MICROSTRUCTURE AND PROPERTIES OF TMP PAPERS

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements of the degree of
Master of Engineering

Department of Chemical Engineering
McGill University
Montreal, Quebec
July 2000

0-612-70652-4

To Robert

ABSTRACT

Paper is comprised of quasi-randomly distributed fibres, fines and different additives. The properties of paper depend on the type of fibres used, their uniformity of distribution, the amount and type of fines and fillers. It is difficult to predict how a particular component will behave in a mixture. This will depend on the form of material introduced (flocculated or dispersed) and on what kind of interactions will take place. These factors can be controlled by various wet-end strategies based on known colloidal behaviour of various additives. Thus, applying this knowledge to papermaking, one should be able to predict and control final structures of paper, which will be reflected in optical and mechanical properties.

A thorough understanding of the effects of different materials, such as fines and fillers, on optical and mechanical properties of paper can only be obtained from a systematic study. Therefore, this research focused on elucidating the relationship between the nature and amount of fines and fillers and paper properties. The studies were mainly limited to papers made from thermomechanical pulps (TMP), although occasionally comparisons with other pulps were made as well.

RÉSUMÉ

Le papier est composé d'une distribution quasi-aléatoire de fibres, additifs et particules fines. Les propriétés du papier dépendent du type de fibres utilisés, l'uniformité de leur distribution, la quantité et le type de remplisseur et de particules fines. Il est difficile de prédire le comportement d'un composant particulier dans un mélange. Ceci dépendra de la forme du matériau (floculé ou dispersé) et de la nature des intéractions qu'auront lieu. Ces facteurs peuvent être contrôlés à la partie humide par divers stratégies conçues à partir d'une étude du comportement colloïdal. L'application de cette connaissance à la fabrication du papier permet un contrôle et une prévision de la structure finale du papier et par conséquent, des propriétés mécaniques et optiques.

Une compréhension des effets de différents matériaux, tel que les remplisseurs et les particules fines, sur les propriétés optiques et mécaniques du papier peut être acquise dans une étude systématique. Par conséquant, ce travail vise l'élucidation de la relation entre la nature et la quantité de particules fines et les propriétés du papier. L'accent est mis sur les papiers fabriqués de pâte thermomécanique (TMP), toutefois des comparaisons seront effectuées avec d'autres pâtes.

PREFACE

The thesis was prepared in accordance with Guidelines for Thesis Preparation of McGill University (revised June 2000). Article I. C. "Manuscript-based thesis" reads as follows:

As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research. The structure for the manuscript-based thesis must conform to the following:

1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly-duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis.)

2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges between the different papers are mandatory.

3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts.

The thesis must include the following:

(a) a table of contents;

(b) an abstract in English and French;

(c) an introduction which clearly states the rational and objectives of the research;

(d) a comprehensive review of the literature (in addition to that covered in the introduction to each paper);

(e) a final conclusion and summary;

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail

to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defence. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers.

6. When previously published copyright material is presented in a thesis, the candidate must obtain, if necessary, signed waivers from the co-authors and publishers and submit these to the Thesis Office with the final deposition.

7. Irrespective of the internal and external examiners reports, if the oral defence committee feels that the thesis has major omissions with regard to the above guidelines, the candidate may be required to resubmit an amended version of the thesis. See the "Guidelines for Doctoral Oral Examinations," which can be obtained from the web (http://www.mcgill.ca/fgsr), Graduate Secretaries of departments or from the Thesis Office, James Administration Building, Room 400, 398-3990.

8. In no case can a co-author of any component of such a thesis serve as an external examiner for that thesis.

Credits to others who helped in any way to the work described in this thesis are declared in the section entitled “Acknowledgements”.

The thesis consists of five chapters. Chapter I states objectives of this study, and review of literature and thesis overview are provided. Chapters II, III, and IV describe research and results; they are written in manuscript format. Chapter V presents summary and conclusions.

Contributions of co-authors of manuscripts and extent of these contributions are stated in the section entitled “Contributions of authors”.

CONTRIBUTIONS OF AUTHORS

The manuscript-based format was used for this thesis (Chapters II, III, and IV).

Chapter II "Colloidal behavior of papermaking fines and fillers"

J. Porubska, B. Alince, T.G.M. van de Ven

This work was performed under the supervision of Drs. Van de Ven and Alince, who will be co-authors of the paper. The author performed all experimental work and data analysis and prepared the chapter. Drs. Van de Ven and Alince acted in supervisory role and did minor editing.

This manuscript will be submitted to the journal "Colloids and Surfaces". Also, this work was presented by the author at the ACS 74th Colloid & Surface Science Symposium at the Lehigh University in Bethlehem (PA, USA) on June 21, 2000. Part of this research was presented by the author at the Mechanical Wood-Pulps Network of Centre of Excellence (NCE) Workshop in Toronto (Ontario, Canada) on February 18, 2000.

Chapter III "Effect of model and fractionated TMP fines on sheet properties"

B. Alince, J. Porubska, T.G.M. van de Ven

The initial ideas for doing this work originated from Dr. Alince who as a result is listed as first co-author. As in Chapter II, all experimental work, data analysis, graphs and original text were prepared by the author. Dr. van de Ven acted as co-supervisor.

This manuscript will be submitted to the Fundamental Research Symposium in Oxford. Part of this research was presented by the author at the NCE Papermaking Workshop in Hamilton (Ontario, Canada) on February 16, 1999.

Chapter IV "Light scattering and microporosity of paper"

B. Alince, J. Porubska, T.G.M. van de Ven

Drs. van de Ven and Alince's involvement in Chapter IV was similar to that for Chapter III.

This manuscript will be submitted to the "Journal of Pulp and Paper Science". Also, this research was presented by the author at the Department of Chemical Engineering at McGill University in Montreal (Quebec, Canada) on February 11, 2000. Part of this research was presented by the author as a poster at the 85th PAPTAC Annual Meeting in Montreal (Quebec, Canada) on January 27, 1999.

ACKNOWLEDGEMENTS

I would like to thank:

Drs. T.G.M. van de Ven and B. Alince for guidance, patience, their ability to transfer their knowledge to their students and for editorial help.

Dr. G. Garnier for discussions, encouragement and ensuring that the quality requirements of the Department of Chemical Engineering were respected.

Dr. J. Petlicki, Dr. J. Wood, Dr. M. Polverari, S. St-Amour, L. Godbout, X. Zhang, T. Thompson, E. Walker, S. Shimamoto for professional and technical assistance, and Paprican for technical services.

NCE, NSERC and McGill for financial support.
Also FCAR scholarship was awarded, but was declined because the NSERC scholarship was accepted for that period.

All the members of papermaking and engineering group: Chris, Claudia, Craig, David, Fero, Hedi, Honza, Jindra, Karine, Kenichi, Lojza, Mahmood, Mehdi, Mohammed, Renata, Tom, Tomas and Françoise, Klara, Livia, Monica, Ondrej, Tibor for help, friendship and fun.

My family who believes in me inspite of being far away.

Most of all, Robert and his mother for their support and love.

TABLE OF CONTENTS

ABSTRACT iii
RÉSUMÉ iv
PREFACE v
CONTRIBUTIONS OF AUTHORS vii
ACKNOWLEDGEMENTS ix
TABLE OF CONTENTS x
LIST OF FIGURES xiii

Chapter I

INTRODUCTION 1
1. Objectives 2
2. Literature Review 2
   2.1. Thermomechanical pulp (TMP) 2
   2.2. TMP fines 3
   2.3. Fillers in paper 8
   2.4. Colloidal behavior of fines and fillers 9
3. Thesis Overview 10
4. References 10

Chapter II

COLLOIDAL BEHAVIOR OF PAPERMAKING FINES AND FILLERS 14
Abstract 15
1. Introduction 16
2. Experimental 17
   2.1. Materials 17
   2.2. Methods 18
3. Results and discussion 19
   3.1. Characterization of fines 19
   3.2. Flocculation of fines by PEI 23

3.3. Flocculation of fines by PAM 29
3.4. Flocculation of fillers 32
3.5. Flocculation of mixtures of fines and fillers 35
4. Conclusions 38
5. Acknowledgements 39
6. References 39

Chapter III

EFFECT OF MODEL AND FRACTIONATED TMP FINES ON SHEET PROPERTIES 42
Abstract 43
1. Introduction 44
2. Experimental 45
2.1. Materials 45
2.2. Methods 46
3. Results and discussion 46
4. Conclusions 60
5. Acknowledgements 60
6. References 60

Chapter IV

LIGHT SCATTERING AND MICROPOROSITY OF PAPER 62
Abstract 63
1. Introduction 64
2. Experimental 65
2.1. Materials 65
2.2. Methods 66
3. Results and discussion 68
4. Conclusions 78
5. Acknowledgements 78
6. References 78

Chapter V

SUMMARY AND CONCLUSIONS 80

Appendix

EXPERIMENTAL METHODS 82
1. Polyelectrolyte titration 83
2. Photometric dispersion analyzer (PDA) 83
3. Light scattering 84
4. Tensile strength 86
5. Porosimetry 88
6. References 89

LIST OF FIGURES

CHAPTER I

Figure 1. Cross-section of a sheet showing different effects of fines, A – bridging effect, B – blocking effect, C – filling effect [18].

Figure 2. Effect of TMP or kraft fines additions on TMP or kraft fibre network [24].

CHAPTER II

Figure 1. Adsorption isotherm of PEI on thermomechanical fines at pH 6 in deionized water.

Figure 2. Electrophoretic mobility of thermomechanical fines as a function of PEI concentration in deionized (DW) and tap water (TW).

Figure 3. Electrophoretic mobility of microcrystalline cellulose (MCC) as a function of PEI concentration in deionized (DW) and tap water (TW).

Figure 4. Stability ratio W of fines as a function of PEI concentration in deionized (DW) and tap water (TW).

Figure 5. Stability ratio W of washed fines as a function of PEI concentration in deionized water at pH 3.

Figure 6. Stability ratio W of microcrystalline cellulose (MCC) as a function of PEI concentration in deionized (DW) and tap water (TW).

Figure 7. Electrophoretic mobility of thermomechanical fines and microcrystalline cellulose (MCC) as a function of PAM concentration in tap water.

Figure 8. Stability ratio W of thermomechanical fines and microcrystalline cellulose (MCC) as a function of PAM concentration in tap water.

Figure 9. Electrophoretic mobility of clay as function of PAM or PEI concentration in tap water.

Figure 10. Stability ratio W of clay as a function of PAM or PEI concentration in tap water.

Figure 11. Stability ratio W of mixtures of fines/clay and MCC/clay as a function of addition of fines or MCC in deionized water. Sequence of addition: 1. Fines or MCC, 2. Clay (50 mg/L) treated with PEI.

CHAPTER III

Figure 1. Effect of beating, introduction of filler, chemical and mechanical fines on bonded and unbonded surface area, and consequently on tensile strength and opacity.

Figure 2. Micrographs: A – microcrystalline cellulose, B – high specific surface area fines, C – low specific surface area fines, D – microfibrillated cellulose.

Figure 3. Tensile strength as a function of different types of fines introduced into TMP fibers (left) and kraft fibers (right).

Figure 4. Light scattering coefficient as a function of fines introduced into TMP fibers (left) and kraft fibers (right).

Figure 5. Tensile strength versus light scattering coefficient for TMP fibers (left) and kraft fibers (right) containing different fines.

Figure 6. Tensile strength as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

Figure 7. Light scattering coefficient as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

Figure 8. Tensile strength versus light scattering coefficient for TMP fibers (left) and kraft fibers (right) containing HSF and PCC.

Figure 9. Opacity as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

Figure 10. Brightness as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

CHAPTER IV

Figure 1. Micrographs: A – microcrystalline cellulose, B – high specific surface area fines, C – low specific surface area fines, D – microfibrillated cellulose.

Figure 2. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of total area of pores. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

Figure 3. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of fractionated fines as a function of total porosity. HSF - high specific surface area fines, LSF - low specific surface area fines.

Figure 4. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of calcium carbonate treated with polyacrylamide or with polyethylenimine as a function of total porosity.

Figure 5. Micrographs of handsheets formed from long fibres (LF) and calcium carbonate treated with polyacrylamide or polyethylenimine. A – 44% $CaCO_3$/PAM, B – 32% $CaCO_3$/PEI.

Figure 6. Micrographs of cross-sections of handsheets formed from long fibres (LF) and calcium carbonate treated with polyacrylamide or polyethylenimine. A – 44% $CaCO_3$/PAM, B – 32% $CaCO_3$/PEI.

Figure 7. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of microfibrillated cellulose (MFC) as a function of total porosity.

Figure 8. Specific light scattering coefficient expressed per void volume as a function of equivalent spherical diameter of voids [10].

Figure 9. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of pores area, for diameters of pores larger than 0.1 μm. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

Figure 10. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of pores area, for diameters larger than 0.2 μm. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

APPENDIX

Figure 1. Experimental setup for stability measurements. 1 – beaker with suspension, 2 – stirrer, 3 – pump, 4 – photometric dispersion analyzer, 5 – recorder.

Figure 2. Typical stress-strain behavior of paper [6].

CHAPTER I

INTRODUCTION

1. Objectives

The main objectives of this thesis are:

1. To study systematically the flocculation behavior of fines, fillers and their mixtures.
2. To prepare papers having different structures in order to quantify how fines and fillers affect mechanical and optical properties.
3. To characterize the microstructure of TMP papers containing fines and fillers by means of scanning electron microscopy (SEM).
4. To elucidate the relationship between microstructure and properties of papers containing fines and fillers.

2. Literature Review

2.1. Thermomechanical pulp (TMP)

TMP is a high yield pulp (97.5%), obtained from chips by preheating with steam (at 145-155°C) and refining under pressure at elevated temperatures [1].

Mechanical pulps are widely used as a main component in newsprint, magazine, printing and writing papers because of their unique properties and their lower cost in comparison to chemical pulps. Also, studies have shown that TMP has the potential to be used in manufacturing tissue paper [2]. Because of the high demand for mechanical pulps, much research is carried out to determine their effect on the properties of paper, to determine the optimum conditions for their effective performance and to characterize and improve (or optimize) their properties.

Properties of TMP fibres

Non-treated TMP fibers contain curls, kinks and microcompressions, which can be removed by hot water treatment during disintegration. This process is called latency removal and it results in 3 to 5% increase in fiber length, 60% increase in fiber flexibility and improves strength properties of a sheet [3].

A typical value for a specific surface area of fibers is 1 m^2/g [4]. With refining, the specific surface area of mechanical fibers increases, which is explained by further development of fibrils on fibers [5].

TMP versus kraft pulps

Fiber collapse of pulps has been recognized as an important factor in the development of pulp and sheet quality. The ability of fibers of different pulps to collapse was measured and compared. Results demonstrated that chemically treated fibers are collapsed to a greater extent at low pressures than mechanical pulp fibers. At higher pressures the chemically treated fibers collapsed completely while mechanical pulp fibers did not exceed 80% collapse even at 5000 kPa [6].

Measurements of wet fiber flexibility showed also the difference between kraft and thermomechanical pulps. Tam Doo and Kerekes found that mechanical pulps were 20 to 30 times stiffer than kraft pulps. Dimensions of fibers are one of the factors affecting flexibility. Fibers with thicker walls and larger diameter are stiffer. Pulping conditions play also an important role in determining stiffness of fibers. Increasing yield leads to an increasing stiffness [7].

2.2. TMP fines

Fines are generally defined as the fraction which passes through the 200 mesh screen (74 μm openings) of the Bauer-McNett fractionator. Sometimes, a 100-mesh screen is used. According to the Tappi Methods, fines are the particles that will pass a round hole 76 μm in diameter [8]. According to Luukko's review [9], there is no clear definition of fines since there are several approaches to their separation and characterization. The percentage by weight of the fines fraction of the whole mechanical pulp may be up to 40%.

The importance of mechanical pulps has been recognized to be due almost exclusively to the unique properties of its fines fraction [10]. The amount and quality of fines affect most paper properties. Papers made only from the long fiber fraction have very low strength properties. Surface tension forces and wet pressing are not sufficient to improve fibers bonding in these fines free handsheets. Fines are required to strengthen the paper network [11].

Fines also contribute to the wet web strength. Their addition increases both the wet web tensile and the tensile energy absorption index (TEA) [12]. The level of contribution to wet web properties depends on the proportions of fines in the furnish and the degree of their development and quality.

Many properties of paper can also be affected by the degree of development of fibers. Pulps containing less developed fibers depend more on the fines fraction than those with well-developed fibers [13]. Development of the long fiber fraction improves the strength properties of thermomechanical pulps, but for optical properties fines must be added to the furnish [14].

Classification of fines

Brecht and Klemm [15] characterized the mechanical pulp fines into two categories: "flour stuff" and "slime stuff". The "flour stuff" consists of powder-like, granular pieces of fiber, and lignin-rich particles with low bondability; "slime stuff" is made of cellulose-rich fine fibrils with high bondability.

Using the work of Brecht and Klemm, Luukko and Paulapuro described TMP fines as a mixture of fibrillar and flake-like particles and studied their properties and effect on the paper properties [16].

Wood et al. classified TMP fines according to their specific surface area, using a small hydrocyclone. Fines were classified as high, medium and low specific surface area fines [17]. Particles of size ranging from 0.5-200 μm were observed.

Fines can also be divided into primary and secondary fines. Primary fines are naturally present in disintegrated mechanical pulps (or unbeaten chemical pulps), while secondary fines result from the refining (beating) of fibers [4].

Properties and role of TMP fines

Fines are considered to have the greatest effect on the fiber bonds. The presence of fines within paper has three main effects on sheet structure. These effects are shown in Figure 1. Fines may shorten the distance between two fibers as illustrated on Figure 1A. Figure 1B shows an increased thickness of the paper structure due to fines which can "bridge" fibers. The other effect represented in the right side of Figure 1B is called "blocking". Both effects, bridging and blocking, are similar in their ability to create bridges

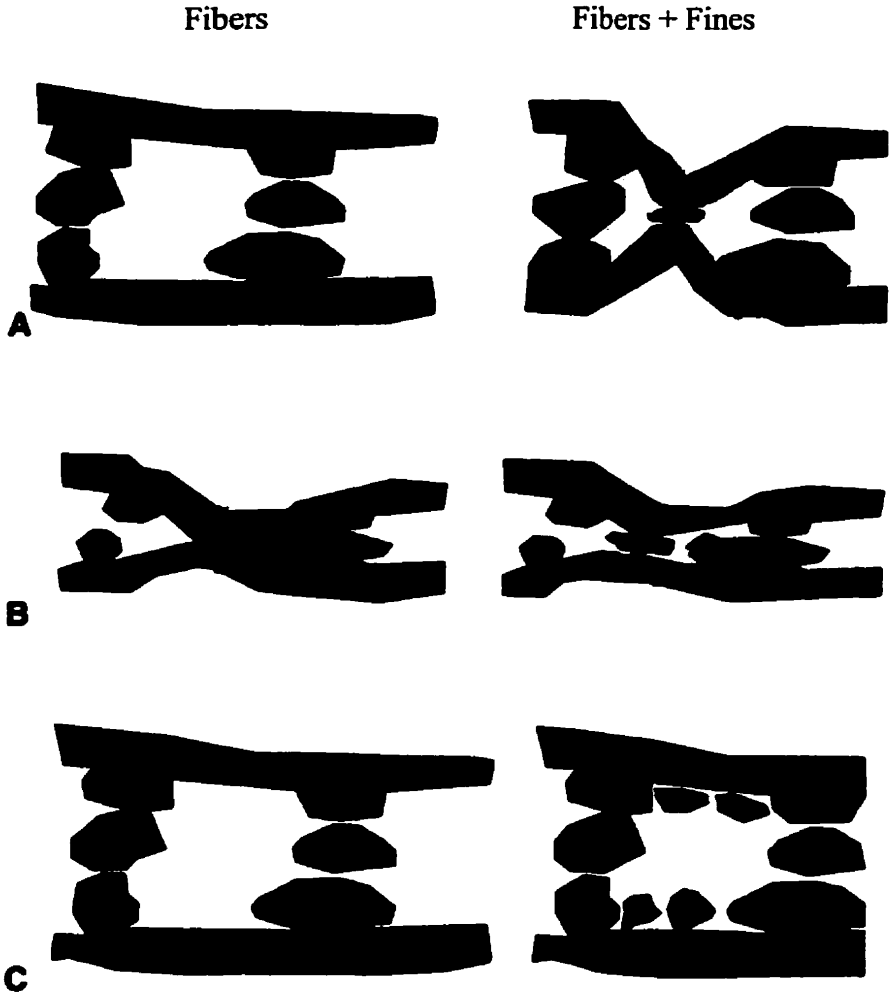

Figure 1. Cross-section of a sheet showing different effects of fines, A – bridging effect, B – blocking effect, C – filling effect [18].

by fines. To distinguish between the two, one has to see what would happen if no fines were present. If the presence of fines creates new bonds which would not occur between fibers otherwise, the effect is called bridging. If bonds are formed in the absence or presence of fines, the effect of fines is called blocking. Fines might also fill interstices between fibers and not create new bonds, which is shown on Figure 1C. This effect is called "filling" [18]. The structural role of fines has also been demonstrated in SEM photomicrographs. In addition to the previously mentioned effects, fines can deposit on the outside surface of a fiber. This effect is called "coating". Shorter fibers, which are considered to be fines as well, are able to perform structurally as fibers and in SEM photomicrographs are found to resemble fibers [19].

Specific surface is an important parameter of fines. The fines have a large surface area in comparison to other fractions and this factor makes them important for improving the properties of paper. It has been calculated theoretically that the specific surface of the fines fraction is 12-14 m^2/g [20]. This value is close to the values of 14-19 m^2/g determined by indirect permeability measurements [21].

Fines are lignin-rich relative to the long fiber fractions. Chemical analysis of thermomechanical pulps showed the lignin/carbohydrates (L/C) ratio to be 32/59 and for the three fractions this ratio decreases in the order fines > middle fraction > long fiber fraction [22]. According to a review article [23], the lignin content of thermomechanical pulp fines varies between 31-39%.

Luukko [9] emphasizes the property of proportion of fibrils, which could be one of the most important for determining the effect of fines on paper properties.

TMP versus chemical pulp fines

In chemical pulps, the amount of fines is lower than in mechanical pulps (around 10% compared to 30-40%). The ability of mechanical pulps to swell in water is reduced compared to chemical pulps due to a high content of hydrophobic lignin and extractives in mechanical pulp fines.

Fines play an important role in determining the physical and optical properties of paper. Retulainen et al. [24] studied the effects of type and amount of fines on paper properties using TMP and softwood bleached kraft fines and fibers. As shown in Figure 2, softwood bleached kraft or TMP fines were added to softwood bleached kraft or TMP fibers. Fines affected both the mechanical and optical properties of paper. Both properties are presented in terms of tensile index and light scattering coefficient, respectively. Addition of kraft fines increased tensile strength greatly while light scattering coefficient was slightly reduced. In contrast, the addition of TMP fines had a positive effect on both properties.

As Retulainen et al. have shown in previous studies [25], the addition of softwood kraft fines to softwood kraft long fibers up to a level 20% resulted in improved strength properties and a slight reduction in light scattering coefficient. Addition of more than 20% fines resulted in a slight improvement of tensile strength, but a further reduction in light scattering coefficient. Also, it was shown that tensile strength was linearly related to the sheet density. Addition of fines from chemical pulps increased the sheet density to a greater extent than the addition of fines from mechanical pulps, thus chemical fines contribute more to the increase of tensile strength. On the other hand, fines from mechanical pulps yielded a larger increase of light scattering, but no strong correlation was found with sheet density.

Mohlin compared light scattering of sheets made of thermomechanical pulps with no fines and containing two different amounts of fines. Plotting light scattering coefficient as a function of density yielded a linear correlation for the same type of pulp [26].

Confocal laser scanning micrographs showed that better contacts were created between TMP fibers when fines were added. Kraft fines were more effective in increasing the contact area than TMP fines [10].

Retulainen et al. also showed that the primary effect of chemical pulp fines is to increase tensile strength and of TMP fines to improve light scattering coefficient. Using a blend of these two fines lead to the increase of both, strength and light scattering coefficient [27].

2.3. Fillers in paper

Fillers are added to pulp suspension primarily to improve optical properties of paper. Furthermore, they improve sheet formation, improve printability and lower the cost of the

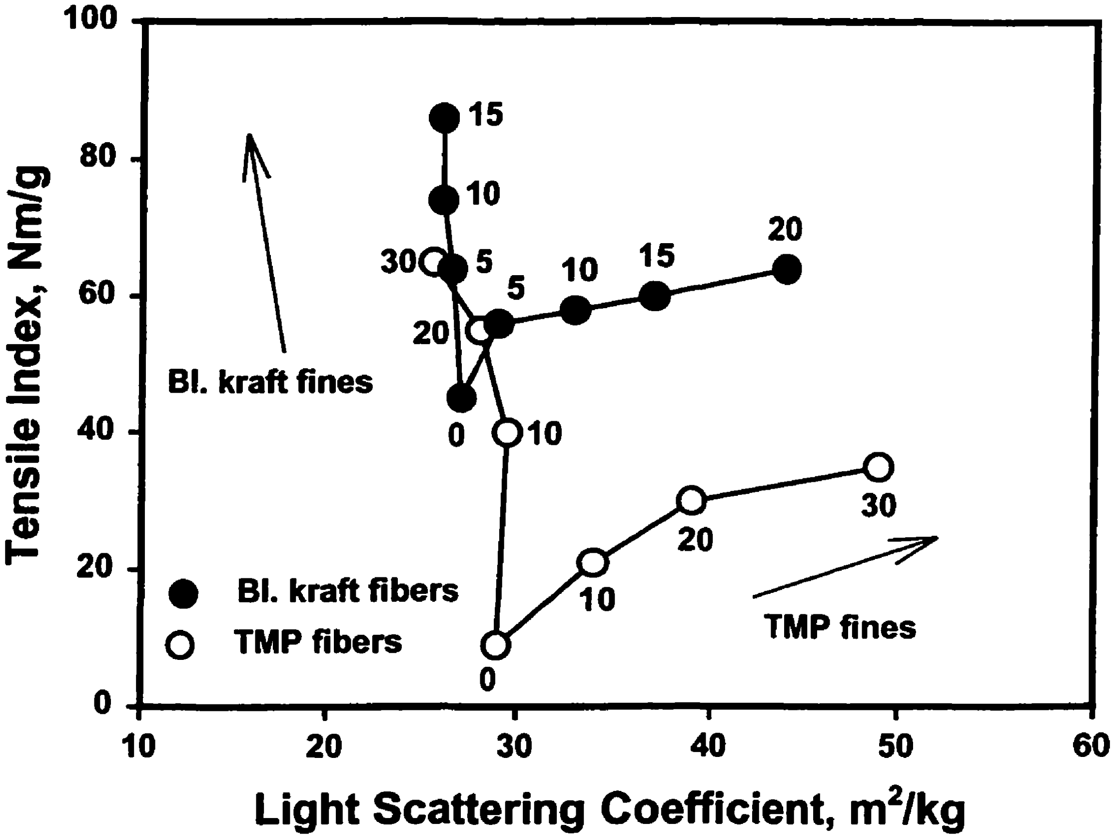

Figure 2. Effect of TMP or kraft fines additions on TMP or kraft fiber network [24].

final product [28]. Usually, 10 to 15% of fillers is added to pulp suspension, in some instances 20 to 30% is used.

Important characteristics of fillers are: particle size and distribution, shape, refractive index, brightness, specific surface area, surface charge and abrasion.

The most widely used fillers in papermaking are clay and calcium carbonate [29].

Calcium carbonate

Natural calcium carbonate is produced from natural chalk or limestone by grinding and fractionation. Precipitated calcium carbonate can be produced from soda mill lime sludge or by special precipitation processes. Precipitated calcium carbonate is less abrasive than the ground one [29]. Calcium carbonate has to be used in alkaline or neutral type of papermaking because it is soluble at low pH. Furthermore, it is attracting attention for acid-free paper manufacturing which is currently in high demand. [30].

Clay

Clay is a naturally occurring material with a basic structure of hydrated aluminosilicates [31]. There are two types of clays – primary, that remain in the place they were formed, and secondary (or sedimentary) that have been transported from the original place and deposited in other sedimentary rocks [32].

2.4. Colloidal behavior of fines and fillers

Fillers and fines can be considered colloidal particles because of their small size. As in other colloidal materials, aggregation can occur under appropriate conditions. Aggregation (or agglomeration) is defined as a gathering of small particles into larger units. Flocculation is similar process but usually occurs in a liquid medium [30].

Aggregation behavior is an important consideration for paper properties. It can be controlled by changing various parameters in papermaking procedures: type of polymer added, shear rate, sequence of addition, type of medium (e.g. tap or deionized water), etc.

Usually, polymers are used as retention aids, as they are able to change the charge of particles and the size of aggregates, thus retaining a larger fraction of additives in a sheet.

Polyethylenimine (PEI) and polyacrylamide (PAM) are retention aids widely used in the papermaking industry. The main role of PEI in papermaking is to modify electrostatic charge. Also, it can be used to prepare well-dispersed suspensions of fillers.

To prepare flocculated suspensions of negative fillers, positively charged PAM can be used as an effective flocculant, which adsorbs on particles by a bridging mechanism. The influence of cationic PAM additions on fiber–fiber or fiber-fines suspensions was studied by King et al. [33]. Addition of positively charged PAM to negatively charged fibers or fines resulted in an adsorption of PAM. An optimum concentration for maximum flocculation of fibers-fibers or fibers-fines was found. However, increased agitation led to a redispersion of fibers in fibers-fibers systems even with increasing concentrations of PAM while fines were not disrupted in fibers-fines systems. This was explained by an increased surface area of fines, which allowed increased polymer adsorption and enhanced polymer bridge strength. Also, size played a role in agitation, smaller particles (fines) experienced a smaller degree of disruption.

3. Thesis Overview

This Chapter focuses on background information related to this study. Objectives of our research are stated.

In Chapter II, the homo- and hetero - flocculation behavior of fines and fillers and the influence of PAM and PEI are discussed. Stability and electrophoretic mobilities measurements for particles in deionized and tap water are presented and explained.

In Chapter III, the effect of different materials (model fines and TMP fines) on optical and tensile properties of TMP and kraft papers is shown and discussed.

In Chapter IV, the correlation between microstructure of thermomechanical papers (varied by addition of different types of materials and characterized by means of porosimetry) and light scattering behavior of this paper was found.

In Chapter V, summary and conclusions are presented.

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CHAPTER II

COLLOIDAL BEHAVIOR OF PAPERMAKING FINES AND FILLERS

Abstract

Measurements of the effects of polyacrylamide and polyethylenimine on the colloidal stability of fines (microcrystalline cellulose or thermomechanical fines), fillers (clay) and their mixtures were performed in order to evaluate their state of flocculation or dispersion. A photometric dispersion analyzer was used to monitor changes in the sizes of the particles.

Measurements confirmed that it was possible to homoflocculate all used materials separately as well as to heteroflocculate them. As expected, higher additions of PAM or PEI lead to steric or electrostatic stabilization of microcellulose and clay suspensions, but it was not possible to stabilize the suspension of fines using high additions of PAM or PEI. In tap water much more PEI or PAM is needed to reach optimum flocculation conditions than in deionized water.

1. Introduction

Paper is a mixture of fibers, fines, often with fillers and different additives. Fibers, fines and most fillers are negatively charged, thus electrostatic forces keep them apart and retention in a sheet is not efficient. In order to keep particles of a colloidal nature (such as fines and fillers) in paper, retention aids are used to flocculate them. Several retention aids, also referred to as flocculants, are used in papermaking: polyacrylamide (PAM), polyethylenimine (PEI), polyethyleneoxide (PEO), etc. Generally, two types of mechanisms of polymer – induced flocculation are recognized in the literature: bridging and charge neutralization/patch flocculation. In the bridging mechanism, an adsorbed polymer creates a link between particles. Generally, high molecular weight and low cationic charge density polymers act by bridging [1]. For example, PEO [2, 3] or weakly charged PAM [4] follow this mechanism. In the charge neutralization mechanism, particle charge is neutralized by a polymer. If a polymer of charge opposite to that of the particles covers the particle partially (creates "patches"), electrostatic interactions between patches on particles and non-covered surfaces of other particles cause the flocculation, also called "patch flocculation" [5]. Neutralization and/or patch flocculation are usually the mechanisms of operation of low or moderately high molecular weight and high charge density polymers [6]. PEI is a typical polymer behaving according to this mechanism.

If colloidal particles are fully covered by polymer, then redispersion can occur due to steric stabilization or due to complete reversal of particle charges.

The flocculation behavior of fibers [7, 8, 9] and fillers [10, 11] by PEI, PAM and a PEO/cofactor system have been studied previously.

The flocculation of fines was studied using a PEO/cofactor system [12]. However, the flocculation behavior of fines induced by PAM or PEI is not discussed in the literature. Therefore, the objective of this work was to study the homoflocculation and heteroflocculation of fines and fillers by PAM and PEI to determine whether or not fines behave similarly as fillers.

2. Experimental

2.1. Materials

Fines

Microcrystalline cellulose (FMC Corporation) with average particle sizes 6 µm (MCC) was used to model small "chunky-like" portions of fines.

The P200 (pass 200 mesh screen) fraction of thermomechanical fines was used in the experiments. The fines were separated from thermomechanical pulp with a float wash equipped with 200 mesh (openings of 74 µm) screen. TMP fines contain various types of materials, i.e. fragments of fibers, fibrillar material, ray cells, pieces of fiber wall of sizes 5-100 µm [13]. Different values for surface area of fines are reported in the literature and will be discussed in this chapter.

Fillers

Filler clay Hydrite UF (Georgia Kaolin) with mass average equivalent spherical diameter 0.2 µm was used as filler. The specific surface area is 16 m^2/g [14] (determined by nitrogen adsorption).

Polymers

Polyacrylamide (PAM) (Percol 292, Allied Colloids) with molecular weight of approximately 3×10^6 [11] and degree of substitution of 25% was used. Stock solutions of 0.1% were prepared by wetting the beads of polymer with ethanol and adding deionized water. The solution was mixed for about 30 min. in order to ensure complete dissolution of the polymer. Diluted solutions (0.01, 0.001%) were prepared from the 0.1% stock solution. Solutions were prepared an hour before experiments and the pH was maintained at 6-7 to minimize the alkaline hydrolysis process, which can affect the charge density of the polymer [15].

Polyethylenimine (PEI) Polymin P (BASF) was used. This is a highly charged branched cationic polyelectrolyte with mass average molecular weight $M_w = 600\,000$ from light-scattering [16]. A stock solution of 1% was prepared from a liquid sample of 25% concentration by adding an appropriate amount of deionized water. Solutions of 0.1, 0.01, and 0.001% were subsequently prepared from the 1% stock solution. The charge of PEI depends on pH, as amino groups are protonated at lower pH. To ensure a positive charge of PEI, the pH was kept neutral.

2.2. Methods

Changes in the state of aggregation of a suspension of fines, fillers, or their mixtures were monitored by a Photometric Dispersion Analyzer (PDA) described in [17, 18, 19]. A suspension flowed from the outlet of a 2L beaker through the photocell of the PDA. The PDA monitors the fluctuations in intensity of light transmitted through a flowing suspension. The root mean square (rms) value of the fluctuating signal is a sensitive indicator of the state of aggregation of the suspension. Measured is the ratio R of the rms value of the intensity fluctuations, V_{rms} to the dc output which corresponds to the average transmitted light intensity $\bar{V}$.

$$R = V_{rms}/\bar{V} \quad (1)$$

Changes in the size of flocs as a function of time were detected and the flocculation rate was determined. The stability ratio W for a particular flocculation rate k_i was calculated as

$$W = k_{fast} / k_i \quad (2)$$

where k_{fast} is the fast flocculation rate, for which $\log W = 0$. Usually, k_{fast} is the rate when all electrostatic repulsions are screened by salt or reduced to zero by polyelectrolyte (e.g. PEI). When $\log W = \infty$, the suspension is stable. In some cases, $\log W < 0$ (ultrafast flocculation). This happens when there is long range attraction, e.g. due to bridging by polymers which extend far from the particle surface.

The flocculation behavior of different materials depends on the conditions under which they are measured, i.e. pH [20, 21], shear rate, flow rate, concentration of a suspension [22], purity of water [23]. A neutral pH was maintained in our experiments unless otherwise specified. The mixing rate (100 rpm) and flow rate (100 mL/min) were also kept constant. The concentration of the suspension was 0.2 g/L. Experiments with PAM were performed in tap water considering that PAM is not very sensitive to the type of water [11]. On the other hand, when PEI was used, experiments were carried out with two types of water – tap (conductivity ~ 260 μS/cm) and deionized (conductivity ~ 4 μS/cm). The conductivity of tap water is equivalent to the conductivity of a 3 mM sodium chloride solution.

Before performing heteroflocculation experiments between fines and fillers, stabilized suspensions had to be prepared. Clay was treated with a high amount of PEI at high shear in order to obtain a redispersed system. Then, excess PEI was removed by filtration. To follow the kinetics of heteroflocculation, a constant amount of clay (50 mg) treated with PEI was added to different amounts of MCC or fines. The effect of the consistency of a suspension on the ratio signal of the PDA was very low. Rather, the ratio was found to be affected only by particle aggregation, so that ratio values could be compared. Only deionized water was used for heteroflocculation experiments in order to avoid the flocculation of clay treated with PEI due to the type of water, since flocculation of clay treated with PEI has been observed in tap water.

Electrophoretic mobility (EM) of particles was measured using a MK II Microelectrophoresis Apparatus (Cambridge, UK), equipped with a flat cell.

The polyelectrolyte titration method was employed to determine the adsorption isotherm. PEI was added to a suspension and allowed to adsorb for 30 minutes at a mixing rate of 100 rpm. The supernatant was separated from the fines by centrifugation. The amount of PEI left in the supernatant was then determined. In this method, titration of a cationic polymer (PEI) with an anionic polyelectrolyte – potassium polyvinyl sulfate (PVSK) in the presence of an indicator/buffer – orthotoluidine blue at pH 4 was carried out.

3. Results and discussion

3.1. Characterization of fines

Figure 1 shows the adsorption isotherm of PEI on thermomechanical fines at pH 6 in deionized water.

The mechanism of polydisperse PEI adsorption on non-porous glass fibers and

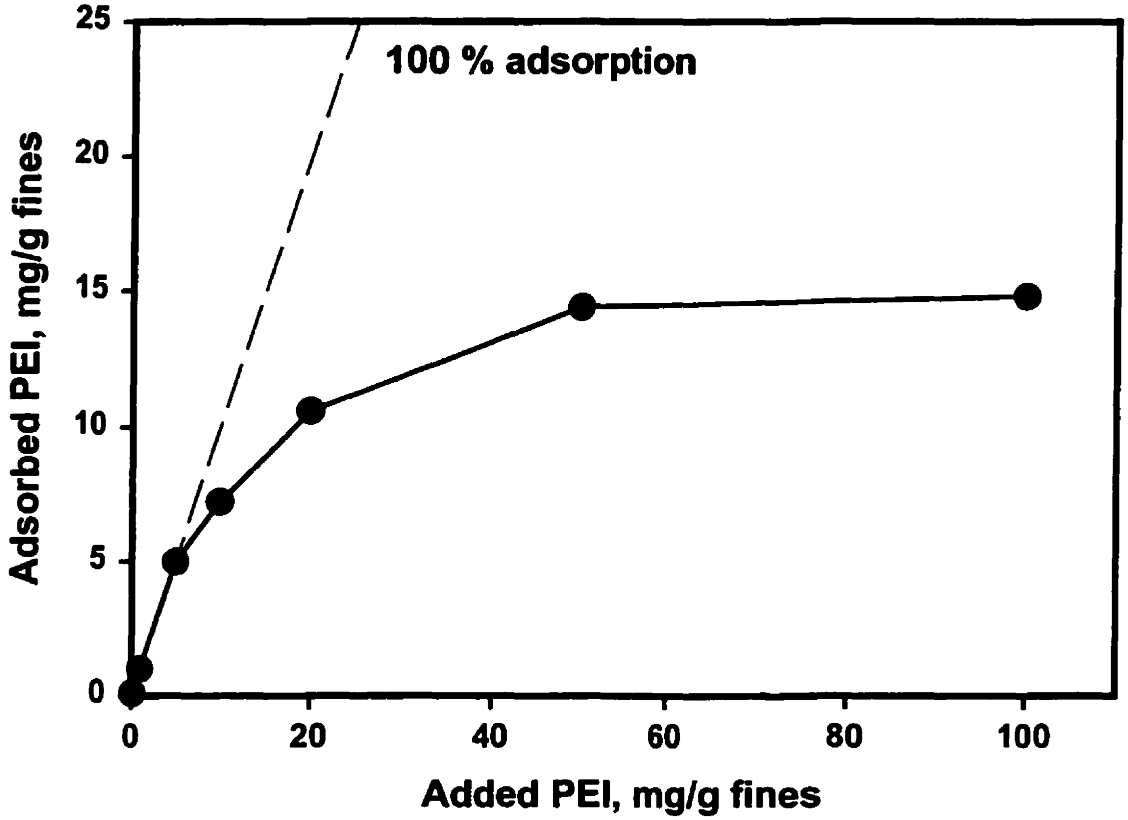

Figure 1. Adsorption isotherm of PEI on thermomechanical fines at pH 6 in deionized water.

porous pulp fibers was discussed in [21]. This work explains the shapes of adsorption isotherms in terms of adsorbing high and low molecular weight PEI at different stages. Fines are similar to fibers, i.e. they have a porous structure, and hence a similar approach can be applied to explain the adsorption isotherm in Figure 1. It can be divided into 4 parts. The first part is characterized by 100% adsorption (i.e. 0-5 mg adsorbed PEI/g fines). In this region, the PEI concentration is low and the concentration of high molecular weight material is much higher than the concentration of low molecular weight material. This high molecular weight material adsorbs on the external surface of the fines. As the concentration of PEI increases, the amount of low molecular weight material in suspension increases. This material adsorbs in between high molecular weight PEI on the external surface. This describes the region of the adsorption curve in the range of 5-11 mg adsorbed PEI/g fines. In the third stage (above 11 mg adsorbed PEI/g fines), as the concentration of polymer increases, the concentration of low molecular weigh material increases and this fraction starts entering the pores in the fines. The fourth stage corresponds to the plateau-value, reached when the interior of the fines is saturated. Assuming that the specific adsorption of high molecular weight PEI is 0.4 mg/m^2 at pH = 6 [21], we can conclude that the external surface area of the fines is ~ 12.5 m^2/g. Other studies reported surface areas of 12-14 m^2/g from microscopic observations [24] or 14-19 m^2/g by indirect permeability measurements [25].

Electrophoretic mobility of fines as a function of PEI concentration and type of water are shown on Figure 2. Fines (without polymer) are more negatively charged in deionized water than in tap water. There is an effect of ions present in water on the electrical double layer. The double layer is created by counterions (that have opposite charge to that of the particle) close to the surface of the particle. When more of these ions are present, as in the case of tap water, the double layer thickness is compressed and particles slow down when exposed to an electric field. As the concentration of polyelectrolyte (PEI) increases, the negative charge of fines diminishes. At a certain concentration of PEI the electrophoretic mobility of fines reaches zero. We will refer to this point as the isoelectric point (IEP), not as the point of zero charge, since they are not identical [26]. We note that the amount of PEI added to fines in order to reach the IEP is lower in deionized water (~ 3 mg PEI/g fines) than in tap water (~ 8-9 mg PEI/g fines). This is again caused by the presence of some negative

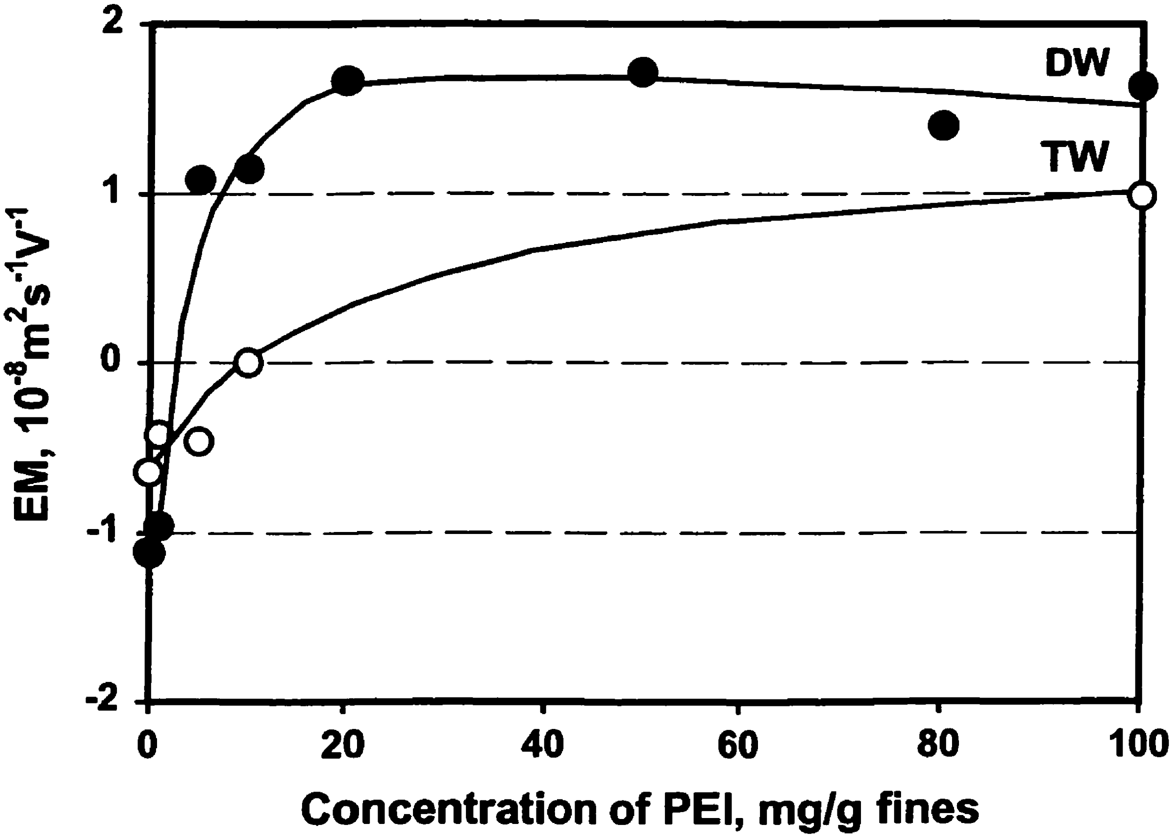

Figure 2. Electrophoretic mobility of thermomechanical fines as a function of PEI concentration in deionized (DW) and tap water (TW).

ions in tap water. Possibly PEI adsorption is reversible in tap water, similar to the case of water containing high concentration of NaCl [21].

The results of electrophoretic mobility of fines in deionized water (Figure 2) support the adsorption isotherm data. The IEP corresponds approximately to the state of particles being partially covered by PEI, thus keeping some positive and some negative patches on their surface. At 5 mg PEI/g fines particles are fully coated by polymer, which corresponds to a positive electrophoretic mobility ($\sim 1\mathrm{x}10^{-8}\mathrm{m}^2\mathrm{s}^{-1}\mathrm{V}^{-1}$).

Electrophoretic mobilities of model fines (MCC) are shown on Figure 3 in deionized water and in tap water. Both plots have similar characteristics as the plots in Figure 2. Particles of MCC are negatively charged in both types of water without a polymer. The negative charge of particles is more pronounced in deionized water for reasons discussed above. When compared to fines, lower amounts of PEI are needed to reach the IEP for MCC. This is probably due to differences in surface areas for these two materials (fines have a larger specific surface area than MCC). Considering the effect of water type, the point of zero charge is reached at 0.05 mg PEI/g MCC in deionized water and 2 mg/g MCC in tap water. This amount does not compare with experiments for fines where the PEI amount required to reach the IEP is just three times as high in experiments in tap water. Presumably ions or other dissolved material affect the adsorption and/or desorption rates of PEI. More studies need to be done to explain this result.

3.2. Flocculation of fines by PEI

The effects of PEI on the flocculation of fines are shown in Figure 4 for deionized water and tap water. The fastest flocculation rate constant k_{fast} was taken for the system of fines in deionized water.

The maximum flocculation rates measured for two systems correspond to the additions of 1-5 mg PEI/g fines in deionized water and 10 mg PEI/g fines (or perhaps somewhat less) in tap water. There is a little difference in flocculation rates attained in deionized and tap water.

It can be seen that lower amounts of PEI are needed to reach the fast rate of destabilization of fines suspensions in deionized water than tap water for reasons already

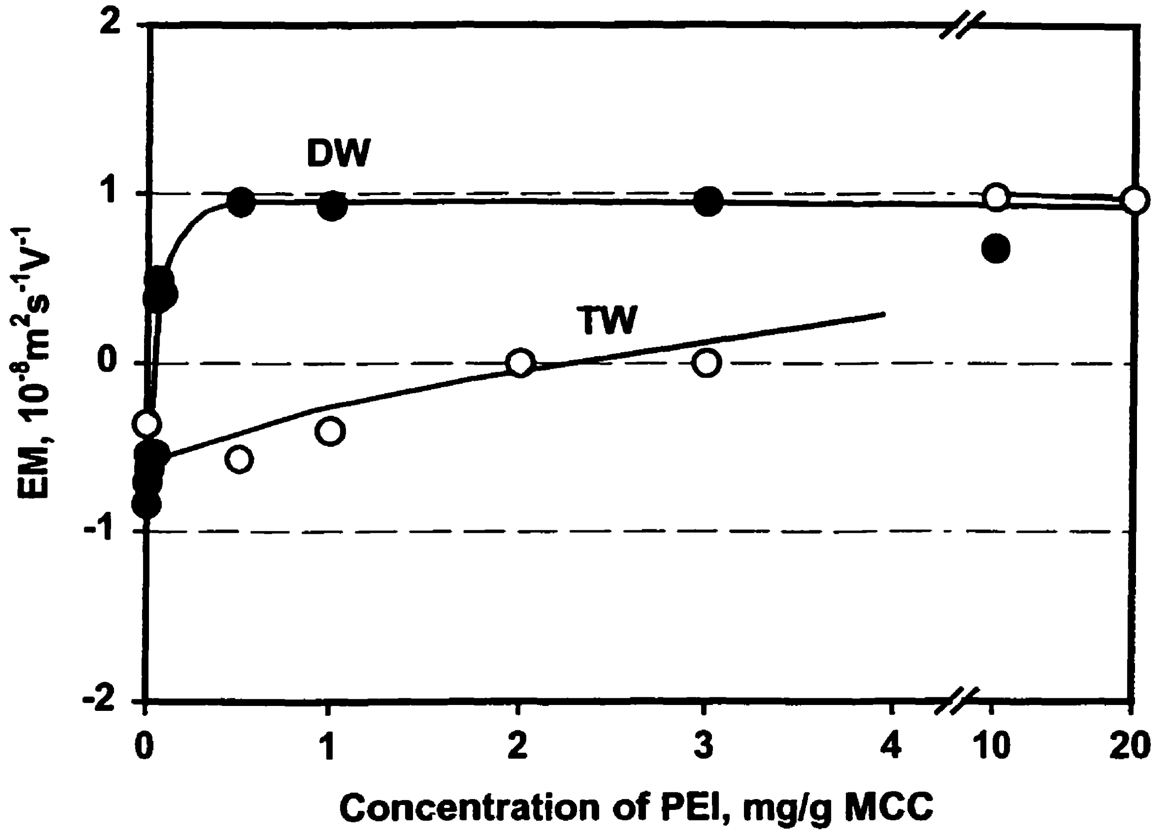

Figure 3. Electrophoretic mobility of microcrystalline cellulose (MCC) as a function of PEI concentration in deionized (DW) and tap water (TW).

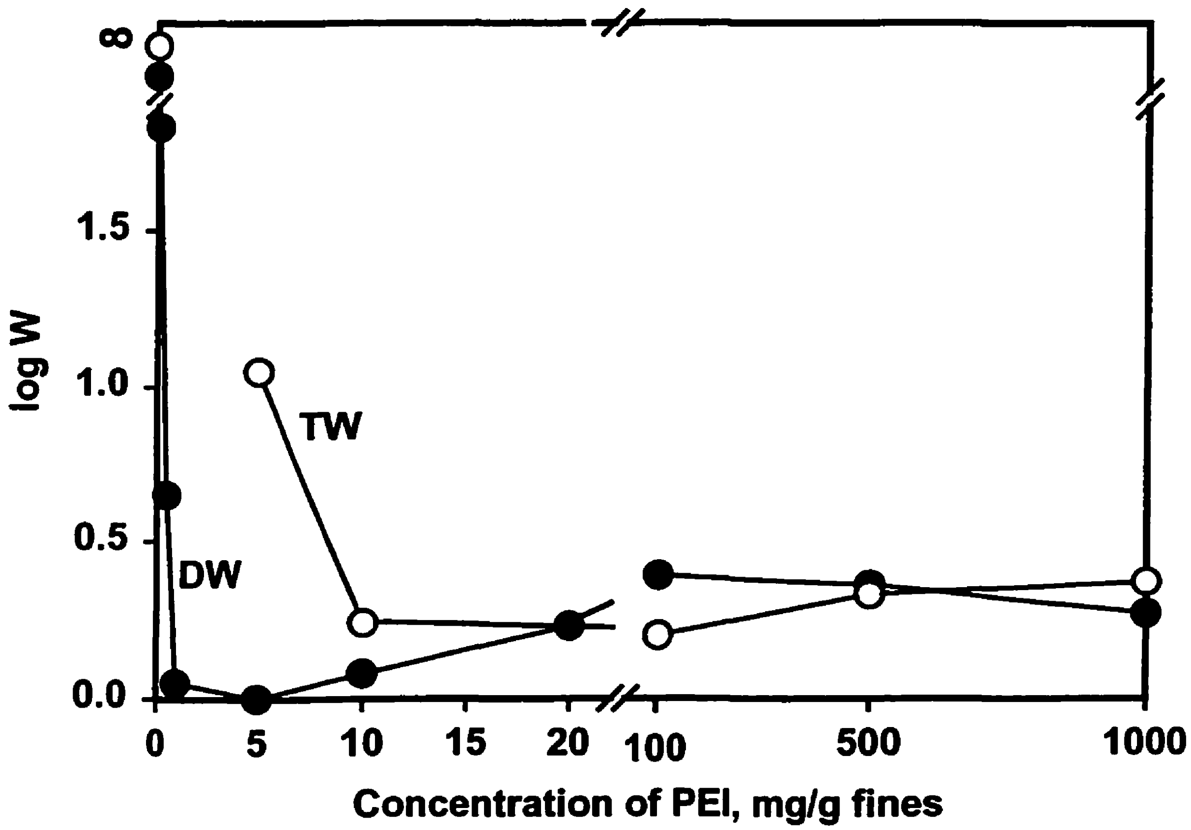

Figure 4. Stability ratio W of fines as a function of PEI concentration in deionized (DW) and tap water (TW).

discussed. Higher amounts of PEI (up to 1000 mg PEI/g fines) are not sufficient to stabilize a suspension. When looking at measurements of electrophoretic mobilities (Figure 2), we can see that the amount of PEI needed to reach the fast flocculation rate are in the range of amounts of PEI added to fines to reach the IEP in both deionized and tap water. This indicates that electrostatic interactions dominate the process. At higher doses of PEI, fines become positive, but do not restabilize. The exact cause of this is unclear. Attempts of washing the fines in deionized water in order to remove possible unwanted substances were made. Also, as mentioned in [21, 27], the size of PEI molecules increases at low ionic strength, low pH or PEI concentration which results in reduced adsorption on fiber surfaces. Figure 5 presents the stability ratio for washed fines at low ionic strength and pH = 3. The fastest flocculation rate constant k_{fast} was taken for the system of fines in deionized water at the neutral pH. The system in Figure 5 shows a very similar flocculation behavior as in Figure 4. This excludes the possibility of the effect of ionic strength, pH or dissolved substances on the anomalous flocculation behavior of fines at high PEI concentrations. The effect of the heterogeneity of fines and the possibility of creating entanglements within the suspension should be considered. Even a system without added polymer might be subject to entanglements, which would mean that the PDA signal corresponds to a certain dynamic equilibrium within the suspension. This equilibrium is then assumed to represent a dispersed system ($\log W = \infty$). As polymer is introduced, the external surfaces of fines will be coated and this will change their electrical properties (Figure 2). As more polymer is introduced and a monolayer of high molecular weight polymer is present on the outer surface (fines are positively charged), low molecular weight polymer starts entering outer and inner surfaces which will lead to higher "consumption" of polymer, but polymer-coated inner surfaces will not enhance the positive charge of fines. Although fines are positively charged and they should restabilize, possibly PEI coated fines are more prone to entanglements and appear to be flocculated.

Figure 6 shows the stability ratio W for measurements with MCC performed in deionized and tap water. The fast flocculation rate constant k_{fast} was taken for the system of MCC in deionized water. Although it looks like MCC flocculates faster in tap water, this is not necessarily the case. There still could be a different addition of PEI close to the value of

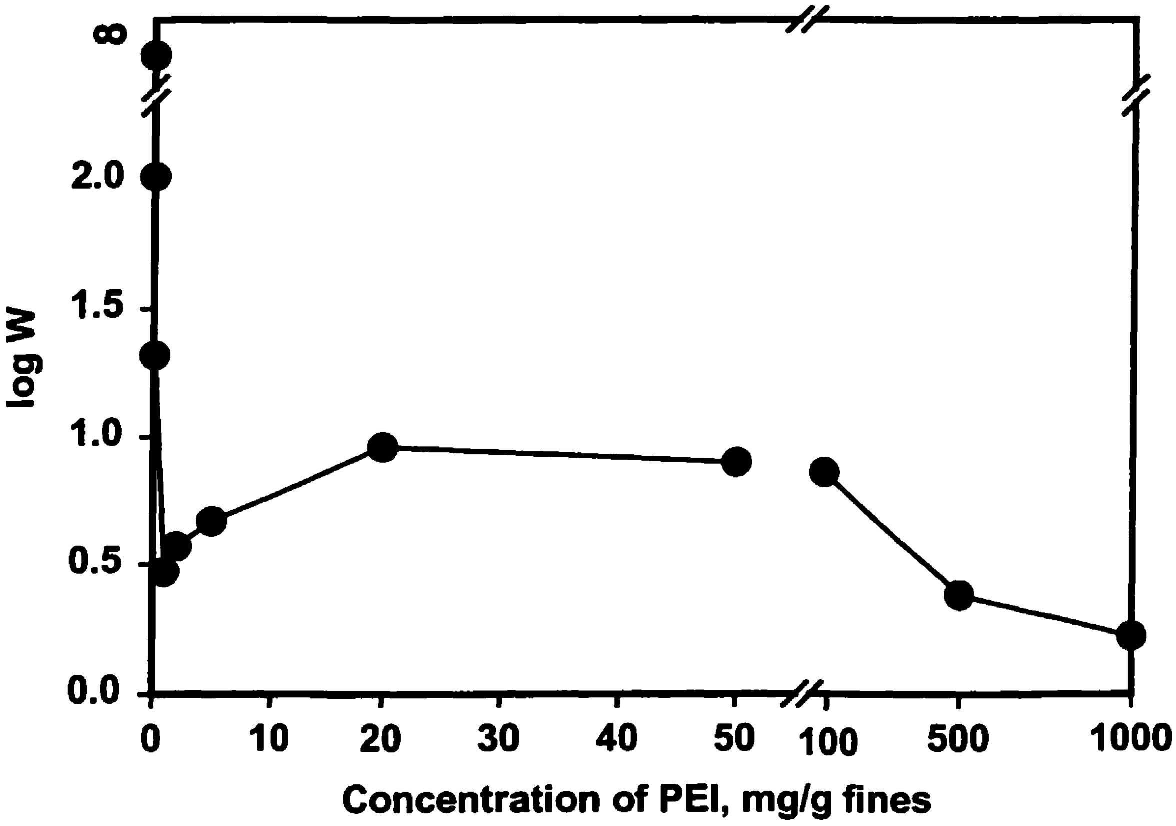

Figure 5. Stability ratio W of washed fines as a function of PEI concentration in deionized water at pH 3.

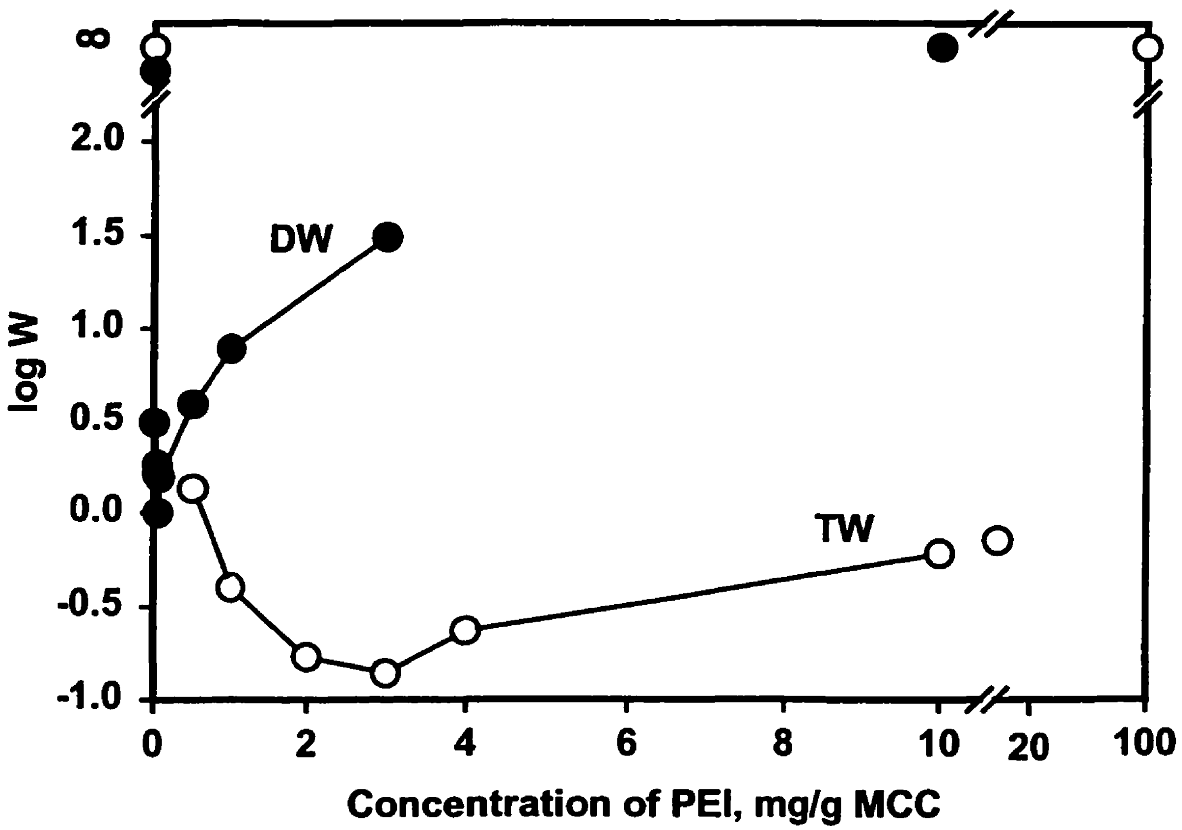

Figure 6. Stability ratio W of microcrystalline cellulose (MCC) as a function of PEI concentration in deionized (DW) and tap water (TW).

0.06 mg PEI/g MCC (the maximum for deionized water) at which a faster rate of destabilization could be reached.

The maximum flocculation rate occurs upon the addition of 0.06 mg PEI/g MCC and 2-3 mg PEI/g MCC in deionized and tap water, respectively. The lower ionic strength medium permits attainment of maximum flocculation rate and stabilization faster. Comparing the amounts of PEI needed to reach the maximum destabilization (Figure 6) and to reach the IEP of MCC (Figure 3), we can see they are in similar ranges. This agrees with the mechanism that the action of PEI is controlled by electrostatic forces. We can notice that at high PEI dosages restabilization occurs due to charge reversal. At an addition of 10 mg PEI/g MCC in deionized water, particles were stable, whereas in tap water, a higher amount of PEI (100 mg PEI/g MCC) was required to reach a stable suspension.

3.3. Flocculation of fines by PAM

In the previous section, we compared the behavior of fines in deionized and in tap water. In this section we compare the behavior of fines with model fines (MCC). Experiments with PAM were performed only in tap water since PAM is not very sensitive to type of water [11].

Figure 7 shows the change of charge of fines and MCC as a function of PAM addition. The IEP is reached upon addition of ~ 4-5 mg PAM/g fines and ~ 2 mg PAM/g MCC.

Flocculation of MCC and fines in tap water in the presence of PAM is shown in Figure 8. For each system (MCC and fines), a different fast flocculation rate k_{fast} was chosen because of differences in adjustments (gains) of the PDA.

In the absence of polymer, the suspension is assumed to be dispersed, thus log W = ∞. Upon addition of PAM the system destabilizes, flocculation is induced and reaches its maximum rate (log W = 0) for PAM additions of 5-10 mg/g fines and ~ 5 mg /g MCC. These amounts are higher than the amounts added to fines and MCC to reach the IEP (Figure 7). This indicates that PAM operates via a different flocculation mechanism and that electrostatic forces are less important in this case. Polymer bridging is involved in this type of flocculation. As expected, higher additions of PAM (500 mg/g) lead to a steric stability

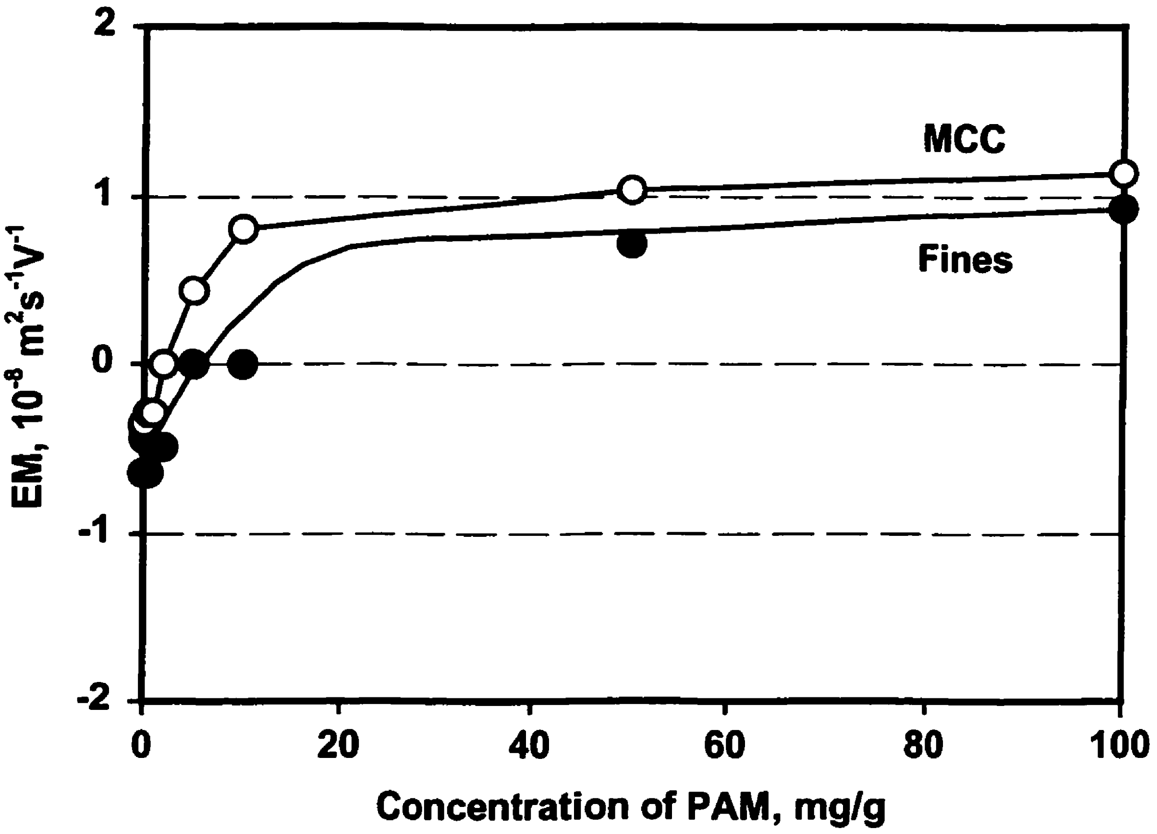

Figure 7. Electrophoretic mobility of thermomechanical fines and microcrystalline cellulose (MCC) as a function of PAM concentration in tap water.

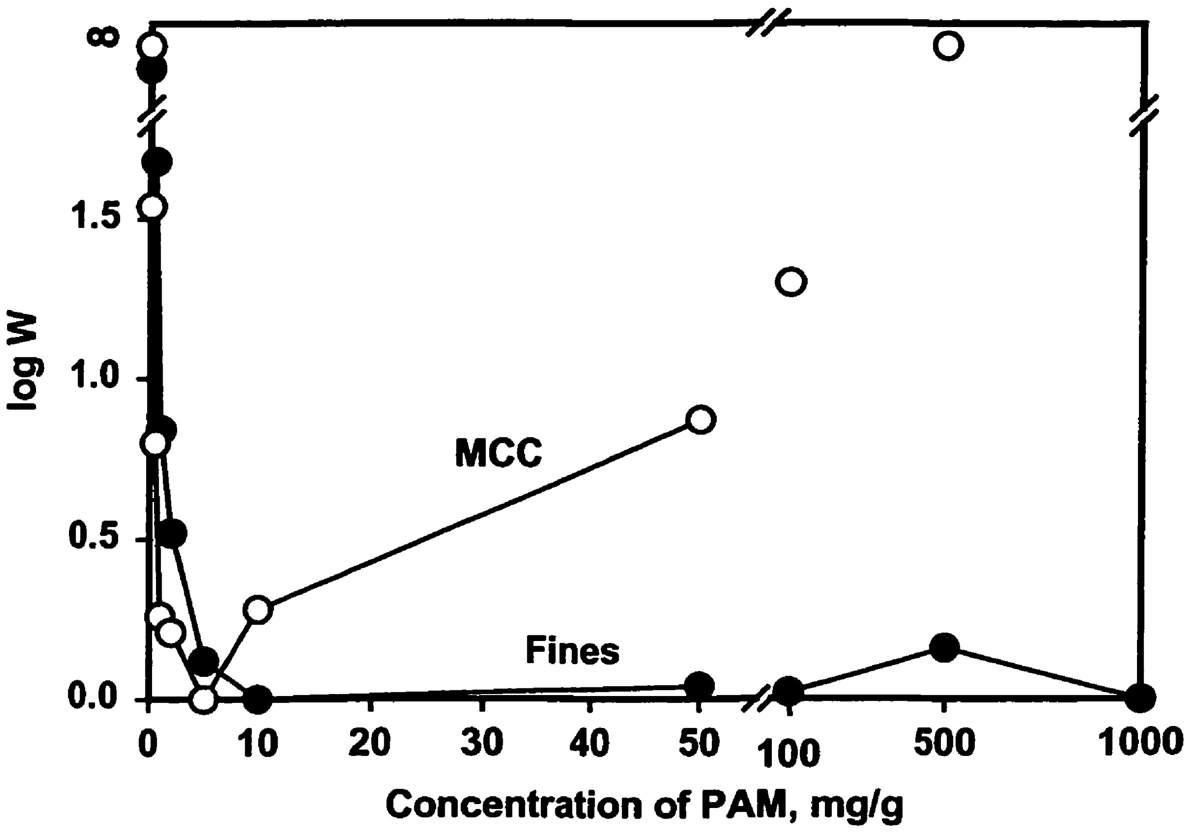

Figure 8. Stability ratio W of thermomechanical fines and microcrystalline cellulose (MCC) as a function of PAM concentration in tap water.

in the case of MCC. Our experiments showed that fines were not stabilized, even at addition of 1000 mg PAM/g fines. Earlier studies showed that PAM-coated fines deposited on PAM-coated fibers [28] that have the same surfaces properties as fines. This suggests the possibility of deposition of PAM-coated fines on PAM-coated fines, thus causing flocculation. Other studies of fiber-to-fiber and fiber-to-fines cationic PAM induced flocculation showed a similar effect of fines [9]. When fines were present higher polymer concentrations did not lead to fines detachment from fibers and the suspension remained flocculated. On the other hand when polymer was added to fibers, redispersion occurred at higher polymer concentrations. This was ascribed to the large surface area of fines, which allows more polymer to be adsorbed and the strength of the polymer bridge to increase. Under the conditions of these experiments the shear was not high enough to disrupt the flocs created by fibers and fines. It is still not clear why flocs created by fines alone cannot redisperse at high amounts of added PAM. The creation of a strong polymer bridge could be an explanation. Also, as proposed earlier, entanglements could play a role in keeping a suspension of fines flocculated. Another reason could be that the polymer layer is not thick enough to eliminate van der Waals attractive forces.

3.4. Flocculation of fillers

Flocculation and EM measurements of clay were performed in tap water only because PAM is not very sensitive to type of water. Additions of PEI to clay suspension in deionized water are described in [20]. The IEP of clay in deionized water was reached at the addition of 1 mg PEI/g clay at pH 6.

Electrophoretic mobilities for clay particles in tap water upon additions of PAM and PEI are presented in Figure 9. The amount of PEI needed to reach the isoelectric point of clay is above 25 mg PEI/g clay, but amounts of 10-25 mg PEI/g clay already make clay less negatively charged.

Figure 10 shows the stability ratio as a function of added PEI and PAM to the clay suspension in tap water. When no polymer is present, the suspension is stable. When positive polymers are added, either PEI or PAM, clay particles start to flocculate. The fastest rates of flocculation are reached upon addition of 15 mg PEI/g clay or 5 mg of PAM/g clay. At

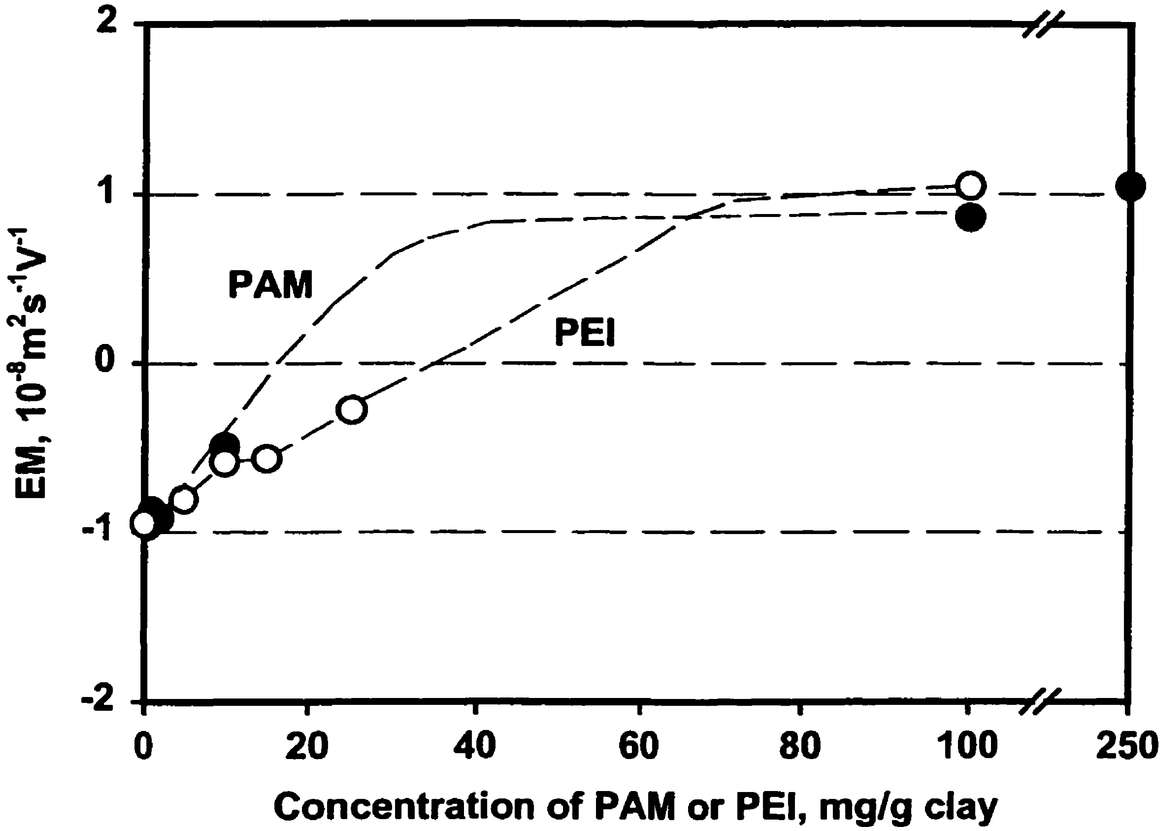

Figure 9. Electrophoretic mobility of clay as a function of PAM and PEI concentration in tap water.

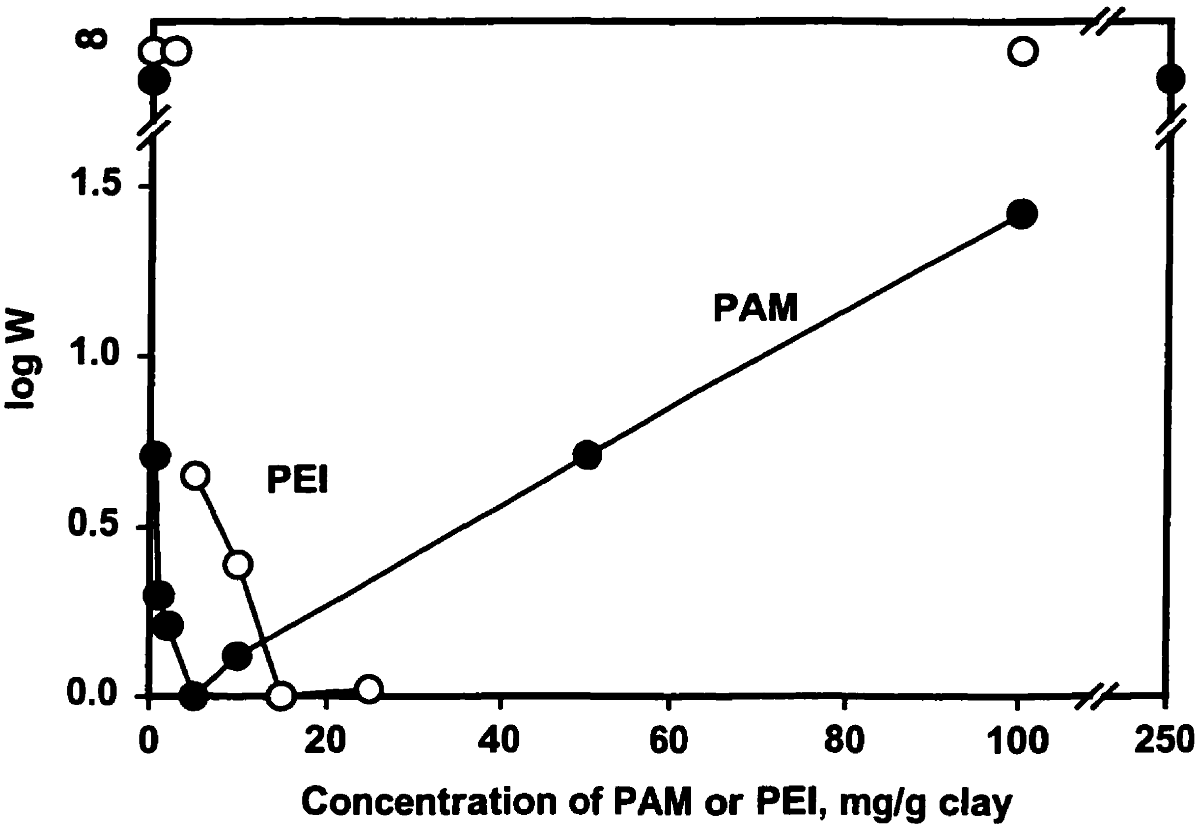

Figure 10. Stability ratio W of clay as a function of PAM or PEI concentration in tap water.

the fastest flocculation rate the electrophoretic mobility of clay particles corresponds to $-0.5\times10^{-8}m^2s^{-1}V^{-1}$ (for 15 mg of PEI) and to $-0.8\times10^{-8}m^2s^{-1}V^{-1}$ (for 5 mg of PAM) from Figure 9. The amount of PEI required to reach the fastest flocculation rate corresponds to the state of clay particles, in which the charge of particles is low enough to initiate flocculation. This indicates again the importance of electrostatic interactions in the PEI adsorption mechanism. On the other hand, the electrophoretic mobility of clay particles corresponding to the fastest flocculation induced by PAM did not change much from the original negative value of $-1\times10^{-8}m^2s^{-1}V^{-1}$ which indicates that the bridging mechanism plays an important role. Data reported in [21] suggest that the maximum rate of destabilization of clay in distilled water is reached when 1 mg PEI/g clay is added at pH = 6. This amount is more than 20 times less than the amount observed here in tap water. Slightly higher amounts could be explained by the presence of some ionic impurities in tap water, which would interact with PEI instead of clay. The amount of 15 mg PEI/g clay is too high to be caused only by the ionic strength of tap water. Possibly, a reversible adsorption of PEI takes place under these conditions, as in the presence of high salt concentrations [21].

Increasing the amounts of positive polymer lead to steric or electrostatic repulsion and the suspension becomes stable. In our case, amounts of 100 mg PEI/g clay or 250 mg PAM/g clay are needed for clay to be electrostatically or sterically stabilized.

3.5. Flocculation of mixtures of fines and fillers

The stability of suspensions consisting of two components (MCC/clay, fines/clay) is shown on Figure 11. The flocculation rate depends on the ratio and surface area of oppositely charged particles present in suspension. MCC or fines are negatively charged while clay is positively charged due to the adsorbed positive PEI. When no MCC or fines are present in the suspension, clay treated with PEI is stable in deionized water. Upon mixing 50 mg of the PEI-coated clay with 50 mg of MCC, the system remains stable. Clay particles provide full coverage of MCC particles which makes the suspension stable. On the other hand, addition of the PEI-coated clay to 50 mg of fines causes the suspension to flocculate. This difference might be caused by differences in the surface areas of MCC and fines. As seen from Figure 8, the amount of PAM needed to reach the fastest flocculation of fines is

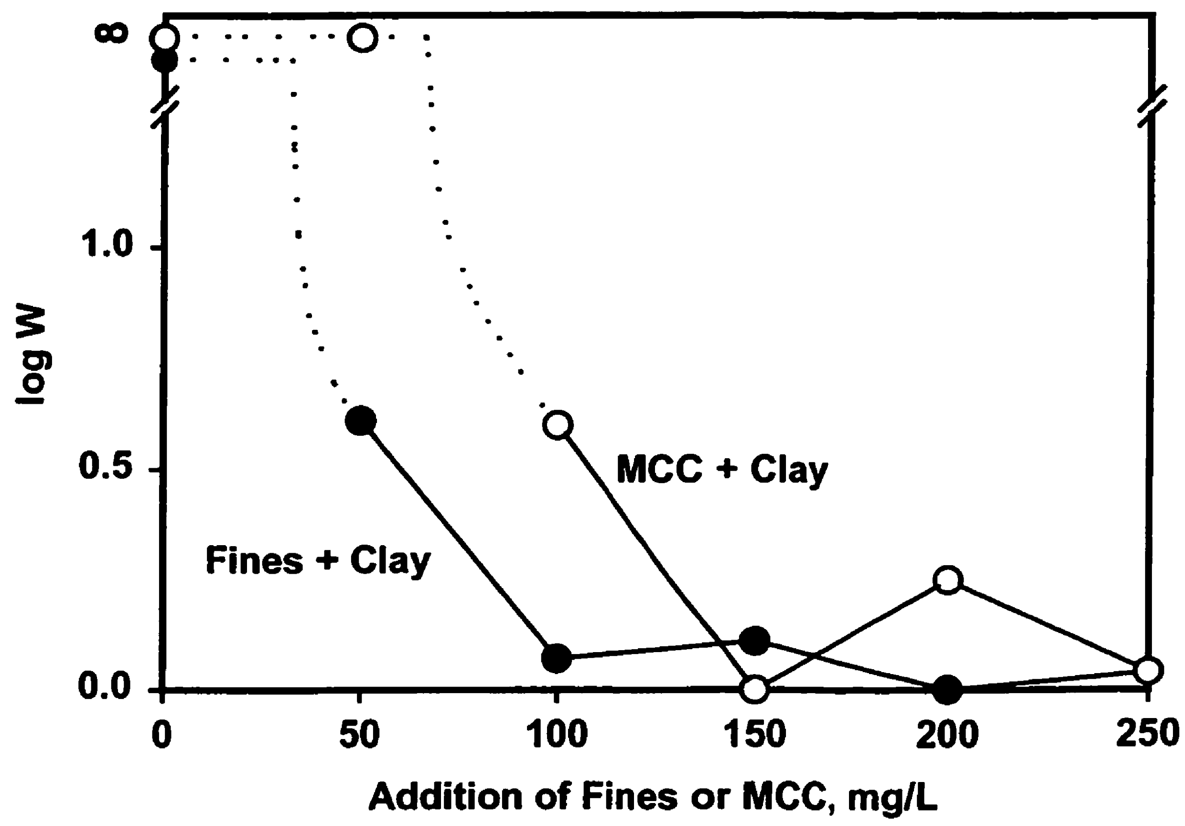

Figure 11. Stability ratio W of mixtures of fines/clay and MCC/clay as a function of addition of fines or MCC in deionized water. Sequence of addition: 1. Fines or MCC, 2. Clay (50mg/L) treated with PEI.

approximately double that needed for the fastest flocculation of MCC. This indicates that the surface area of fines is about twice as large as the surface area of MCC. Thus, the presence of 50 mg of fines will provide more negative surfaces for interaction with positive clay particles, than 50 mg of MCC. An amount of 50 mg of positive clay particles is not sufficient for full coverage of 50 mg of fines and the suspension will flocculate. Upon increasing amount of MCC or fines, addition of clay makes the suspension flocculate faster until it reaches the maximum flocculation rate and higher amount of MCC or fines (over 100 mg fines/L, or over 150 mg MCC/L) no longer change the flocculation rate. PEI-coated clay particles form a bridge between bare fines or bare MCC.

The adsorption of PEI-coated clay on MCC or fines particles can be described by the following equation:

$$\frac{dN_f}{dt} = -\alpha k N_f^2 \qquad (3)$$

where $\frac{dN_f}{dt}$ is the decrease in number of particles (fines or MCC) Nf, with time t, k is the adsorption rate constant. The adsorption efficiency α can be written as:

$$\alpha = 2\,\theta\,(1-\theta) \qquad (4)$$

where $(1-\theta)$ is the fraction of the surface of fines or MCC that is bare. θ is the coverage of fines or MCC by PEI-coated clay and it is inversely proportional to Nf:

$$\theta \propto 1/Nf \qquad (5)$$

If we assume that clay adsorption on fines or MCC is faster than fines flocculation, since fines do not flocculate without clay, then we can determine certain critical fines or MCC concentrations $[\text{fines}]_{\text{crit}}$ below which $\theta = 1$ and $\alpha = 0$. This corresponds to a value of $W = \infty$ that describes a stable suspension. Above $[\text{fines}]_{\text{crit}}$, θ decreases with Nf. For a large number of particles of fines or MCC N_f, the coverage θ is small. Then equation (3) reduces to:

$$\frac{dN_f}{dt} \approx -2\theta k N_f^2 \qquad (6)$$

Using (5) we can rewrite (6) as:

$$\frac{dN_f}{dt} \approx -\frac{k^*}{N_f} N_f^2 = -k^* N_f \qquad (7)$$

where k^* is a redefined rate constant. In our experiments, ratio R was monitored with time. The change of this ratio with time can be expressed as:

$$\frac{dR}{dt} \propto \frac{1}{N_f}\frac{dC}{dt} \propto k^* \qquad (8)$$

where C is number of clay particles. k^* is independent of fines concentration and constant for a fixed clay concentration. Above $[\text{fines}]_{\text{crit}}$ and at a constant clay concentration, log W will decrease with increasing amount of fines or MCC, until it reaches a constant value. Knowing the specific surface areas of clay (16 m^2/g) and fines (12 m^2/g) and MCC particles (assuming 6 m^2/g) we can predict the trend in log W (dotted curves on the Figure 11) and the values of $[\text{fines}]_{\text{crit}}$, and $[\text{MCC}]_{\text{crit}}$. The surface area of 50 mg of clay is about 0.8 m^2, from which 0.4 m^2 is available for adsorption on fines or MCC. $[\text{MCC}]_{\text{crit}}$ must be lie between 50-100 mg (from Figure 11) and $[\text{fines}]_{\text{crit}}$ between 1-50 mg. Critical values of fines and MCC based on full coverage by clay are: $[\text{fines}]_{\text{crit}} \sim 33$ mg/L, which corresponds to a surface of 0.4 m^2, and $[\text{MCC}]_{\text{crit}} \sim 66$ mg/L.

4. Conclusions

Controlled homo- and hetero-flocculation experiments of MCC, clay and MCC/clay, fines/clay induced by PEI or PAM confirmed that these systems follow the mechanisms previously described in the literature. Contrary to theory, thermomechanical fines at high concentrations of polyelectrolytes did not undergo redispersion. This behavior of fines has not been previously described in the literature. The fibrillated nature of fines may lead to entanglements within the suspension and allow a certain dynamic equilibrium to be reached. Addition of polymer could shift this equilibrium, keeping the suspension flocculated due to entanglements. Particles will change their charge from negative to positive, but the positive charge is not strong enough to keep the particles apart and forces keeping them entangled might prevail. Particles of MCC and clay required large amounts of PEI to reach the isoelectric point in tap water as compared to deionized water which might be caused by reversible adsorption/desorption of PEI. This result needs to be explored in future work.

5. Acknowledgements

The authors wish to thank Dr. M. Polverari and PAPRICAN for allowing us to use instrumentation and providing assistance with adsorption measurements. Financial contributions from the Mechanical Wood-Pulps Network of Centres of Excellence and NSERC PGS scholarship (for Jana Porubska) are gratefully acknowledged.

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CHAPTER III

EFFECT OF MODEL AND FRACTIONATED TMP FINES ON SHEET PROPERTIES

Abstract

Two model fines, representing microfibrils and microgranules, and two fractions of TMP fines were used to demonstrate their effect on tensile strength and optical properties of handsheets formed from TMP and kraft fibers. The model microfibrils behave as a binder between fibers, thus improving tensile strength. The light scattering of kraft handsheets decreases but that of TMP handsheets increases. The model microgranules behave as a pigment by improving light scattering but preventing interfiber bonding. TMP fines, containing both types are capable of increasing tensile strength and light scattering simultaneously. The relation between tensile strength and light scattering depends on the proportion of fibrillated fines and granulated fines. The fractionated TMP fines of high surface area are shown to be very effective in improving the handsheet properties and the relation between tensile strength and light scattering is superior to that achieved by calcium carbonate filler.

1. Introduction

The effect of fines on a number of paper properties is well recognized, yet their actual role is not fully understood because of their heterogeneous nature. The often used definition of fines, being the fraction of pulp passing through a 200 mesh screen, includes particles of different shapes, dimensions, chemical composition, surface properties, etc. This is particularly true in the case of mechanical fines composed of broken fibers, cell wall fragments, middle lamellae fragments, parenchyma, ray cells and bordered pits. Because of the wide range of different types of particles there is no standard classification for them. It has been suggested, however, that in a broad sense the fines can be divided into slime stuff and flour stuff [1]. Alternatively, the two categories can be described as fibrils and flakes [2,3] or ribbons and chunks [4]. The slime stuff consists mainly of swellable and flexible fibrillar particles originating from the cellulose-rich fiber wall. The flour stuff contains flake-like particles, i.e., fiber fragments and pieces of cell wall and middle lamella. Within each category there are particles of different sizes. In general, the slime stuff is considered a good bonding material while the flour stuff has poor bonding ability.

A number of studies dealing with the effect of mechanical fines on paper properties have been reviewed by Luukko [2]. In most of the contributions, the whole fraction of fines was used because of the difficulty to separate fines into distinct categories. The general conclusion is that in mechanical papers, where their content could be very high, fines are very important components dominating the paper properties. It has also been shown that the mechanical and optical properties of paper depend on the type of fines (kraft or TMP) rather than the type of fibers [5]. Introducing kraft fines in paper results in increased tensile strength and decreased light scattering in both chemical and mechanical fiber networks. On the other hand, TMP fines incorporated into a network of either kraft fibers or TMP fibers will increase both the tensile strength and the light scattering. However, when TMP fines are divided into two fractions, one consisting predominantly of fibrillar material and the other of flake-like material, a distinctly different effect on sheet properties is observed [3]. The fibrils are responsible for improving strength while the flakes improve the optical properties. This suggests that fractionated TMP fines could be used as an additive to control specific properties.

The objective of the present work is to investigate the effect of two fractions of TMP fines with different proportions of fibrillated and flake-like material. Two other model fines representing either fibrils or granules are microfibrillated cellulose and microcrystalline cellulose. Their effect on mechanical and optical properties of handsheets formed from either chemical or mechanical fibers is the main focus of this investigation.

2. Experimental

2.1. Materials

Fibers

Thermomechanical and unbeaten kraft fibers without fines were used. Fines were removed using a float-wash fractionator equipped with a 100 mesh screen. The amount of TMP fines passing the 100 mesh screen was 27%.

Fines

Two types of TMP fines fractionated in a small hydrocyclone [6] were used. The fraction of fines of high specific surface (HSF) containing pieces of fiber, fibrillar material and pieces of fiber wall of various sizes down to less than 0.5 μm represents 57% of the total mass of fines. The fraction of fines of low specific surface (LSF) containing mostly ray cells and intact pieces of fiber 10 to 200 μm in length represents 21% of the total fines. The specific surface was determined by turbidimetry [7].

Two model fines representing fibrillar and granular portions were used. Microfibrillated cellulose KY 100S (supplied by Daicel Chemical Industries, Japan) with average length 0.5 mm and diameter 0.01-0.1 μm (MFC), and microcrystalline cellulose (FMC Corporation) with average particle sizes 6 μm (MCC) and 100 μm (MCC-100).

Filler

Precipitated calcium carbonate PCC (Specialty Minerals) with average size of 1.6 μm was used.

2.2. Methods

Handsheets from mixtures of either TMP or softwood bleached kraft (SBK) long fibers and fines were prepared in a British Sheet Machine according to the standard method (CPPA C.4) and tested for tensile strength and optical properties. Handsheet consisted of 1 g of long fibers and different amounts of fines. No retention aid was used (to prevent the effect of flocculation) and consequently to achieve high content of fines, considerable amounts were used (up to 0.75 g, 1 g, and 5 g of fines, MCC and filler, respectively).

The amounts of retained fines, MCC and MFC were determined from the dried sample assuming that 1 g of fibers was always retained. The amount of retained calcium carbonate was determined by ashing the sample at 500°C.

3. Results and discussion

When dealing with the relation between tensile strength and opacity it is reasonable to consider the role of the surface area of fibers. In a random assembly of fibers, part of a fiber surface is in contact with another fiber at the point where they cross. Within this area hydrogen bonds between fibers can form. The number of interfiber bonds determines how strongly the fibers stick to each other and consequently the tensile strength increases with bonded area. The fiber surface outside the bonded area is in contact with air and thus presents an interface where scattering of light takes place. In the absence of light absorption (well bleached fibers) the light scattering is directly related to opacity.

The relation between bonded and unbonded area is sufficient to explain the effects caused by beating, filler and fines introduction The inverse relation between tensile strength and opacity (which for white fibers is a function of light-scattering) is well known for chemical pulp fibers subjected to different levels of beating. Beating results in increased bonded areas due to better conformability and plasticity of the fiber wall and its fibrillation. This means that less of the fiber surface is available for scattering the light and thus the opacity decreases while tensile strength increases.

The effect of pigments incorporated into paper can be also viewed as a relation between bonded and unbonded area. Pigment contributes an additional interface for light scattering and therefore the opacity increases. However, the pigment particles prevent interfiber bonding and consequently tensile strength decreases. The result is again an inverse relation between tensile strength and opacity.

Chemical fines predominantly increase tensile strength. The chemical fines are mostly fibrillar with a high surface area. However, upon drying they collapse on the fiber surface and therefore they do not represent an additional interface for light scattering. Their collapse, though, enables them to form bridges between fiber surfaces, which will happen most likely around the points of fiber crossing where the surfaces are close. The result is then increased interfiber bonding but without a considerable decrease of unbonded fiber surface.

Mechanical fines perform differently due to the presence of both the collapsible fibrils and noncollapsible flakes. They increase both the interfiber bonding and the area for light scattering, thus tensile strength and opacity improve simultaneously. The effect of pigments, chemical fines and mechanical fines introduced into an assembly of fibers is shown schematically in Figure 1.

In order to demonstrate the contribution of fibrils and flakes separately, two model fines were used - microfibrillated cellulose (MFC) and microcrystalline cellulose (MCC). Their performance is observed by introducing them into long kraft and TMP fibers and compared with TMP fines classified into fractions of different specific surface [6]. Fractions of high surface (HS) and low surface (LS) area were used. From the micrographs shown in Figure 2 it is apparent that the LS fraction of TMP fines contains mostly ray cells and intact pieces of fiber. The HS fraction contains fiber wall fragments and more of the fibrillated material.

In Figure 3 the tensile strength is shown as a function of fines content in handsheets formed from TMP long fibers and unbeaten long kraft fibers. The results are consistent with the assumption that fibrils contribute to bonding between fibers and consequently tensile strength, as shown in the case of MFC. On the other hand, the granular particles of MCC interfere with interfiber bonding and tensile strength decreases. The effect of HSF and LSF of TMP is between the two extremes. For comparison, the tensile strength of nonfractionated original TMP containing 0.35 g fines per gram of fiber is included as a single point.

In Figure 4 is shown the light scattering behavior of the handsheets. Again, the trend is obvious. The MCC acts as a pigment by increasing the solid-air interface while the

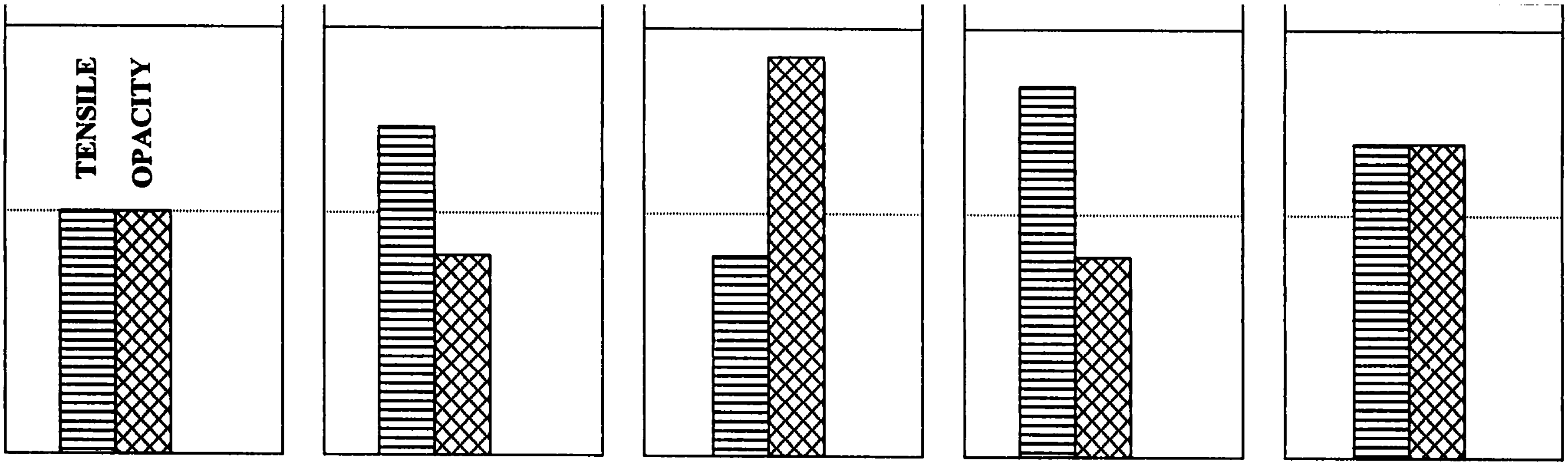

Figure 1. Effect of beating, introduction of filler, chemical and mechanical fines on bonded and unbonded surface area, and consequently on tensile strength and opacity. ▬ bonded area.

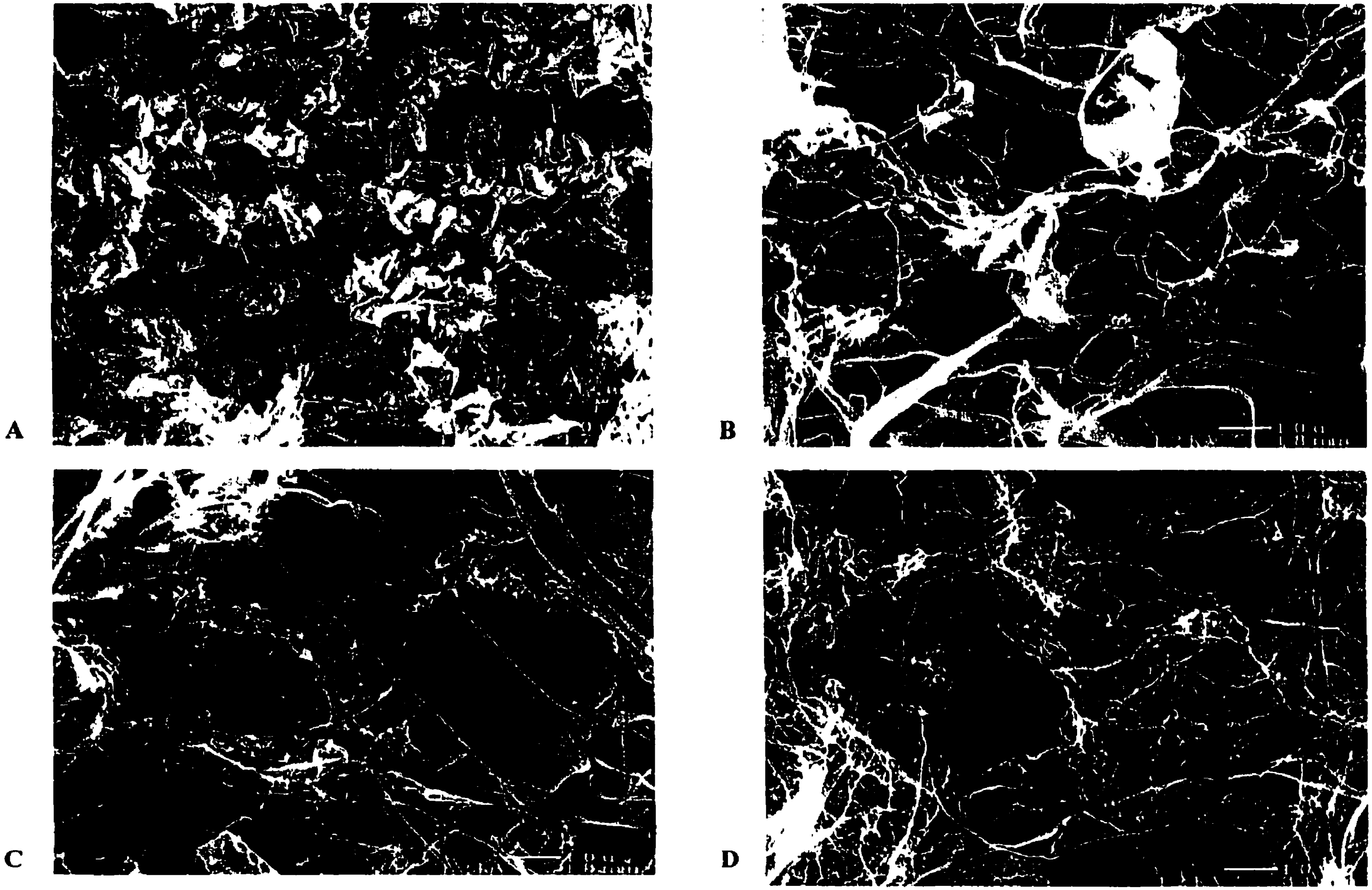

Figure 2. Micrographs: A – microcrystalline cellulose, B – high specific surface area fines, C – low specific surface area fines, D – microfibrillated cellulose.

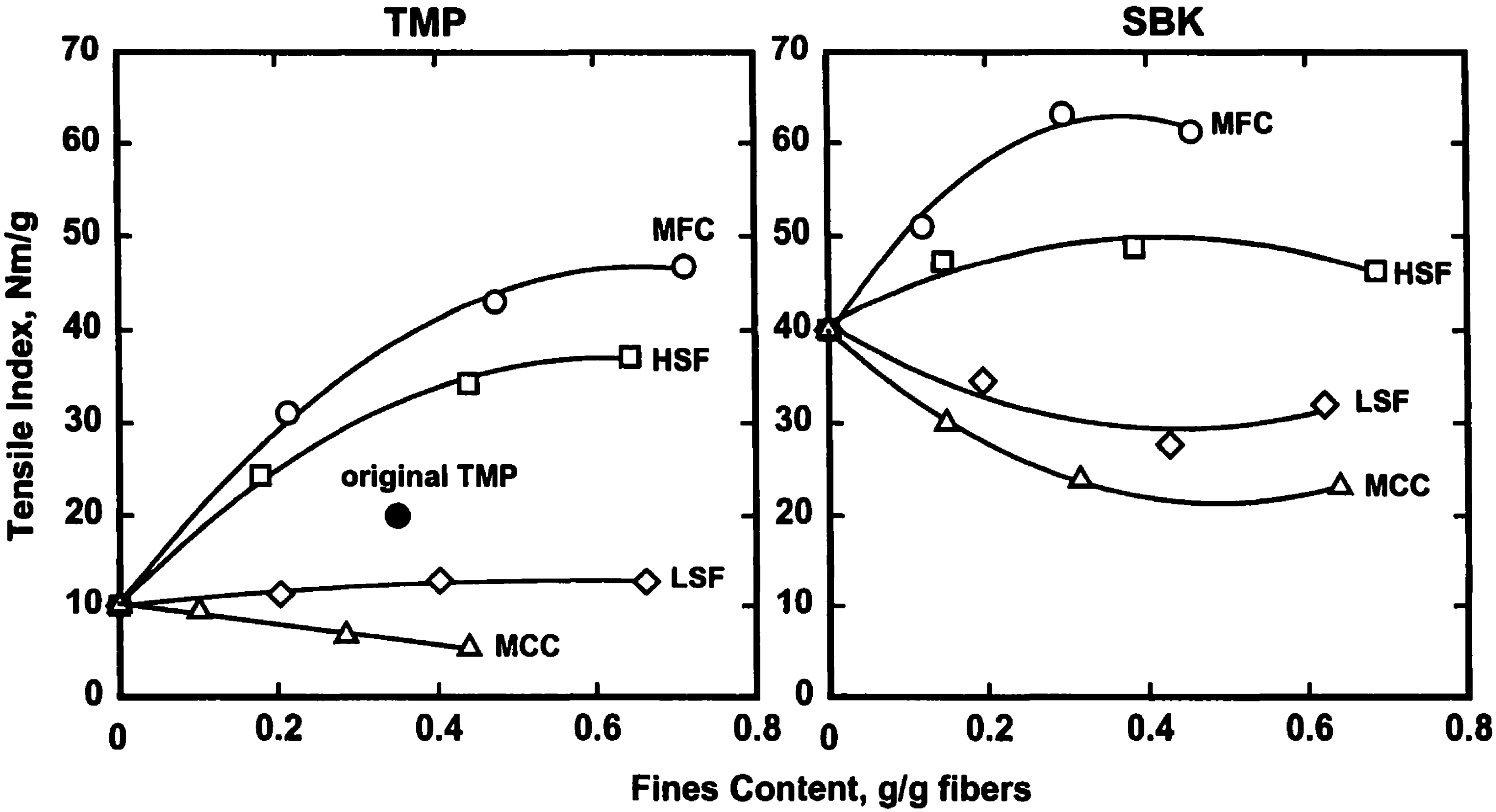

Figure 3. Tensile strength as a function of different types of fines introduced into TMP fibers (left) and kraft fibers (right).

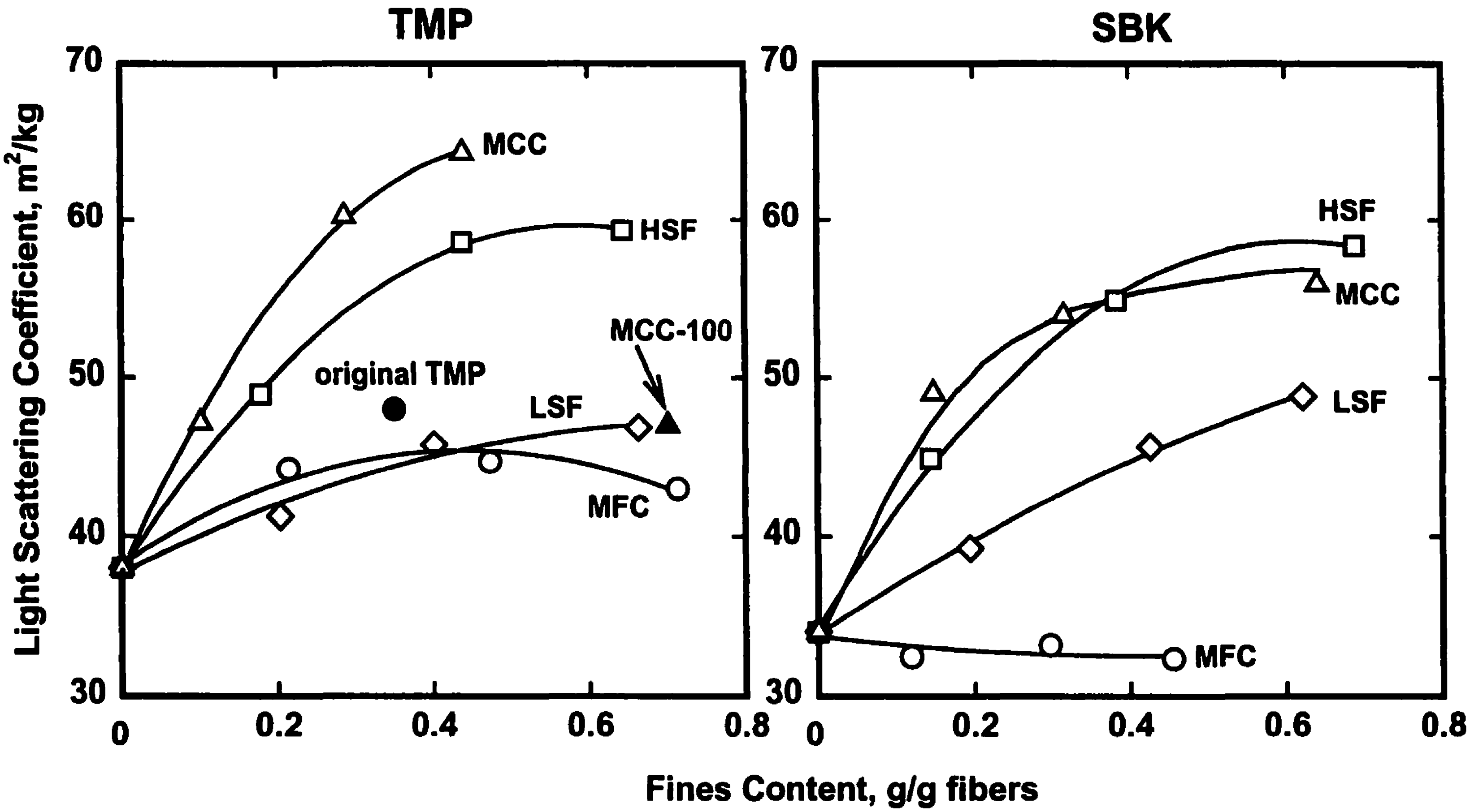

Figure 4. Light scattering coefficient as a function of fines introduced into TMP fibers (left) and kraft fibers (right).

collapsible MFC affects the interface only marginally. The HSF contain small particles with considerable surface area and therefore their contribution to light scattering is high, and when incorporated into kraft fibers it even matches that of MCC. On the other hand, the particles in LSF are large and therefore their low surface contributes little to the total.

The contributions of small and large particles can be demonstrated by comparing the effect of two MCCs having an average particle size of 6 μm and 100 μm, and shown for TMP handsheets in Figure 4. The calculated specific surface area of cellulose spheres, 6 μm in diameter, is 15 times the area of spheres 100 μm in diameter. This means that the increase of total surface area by large MCC is insignificant in comparison to the smaller ones. The light scattering for original TMP containing 0.35 g fines per gram of fiber is also shown. In general, the outstanding performance of HSF, particularly the ability to improve tensile strength and light scattering simultaneously, derives from the presence of both the collapsible fibrils and the granules small enough to possess a considerable surface.

By considering the performance of fines in kraft and TMP handsheets in Figure 4, one may conclude that although similar in trend, there is a difference. Without a more detailed analysis it is difficult to explain why the LSF are more effective in kraft handsheets where the difference between LSF and MFC is obvious while in TMP handsheets it is not. Also, why the MFC in kraft handsheets has little effect on light scattering while in TMP handsheets the presence of MFC results in increased light scattering is not entirely clear. One can speculate that this is due to different characteristics of the fibers, particularly their flexibility, stiffness, conformability and other factors that may determine how the fines and their fractions may be accommodated in the fiber network.

The relation between tensile strength and light scattering is of practical significance if both properties are important. This relation allows, for example in filled papers, to select a pigment which for a given improvement in optical properties causes the least drop in tensile strength.

In Figure 5 is shown the tensile strength versus light scattering for handsheets from kraft and TMP fibers. In the kraft handsheets the MFC performs as expected by increasing tensile strength accompanied by a small decrease in light scattering. The MCC acts as a pigment - increases light scattering and decreases tensile strength. However, it is the different

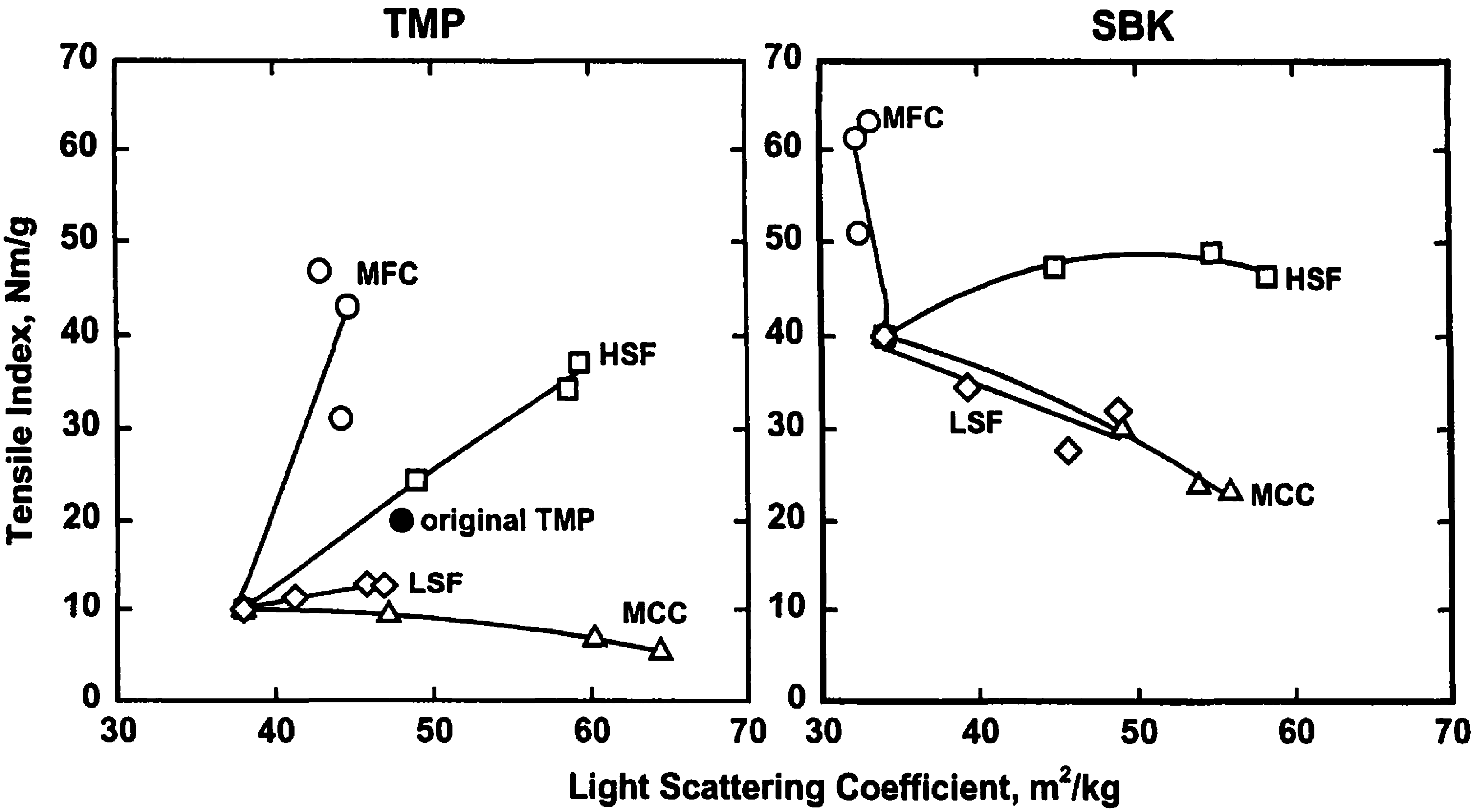

Figure 5. Tensile strength versus light scattering coefficient for TMP fibers (left) and kraft fibers (right) containing different fines.

performance of HSF and LSF which is of interest. It indicates that the LSF introduced into kraft fibers are detrimental to tensile strength while the improvement in scattering is not great. Their introduction into TMP fibers results in rather small improvements in light scattering and tensile strength. On the other hand, the HSF in kraft fibers are effective in light scattering but the tensile strength is not impaired. Their positive effect is even more pronounced in TMP handsheets where both the light scattering and tensile strength improve considerably. This observation naturally leads to the conclusion that it would be beneficial to separate fines from TMP pulp, remove the LSF fraction and then combine the remaining HSF fraction with the long fibers. The relation for original TMP shown as a single point is similar to that of HSF but it should be realized that the handsheet from unfractionated TMP contains 0.35 g fines per gram of fiber, while it is enough to add about 0.15 g HSF to one gram of long TMP fibers to reach similar values.

Because the HSF fraction acts also as filler by increasing the light scattering, it is of interest to compare its performance with that of a conventional filler - precipitated calcium carbonate (PCC). Figure 6 shows the tensile strength of handsheets from kraft and TMP fibers as a function of PCC and HSF. Figure 7 shows the light scattering coefficient for the same handsheets. Figure 8 shows the plot of tensile strength against light scattering which indicates that HSF are superior to PCC because with increasing light scattering there is no loss of tensile strength. However, it has to be realized that for obtaining the same value of light scattering, say 60 m^2/kg, which is about the maximum reached with HSF in kraft handsheets it would be necessary to incorporate 0.6 g HSF as opposed to about 0.12 g PCC per gram fiber (Figure 7). The superior performance of HSF is even more pronounced in handsheets formed from TMP fibers. Besides the increased light scattering there is a considerable improvement in tensile strength. Although the same applies as above, i.e. more HSF are required to reach a given value of light scattering, HSF improve tensile strength at the same time. However tempting it is to suggest that HSF can be used instead of mineral pigments, one drawback is rather serious and becomes obvious from considering the opacity as shown in Figure 9 and light scattering shown in Figure 7. Although the HSF are less effective in light scattering, the opacity is similar to that produced by PCC. This is due to the fact that besides scattering the light, the TMP fines also absorb the light. Therefore, the

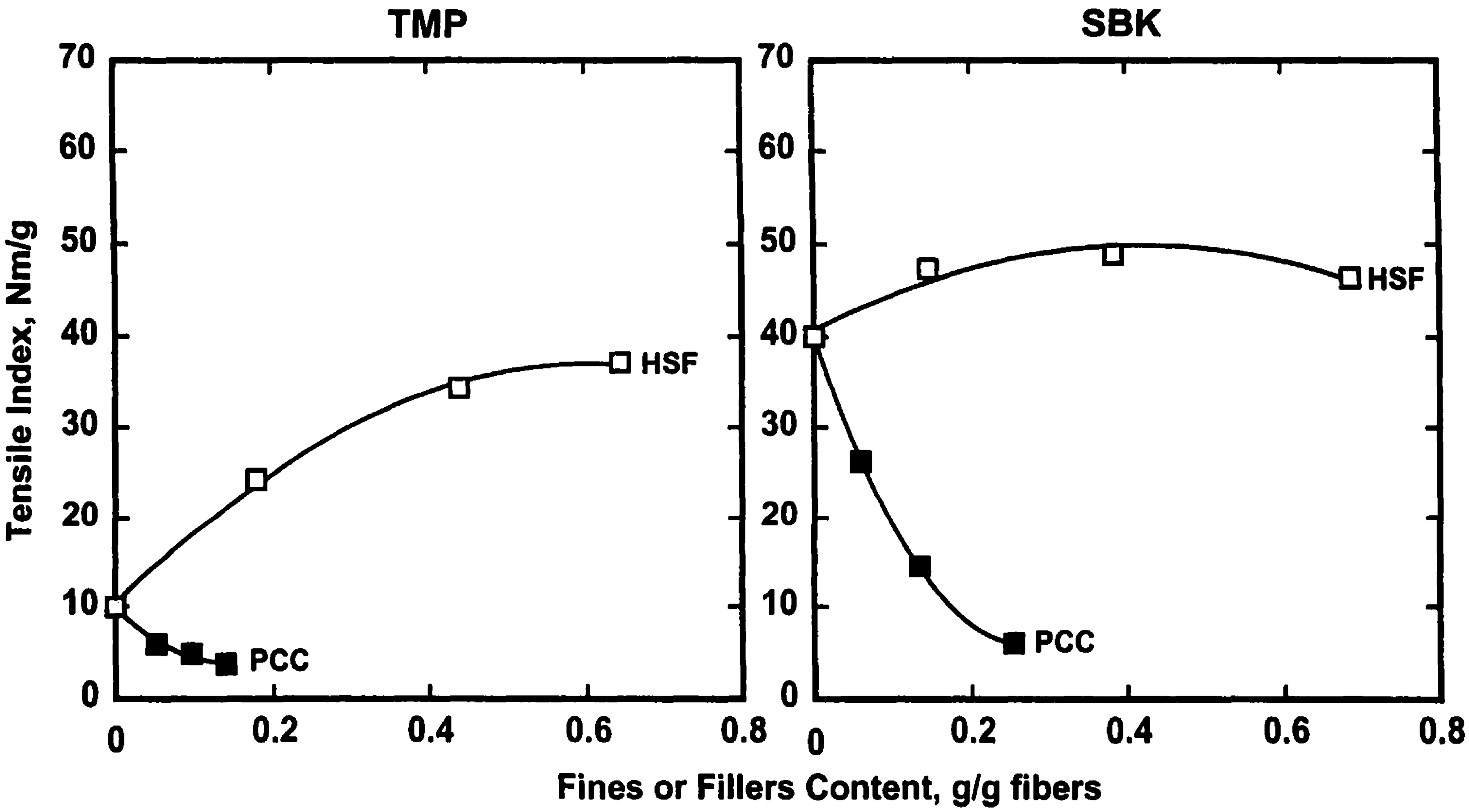

Figure 6. Tensile strength as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

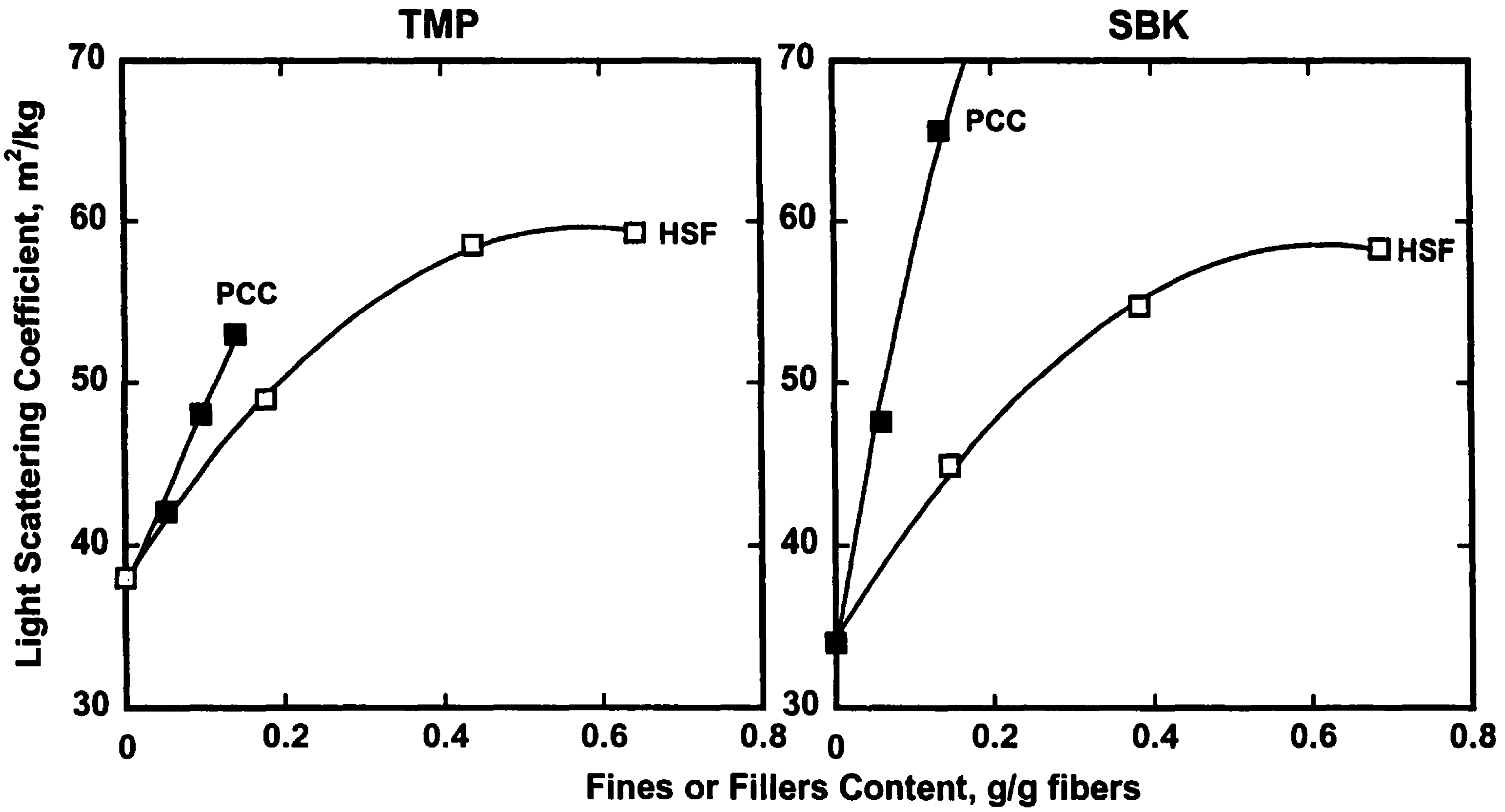

Figure 7. Light scattering coefficient as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

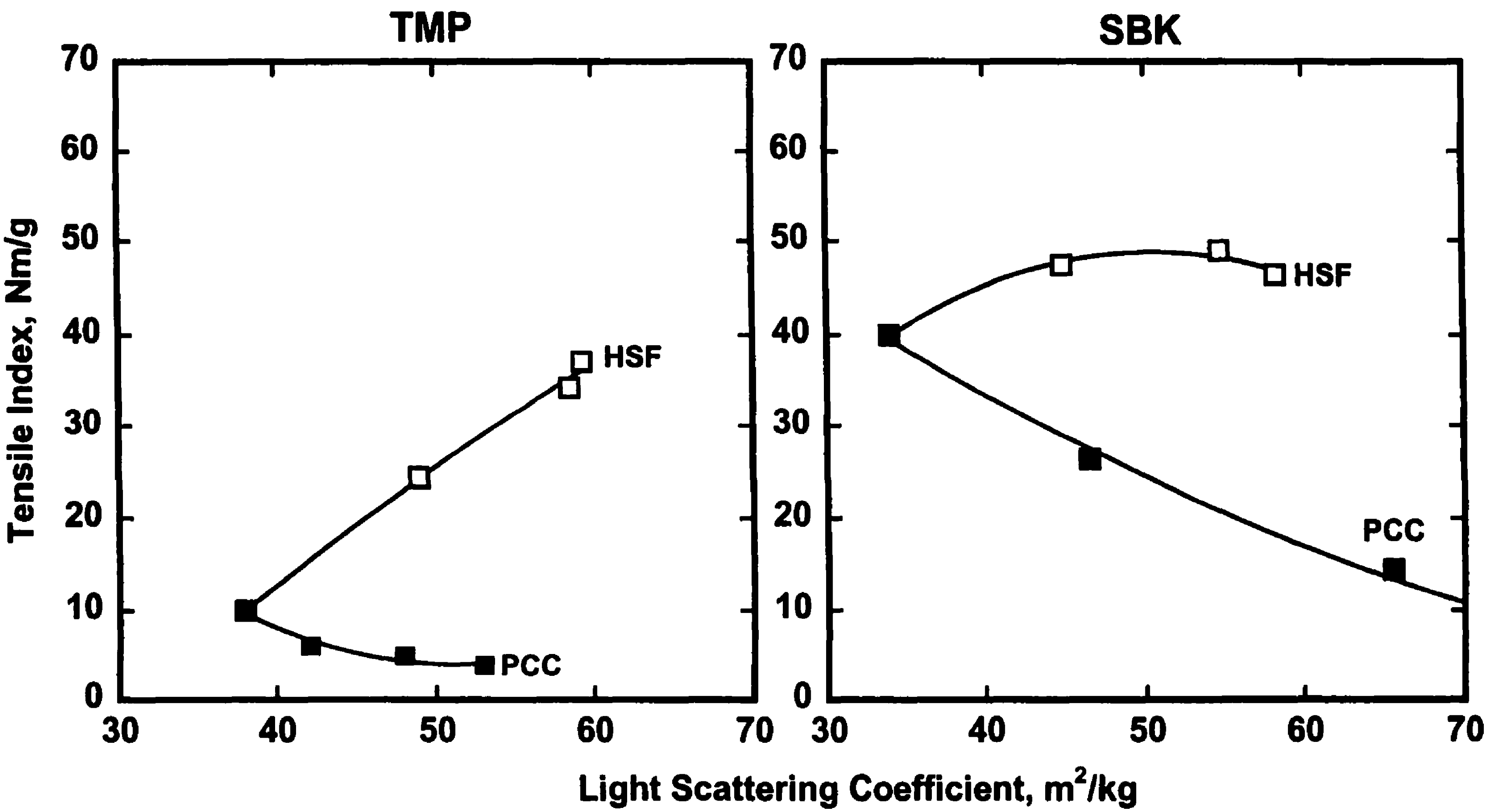

Figure 8. Tensile strength versus light scattering coefficient for TMP fibers (left) and kraft fibers (right) containing HSF and PCC.

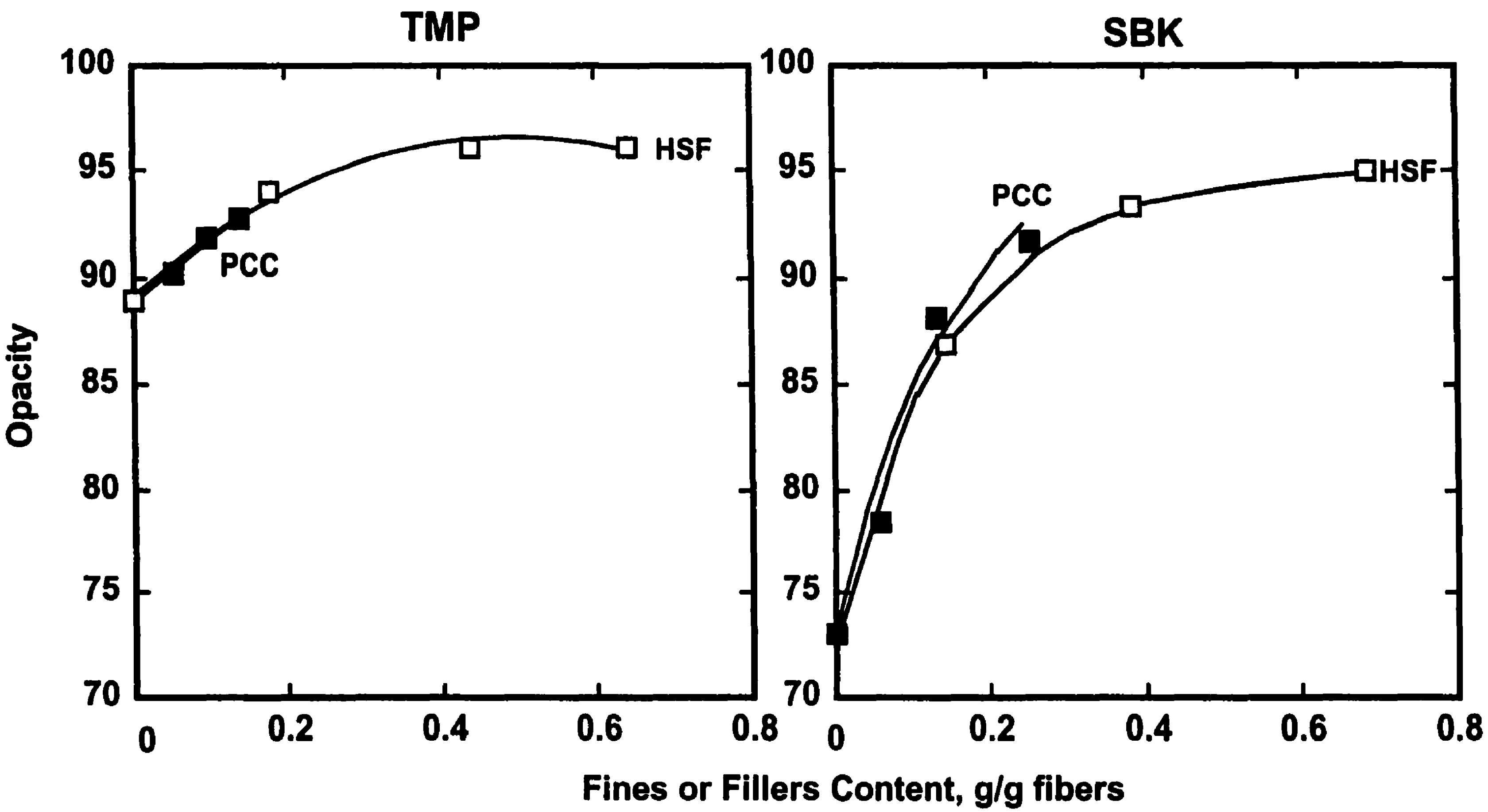

Figure 9. Opacity as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

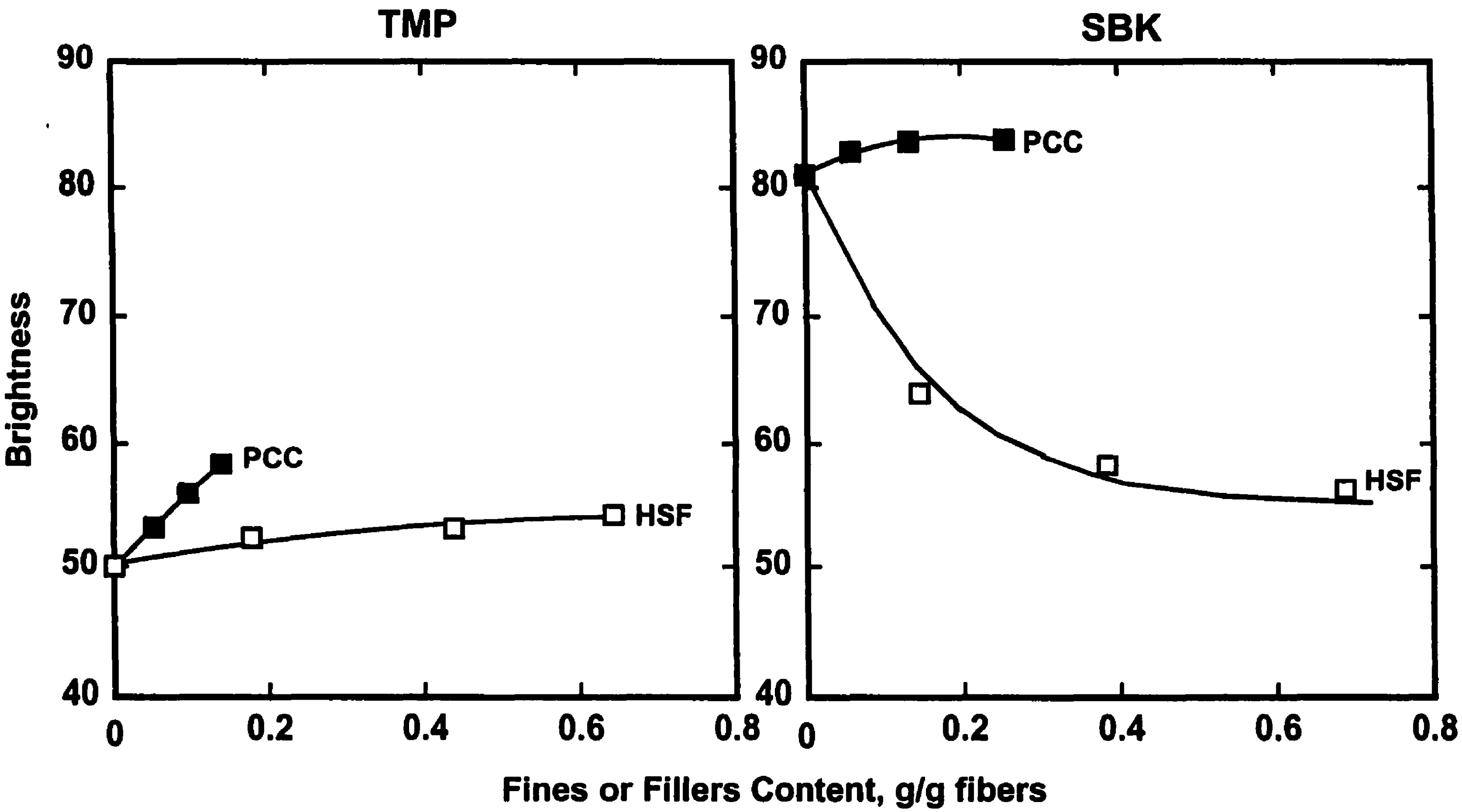

Figure 10. Brightness as a function of HSF and PCC introduced into TMP fibers (left) and kraft fibers (right).

brightness of TMP handsheets containing fines does not improve contrary to handsheets filled with PCC, as shown in Figure 10. In the case of kraft fibers containing TMP fines, the brightness decreases considerably. In principle, this difficulty could be overcome in bleaching the HSF separately, but as a consequence the opacity will suffer.

4. Conclusions

Fines in the form of microfibrils are responsible for improving bonding between fibers. Fines in the form of microgranules improve light scattering because they introduce additional solid-air interface. In order to be effective they must be small and thus possess large surface areas.

TMP fines are a mixture of fibrillated and granular particles and thus contribute to improvement of both the tensile strength and the scattering of light. However, for optimum performance it is beneficial to separate the TMP fines into a fraction of high surface area, which contains mostly the microfibrils and small granules. This HSF fraction is superior to calcium carbonate filler because it can increase opacity to similar values, and simultaneously also improve tensile strength, however at the cost of reducing brightness in kraft papers.

5. Acknowledgements

The authors thank S. Shimamoto from Daicel Chemical Industries Ltd. for providing the microfibrillated cellulose, J. Wood, X. Zhang, T. Thompson and E. Walker from Paprican for help with fines fractionation and SEM, and the Mechanical Wood-Pulps Network of Centres of Excellence for financial support.

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CHAPTER IV

LIGHT SCATTERING AND MICROPOROSITY OF PAPER

Abstract

In a sheet of paper, the scattering of light takes place at the air-solid interface. Provided that the paper is composed from components of similar refractive index, then the total light scattering should be a function of the air-solid interface, and consequently, the porosity.

Handsheets of different microstructures were made from TMP fibers, a variety of fines, and fillers to test this assumption. No correlation was found between the specific light scattering coefficient and the total porosity or the total surface area determined by mercury porosimetry. However, when only the surface within the optically effective pores is considered, a direct relation is observed regardless of the components forming the paper. Thus, the optical performance can be regulated by affecting the microstructure, particularly through the formation of pores having an optimum size.

1. Introduction

In an assembly of randomly oriented fibers scattering of light takes place at the interface of fiber surface and air. Therefore, the total amount of scattered light per unit mass will depend on the extent of such an interface. An example of this dependency is provided by the well-known inverse relation between light scattering and tensile strength, because both are functions of the fiber surface. By increasing the fraction of surface in contact (interfiber bonded area), either by beating or pressing, the tensile strength increases, but less of the surface becomes available for scattering and thus the opacity decreases. The introduction of filler results in an increase in opacity simply because of an additional light-scattering interface.

Fraction of light reflected at the interface of two media having different refractive indices R at normal incidence is given by Fresnel equation:

$$R = (n_r-1)^2/(n_r+1)^2$$

where $n_r = n_l/n_2$, and n and n are the refractive indices of the two adjacent materials. The total amount of scattered light S is proportional to the product of reflectance and the reflecting area A

$$S \propto RA$$

This relation has been verified on model glass fibers and a number of pulp fibers by plotting the surface area determined by nitrogen adsorption versus the specific light scattering coefficient [1-3]. A good correlation between the specific light scattering coefficient and the specific surface area of pores larger than 0.2 μm, determined by mercury porosimetry, was reported in the case of filled papers [4] and mechanical papers [5].

It is of interest to test this relation with more complex structures composed of fibers, fines and pigments, and to verify if it is generally applicable. The mutual arrangement of these components may result in different microstructures, depending on the uniformity of the distribution, the state of flocculation of individual components or coflocculation among them. This means that even using the same composition, the surface in contact with air could differ.

It has already been suggested [6] that, from an optical point of view, a highly filled paper can be treated as a microporous system, as is done with a pigmented coating. In conventional paper coatings formulated with low refractive index pigments, such as clay and calcium carbonate, the scattering sites are the numerous microvoids, which are occluded within the continuous pigment-binder matrix. It has been shown [7] that the increased specific light scattering is directly proportional to the increased porosity of coating, which also means that the total interface for light scattering increases with the number of voids. If paper is also viewed as a continuous matrix of solid components, then its porosity and the internal surface associated with the pores would determine the light scattering efficiency.

For the purpose of verifying this concept, a variety of structures were formulated using TMP fibers, different types of fines and fillers ($CaCO_3$ and clay) treated with different polyelectrolytes in order to either disperse or to flocculate the filler particles. All the components have a similar refractive index and therefore the fraction of light reflected at the interface with air is also similar. Thus, the total amount of scattered light should be proportional to the reflecting area.

The total porosity and surface area, as well as the distribution of pore size and the internal surface associated with a pore of given size, were evaluated by the method of mercury intrusion.

2. Experimental

2.1. Materials

Fibers and fines

Thermomechanical pulp was separated into long fiber fraction (LF) and fine fraction. To obtain larger quantities of fines, a float-wash fractionator equipped with a 100-mesh screen was used.

The fines were fractionated in a small hydrocyclone [8]. Two types of fines were used for our experiments: high and low specific surface area (HSF, LSF). The material of LSF is mostly ray cells and intact pieces of fiber, 10 to 200 μm in length. The material of

HSF is pieces of fiber with well-developed surfaces, fibrillar material, and pieces of fiber wall of various sizes, down to less than 0.5 μm. The micrographs of HSF and LSF are shown in Figure 1.

Microcrystalline cellulose (MCC)

Obtained from FMC Corporation, the average particle size is 6 μm. Refractive index n = 1.55.

Microfibrillated cellulose KY 100S (MFC)

Supplied by Daicel Chemical Industries Ltd., the average length is 0.5 mm and the average diameter is 0.01-0.1 μm. Refractive index n = 1.55.

Fillers

Two types of precipitated calcium carbonate (PCC) Hydrocarb HO and LO from Specialty Minerals were used. The average equivalent spherical diameter determined using a centrifuge photosedimentometer B1-DCP (Brookhaven), is 1.3 μm for HO and 2.5 μm for LO. The refractive index n = 1.56. Filler clay BN from English China Clay with an average equivalent spherical diameter 2.3 μm and refractive index n = 1.56. The fillers were treated with either polyethylenimine (PEI) or polyacrylamide (PAM). PEI provides positively charged and dispersed fillers, while PAM caused flocculation resulting in increased sizes of $CaCO_3$ to 3-5 μm.

2.2. Methods

A variety of paper structures were prepared using thermomechanical pulp – long fiber fraction and different material – dispersed fillers, flocculated fillers, fractionated fines, model fines: granulated (MCC) and fibrillated (MFC). The handsheets were made in a standard British machine, restrained between drying rings and dried at a standard temperature. The optical properties of the dry paper samples were determined using Technibrite Micro TB-1C (Technidyne Corporation). The porosity and the area of pores were determined by mercury porosimetry using PoreSizer 9320 (Micromeritics).

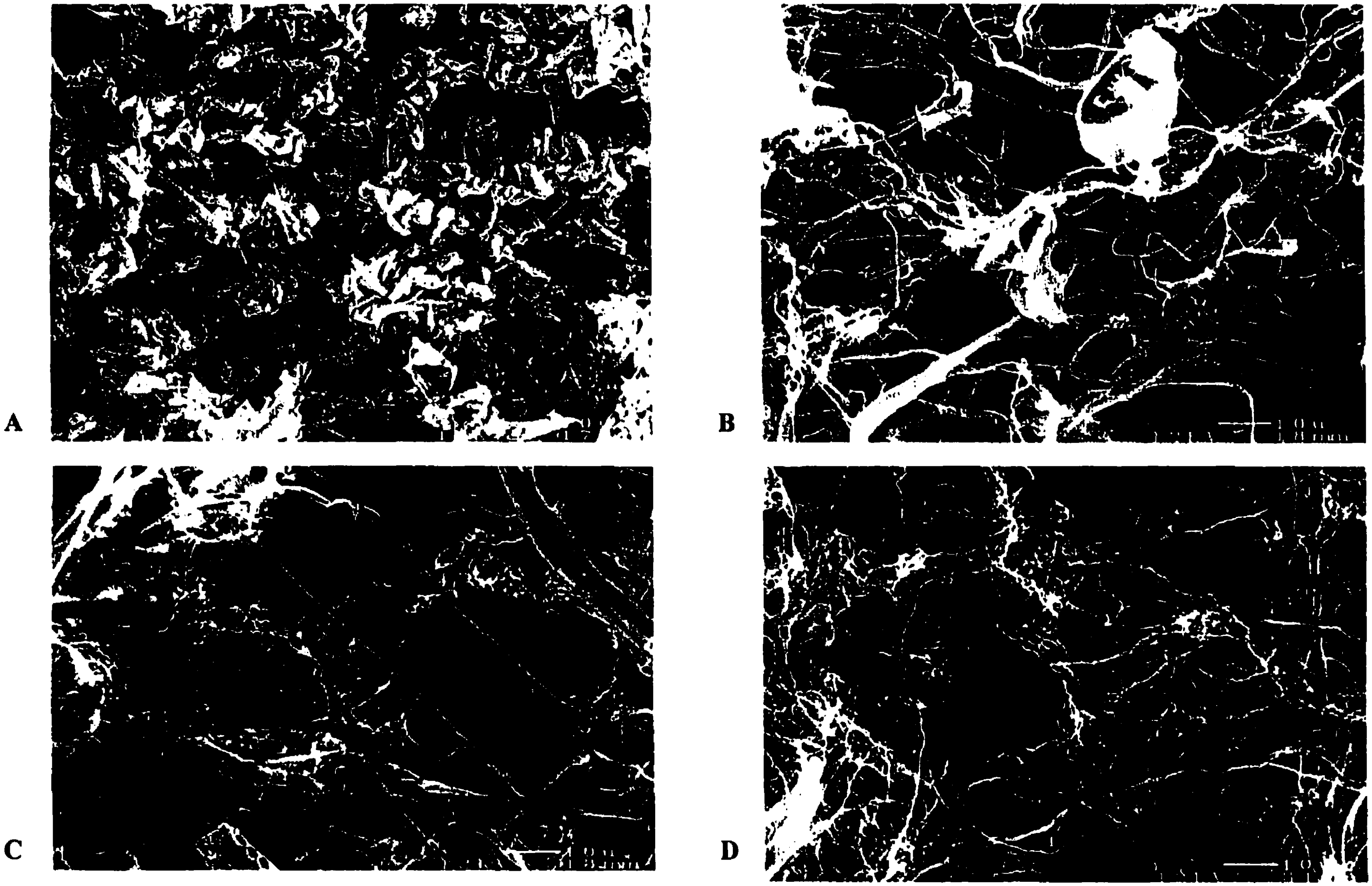

Figure 1. Micrographs: A – microcrystalline cellulose, B – high specific surface area fines, C – low specific surface area fines, D – microfibrillated cellulose.

3. Results and discussion

The direct relation between the surface area determined by nitrogen adsorption and the specific light scattering has been reported for a number of fibers [1-3]. However, when the total surface area determined by mercury intrusion is plotted against the light scattering coefficient (LSC) for a variety of structures, as shown in Figure 2, there is a considerable deviation from linearity.

Since the relation in Figure 2 is of questionable value, let us compare the LSC with porosity, which has been shown to be directly related in the case of pigment coating [7]. In Figure 3, the introduction of fines show that although the porosities are not much different, the LSC differs considerably. Actually, the trend is opposite to what is expected because the LSC increases while the porosity decreases. The same is observed in the case of handsheets filled with $CaCO_3$ or clay treated either with PAM or PEI, shown in Figure 4. The LSC increases from around 30 m^2/kg, to almost 100 m^2/kg while porosities remain similar. The micrographs of some of the samples are shown in Figure 5 and their cross-sections in Figure 6. Figure 7 shows the LSC versus porosity for samples formed from TMP and microfibrils. Here, the porosity changes while the LSC remains similar.

In view of the data presented, the obvious question is whether it is reasonable to expect any relation between porosity and the light scattering efficiency in the case of composites formed from a number of components having a similar index of refraction. In other words, can we treat the paper similarly to the pigmented coatings, i.e., as a continuous matrix of solids containing voids which are responsible for scattering the light?

The answer would require recognizing that not all voids are equal. It has been shown theoretically [9] as well as experimentally [10] that optically effective are only such voids the size of which is in the proximity of wavelength of visible light. As seen in Figure 8, the light scattering coefficient of model coating formulated from spherical polystyrene latex particles of different sizes is a function of void size. Voids having an equivalent spherical diameter of less than 0.1 μm are not effective in scattering the light. This means that the opposite air-solid interfaces within the voids, where the scattering of light takes place, are too close to be optically effective. With increasing void size the

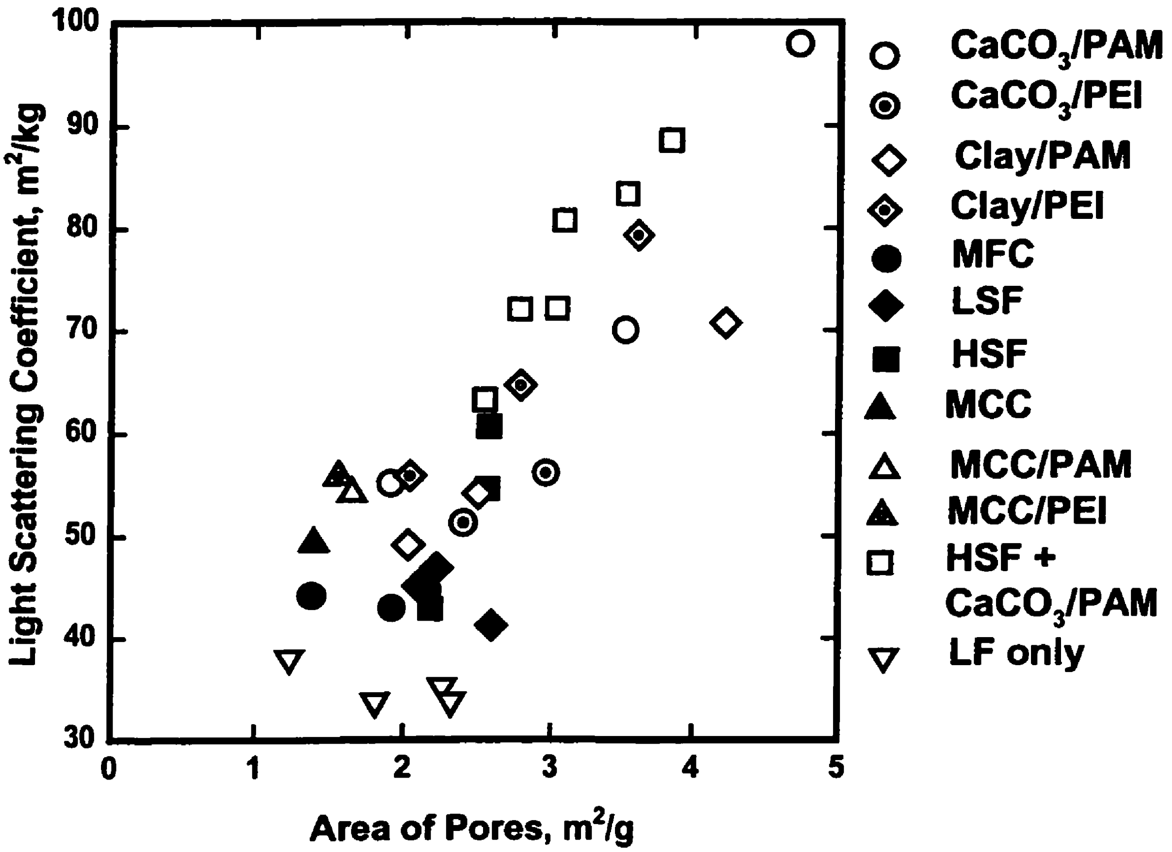

Figure 2. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of total area of pores. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

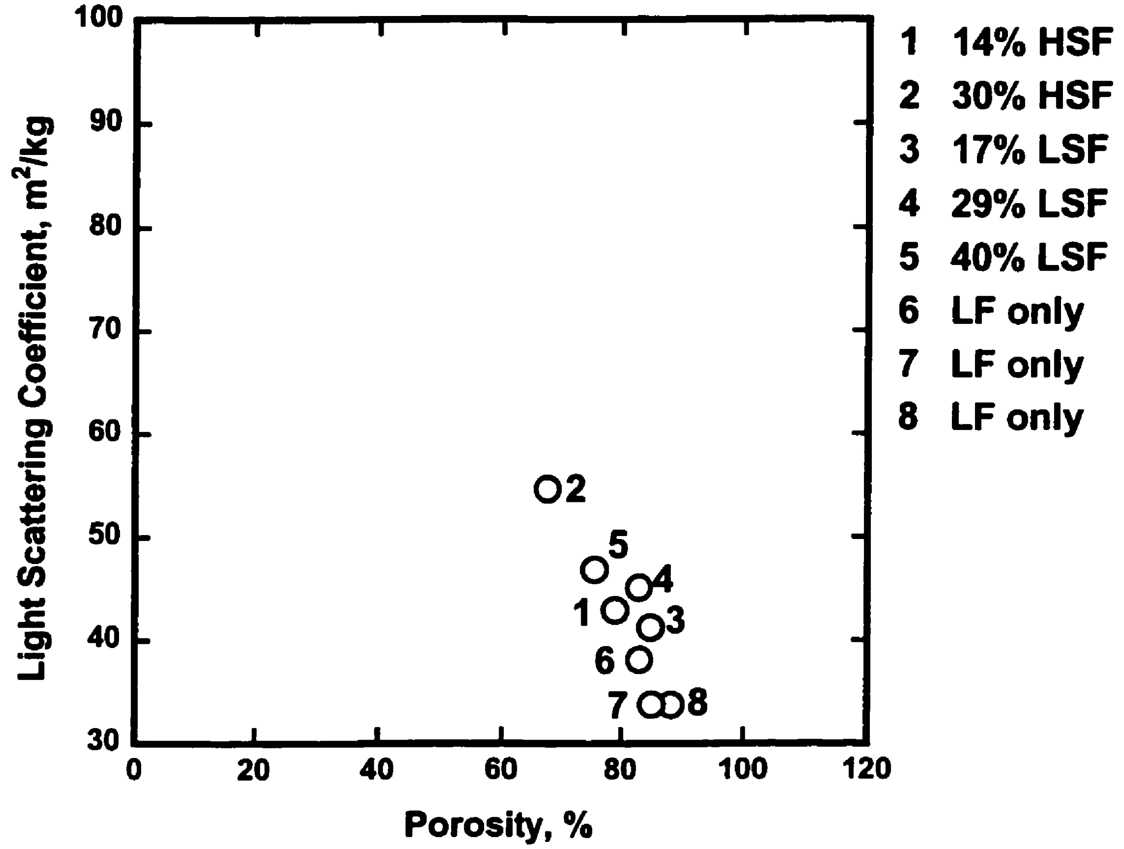

Figure 3. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of fractionated fines as a function of total porosity. HSF - high specific surface area fines, LSF - low specific surface area fines.

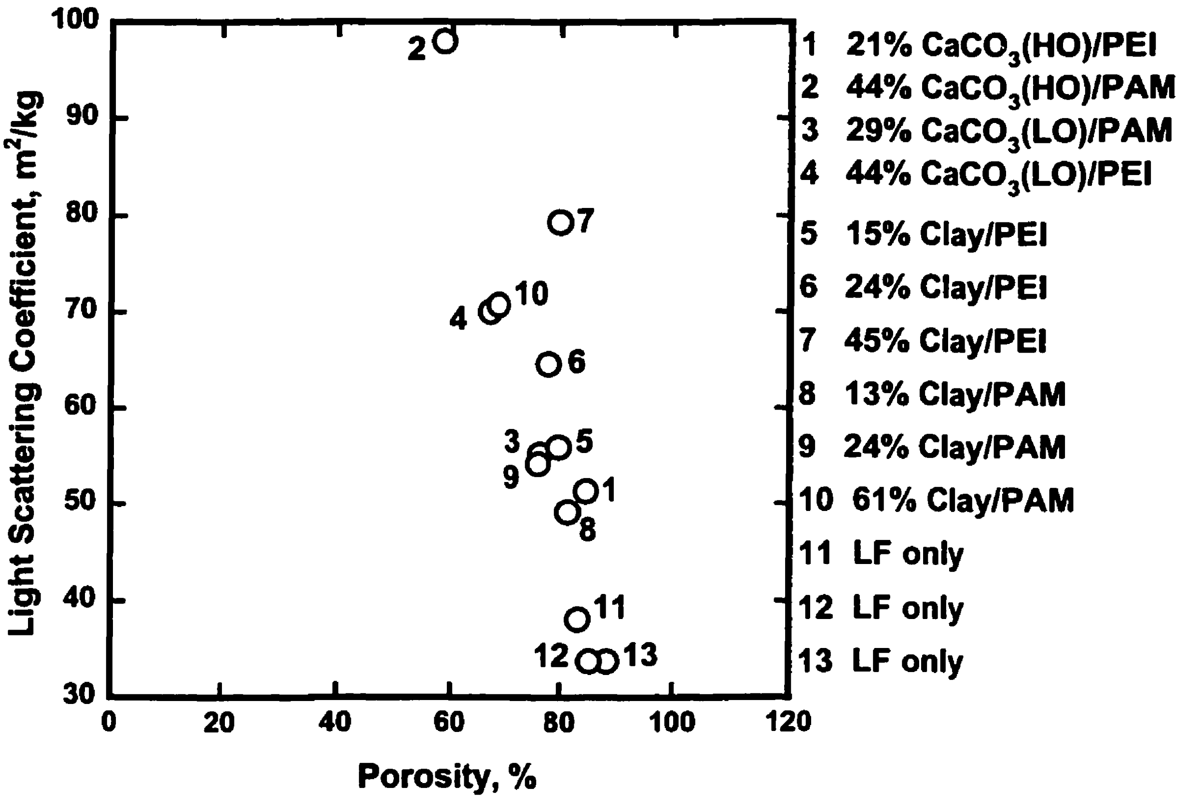

Figure 4. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of calcium carbonate treated with polyacrylamide or with polyethylenimine as a function of total porosity.

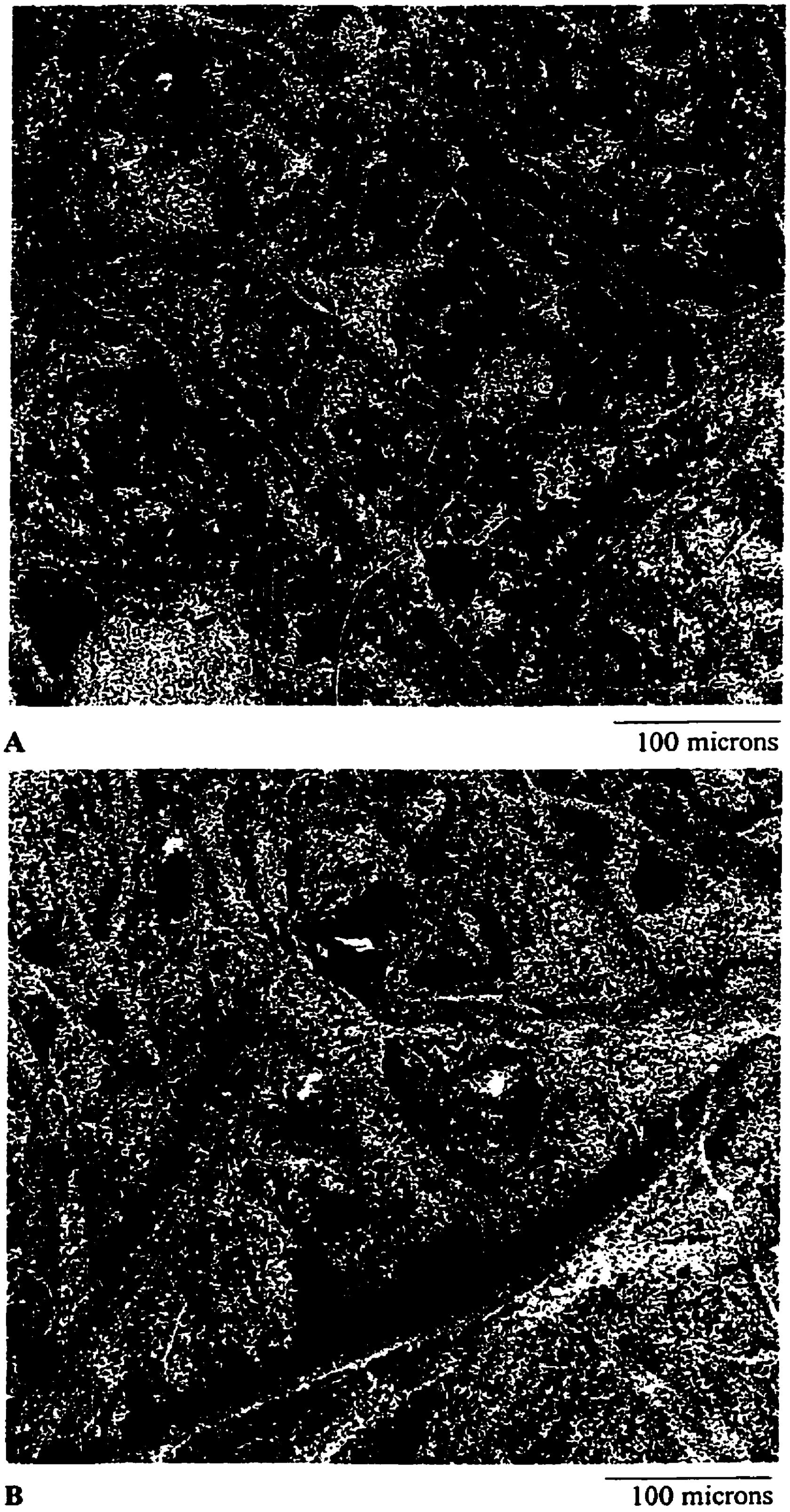

Figure 5. Micrographs of handsheets formed from long fibres (LF) and calcium carbonate treated with polyacrylamide or polyethylenimine. A – 44% $CaCO_3$/PAM, B – 32% $CaCO_3$/PEI.

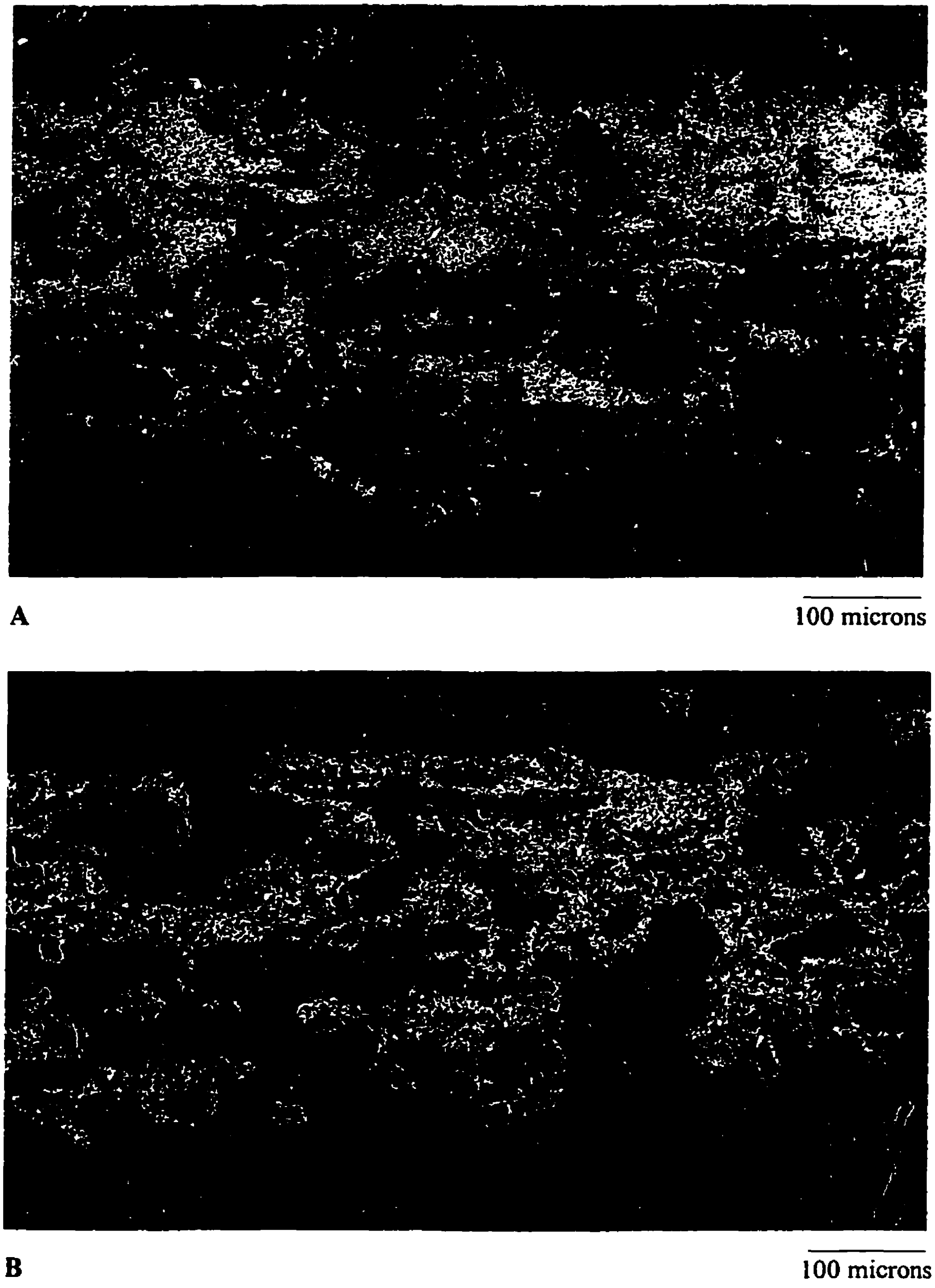

Figure 6. Micrographs of cross-sections of handsheets formed from long fibres (LF) and calcium carbonate treated with polyacrylamide and polyethylenimine. A – 44% $CaCO_3$/PAM, B – 32% $CaCO_3$/PEI.

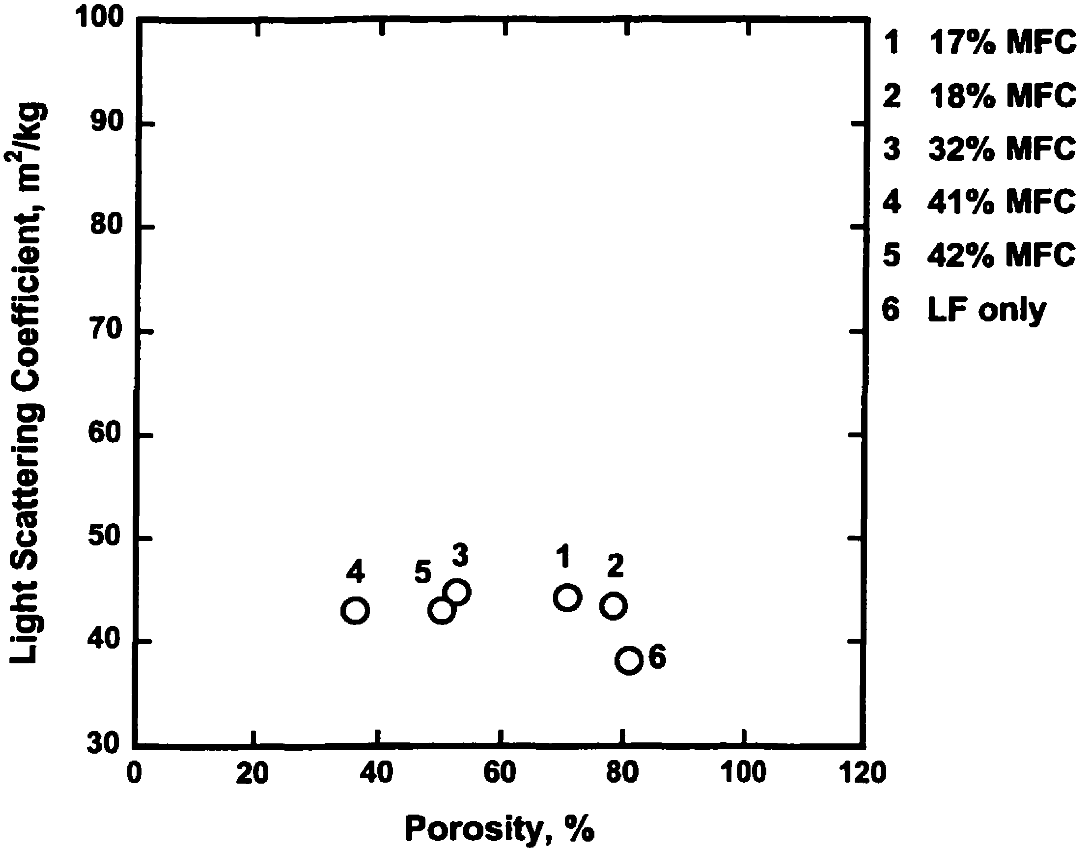

Figure 7. Light scattering coefficient of handsheets formed from long fibres (LF) and different amounts of microfibrillated cellulose (MFC) as a function of total porosity.

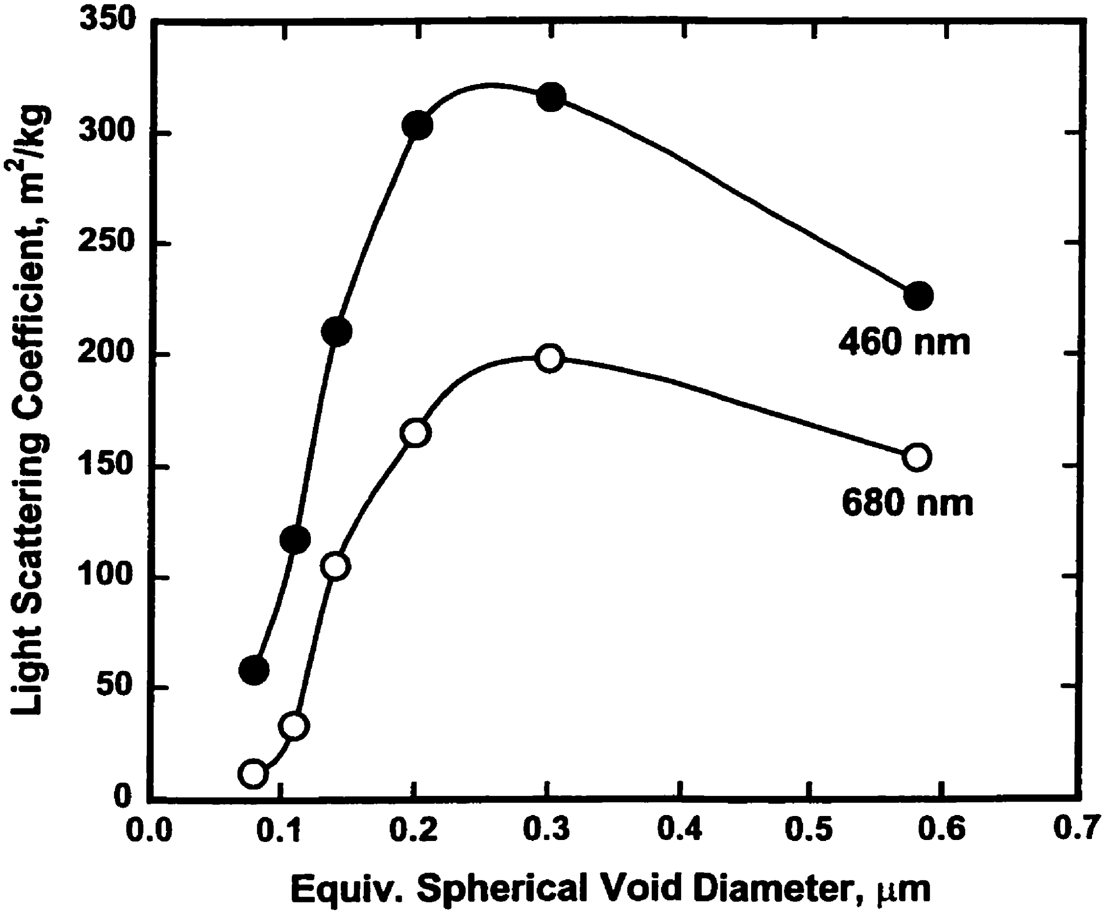

Figure 8. Specific light scattering coefficient expressed per void volume as a function of equivalent spherical diameter of voids [10].

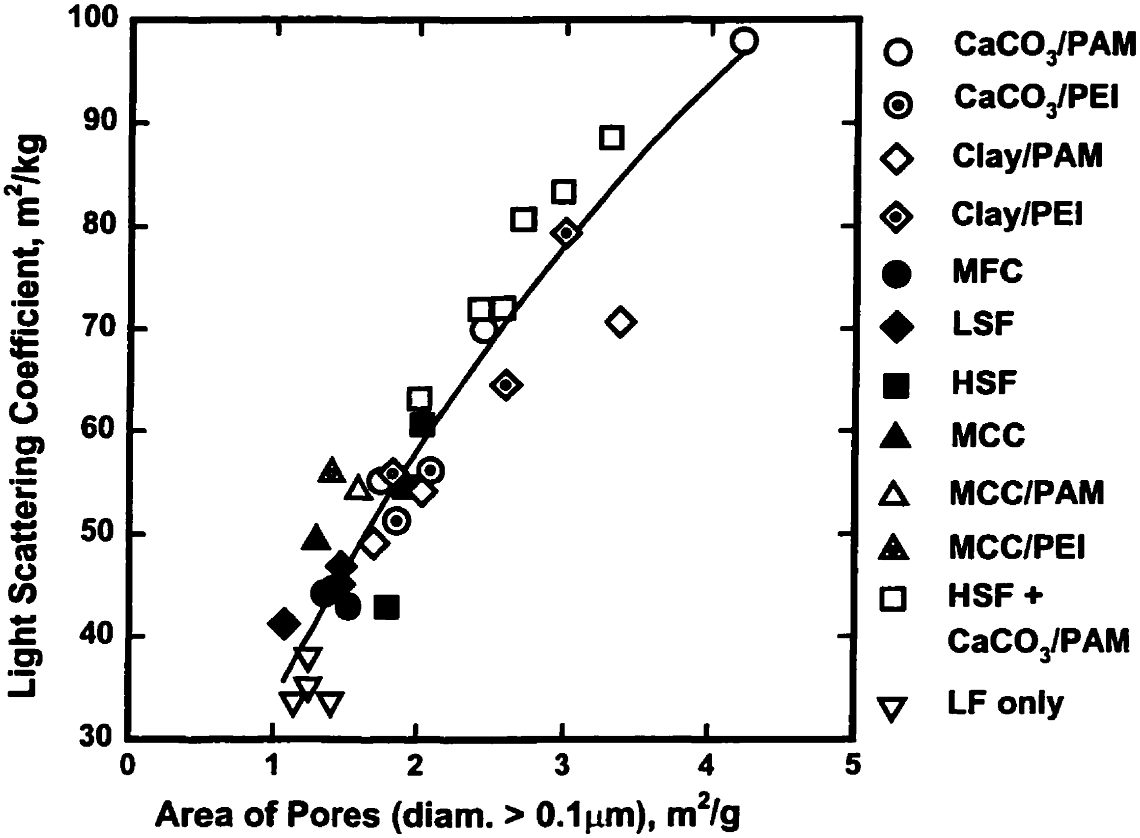

Figure 9. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of pores area, for diameters of pores larger than 0.1 μm. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

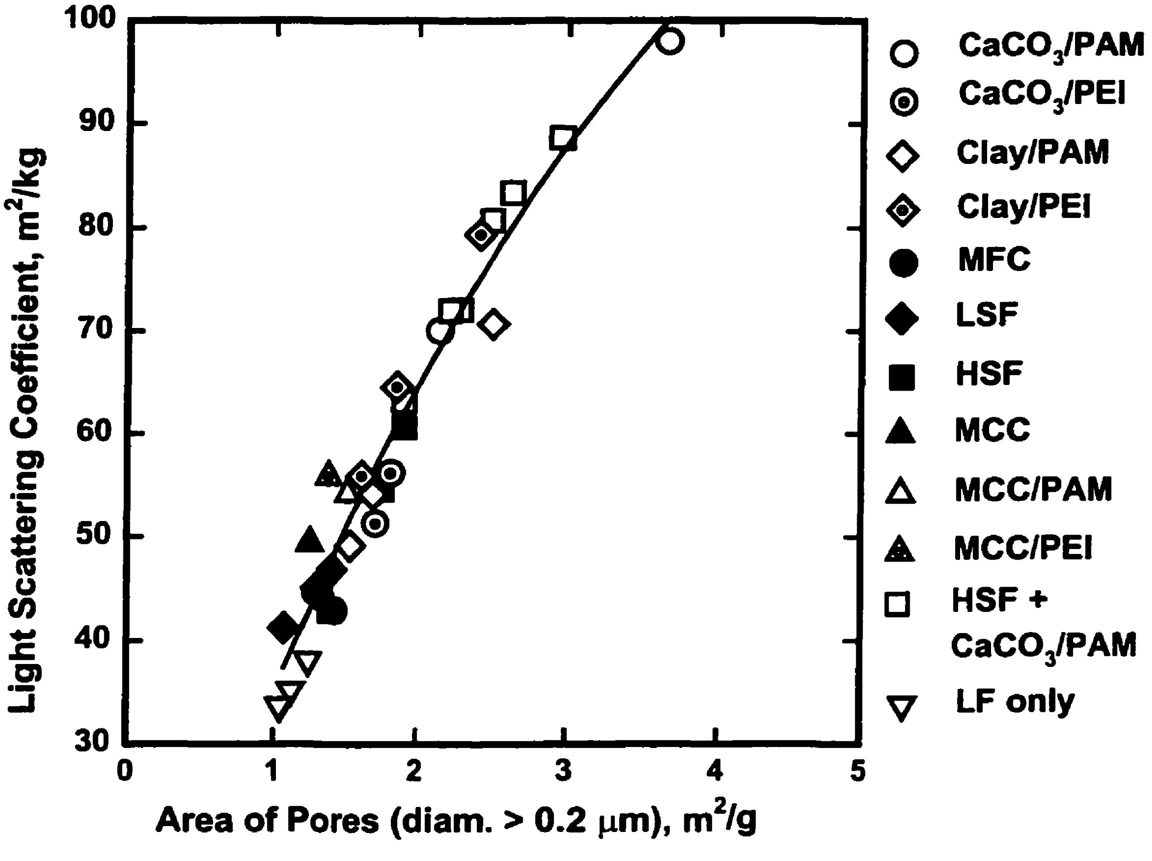

Figure 10. Light scattering coefficient of handsheets formed from long fibres (LF) and different components as a function of pores area, for diameters larger than 0.2 μm. MFC - microfibrillated cellulose, LSF - low specific surface area fines, HSF - high specific surface area fines, MCC - microcrystalline cellulose.

light scattering efficiency increases reaching a maximum around 0.2-0.3 μm (at 460 nm wavelength).

In order to analyze the relation between LSC and air-solid interfaces it is, therefore, necessary to exclude the surface area within the pores too small to be optically effective. This is done in Figure 9 where the surface area of pores larger than 0.1 μm of equivalent spherical pore diameter is plotted against the LSC of handsheets formulated from a variety of components. Now, the direct relation between light scattering and pore area is obvious. The correlation is better when the surface area of pores larger than the optically most effective ones, i.e., 0.2 μm, is considered, as shown in Figure 10.

4. Conclusions

From an optical point of view, paper, composed of a variety of components having similar refractive indices, can be treated as a matrix containing a variety of pores. The air-solid interface in pores smaller than 0.1 μm does not contribute to the scattering of light. However, the light-scattering efficiency is directly related to the extent of the surface area associated with optically effective pores. Therefore, the paper can be considered as a continuous solid phase containing air voids that are the scattering elements.

5. Acknowledgements

This work was financially supported by the Mechanical Wood-Pulps Network of Centres of Excellence. Thanks are due to S. Shimamoto from Daicel Chemical Industries, Ltd. for providing the microfibrillated cellulose, J. Wood, X. Zhang and T. Thompson for help with fines fractionation, and E. Walker for the SEM.

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CHAPTER V

SUMMARY AND CONCLUSIONS

The objectives of this work were to study the flocculation behavior of fines, fillers and their mixtures, to prepare papers with different structures in order to see the effect of fines and fillers on paper properties, to characterize the microstructure of TMP papers by scanning electron microscopy, and elucidate the relationship between the microstructure and properties of papers.

Flocculation behavior of fines, fillers and their mixtures is described in Chapter II. Two polymers, polyacrylamide and polyethylenimine, were used to change the rate of flocculation of fines (MCC and TMP fines) and fillers (clay). Measurements confirmed that it was possible to homoflocculate all materials separately as well as to heteroflocculate them. This knowledge was applied in Chapter IV, where different structures of papers were formed.

In Chapter III, two types of model fines and two types of thermomechanical fines were used to investigate their effect on the mechanical and optical properties of thermomechanical and kraft papers. It was shown that the shape and the degree of fibrillation play an important role in tensile strength and light scattering. High specific surface area fines were shown to be very effective in improving tensile strength and light scattering simultaneously.

In Chapter IV, different structures of thermomechanical papers were prepared by introducing different types of fines, fillers or their mixtures in different forms (dispersed or flocculated). The microstructure of these papers was characterized by SEM. The assumption, that the total light scattering is a function of the air-solid interface was tested. A direct relation was observed between the optical performance of paper and pores of different sizes. Only optically active pores (above 0.1 μm) contribute to the light scattering. The most effective pores were found to be those having sizes 0.2-0.3 μm.

APPENDIX

EXPERIMENTAL METHODS

1. Polyelectrolyte titration.

The polyelectrolyte titration method is based on the formation of complexes between polycations (such as polyethylenimine (PEI)) and polyanions (such as potassium poly(vinyl sulfate) (PVSK)) and on determination of the equivalent point (endpoint) by the adsorption of a dye onto a chromotrope polyelectrolyte. The detection limit for ethylenimine-type substances is 50 ppb. The method of colloidal titration can be applied in wastewater analysis, papermill whitewater analysis, or determination of the state of adsorption of polyelectrolytes.

PEI is a highly branched water-soluble polymer of variable molecular weight. It contains primary, secondary, and tertiary amino groups. The charge of PEI depends on pH, because amino groups become protonated at low pH. Point of zero charge is at pH close to 11. Thus, PEI is positively charged at lower pHs, which corresponds, to papermaking conditions. PEI has strong affinity for anionic materials. Positively charged PEI adsorbs on oppositely charged surfaces in a flat configuration. It is a very effective flocculant.

PEI Polymin P was used as a cationic polyelectrolyte. The concentration of a stock solution was 0.1 g/L. PVSK was used as an anionic polyelectrolyte. Orthotoluidine blue (Blue O) was used as an indicator/buffer. Solution of buffer of pH 4 was prepared containing potassium acid phtalate ($KHC_8H_4O_4$) and indicator Blue O. The buffer maintained constant pH throughout the titration. Also, low pH provides a good environment for PEI to be highly protonated, thus allowing easy complex-formation.

An automatic polyelectrolyte titrator designed and constructed by BASF was used. It is connected to a chart recorder which permits the observation of the endpoint of titration. At the endpoint of the titration, an excess of PVSK is first added to the solution and it is identified by a change of color (from blue to pink). The method is based on measuring the light transmittance of red light, relative to green light (when the isobestic point is related, i.e. for that wavelength no changes occur when the PVSK/Blue O complex is formed) [1].

2. Photometric dispersion analyzer (PDA)

The principle of PDA is based on monitoring the fluctuations in the intensity of light transmitted through a flowing suspension. The light intensity is monitored by a sensitive photodiode, and the output is converted to a voltage proportional to the intensity. The output voltage has a large dc component corresponding to the average transmitted light intensity (related to the turbidity of the suspension) and much smaller ac component due to the random variations in particle numbers. The ac component is separated from the dc component and amplified. What is actually measured is the ratio R of RMS to the dc output

$$R = RMS/DC \qquad (1)$$

The root mean square (RMS) value of the fluctuations is sensitive to changes in particle aggregation, the smaller the average number of particles, the larger RMS amplitude of the ac signal. Thus, the RMS value increases as particles aggregate. Conversely, dispersion causes a substantial decrease in the RMS value [2].

The experimental setup is shown in Figure 1. The suspension of fines or fillers is mixed in a beaker and pumped to the PDA. Changes – either flocculation or dispersion, are monitored, and the suspension is returned to the beaker.

3. Light scattering

When light strikes a paper surface, four processes can occur: reflection, transmission, scattering and absorption. The most important result, with regard to brightness and opacity, is scattering. Scattering of light by paper is a combination of multiple reflection and refraction as light rays pass from air into cellulosic fibres and fillers [3]. The scattering coefficient was originally defined by Kubelka and Munk [4]. The following equations are used in the instrument Technibrite Micro TB-1C software to compute the scattering coefficient S:

$$S = 1000\,(SW/W) \qquad (2)$$

where SW is the scattering power, and W is the basis weight of paper in g/m^2. The scattering power is defined as:

$$SW = [0.5/b]\ \ln[(x+1)/(x-1)] \qquad (3)$$

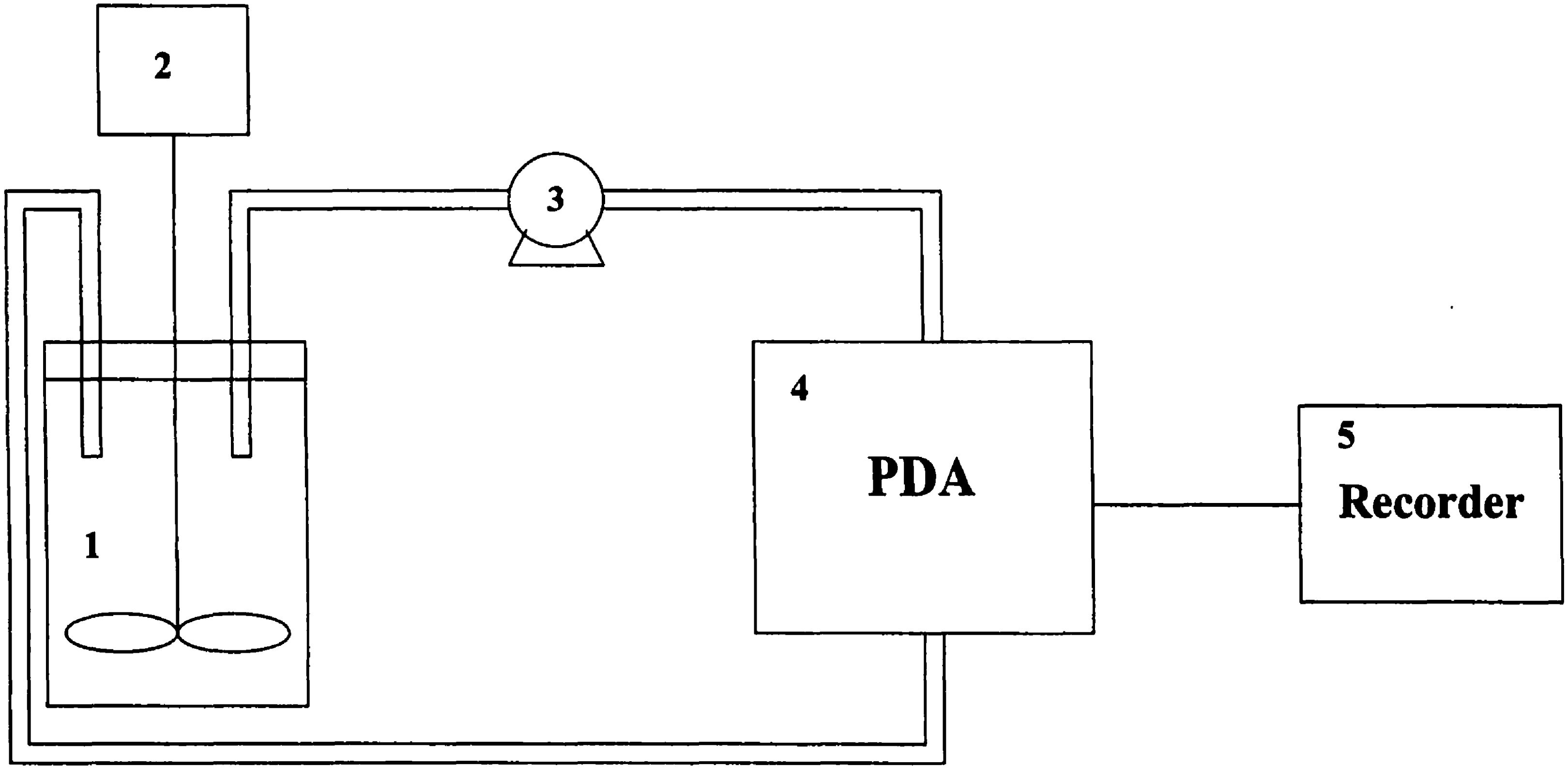

Figure 1. Experimental setup for stability measurements. 1 – beaker with suspension, 2 – stirrer, 3 – pump, 4 – photometric dispersion analyzer, 5 – recorder.

Values b and x are based on reflectance measurements:

$$b = 0.5\,[1/R_\infty - R_\infty] \qquad (4)$$

$$x = [1 - aR_0]/[bR_0] \qquad (5)$$

where R_∞ is the reflectance value obtained with multiple sheet backing, R_0 is the reflectance value obtained with zero reflectance backing, also called reflectivity, and a is calculated as follows:

$$a = 0.5\,[1/R_\infty + R_\infty] \qquad (6)$$

The optical system of the Technibrite Micro TB-1C is based on a large integrating sphere of 150 mm diameter which is coated with a high reflectance barium sulphate paint. Two quartz tungsten halogen lamps direct beams of light through the holes on each side of the sphere. Highly diffuse illumination of the sample, which covers a 34 mm diameter opening, is produced by multiple reflections from the sphere wall. The light reflecting from the sample is viewed by the photocell. A selected filter is inserted into the light beam [5]. Reflectance and reflectivity values are measured. Other optical parameters can be calculated using the Kubelka-Munk equations.

4. Tensile strength

Tensile strength is a measure of sheet resistance to stress produced by tension. It is defined as a maximum stress developed before the sheet ruptures. Typical stress-strain behavior of paper is shown on Figure 2. Load and elongation can be measured by a constant rate of elongation tester [6]. A tensile testing machine model T2001 (JJ Instruments) was used. The tensile tester is capable of applying a force of 2000 N. A load cell with a maximum force 200 N was sufficient to test the paper. A testing speed of 15 mm/min was chosen. The strips of paper 10 mm wide and minimum 12 cm long were tested between a fixed base-plate and vertically moving crosshead [7]. The jaws of the tensile tester were adjusted 100 mm

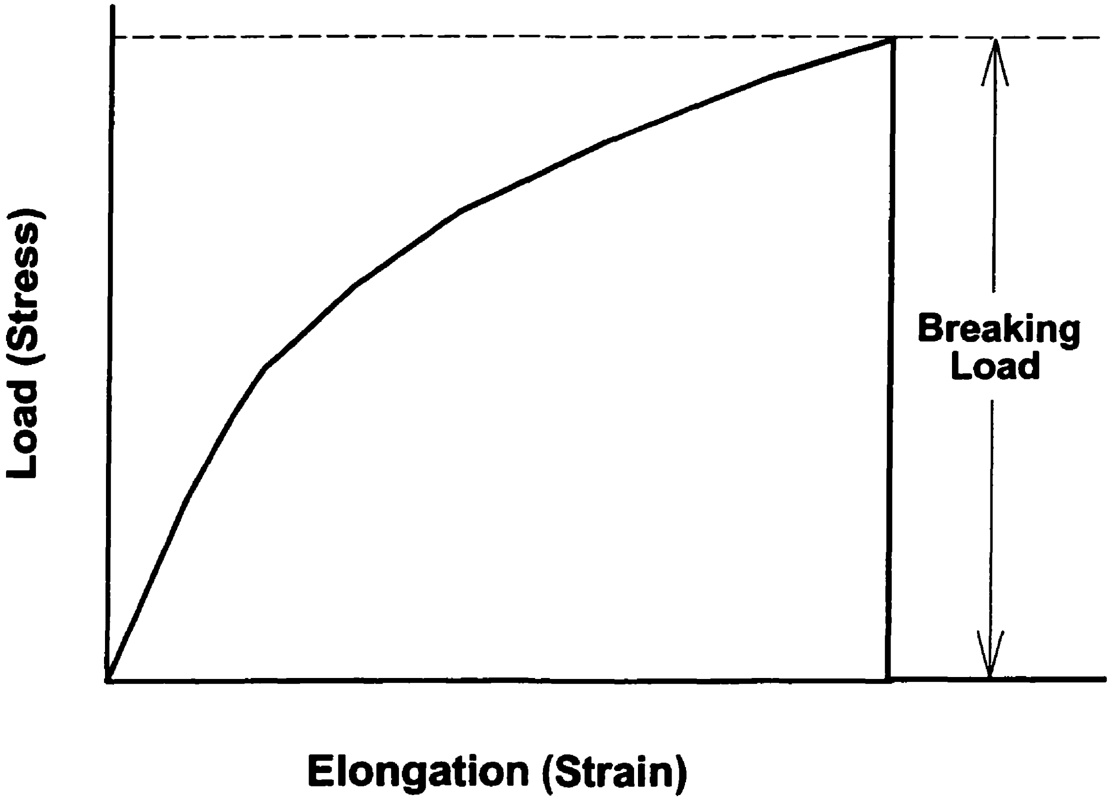

Figure 2. Typical stress-strain behavior of paper [6].

apart. The maximum load is measured by an electronic strain gauge type cell. Also, extension is measured. Tensile strength TS (kN/m) is calculated from the formula:

$$TS = P/(1000w) \tag{7}$$

where P is tensile load in N, w is width of sample in m. Tensile index TI (Nm/g) can be calculated from the tensile strength TS and basis weight of paper W (g/m^2):

$$TI = (1000\ TS)/W \tag{8}$$

5. Porosimetry

Porosity is the ratio of pore volume to total volume.

The porosity and the area of pores in papers was determined by mercury porosimetry using a PoreSizer 9320 (Micromeritics). The mercury intrusion method is commonly used to characterize a porous material. A porosimeter is a device capable of generating suitably high pressures and measuring the volume of mercury taken up by the pores. A mercury atom is about 3.14 Å in diameter. The detectable size of pores depends on the pressure used to force mercury into the pores of the sample and on penetrometer deformation under high pressures [8]. A pressure of 30,000 psi was used for our samples, which corresponds to a 0.02 μm diameter pores accounting for the deformation of penetrometers.

The method is based on the capillary law governing liquid penetration into small pores. This law can be expressed by the Laplace equation:

$$D = -(1/P)\ 4\gamma \cos\varphi \tag{9}$$

where D is pore diameter, P is the applied pressure, γ is the surface tension, and φ is the contact angle. The volume of mercury V penetrating the pores is measured directly as a function of applied pressure. The surface tension of mercury varies with purity. A value of 480 mN/m was used. The contact angle between mercury and the solid depends on sample composition. For a cellulose-mercury system the contact angle $\varphi = 140°$.

It is hard to evaluate the shape of pores. Pores are rarely cylindrical. The equation (9) represents a generally accepted model [9]. From the pore volume V and the pore diameter D, the surface area of the pores, A, can be found from

$$A = 4V/D \tag{10}$$

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