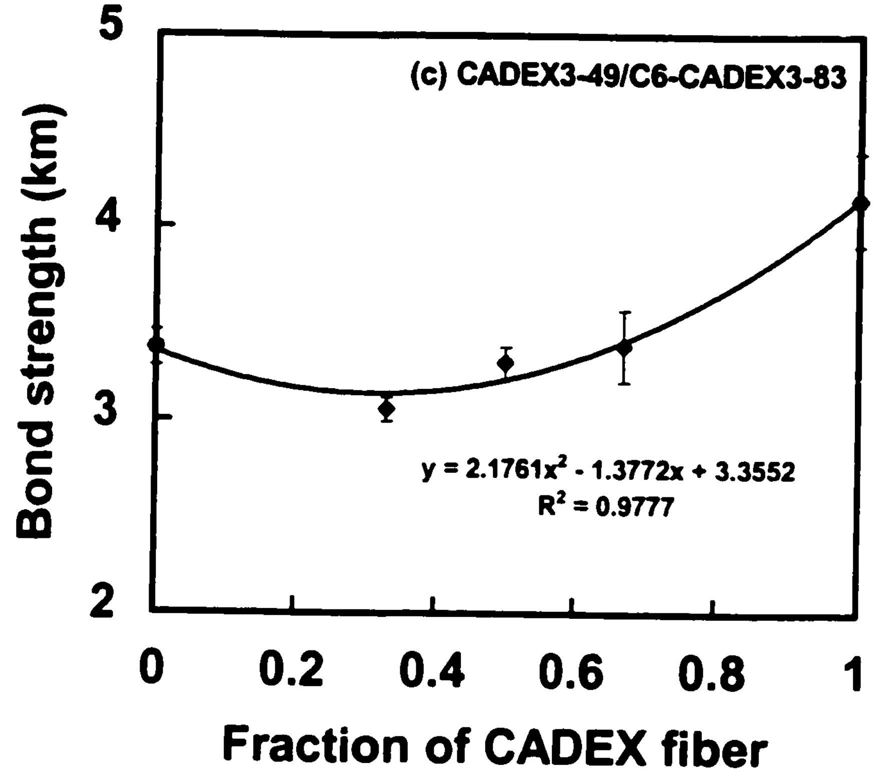


Figure 6. 5 The measured bond strength of the paper as the function of mixing ratio for different incompatible polymer pairs. Figure 3(a) is CADEX3-49/C4-CADEX3-62; Figure 3(b) CADEX3-49/C4-CADEX3-76, and Figure 3(c) CADEX3-49/C6-CADEX3-83. The bond strength was calculated with Page equation.

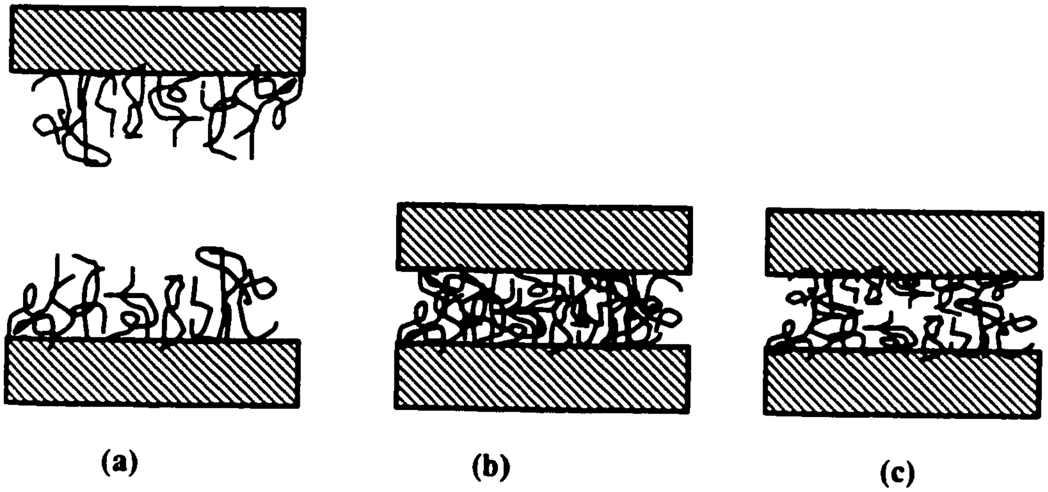


Figure 6. 6 The formation of fiber-fiber bonds between dextrans during water being removed. (a) high water content, no interaction between two dextrans; (b) mixing of the two identical dextrans; (c) interfacial bonding between the incompatible dextrans.

Table 6. 1 **The characteristic properties of dextrans used in current work.**

Dextrans	**MW**	**Charge density (meq/g)**	**DS**
CADEX3-49	2,000,000	0.284	0
C4-CADEX3-62	2,000,000	0.284	0.42
C4-CADEX3-76	2,000,000	0.274	0.66
C6-CADEX3-83	2,000,000	0.214	0.27

Table 6. 2 **Elastic moduli of paper made from the mixture pulp at different mixing ratio.**

Incompatible polymer pairs	**E-modulus of mixture pulp at different fraction of CADEX fiber GPa**				
	1	**0.67**	**0.5**	**0.33**	**0**
CADEX3-49/ C4 -CADEX3-62	2.07	1.88	1.85	1.83	1.85
CADEX3-49/ C4-CADEX3-76	2.07	1.86	1.86	1.79	1.96
CADEX3-49/ C6-CADEX3-83	2.07	1.87	1.77	1.83	1.82

Table 6. 3 **The calculated mixture bond strength with Page equation and the bond strength of each type of bonding.**

Incompatible polymer pairs	**Bond strength of the mixture pulp at different fraction of DEX fiber (km)**					**Bond strength for individual bond (km)**		
	1	**0.67**	**0.5**	**0.33**	**0**	**Bdd**	**Bcc**	**Bcd**
CADEX3-49/ C4-CADEX3-62	4.15	3.21	3.07	2.86	3.47	4.16	3.45	2.17
CADEX3-49/ C4CADEX3-76	4.15	3.28	3.16	2.92	3.16	4.15	3.16	2.51
CADEX3-49/ C6CADEX3-83	4.15	3.39	3.3	3.06	3.37	4.15	3.36	2.67

Table 6. 4 The effect of incompatible polymers on the tensile strength of paper.

CADEX3-49/C4-CADEX3-62

Pressing pressures (kPa)	800					1600				
Fraction of CADEX pulp	0	0.33	0.5	0.67	1	0	0.33	0.5	0.67	1
Density (kg/m^3)	510	525	522	529	513	596	594	602	601	596
Tensile index (Nm/g)	22.0	19.9	21.0	22.9	26.1	29.4	26.0	27.7	27.3	33.8
E-modulus (GPa)	1.57	1.62	1.63	1.71	1.86	2.17	2.21	2.25	2.31	2.34
TAE (J/m^2)	24.9	18.1	21.3	27.9	26.3	43.7	30.5	36.6	31.3	46.4

CADEX3-49/C4-CADEX3-76

Pressing pressures (kPa)	800					1600				
Fraction of CADEX pulp	0	0.33	0.5	0.67	1	0	0.33	0.5	0.67	1
Density (kg/m^3)	498	519	523	529	513	559	603	599	604	596
Tensile index (Nm/g)	21.2	19.5	21.4	22.7	26.1	27.5	27.6	28.5	29.4	33.8
E-modulus (GPa)	1.47	1.52	1.63	1.68	1.86	2.05	2.25	2.29	2.32	2.34
TAE (J/m^2)	24.7	18.1	24.0	26.4	26.3	34.0	35.0	37.5	41.6	46.4

CADEX3-49/C6-CADEX3-83

Pressing pressures (kPa)	800					1600				
Fraction of CADEX pulp	0	0.33	0.5	0.67	1	0	0.33	0.5	0.67	1
Density (kg/m^3)	517	551	547	547	513	614	607	607	608	596
Tensile index (Nm/g)	21.0	23.4	24.4	24.8	26.1	31.3	29.6	30.3	33.0	33.8
E-modulus (GPa)	1.53	1.84	1.74	1.84	1.86	2.39	2.30	2.39	2.49	2.34
TAE (J/m^2)	25.5	28.7	34.0	31.3	26.3	46.2	46.6	43.1	52.7	46.4

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Chapter 7. Conclusions And Contributions

The novel idea in this project is to apply the concepts developed in the disciplines of polymer science to understanding the role of polymers in enhancing the strength of paper. The goal we set at the beginning was fulfilled, and the conclusions have been given in each of the chapters. The following provides a brief review and comments about the project, as well as recommendations for further work.

7.1 Main conclusions and recommendations

It is well known that the essential concern about adhesion resulting from the diffusion of surface polymers is whether they are compatible. However, this work is the first time an attempt has been made to demonstrate diffusion effects in paper. After applying two incompatible polymers, dextran and hydrophobic dextran, to the fiber network, we found that the bond strength between identical polymers was stronger than that between incompatible polymers. The bond strength between dextran and hydrophobically modified dextran was about 30% lower than the bond strength between hydrophobic dextran and 40% lower than that between dextran. The Page equation, along with a binomial model, was successfully used to split the value of the overall bond strength into three components corresponding to the three possible types of fiber/fiber bonds.

The incompatibility of hydrophobically modified dextran, with different degree of substitution of a number of different substituents, and dextran was characterized using the phase diagrams of the biphase formed from an aqueous mixture of the two. It was observed that the tendency for phase separation increased with the molecular weight, the degree of substitution and the chain length of the fatty acids that were used to introduce the hydrophobic groups.

The role of polymer compatibility in the strength development of fiber-fiber bonding illustrated in this work provided direct evidence for polymer diffusion across the interface of two fibers. In practice, this work suggests that the impact from the interaction of polymers between fibers is very important in determining the strength of interfiber bonding.

One of the most important characteristics of a polymer is its molecular weight. Surprisingly, varying the molecular weight of dextran, in the range from 77,000 to 2000,000, produced no changes in the tensile strength of paper. Thus the ultimate tensile strength obtained when the fiber surface was saturated with dextrans was not affected by the mw of the dextran used. In contrast, the internal bond strength, the Scott bond, increased as the molecular weight increased. Varying the molecular weight also affected the fiber-surface coverage of dextran due to the porosity of fibers.

It is proposed that the strength enhancing effect is caused by the strength enhancement per relative bonded area due to the more effective interfiber bonding of dextrans compared to fiber alone. The results from this work suggest that a high molecular weight polymer is more efficient in strengthening paper than is a low molecular weight one since the same tensile strength can be obtained with less polymer adsorption.

Due to the penetration of a large amount of small molecular weight dextran into the fiber wall during the adsorption, the question arises as to whether the presence of dextran will affect the zero span strength of fibers. Although it is generally believed that the addition of polymers to a fiber does not change the strength of the fiber itself, there is no systematic data so far which allows us to understand how changing the molecular weight of polymers changes their effect on the strength of fibers. Further work on this aspect is recommended, that is, how the molecular weight might effect the zero-span strength of fibers when they are saturated with dextran. This work could determine whether penetration of low molecular weight dextran into fibers can enhance the strength of the fibers themselves which in turn would contribute to the strength enhancement of paper. Another suggestion for further work is a study of the z-directional tensile strength, a test to measure the internal bond strength in the transverse direction. It is believed that this test gives more precise and reproducible results than any other test methods in evaluating the internal bond strength of fiber-fiber bonding.

In contrast to the observation obtained when dextran was adsorbed on fibers, the tensile strength of paper impregnated with dextran depended on the molecular weight of dextran. It was found that at the same dextran content, the higher molecular weight of dextran, paper impregnated with the higher molecular weight dextran was stronger than that obtained from the lower molecular weight one. The strength enhancement was attributed to the increase both in the relative bonded area and in the number of intermolecular bonds. Furthermore, this work suggested that the distribution of polymer added with impregnation might be different from that added by adsorption; while the polymer distributes uniformly on fiber in the case of adsorption, it might give uneven distribution within fiber network in the case of impregnation. For high molecular weight dextran, impregnation may lead to the formation of additional bonded areas, whereas low molecular weight dextran may penetrate into fiber walls and pass through the existing bonded area.

This work suggests that impregnation may give a polymer distribution that is more efficient in strengthening the fiber network. However, further evidence is required to support this hypothesis. It is recommended that the densities of the impregnated paper and the paper made from dextran treated fiber are controlled so that the tensile strength be compared at the same sheet density.

It is interesting to note that the influence of charge density in the investigated range was similar to that of the molecular weight in the way that it affected the tensile strength of paper by changing the amount of dextran adsorbed on fiber surfaces. Dextran with low charge density results in a higher maximum amount of adsorption than dextran of high charge density, which in turn brings about the higher tensile strength of paper. However, the cationic charge itself does not participate in the formation of fiber-fiber bonding and has no direct impact on the strength development. The results from this work suggest that low charge density polymers are more efficient in enhancing the fiber-fiber bonding strength than high charge density due to their high retention on fiber surfaces. Although a similar conclusion has been reported by other researchers, no systematic research has been done to support it.

The charge densities of the dextrans used in this investigation, from 0.16-0.49 meq/g, were in the same range as those of commercial starch. An investigation over a wider range of charge densities is suggested.

Hydrophobic dextrans prepared in this work functioned as strength enhancing polymers when they saturated the fiber surfaces, although their strength enhancing ability was less than that of dextran itself. The fiber-fiber bond strength between the hydrophobic dextran from both the tensile strength and Scott bond testing was found to be inversely proportional to the degree of hydrophobicity and surface energy of the modified dextran. Since the hydrophobic dextran which we prepared remained water-soluble, it was proposed that hydrophobic modification did not change the mobility, or the diffusion of the modified dextran molecules in water. The weaker interfiber bonding formed between fibers coated with hydrophobic dextran was believed to be the result of the reduction in the number of hydrogen bonding sites.

7.2 Contributions

1. For the first time, the role of polymer compatibility in the strength development of interfiber bonding was proposed and demonstrated. The bond strength formed between the incompatible polymer pair (dextran and hydrophobically modified dextran) was lower than that obtained from each single polymer in the pair. This work provided direct evidence for polymer diffusion across the interface of two fibers.

2. The Page equation, combined with the model developed in this work, was extended to calculate the interfiber bond strength between fibers bearing different surface polymers.

3. This work is the first time that the influence of molecular weight on the strength of paper was systematically investigated. It was found that when the molecular weight of the dextran was anywhere in the range 77,000 to 2,000,000, the same ultimate tensile strength was obtained when fiber surfaces were saturated with dextran.

4. The Scott bond strength was found to vary linearly with the logarithm of the molecular weight in the range 77,000 to 25,000,000.

5. For the first time, polymers with different degrees of hydrophobic substitution were applied to fiber networks as strength enhancing polymers, and a linear relationship between the fiber-fiber bond strength and the surface energy of the hydrophobic polymers was demonstrated.

6. The role of the charge density in the development of the strength of fiber-fiber bonding was clarified. The charge density affected the maximum amount of dextran which could be adsorbed by fibers, but did not affect the extent of fiber-fiber bonding.