PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL CELLULOSE FROM SUGARCANE BAGASSE

By

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ABSTRACT

A 38 % of cellulose was successfully extracted from sugarcane bagasse through alkali treatment followed by the nitric acid hydrolyzed process. The cellulose was then converted to carboxymethyl cellulose (CMC) by mercization with various sodium hydroxide (NaOH) concentrations and subsequently etherified with monochloroacetic acid. The presence of C=O bond at wavenember of 1606 – 1632 cm^{-1} in infrared radiation (IR) spectrum confirmed the conversion of cellulose to carboxymethyl cellulose. The absolute degree of substitution (DS_{abs}) of CMC was found to increase with increasing concentrations of NaOH up to 25 % (w/v) of NaOH and decreased at higher NaOH concentration. The molecular weight, mechanical properties and water vapor permeability (WVP) were found to have the same trend as DS_{abs}. This is because higher the NaOH concentration causes the crystalline cellulose to become more amorphous, thus more carboxymethyl group substituted on the cellulose backbone which results a higher DS_{abs} and molecular weight as well as WVP. Higher DS_{abs} provide a stronger inter-molecular interaction between carboxymethyl and hydroxyl groups which result a higher mechanical properties. The synthesized CMC which results a highest tensile strength was then blended with corn starch at various compositions. Blending corn starch with CMC improved the tensile strength and also water vapor transmission of corn starch films. The WVP of the CMC/corn starch blend films decreased with increasing CMC content up to 40 % (w/w) of CMC content. This is because CMC acts as filler at low content, which disperse well in the corn starch matrix and blocked the water vapor transmission. However, excessive filler easily congregates which in turn decreased the effectiveness of CMC content. The melting and degradation temperature of corn starch decreased as CMC content increased up to 40 % (w/w) of CMC due to poor stability of CMC.

ABSTRAK

Sebanyak 38 % daripada selulosa telah berjaya dikeluarkan dari hampas tebu melalui reaksi alkali diikuti dengan asid nitrik hidrolisasi proses. Selulosa itu kemudian diubah kepada selulosa carboxymethyl dengan mercization menggunakan pelbagai kepekatan natrium hidroksida dan seterusnya etherified dengan asid monochloroacetic. Kehadiran C=O pada 1606 - 1632 cm^{-1} dalam sinaran inframerah spektrum mengesahkan penukaran selulosa kepada selulosa carboxymethyl. Tahap penggantian kumpulan carboxymethyl (DS_{abs}) daripada selulosa carboxymethyl telah didapati meningkat dengan peningkatan kepekatan NaOH sehingga 25 % (w/v) NaOH dan menurun pada kepekatan NaOH yang lebih tinggi. Berat molekul, sifat mekanik dan kebolehtelapan wap air (WVP) didapati mempunyai trend yang sama seperti DS_{abs}. Ini adalah kerana lebih tinggi kepekatan NaOH menyebabkan selulosa kristal menjadi lebih amorfus, jadi lebih banyak kumpulan carboxymethyl digantikan pada tulang belakang selulosa yang mengakibatkan DS_{abs} yang lebih tinggi dan juga berat molekul serta kebolehtelapan wap air. DS_{abs} yang tinggi menyebabkan interaksi yang lebih kukuh antara kumpulan carboxymethyl dan hidroksil yang menyebabkan sifat-sifat mekanikal yang lebih tinggi. Selulosa carboxymethyl disintesis yang mempunyai kekuatan tegangan yang tinggi kemudian dicampur dengan tepung jagung dalam pelbagai komposisi. Kanji jagung yang dicampur dengan selulosa carboxymethyl menambahkan kekuatan tegangan dan juga penghantaran wap air filem kanji jagung. WVP daripada campuran selulosa carboxymethyl/jagung filem menurun dengan peningkatan kandungan selulosa carboxymethyl sehingga 40 % (w/w) kandungan selulosa carboxymethyl. Ini adalah kerana tindakan selulosa carboxymethyl sebagai pengisi pada kandungan yang rendah, yang bercampur dengan baik dalam matriks kanji jagung dan menyekat penghantaran wap air. Walau bagaimanapun, pengisi yang berlebihan mudah congregates jadi menurun keberkesanan kandungan selulosa carboxymethyl. Lebur dan kemerosotan suhu kanji jagung menurun pada kandungan selulosa carboxymethyl yang meningkat sehingga 40 % (w/w) selulosa carboxymethyl kerana kestabilan selulosa carboxymethyl.

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Thank you.

APPROVAL SHEET

This project entitled "**PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL CELLULOSE FROM SUGARCANE BAGASSE**" was prepared by **KOH MAY HONG** and submitted in partial fulfillment of the requirements for the degree of Bachelor of Science (Hons.) in Chemistry at Universiti Tunku Abdul Rahman.

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UNIVERSITI TUNKU ABDUL RAHMAN

Date: _____________

PERMISSION SHEET

It is hereby certified that **KOH MAY HONG** (ID No: **10ADB04861**) has completed this final year project entitled "**PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL CELLULOSE FROM SUGARCANE BAGASSE**" supervised by Dr. Tan Shu Min from the Department of Chemical Science, Faculty of Science.

I hereby give permission to my supervisor to write and prepare manuscripts of these research findings for publishing in any form, if I do not prepare it within six (6) months from this date, provided that my name is included as one of the authors for this article. The arrangement of the name depends on my supervisor.

Yours truly,

____

(KOH MAY HONG)

DECLARATION

I hereby declare that the project report is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

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KOH MAY HONG

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LIST OF ABBREVIATIONS

AGU	Anhydroglucopyranose unit
ASTM	American Society for Testing of Materials
CMC	Carboxymethyl cellulose
$\mathbf{DS_{abs}}$	Absolute degree of substitution
$\mathbf{DS_{rel}}$	Relative degree of substitution
DSC	Differential scanning calorimetry
DTG	Differential thermogravemetric
EB	Elongation at break
FTIR	Fourier transform infrared spectroscopy
HCl	Hydrochloric acid
IR	Infrared radiation
MCA	Monochloroacetic acid
M_v	Molecular weight
NaCl	Sodium chloride
NaCMC	Sodium carboxymethyl cellulose
NaMCA	Sodium monochloroacetic acid
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance
RH	Relative humidity
SCB	Sugarcane bagasse
T_d	Degradation temperature
TGA	Thermogravimetric analysis
T_m	Melting temperature

TS	Tensile strength
WVP	Water vapor permeability
ΔH_{f}	Heat of fusion
$[\eta]$	Intrinsic viscosity

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, there has been an increase in the level of research on the development of new biodegradable materials for use in packaging, agriculture, medicine and other areas. Generally, biodegradable polymer materials are increasingly important as environmental contamination and waste disposal problems associated with plastics and related products from synthetic polymers become more severe. Natural polymers have various advantages over synthetic polymers due to their low-cost, great availability and biodegradability (Zhou, et al., 2008). Furthermore, oil prices have increased significantly due to the limited nature of fossil fuels, especially petroleum resources. In response to this situation, lignocelluloses biomass from plants has become the main focus of the developing bio-refining industry.

Sugarcane bagasses (SCB) are an abundant agricultural lignocelluloses by-product on the earth. It is a main product to the sugarcane industry which is generated in large quantities during the processing of sugarcane in sugar mills. Bagasses offer the advantages of being a cheap, plentiful and low polluting fuel (Mothe and Miranda, 2009). Commonly, all plant biomass consists of cellulose, hemicellulose, lignin, pectin and protein (Singh and Khatri, 2012). Most of the plant biomass consists of about 33 % of cellulose as the major component of the rigid cell walls (Singh and Singh, 2012).

Cellulose is a linear and high molecular weight polymer as well as natural, renewable and biodegradable material (Rachtanapun, 2009). However, due to its high crystallinity and strong inter- and intra-molecular hydrogen bond, cellulose neither melts nor dissolves in the most common organic solvents, therefore, reduces its applicability (Hattori, Abe and Cuculo, 2004). In order to increase the cellulose applicability, an alternative pathway is to convert the cellulose to its derivatives such as carboxymethyl cellulose (CMC) through chemical derivatization reaction (Singh and Singh, 2012). CMC is important for its water-soluble properties where great applications are applied throughout the food industry, detergents, cosmetics, pharmaceuticals, textiles, paper, adhesives as well as ceramics (Savage, Young and Maasberg, 1954; Yang and Zhu, 2007).

CMC was reported to be synthesized from diverse plant biomasses, which contain 40 – 50 % cellulose, 25 – 40 % hemicellulose and 15 – 35 % lignin on a dry basis (Singh and Singh, 2012). The synthesis of CMC from various agricultural waste cellulose sources such as sugar beet pulp (Togrul and Arslan, 2003), cavendish banana pseudo stem (Adinugraha, Marseno and Haryadi, 2005), cashew tree gum (Silva, et al., 2004), sago waste (Pushpamalar, Langford and Lim, 2006), orange peel (Yasar, Togrul and Arslan, 2007), papaya peel (Rachtanapun, Kumthai and Uthaiyod, 2007) and Mimosa pigra peel (Rachatanapun and Rattanapanone, 2011) have been reported by many researchers.

Corn starch is an essential polysaccharide polymer used to develop edible or biodegradable film due to its ability to provide a continuous matrix, abundant, cheap and biodegradable (Wing, Maiti and Doane, 1988). Nonetheless, the corn starch film is highly waters sensitive and exhibits poor mechanical properties as compared to conventional synthetic polymers, thus it is unsuitable for application such as packaging purposes (Alves, et al., 2006). However, blending of corn starch with CMC is expected to improve its mechanical properties.

1.2 Objectives

The main objectives of this research are as follows:

i. Extraction of the cellulose from SCB.
ii. Modification of the structure of cellulose to produce CMC.
iii. Examination of the effect of various NaOH concentrations on the degree of substitution, viscosity, mechanical properties, thermal properties and water vapor permeability (WVP) of CMC produced.
iv. Preparation of various blends of corn starch and CMC.
v. Examination of the mechanical properties, thermal properties and WVP of CMC/corn starch blend films.

CHAPTER 2

LITERATURE REVIEW

2.1 Raw materials for carboxymethyl cellulose (CMC) production

Chemical functionalization of cellulose is to alter the properties of the macromolecule for different purposes such as the production of cellulose derivatives for a variety of applications. The most common sources of cellulose for industrial uses are from wood pulp (contain 40 – 50 % cellulose) and cotton linters (contain 90 % cellulose) which nowadays are discouraged due to the cost of production and increasing environmental concerns (Singh and Singh, 2012). Besides, renewable materials are gaining importance due to the limited existing quantities of fossil resources. Thus, biomass rich in cellulose such as bamboos, weeds, fibers and agriculture waste become an alternative chemical feedstock as it consists of cellulose, hemicellulose and lignin, which contain various functional groups suitable for chemical functionalization (Varshney and Naithani, 2011).

Table 2.1: Content of cellulose, hemicellulose and lignin in agricultural waste

Agricultural waste	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Corn cobs	45	35	15
Wheat straw	30	50	15
Hardwood stems	45-50	24-40	18-25
Softwood stems	45-50	25-35	25-35
Sugarcane bagasse	40-50	23-35	18-24

Sources: Cheung and Anderson (1997); Mandal and Chakrabarty (2011)

2.2 Sugarcane bagasse (SCB)

2.2.1 General

The sugarcane stalks are divided into two parts, which are an inner pith consisting most of the sucrose and an outer rind with lignocellulosic fibers. Sugarcane is largely grown in tropical and subtropical places where the wet and dry season is alternate such as Brazil, Australia, India, South Africa, Cuba, Peru and Mexico (Ripoli, et al., 2000). Bagasses are a fibrous residue obtained from sugarcane stalks after it is crushed to obtained juice used for sugar and ethanol production (Mothe and Miranda, 2009).

Among sugarcane producing industries, Brazil was the top producer with 625 million tons of sugarcane in the year 2011, followed by India and China (Chandel, Silva and Singh, 2012). Generally, 1 ton of sugarcane will generate 280 kg of humid bagasses. Throughout the world, about 54 million dry tons of bagasses are produced annually (Mulinari, Voorwald and Silva, 2009).

2.2.2 Components of sugarcane bagasse (SCB)

A lignocellulosic material from forestry or agricultural waste, including bagasses provides intermediate chemical building blocks whereby the polymer is hydrolyzed to obtain the desired compounds (Walford, 2008). Lignocellulosic material consists of mainly cellulose, hemicellulose and lignin, which are produced by plants to form cell walls and act as a structural support

(Idi and Mohamad, 2011). The main disadvantage of using lignocellulosic as a natural fiber in the polymer production is the poor compatibility between the fiber and the matrix. Besides, the characteristic of high moisture absorption tendency will also lead to dimensional changes of lignocellulosic based fibers (Rout, Misra and Mohanty, 2001).

Approximately, 40 to 50 % of SCB is the glucose monomer which is in a crystalline structure. Another 25 to 35 % is hemicellulose which is an amorphous polymer usually composed of xylose, galactose, arabinose, glucose and mannose. The remainder is mostly lignin with a lesser amount of mineral, wax and other compounds (Sun, et al. 2004). The typical composition of bagasses fiber is about of 26.6 – 54.3 % cellulose, 22.3 – 29.7% hemicellulose, 14.3 – 24.5 % lignin, 45 – 50 % moisture and 2 – 6 % soluble solids (Katyal, Thambimuthu and Valix, 2003).

Hemicellulose is a heterogeneous polysaccharide composed of different monomers such as D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose and D-glucuronic acid (Sun, et al., 2004). It is a complex polysaccharide made up of various five and six-carbon sugars (Idi and Mohamad, 2011) and has a low degree of polymerization, which often contains side chains in the acetylated form (Sun, et al., 2004). Hemicellulose has a random amorphous structure with little strength, which is easily hydrolyzed by dilute acid as compared to cellulose, which is crystalline, strong and resistant to hydrolysis reaction (Idi and Mohamad, 2011).

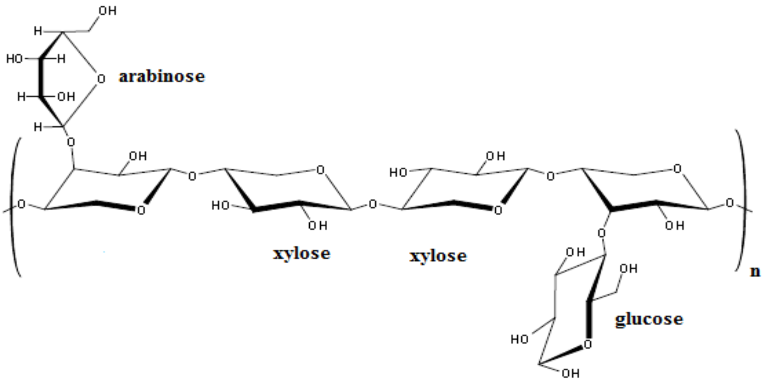

Fig. 2.1: The structure of hemicellulose

Lignin is a highly complex, three-dimensional polymers of three different phenyl-propane units, which is p-coumaryl, sinapyl and coniferyl alcohols (Amen-Chen, Pakdel and Roy, 2001). They are bound together by aryl-aryl, alkyl-aryl and alkyl-alkyl ether bonds. Lignin is embedded in the cellulose and hemicellulose structure which helps to strengthen the cell walls rigidity. Besides, it also prevents the penetration of chemicals that can destroy the cell wall as well as offering protection to the plant against microbial attack (Amen-Chen, Pakdel and Roy, 2001). Lignin content in SCB is roughly about 21 % on average (Cadenas, Mitrani and Pena, 1990). High content of lignin is classified as a factor that against the production of good surface wettability between polymer matrix material and natural fibers (Navarro, Medeiros and Maia, 1991).

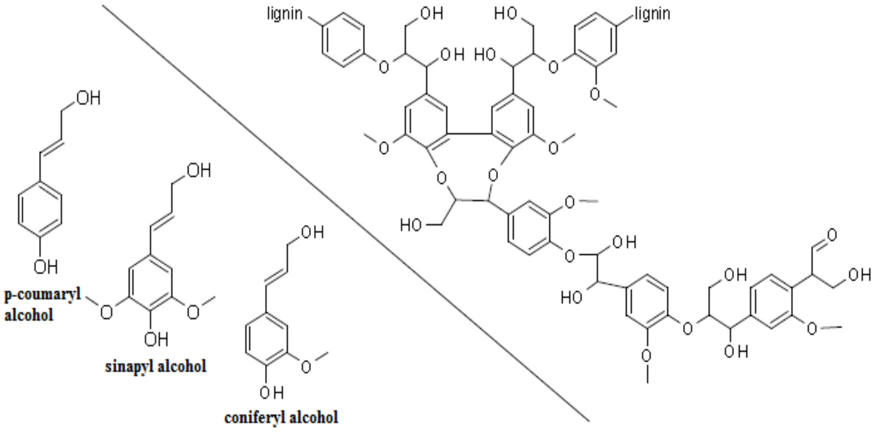

Fig. 2.2: Phenyl-propane precursors (left) and structure of lignin (right)

2.3 Cellulose

2.3.1 General

Cellulose is a natural occurring linear polymer of anhydroglucose that is found abundantly on earth (Kester and Fennema, 1986). Elemental composition of cellulose was first determined by Payen in 1838 to have the empirical formula of $C_6H_{10}O_5$ whereby he found the composition of 44.4 % C and 6.2 % H in an elemental analysis of cellulose (Payen, 1842; Krassig and Schurz, 1986). Furthermore, cellulose was described as a material which is resistant to the extraction with water, ether or ethanol (Payen, 1842).

2.3.2 Structure of cellulose

At a molecular level, cellulose is a simple linear polymer consisting of D-anhydroglucopyranose unit (AGU) linked together with β-(1,4)-glycosidic bonds formed between carbon 1 and carbon 4 of adjacent glucose (Kester and Fennema, 1986) as shown in Fig. 2.3. In the solid state, AGU units are rotated 180º with respect to each other due to the constraints of β-linkage. Each of the AGU units consists of three hydroxyl groups at carbon 2, 3 and 6 positions. The hydroxyl group at carbon 1 of either end of molecule is an aldehyde group which has a reducing characteristic. Conversely, the hydroxyl group at carbon 4 on the other end of the chain consists of alcoholborne hydroxyl group constituent and thus is known as a non-reducing end (Staudinger, 1932).

In cellulosic plant fiber, cellulose is present in an amorphous state as well as crystalline phase through inter- and intra-molecular hydrogen bond; thereby cellulose does not melt before thermal degradation (Fengel and Wegner, 1989). Cellulose is aligned parallel to each other in fibrils, which are surrounded by a matrix of lignin and hemicellulose. In addition, cellulose has properties such as low density, good mechanical properties as well as biodegradability (Zimmerman, Pohler and Schwaller, 2005).

Based on Lennholm and Iversen (1995), there are several types of celluloses, which are type I, II, III, IV and V. However, only type I show the best mechanical properties. Furthermore, cellulose I was found to have a parallel chain orientation while cellulose II is anti-parallel chain. Through the investigation from the infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) found that, the AGU ring exists in the pyranose ring form adopts the $^4C_1$-chair conformation which constitutes the lowest energy conformation, thus are thermodynamically more stable (Michell and Higgins, 1965).

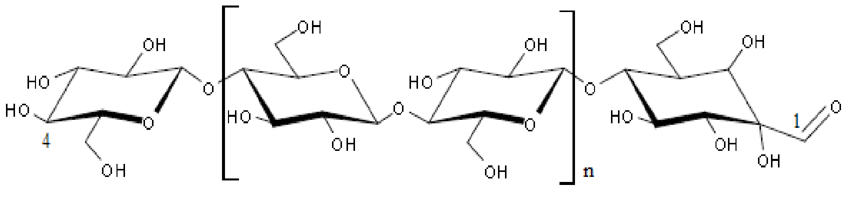

Fig. 2.3: Molecular structure of cellulose showing reducing (right) and non-reducing (left) end groups

The presence of the three equatorial positioned hydroxyl groups in AGU, which is a secondary hydroxyl group at carbon 2 and 3 with a primary hydroxyl group at carbon 6 positions, determined the chemical character and reactivity of the cellulose (Kadla and Gilbert, 2000). Besides, the hydroxyl groups of cellulose also play an important role in the solubility of cellulose, and the β-glycosidic linkages of cellulose are susceptible to hydrolytic attack as shown in Fig. 2.4. Cellulose is insoluble in common organic solvents as well as water due to the formation of various strong inter- and intra-molecular hydrogen bonding (Bono, et al., 2009). Therefore, in order to dissolve the cellulose, the existing hydrogen bonding network must be broken.

2.3.3 Swelling of cellulose

Alkali cellulose is an important swelling complex formed after treatment with NaOH as it increased the reactivity of cellulose towards the chemical reactions as compared to the untreated cellulose (Fengel and Wegener, 1989). This means that, the etherifying or esterifying reagents able to penetrate the swelled cellulose structure more easily and thus substitution of the hydroxyl group of the anhydrous glucose unit becomes easier.

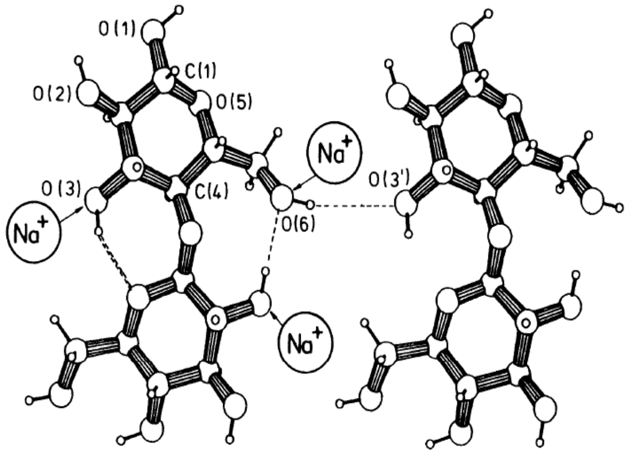

Fig. 2.4: Schematic diagram of Na-cellulose I structure (Fink, Walenta and Mann, 1995)

NaOH treatment of cellulose yields the pure cellulose modification I and II as well as mixtures of cellulose I and II which depends upon the concentration of the NaOH solution.

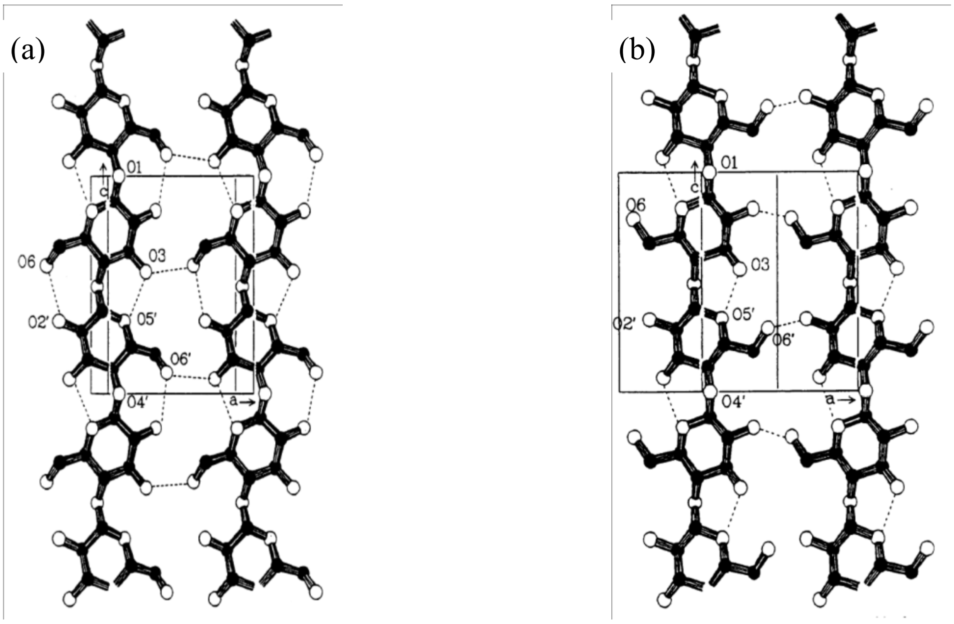

Fig. 2.5: Patterns of hydrogen bonds in (a) cellulose I and (b) cellulose II (Fink, Walenta and Mann, 1995)

Cellulose II appears to have more hydrogen bonding, which contribute to the additional stability of the chain and thus thermodynamically more stable than cellulose I (O'Sullivan, 1997). Besides, due to higher inter-molecular and cross-linking density, cellulose II is less reactive than cellulose I (Kolpack and Blackwell, 1976). As shown in Fig. 2.5 (b), the position of all the hydroxyls favored the formation of inter- and intra-molecular hydrogen bonds within the unit cell structure of cellulose II. Krassig (1993) reported the reduction of the accessible inter-fibrillar surface of the cellulose II due to its low reactivity as the density and hydrogen bonding increased.

2.3.4 Derivatives of cellulose

Cellulose derivatives which are synthesized from natural waste have diverse physiochemical properties due to the wide range of substitutions, molecular weight, and degree of polymerization are valued for their vast application as additives in textile, food, cosmetic and packaging industries (Balser, et al., 1986; Barndt, 1986). Through Williamson etherification reaction (Tijsen, Kolk and Beenackers, 2001), several cellulose derivatives which are soluble in common solvents may be produced, such as carboxymethyl cellulose (CMC), methylcellulose, hydroxypropyl cellulose and hydroxypropylmethyl cellulose (Olivas and Barbosa-Canovas, 2005).

During 1920-1930s, the first cellulose ether which gains economic significant was carboxymethyl cellulose (CMC) followed by methyl cellulose and hydroxyethyl cellulose. These three types of cellulose ether and their mixed derivatives such as methylhydroxyethyl, methylhydroxypropyl and hydroxypropylmethylcellulose still dominate the market due to their multifunctional properties. Schweizer and Sorg (1995) reported the worldwide production of cellulose ethers to be over 300,000 metric tons annually. Besides, they are kinetically and thermodynamically more stable and easier to be prepared and characterized.

Table 2.2: Commercially marketed cellulose ethers (Arthur, 1986)

Cellulose ethers	Functional group	DS	Solubility
Carboxymethyl cellulose	$-CH_2COONa$	0.5-2.9	Water
Methyl cellulose	$-CH_3$	1.5-2.4	Hot water
Ethyl cellulose	$-CH_2CH_3$	2.3-2.6	Organic solvents
Hydroxyethyl cellulose	$-CH_2CH_2OH$	0.5-0.7	Water
Hydroxypropyl cellulose	$-CH_2CH_2CH_2OH$	1.5-2.0	Water

2.4 Carboxymethyl cellulose (CMC)

2.4.1 General

CMC is one of the most important cellulose derivatives, which have an immense importance to the industry and also in our everyday life. CMC is a linear, long chain, water soluble, anionic polysaccharide derived from cellulose (Bono, et al., 2009). In addition, the purified cellulose is a white to cream colored as well as tasteless, odorless, and it is a free-flowing powder (Keller, 1986). Furthermore, due to its water-soluble heteropolysaccharides with high molecular weight properties, thus CMC is often blended with starch to provide desirable texture, enhanced product quality and stability, control moisture and also water mobility (Bertuzzi, Castro and Gottifredi, 2007).

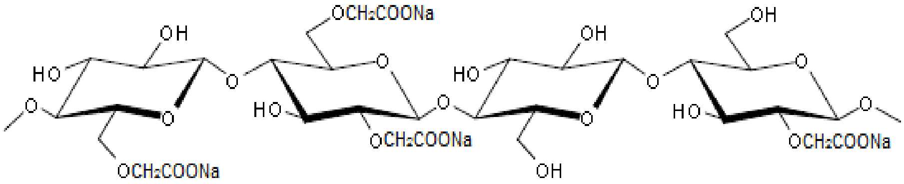

Fig. 2.6: Molecular structure of carboxymethyl cellulose (Na salt, NaCMC)

2.4.2 Synthesis process

Several methods have been used to synthesized CMC, including homogeneous carboxymethylation (Heinze, Liebert and Meister, 1999), fluidized bed technique (Durso, 1981), sheet carboxymethylation (Collings, Freeman and Anthonisen, 1942), rotating drum technique (Swinehart and Allen, 1950), solvent-less method using a double screw press (Edelman and Lindroos, 1990) and a paddle reactor (Holst, Lask and Kostrzewa, 1978).

Ladish, et al. (1989) proved that alkali brings about the swelling of native cellulose fiber, which causes modifications of the crystallinity of cellulose structure and increased the accessibility of fibers to chemicals. A 1.25 M sodium hydroxide (NaOH) concentration at temperatures between 25 – 85 °C solubilized lignin and hemicelluloses. The preparation of CMC involves two reaction steps, which are mercization and etherification by a slurry process (Heinze and Koschella, 2005). In the slurry method, cellulose is suspended in a mixture of NaOH-water-alcohol systems at 20 – 30 ºC with an excess of alcohol (ethanol or isopropanol), to ensure a good mixing efficiency (Mann, Kunze and Fink, 1998).

In the mercerization process, the liquid phase (water-alcohol mixture) which acts as a solvating agent, dissolves the NaOH and distributes it evenly to the cellulose hydroxyl groups forming alkali cellulose. The aqueous NaOH will penetrate the crystalline structure of cellulose, which then solvates its hydroxyl groups and thus makes them available for etherification reaction by breaking the hydrogen bonds (Savage, Young and Maasberg, 1954).

Furthermore, the alkali cellulose produced is reactive towards monochloroacetate acid (MCA), which is added in the second step either as free acid, MCA or its salt, sodium monochloroacetate acid (NaMCA) to form carboxymethyl cellulose ethers. NaOH reacts simultaneously with MCA to form two by-products, which are sodium glycolate and sodium chloride (Krassig, 1993). CMC is produced by Willamson etherification according to the following mechanisms (Stigsson, Kloow and Germgard, 2001).

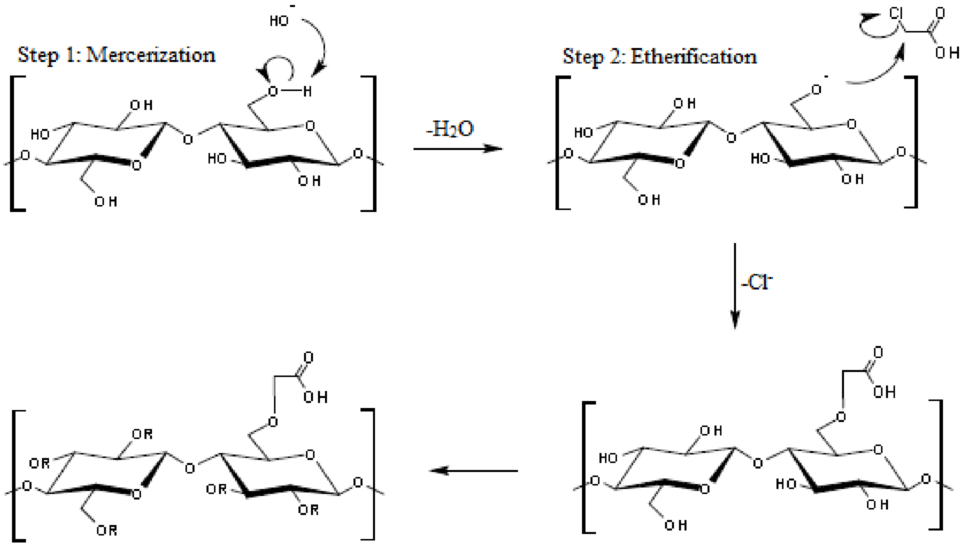

Fig. 2.7: Carboxymethylation reaction where R could be H or CH_2COOH if the carboxymethylation progresses

Side reaction, hydrolysis of MCA occurs, where sodium glycolate and sodium chloride are formed as shown in Eq. (2.1).

$$\mathrm{NaOH} + \mathrm{ClCH_2COOH} \rightarrow \mathrm{HO-CH_2COONa} + \mathrm{NaCl} \qquad (2.1)$$

Furthermore, in this carboxymethylation process, NaOH is consumed; thereby the initial charge of NaOH has to be high to maintain the alkaline pH throughout the reaction (Klemm, Philip and Wagwnknecht, 2001). If the pH during the etherification reaction is acidic, an internal etherification will occur and causes the CMC molecules to be cross-linked. Therefore, pH in the reaction system is important during etherification reaction. According to Klemm, Philip and Wagwnknecht (2001), the reaction requires at least 0.8 mole of NaOH per molecule of AGU to remain the alkalinity if the etherifying agent used is NaMCA. However, if MCA is used instead, thus extra mole of NaOH per mole of AGU must be added to neutralize the acid.

Based on Olaru (2001), the rate of mercerization reaction in ethanol is lower than isopropanol since sodium hydroxide is more favorable to dissolve in ethanol. The use of ethanol during mercerization stage will give a homogeneous NaOH-water-ethanol system. Whereas using isopropanol, a heterogeneous system will occur and forms a layer around the fiber composed of highly concentrated NaOH-water phase due to the low solubility of NaOH in a non-polar system (Yokoto, 1985). Therefore, only small amounts of Na^+ and OH^- ions will enter the alcohol phase of isopropanol and favoring a higher concentration of NaOH in the surrounding area of cellulose, which results in a significant decrystallization of cellulose and changes of polymorphism from cellulose to Na-cellulose during mercerization.

In addition, it is also reported that different solvent system will affect the characteristic of CMC during synthesis. The use of isopropanol in CMC synthesis is reported to generate fewer amounts of sodium glycolate by-product, as MCA is enriched in less polar solvent while NaOH in the aqueous phase (Klemm, Phillip and Wagenknecht, 1998). The efficiency of carboxymethylation increases as the polarity of the aqueous medium decreases (Barai, Singhal and Kulkarni, 1997), thus isopropyl alcohol is used since it has a lower polarity than water. Besides, Stigsson, Kloow and Germgard (2001) reported an uneven substitution of the carboxymethyl group on the AGU when isopropanol is used in mercerization whereby enhanced the substitution on the carbon 6 as well as tri-substitution of the hydroxyl groups of AGU. The most common reaction diluents used for this process are isopropyl alcohol, t-butyl alcohol or ethyl alcohol (Thomas, Paquita and Thomas, 2002).

2.4.3 Properties of CMC in aqueous solution

CMC is a water as well as alkali soluble even at low degree of substitution. Trivedi and Patel (1981) studied the effect of degree of substitution, polymer concentration and size of the counter ions from the dissociation constant of CMC potantiometrically. The solubility of CMC depends on the pH as well as degree of substitution. At low pH values CMC precipitates due to intermolecular hydrogen bond formation between the undissociated carboxymethyl groups as shown in Fig. 2.8.

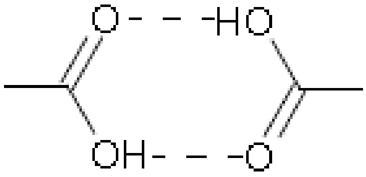

Fig. 2.8: Hydrogen bond formation between two carboxylic acid groups at low pH values

The length of H-O between two acetic acid molecules is 1.64 Ǻ which is in the range of the covalent C-OH bond (1.33 Ǻ), thus these hydrogen bonds are strong and hard to break (Jeffrey and Saenger, 1994). Besides, they also reported that precipitation occurred at pH below 3 for the CMC with DS_{abs} of 0.3 – 0.5, whereas highly substituted CMC with DS_{abs} of 0.7- 0.9 precipitates at pH lower than 1. In neutral aqueous solutions, CMC may form aggregate although the molecular dispersed molecules are arranged in uncoiled linear structures.

Burchard (2003) studied the behavior of cellulose and its aliphatic ethers in solution and reported that the cellulose crystalline section was not fully destroyed during mercerization but form a bundle of aggregated chains with hanging outer chains, which bind water molecules extensively. In 1961, Francis explained that the aggregation and discrete gel particle formation in aqueous CMC solutions depend on the residual crystalline region of cellulose.

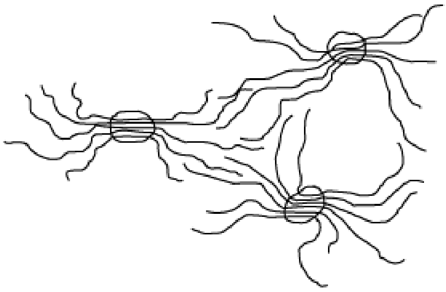

Fig 2.9: The fringed fibril model of aggregated formation of CMC in aqueous media (Francis, 1961)

2.4.4 Applications of carboxymethyl cellulose (CMC)

CMC is an important industrial polymer due to its high viscosity, non-toxic, non-allergenic, biodegradability as well as production at lower cost (Verraest, Peters and Bekkum, 1995). Furthermore, it is a most important water soluble derivative with various applications in paper, food, detergents, cosmetics, and textiles as shown in Table 2.3.

Table 2.3: Applications of CMC in major field of industry

Industry	Application	Function	Reference
Paper	Internal additive	Water binder	Seiichi and Shosuke (2000)
Detergents	Laundry	Soil anti-redeposition aid	Leupin and Gosselink (1999)
Cosmetics	Toothpaste	Thickener, suspension aid	Savage, *et al*. (1954)
Textiles	Printing paste, dye	Water binder, thickener	Yang and Zhu (2007)
Foods	Frozen desserts	Inhibit ice crystal growth	Verraest, *et al*. (1995)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Sugarcane bagasses were obtained from a local market near Westlake Kampar. All chemicals used for the preparation and characterization of CMC were AR grade or equivalent. The sources of all the chemicals used are listed in Table 3.1.

Table 3.1: Sources of chemicals used for the preparation and characterization of CMC

Chemical	**Source**
Sodium hydroxide (NaOH)	R&M Marketing, Essex, U.K
Monochloroacetic acid (MCA)	Merck
Hydrochloric acid (HCl)	Labscan
Glacial acetic acid	Labscan
Absolute methanol	Labscan
Isopropanol	Quality Reagent Chemical
95% ethanol	HmbG Chemicals
Nitric acid	Fisher Scientific

3.2 Methods

3.2.1 Cellulose extraction from sugarcane bagasse (SCB)

The SCB was cleaned and sun-dried for two days. Dried SCB was cut into small pieces and then grounded into powder form using a grinder. A 25 g of sugarcane powder was cooked (95 ºC) with 750 ml of 0.5 M NaOH for two hours at continuous stirring. The dark slurry obtained was filtered and washed with 1 L of distilled water.

The dried cellulose was refluxed with two successive portions of mixture containing 20 % (v/v) of nitric acid in ethanol. The mixture was then filtered and washed with cold distilled water until the filtrate did not turn to pink when phenolphthalein and a drop of 0.5 M NaOH was added to it (Filho, et al., 2007). The residue was dried in an oven at 60 ºC overnight to constant weight. Lastly, the dried cellulose was ground and kept in the polyethylene bag for the cellulose modification in the next process.

3.2.2 Synthesis of carboxymethyl cellulose (CMC) from sugarcane bagasse (SCB) cellulose

CMC from SCB cellulose was synthesized according to the procedure described by Bhattacharyya, Singhal and Kulkarni (1995). First of all, 5 g of cellulose powder from SCB was weighed and added to 150 ml of isopropanol with continuous stirring. Then, 15 ml of (10 %, 15 %, 20 %, 25 % and 30 %

w/v) NaOH was added dropwise into the mixture and further stirred for an hour at room temperature. The carboxymethylation was started when 6 g of MCA was added with continuous stirring for another 1.5 hours. The mixture was covered with aluminum foil and placed into the hot air oven at 60 ºC for 3.5 hours.

The slurry was subsequently soaked in 100 ml of methanol for overnight. On the next day, the slurry was neutralized with 90 % of acetic acid to pH 7 and then filtered using sintered funnel. The final product was washed for three times by soaking in 50 ml of ethanol for 10 minutes to remove undesirable by-products, and then it was washed again with 100 ml of absolute methanol for the last time. The obtained CMC from SCB was filtered and dried at 60 ºC to constant weight and kept in a dry place.

3.2.3 Purification of CMC

Approximately, 5 g of CMC synthesized earlier with various NaOH concentrations was dissolved in 100 ml of 80 ºC of distilled water at constant stirring for 10 minutes. Then, it was centrifuged using an Eppendorf 5430 centrifuges for 1 minute at 4000 rpm. The dissolved CMC were re-precipitated in 100 ml of acetone. Recovered CMC was filtered and dried in a 60 ºC oven until constant weight and was kept in desiccator for characterization process.

3.2.4 Film preparation

2 % (w/v) blend solutions of CMC/corn starch were prepared. For instance, to prepare 80:20 % (w/w) CMC/corn starch, 0.64 g of CMC and 0.16 g of corn starch were dissolved in 39.2 ml of distilled water. The blend solution was stirred constantly at 80 ºC for 15 minutes. Next, the solution was cooled down to room temperature and cast onto polyethylene plates (13 cm x 17 cm). The blend solution was evaporated at room temperature for 36 hours, and then the films were obtained. The films were then peeled and kept in desiccator for characterization.

3.3 Characterization of CMC and CMC/corn starch blends

3.3.1 Determination of degree of substitution (DS) of CMC

3.3.1.1 Potentiometric back titration

Absolute values of the DS of CMC products were determined by the standard method ASTM D1439. A 4 g of the dry powder sodium carboxymethyl cellulose (NaCMC) was stirred in 75 ml of 95 % ethanol for 5 minutes. Then 5 ml of 2 M nitric acid was added to convert NaCMC to its acid form, H-CMC and the solution was boiled. Next, the solution was removed from the hot plate and further stirred for 10 minutes.

The mixture separated into two parts, which was a solid and liquid phase. The liquid phase was removed, and the solid phase was washed with 20 ml of 80 % ethanol at 60 ºC for 5 times. Then the precipitate was washed with a small quantity of anhydrous methanol and filtered. Lastly, the precipitate was dried at 100 ºC for 3 hours and cool in desiccators for half an hour.

About 0.5 g of dry acid CMC was weighed in 250 ml Erlenmeyer flask and 100 ml of distilled water was added and stirred. Then 25 ml 0.3 M NaOH was added and heated to boil for 15 minutes. After the products dissolved, the mixture was titrated with 0.3 M HCl. Phenolphthalein was added to observe the color change from dark pink to colorless. The titration was repeated twice, and the average volume of HCl used was recorded.

3.3.1.2 Fourier transform infrared spectroscopy (FTIR)

The functional groups of the cellulose, CMC synthesized and CMC/corn starch blends were determined using Perkin Elmer Spectrum RXI Fourier Transform Infrared Spectrophotometer. The samples were dried in an oven at 60 ºC to remove the moisture. About 0.2 mg of sample and 2 mg of potassium bromide were mixed and ground finely before the mixture was compressed to form a transparent pellet. The infrared spectra of these samples were measured in the transmission of a wavelength number range between 4000 and 400 cm^{-1}.

3.3.2 Determination of the viscosity average molecular weight (M_v) of CMC

The viscosity of 0.5 % aqueous solution of CMC synthesized were determined using Ubbelohde type capillary viscometer immersed in a 30.0 ± 0.1 ºC thermostated water bath. Intrinsic viscosities of CMC samples were obtained by dissolving the samples in 0.1 M sodium chloride (NaCl) solution followed by dilution series. The range of concentration investigated was from 0.5 – 0.02778 % (w/v). The flow times, t, were recorded with reproducibility ± 0.2 s. The flow times are used to calculate the viscosity, η of the solution.

3.3.3 Mechanical properties

The mechanical properties to be examined included tensile strength (TS) and elongation at break (EB). The mechanical properties were determined using a Tinius Olsen H10KS-0748 light weight tester with the procedure according to the ASTM D638M (ASTM, 2002). The film samples were cut into 15 x 70 mm rectangular strips to be used for tensile testing. All CMC film strips were preconditioned for 48 hours to 0 % relative humidity (RH) in desiccator using silica gel at room temperature (25 ± 2 ºC) before testing.

The thickness of each strip was measured using a micrometer with sensitivity 1 μm at five randomly selected points, which are the center and four corners. At least five replications of each test sample were run. The initial grip separation and test speed was set at 50 mm and 5 mm min^{-1}, respectively. The tensile strength (MPa) was calculated by dividing the maximum load by cross-sectional area of the film. Whereas, the percent elongation at break was expressed as percentage of change of the original length of a specimen between grips at the break.

3.3.4 Thermal properties

3.3.4.1 Differential scanning calorimetry (DSC) analysis

The melting point of SCB, cellulose, CMC synthesized and CMC/corn starch blends were determined using differential scanning calorimetry (Model DSC 823^{e} Mettler Toledo). The calorimeter was calibrated with indium, which has a melting point of 156.6 ºC and ΔH of 28.5 J g^{-1}. The DSC runs were operated under nitrogen gas atmosphere at a flow rate of 20 mL min^{-1}. The reference was an empty aluminum standard 40 µl pan without pin hole. The film samples, approximately 5 mg was cut into small pieces and were hermetically sealed in aluminum pans. The pans were heated from 30 to 250 ºC at the scanning rate of 10 ºC min^{-1}. The DSC thermograms were evaluated to characterize the onset, peak, end temperatures and the enthalpy changes of the phase transitions.

3.3.4.2 Thermogravimetric analysis (TGA)

The thermal stability of CMC synthesized and CMC/corn starch blends were measured with a Mettler Toledo SDTA 851^{e} TGA instrument. The measurements were recorded in a nitrogen gas atmosphere at a flow rate of 20 ml min^{-1}. The sample mass was about 5 mg and it was heated from 30 to 800 ºC at a heating rate of 20 ºC min^{-1}.

3.3.5 Water vapor permeability (WVP) of CMC and CMC/corn starch blends

Water vapor transmission of CMC and CMC/corn starch blends were measured according to ASTM E96-80 (ASTM 1980), modified by Gontard, et al. (1993). Circular cosmetic glass cups with a diameter of 5 cm and a depth of 3.5 cm were used to determine WVP. Films were cut into discs with a diameter slightly larger than the diameter of the cup. After placing 10 g of dried silica gel in each cup, they were covered with film samples and sealed using vacuum grease and aluminum foil. The zero relative humidity (RH) was maintained using dried silica gel in the cup.

The sealed cups, including their contents were weighed and placed in desiccator containing saturated sodium chloride (NaCl) solution. A small amount of solid NaCl was left in the bottom of the saturated solution to ensure that the solution remains saturated all the times. Saturated NaCl solution in the bottom of the desiccator provides a constant RH of 75 % at 25 ± 1 ºC. The cups were weighed in every half an hour for the first two hours and then at every consecutive hour until eight measurements were made. Changes in the weight of the cell were recorded as a function of time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Percentage yield of cellulose and carboxymethyl cellulose (CMC)

The yield of cellulose extracted from the SCB and also the yield of CMC synthesized was measured based on the dry weight basis. The yield of cellulose, expressed in a percentage, was calculated based on the amount of sugarcane bagasse (SCB) using Eq. (4.1). Moreover, the yield of CMC was determined by dividing the net dry weight of CMC with 5 g of dry cellulose as shown in Eq. (4.2).

$$\text{Yield of cellulose (\%)} = \frac{\text{weight of cellulose obtained (g)}}{\text{weight of bagasses used (g)}} \text{ X } 100\% \qquad (4.1)$$

$$\text{Yield of CMC (\%)} = \frac{\text{weight of dried CMC (g)}}{\text{dry weight of cellulose (g)}} \text{ X } 100\% \qquad (4.2)$$

From the measurement, alkali treatment of SCB followed by nitric acid hydrolyzed process recovered 38.0 % of cellulose. Besides, the recovered cellulose was white to yellow in color as shown in the Figs. 4.1 (a) and (b).

Fig. 4.1: (a) Extracted cellulose (b) Grounded cellulose

Table 4.1 shows the percentage yield of CMC synthesized with various NaOH concentrations. The percentage yield of CMC increased with increasing NaOH concentration due to the reaction of cellulose with monochloroacetic acid (MCA) in an alkaline condition causes the substitution of the hydroxyl group of cellulose molecules with carboxymethyl group and attributed to a higher mass (Selke, Culter and Hernande, 2004). Fig. 4.2 illustrates the correlation between percentage yield and absolute degree of substitution (DS_{abs}) of CMC. The results showed that higher the DS_{abs}, higher the yield of CMC.

Table 4.1: The percentage yield of CMC synthesized with various NaOH concentrations

Type of powder	Mass of cellulose (g)	Mass of CMC (g)	Yield (%)
10% NaOH - CMC	5.0010	5.6700	113.38
15% NaOH - CMC	5.0002	6.3757	127.51
20% NaOH - CMC	5.0013	7.2734	145.43
25% NaOH - CMC	5.0002	7.6088	152.17
30% NaOH - CMC	5.0016	7.1221	142.40

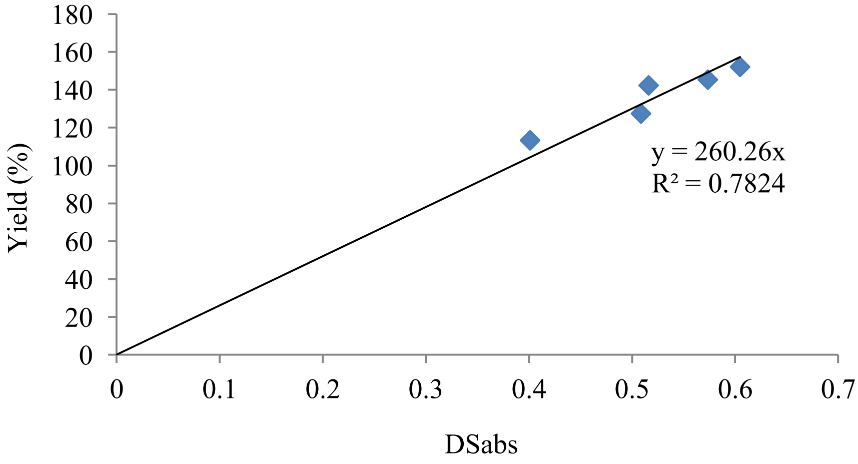

Fig. 4.2: Correlation between percentage yield of synthesized CMC and DS_{abs} of CMC

4.2 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR spectroscopy was widely used in cellulose research as it provides a simple method of obtaining direct information on chemical changes that occur during various chemical treatments (Ristolainen, Alen and Pere, 2002). FTIR spectrum of grounded SCB, Na-cellulose and cellulose were displayed in Figs. 4.3 (a), (b) and (c), respectively. For grounded SCB, the peak centered at 1730 $\mathrm{cm^{-1}}$ is attributed to the C=O stretching vibration of the acetyl and uronic ester group from pectin, hemicellulose or the carboxylic group of ferulic and p-coumaric acids of lignin (Sun, Xu and Baird, 2005).

Similarly, the absorption peak at 1622 $\mathrm{cm^{-1}}$ and faintly at 1509 $\mathrm{cm^{-1}}$ are assigned to aromatic C=C in the plane symmetrical stretching vibration of the aromatic ring present in lignin (Wang, et al., 2009). The peak at 1250 $\mathrm{cm^{-1}}$ present in SCB spectra is associated with the C-O out of plane stretching vibration of the aryl group in lignin (Troedec, et al., 2008). All these peaks are disappearing in the spectra of Na-cellulose and cellulose obtained after alkali and nitric acid treatment respectively. Besides, the presence of 1644 $\mathrm{cm^{-1}}$ peak in the spectra of Na-cellulose and cellulose indicates the OH bending of the adsorbed water (Troedec, et al., 2008).

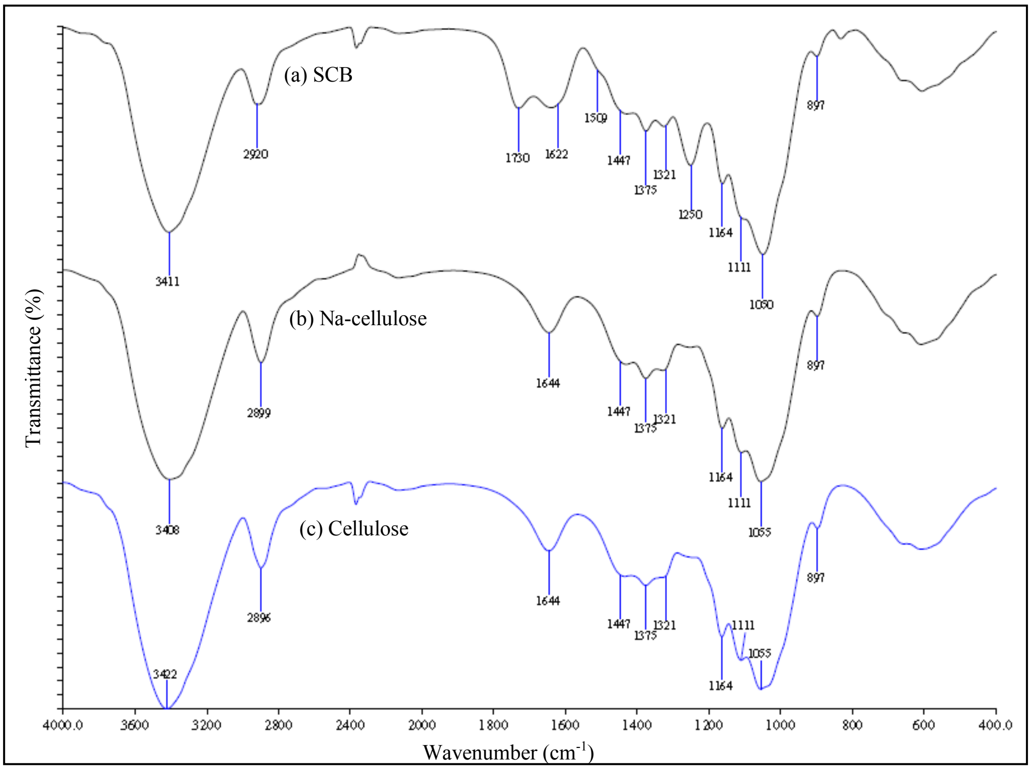

Fig. 4.3: FTIR spectrum of SCB (a), Na-cellulose (b) and Cellulose (c)

Furthermore, the IR spectra of all the CMC samples synthesized (Fig. 4.4) showed the emblematic absorptions of the cellulose backbone as well as the presence of the carboxyl, C=O group at 1606 – 1632 cm^{-1}. According to Pecsok, Shields and McWilliam (1976), carboxyl groups and its salts show two peaks at the wavenumber about 1600 – 1640 cm^{-1} and 1400 – 1450 cm^{-1} which indicates the presence of carboxymethyl substituent. A significant increase in the intensity of C=O band was observed after carboxymethylation as more carboxylic groups was introduced. The bands around 1421 – 1425 cm^{-1} and 1325 cm^{-1} are assigned to CH_2 scissoring and OH bending vibration, respectively.

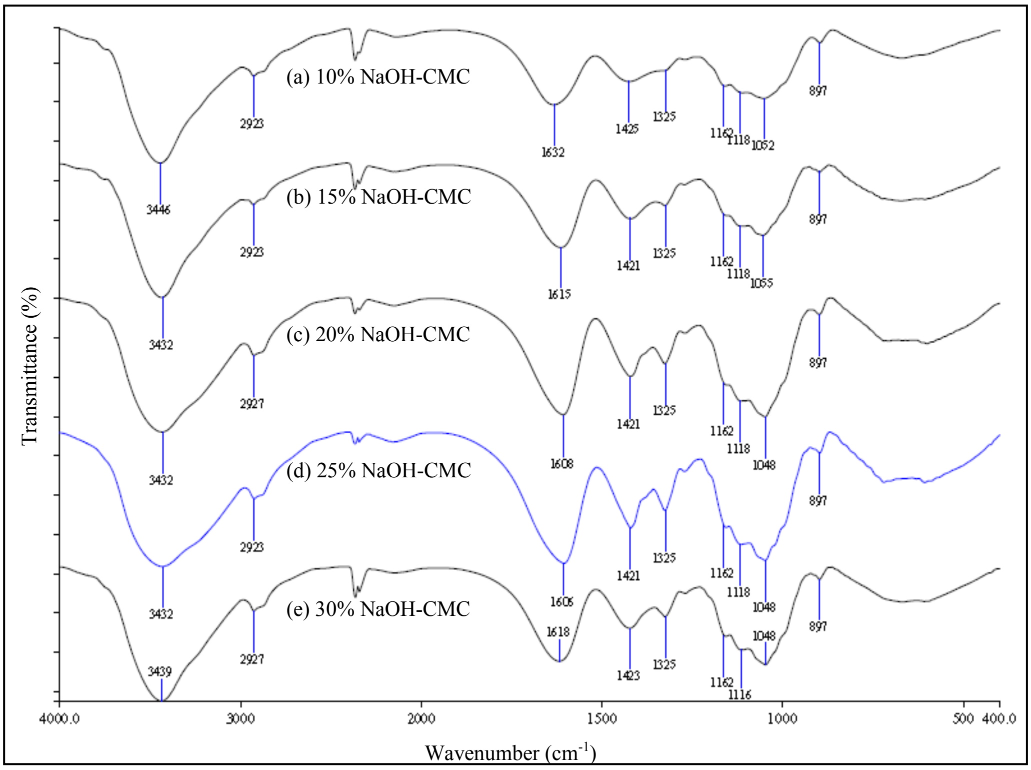

Fig. 4.4: FTIR spectrum of 10 – 30 % NaOH-CMC (a-e)

After adding a range of CMC concentrations to corn starch matrix resulted in similar characteristics in the FTIR spectra as shown in Fig. 4.5. However, blending corn starch with CMC caused a shifting of the band and also increased in the adsorption of COO^- around 1585 – 1589 cm^{-1}. This shows that the asymmetric and symmetric vibrations of C=O and C-O bonds were enhanced due to the disruption of intermolecular hydrogen bonding between carboxylic groups (Tong, Xiao and Lim, 2008). Moreover, the water absorption band of corn starch at 1644 cm^{-1} was disappeared upon the addition of CMC.

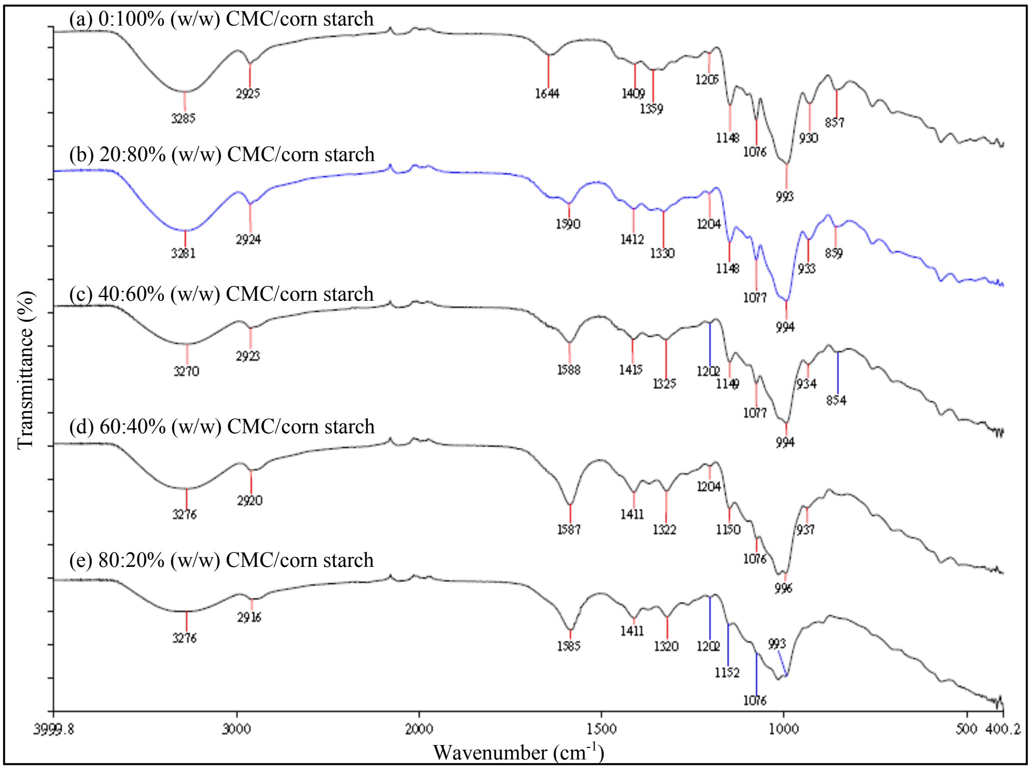

Fig. 4.5: FTIR spectrum of CMC/corn starch blend films

The broad band located within the region of 3500 – 3200 cm^{-1} appeared in all spectra indicates the free OH stretching vibration as well as inter- and intra-molecular hydrogen bonds in cellulose molecules (Pushpamalar, Langford and Lim, 2006). The band at 2896 – 2927 cm^{-1} is attributed to CH stretching vibration (Biswal and Singh, 2004). Besides, the vibration peak at 1375 cm^{-1} was disappeared in all the spectra of synthesized CMC and corn starch blend films. This peak assigned to the CH and C-O bending vibration in the polysaccharide aromatic rings (Nacos, et al., 2006).

The C-C ring breathing band appeared at 1148 – 1164 cm^{-1} and C-O-C glycosidic ether band at 1076 – 1118 cm^{-1} arises from the polysaccharide components was observed in all the spectra (Garside and Wyeth, 2003). In addition, the peak at 993 – 1057 cm^{-1} appears in all the spectra indicates the C-

O-C pyranose ring stretching vibration. Lastly, the wavenumber of about 897 – 937 cm^{-1} associated with the β-(1,4)-glycosidic linkages between the glucose units in cellulose (Viera, et al., 2007).

4.3 Degree of substitution of CMC

The degree of substitution of carboxyl group in CMC can be determined from both infrared radiation (IR) spectra and potentiometric titration. The values obtained from IR spectra are the measurements of relative values of the degree of substitution (DS_{rel}), whereas values obtained from potentiometric titration correspond to the absolute values of the degree of substitution (DS_{abs}) (Rosnah, Gapor and Hassan, 2004). The DS_{abs} and DS_{rel} of CMC powder synthesized with different NaOH concentrations were shown in Table 4.2.

The carboxymethyl content and the DS_{abs} were calculated based on the Eq. (4.3) and (4.4), respectively.

$$\text{Carboxymethyl content (\%CM)} = \frac{[(V_0 - V_\text{n})M \text{ x } 0.059 \text{ x } 100]}{m} \tag{4.3}$$

$$\text{Degree of substitution } (\text{DS}_\text{abs}) = \frac{162 \text{ x \%CM}}{[5900 - (58 \text{ X \%CM})]} \tag{4.4}$$

Where

V_0 = mL of hydrochloric acid used to titrate blank.

V_n = mL of hydrochloric acid used to titrate samples.

M = molar concentration of hydrochloric acid used.

m = sample amount (g)

162 g/mol is the molar mass of the anhydroglucopyranose unit (AGU), and 59 g/mol is the molar mass of $–CH_2COOH$ (Elomaa, et al., 2004).

From the practical point of view, it is preferable to determine the relationship between the absolute values and the relative values of the degree of substitution. Miyamoto, Tsuji and Komai (1996) estimated the DS_{rel} of carboxyl groups in CMC by taking the ratio of absorption spectra as shown in Eq. (4.5):

$$\mathrm{DS}_{\mathrm{rel}} = \frac{A_{1606}}{A_{2927}} - B \tag{4.5}$$

The absorbance at 1606 cm^{-1} is assigned to the stretching vibration of the carboxyl group (COO^-) and 2927 cm^{-1} is assigned to the stretching vibration of methine (C-H). B is a numerical constant correspondent to A_{1606}/ A_{2896} ratio of the cellulose which was found to be zero.

The DS_{abs} for CMC obtained from this work was between 0.4 – 0.6. According to Reuben and Conner (1983), CMC which obtained with alkalization of cellulose followed by carboxymethylation process using MCA was between 0.4 – 1.3. However, DS_{abs} was found to be less than 0.4 in another study (Waring and Parsons, 2001) which is swellable but insoluble. Above this value, CMC is soluble as its hydro-affinity increases with increasing degree of substitution.

The effect of NaOH concentration on DS_{abs} was shown in Fig. 4.6. The DS_{abs} of CMC increased with NaOH concentration and attained a highest DS_{abs} of 0.6 at a NaOH concentration of 25 % (w/v). This is due to the crystalline region in cellulose was changed to amorphous and thus, atom at C2, C3 and C6 of anhydroglucopyranose unit (AGU) could be easily accessed by MCA (Olaru, Stoleriu and Timpu, 1997). However, the DS_{abs} started declining at higher concentration of NaOH (>25 %) which could be due to formation of sodium glycolate as a by-product in the synthesis of CMC and also degradation of cellulose polymer.

Besides, a similar result was also observed in CMC from the banana pseudo stem (Adinugraha, Marseno and Haryadi, 2005), sugar beet pulp (Togrul and Arslan 2003) and sago waste (Pushpamalar, Langford and Lim, 2006). Barai, Singhal and Kulkarni (1997) reported that at high concentration of NaOH, glycolate formation predominated, thus lowering the degree of substitution and CMC content as part of MCA molecule tends to react with NaOH.

Table 4.2: DS_{abs} and DS_{rel} of CMC synthesized with various NaOH concentrations

Type of powder	DS_{abs}	DS_{rel}
10% NaOH - CMC	0.4010	1.0300
15% NaOH - CMC	0.5086	1.0909
20% NaOH - CMC	0.5734	1.2148
25% NaOH - CMC	0.6047	1.2803
30% NaOH - CMC	0.5160	1.1633

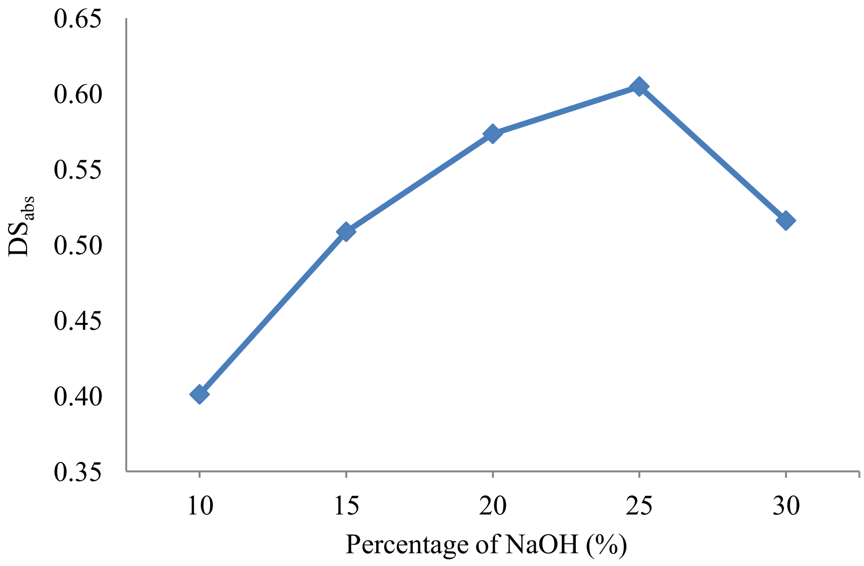

Fig. 4.6: DS_{abs} of CMC powder synthesized with various NaOH concentrations

Fig. 4.7 shows a linear relationship between the absolute and relative value of the degree of substitution. Therefore, this linear correlation yields an equation of $DS_{abs} = 0.4523DS_{rel}$. Pushpamalar, Langford and Lim (2006) also found a similar linear relationship for CMC from sago waste.

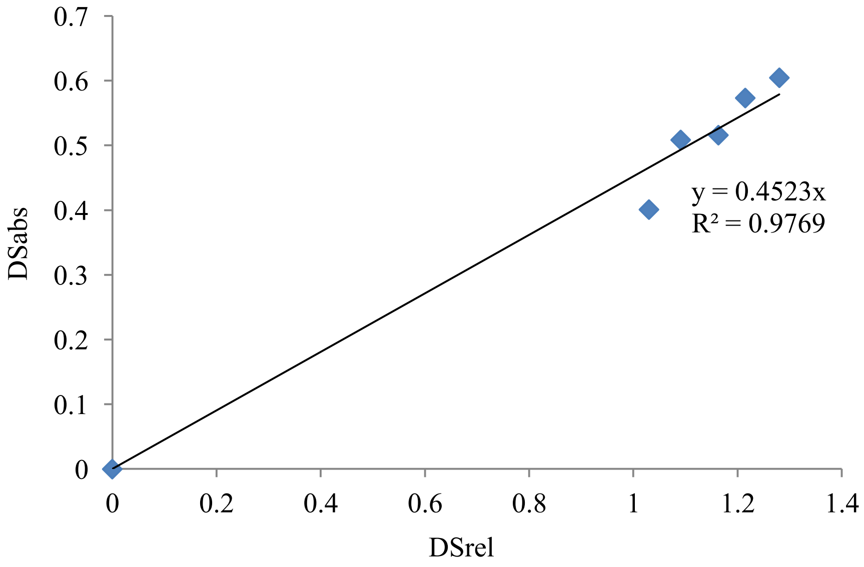

Fig. 4.7: Correlation between absolute and relative degree of substitution for CMC

Table 4.3 shows a comparison between the DS_{abs} value of carboxymethyl cellulose synthesized from SCB cellulose with other sources of cellulose. The DS_{abs} values observed were much different from one another due to different experimental conditions and chemicals used.

Table 4.3: DS value of CMC from different sources of cellulose

Sources of cellulose	DS	Reference
Sugar beet pulp cellulose	0.11 – 0.67	Togrul and Arslan (2003)
Cotton fiber	0.15 – 0.70	Heydarzadeh, et al. (2009)
Water hyacinth	0.24 – 0.73	Barai, et al. (1996)
Banana pseudo stems	0.26 – 0.75	Adinugraha, et al. (2005)
Sago waste	0.33 – 0.82	Pushpamalar, et al. (2006)

4.4 Determination of the viscosity average molecular weight (M_v) of CMC

Viscosity is defined as the resistance against the fluid flow which is affected by the binding between molecules that make up the solution or the solvent-solute relationship (Yasar, Togrul and Arslan, 2007). Intrinsic viscosity was determined by combining the Huggins and Kramer equations.

$$\eta_{\mathrm{red}} = \frac{\eta_{\mathrm{sp}}}{C} = [\eta] + k_{\mathrm{H}}[\eta]^2 C \tag{4.6}$$

$$\eta_{\mathrm{inh}} = \frac{\ln\eta_{\mathrm{r}}}{C} = [\eta] - k_{\mathrm{k}}[\eta]^2 C \tag{4.7}$$

$$b = k_{\mathrm{H}}[\eta]^2 \tag{4.8}$$

where $\eta_r = t/t_0$, $\eta_{sp} = \eta_r - 1$, t and t_0 are the flow time for the CMC solution and pure solvent, respectively. Extrapolation of both reduced $[\eta_{red}]$ and inherent $[\eta_{inh}]$ viscosities to zero concentration provide the intrinsic viscosity, $[\eta]$. The constant b in the Eq. (4.8) represents the gradient of the Huggins curve.

The viscosity average molecular weights (M_v) of CMC synthesized were determined by using the corresponding Mark-Houwink equation (Eq. 4.9). The Mark-Houwink constant, K and α for CMC were 5.37 x 10^{-4} dL g^{-1} and 0.73, respectively (Eremeeva and Bykova, 1998).

$$[\eta] = KM_v^{\alpha} \tag{4.9}$$

The molecular weights of CMC synthesized with different NaOH concentrations were listed in Table 4.4. The intrinsic viscosity of CMC increased with increasing NaOH concentration up to 25 % of NaOH concentration. The intrinsic viscosity of CMC solution increased as the DS_{abs} increased. This is because of greater amount of carboxymethyl groups substituted on the hydroxyl groups of the cellulose polymer (Adinugraha, Marseno and Haryadi, 2005). Moreover, these carboxymethyl groups which act as a hydrophilic group increased the ability of CMC to immobilize more water in the system (Latif, Anwar and Noor, 2007).

However, beyond 25 % of NaOH concentration used in the carboxymethylation synthesis causes the intrinsic viscosity of CMC to decrease. This is due to the effect of polysaccharide degradation at higher concentration of NaOH (Bono, et al., 2009). Furthermore, the intrinsic viscosity of CMC was found to have the same trend as DS_{abs} for the increase in the concentration of NaOH. This was in agreement with the study by Rachtanapun, Lungkamin and Suriyatem (2012).

According to Chee (1990), theoretical considerations of flexible polymers within good solvents will lead to a k_H value in the range of 0.3 – 0.5. Based on the result listed in Table 4.4, the Huggins coefficient, k_H calculated for all the synthesized CMC were within this range therefore, the reliability to the data was confirmed.

The molecular weight of CMC synthesized with various NaOH concentrations were in the range of 30,613 – 87,318 g mol^{-1}. This M_v range was categorized as low viscosity average molecular weight of CMC since low molecular weight CMC has a M_v of about 90,000 g mol^{-1} (Aqualon, 1988). Medium-weight CMC will have a M_v of about 250,000 g mol^{-1} while high molecular weight CMC has a M_w of about 700,000 g mol^{-1}.

Table 4.4: $[\eta]$ and M_v of CMC synthesized with various NaOH concentrations

Type of powder	**$[\eta]$ (dL g^{-1})**	**k_H**	**M_v (g mol^{-1})**
10% NaOH - CMC	1.01085	0.40428	30 613
15% NaOH - CMC	1.74210	0.42937	64 524
20% NaOH - CMC	1.96545	0.44693	76 118
25% NaOH - CMC	2.17260	0.36753	87 318
30% NaOH - CMC	1.91705	0.43653	73 562

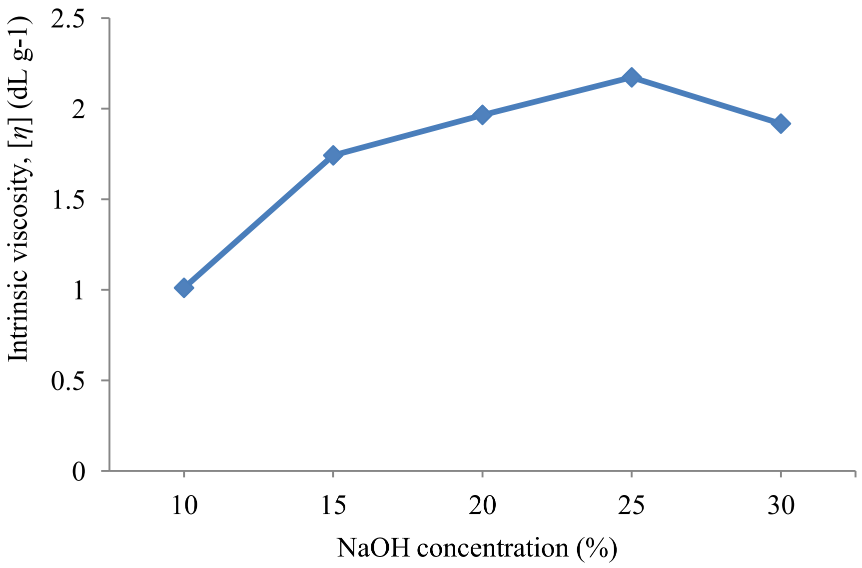

Fig. 4.8: Intrinsic viscosity, [η] of CMC synthesized with various NaOH concentrations

4.5 Mechanical properties

4.5.1 The effect of NaOH concentrations on mechanical properties of CMC films

The effect of various NaOH concentrations on the tensile strength (TS) and the elongation at break (EB) of the CMC films were studied. However, there is no trend for the elongation at break of various CMC synthesized at different NaOH concentrations. These results were similar to the mechanical properties studied for CMC film from the durian rind by Rachtanapun, Luangkamin and Suriyatem (2012).

The tensile strength (TS) of the CMC films increased with increasing concentrations of NaOH up to 20 % (w/v) of NaOH as shown in Fig. 4.9. The increased in TS value was interrelated with an increasing DS_{abs} value due to the substituted carboxymethyl group in AGU, which affects an increase in the ionic character and intermolecular forces between the polymer chains (Adinugraha, Marseno and Haryadi, 2005). Nonetheless, above 20 % of NaOH, the TS started to decrease due to polymer degradation at high NaOH concentration. According to Barai, Singhal and Kulkarni (1997), at high concentration of NaOH, formation of sodium glycolate by-products increases providing a decreasing in CMC content and thus lowering the inter-molecular forces.

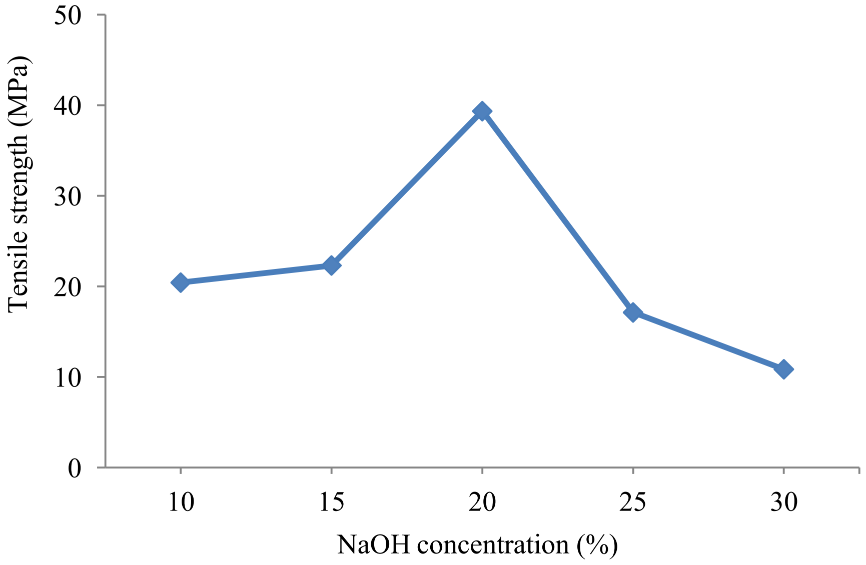

Fig. 4.9: Tensile strength of CMC films synthesized with various NaOH concentrations

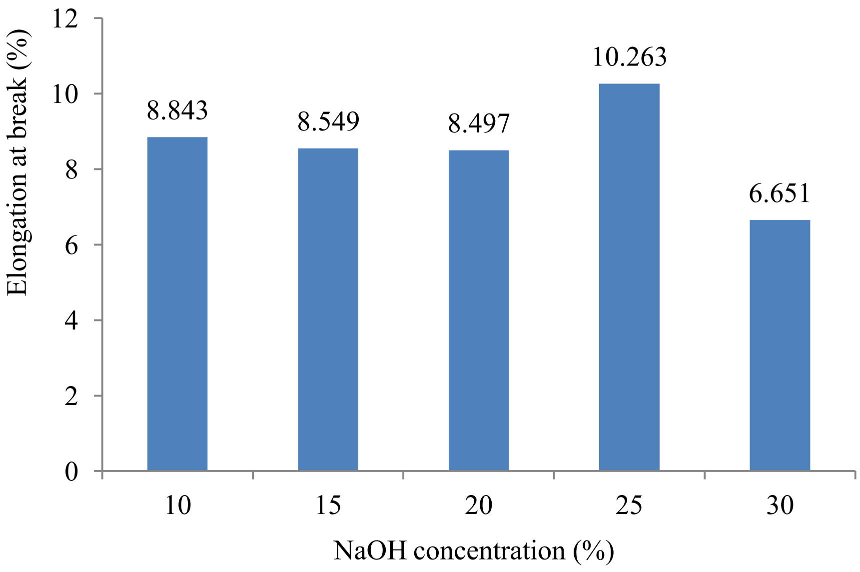

Fig. 4.10: Percent elongation at break of CMC films synthesized with various NaOH concentrations

4.5.2 The effect of CMC content on mechanical properties of CMC/corn starch blend films

The effect of CMC content on tensile strength (TS) and elongation at break (EB) of CMC/corn starch blend films were shown in Figs. 4.11 and 4.12, respectively. Fig. 4.11 shows that the tensile strength of corn starch films was improved with the increase of CMC content. This was due to the formation of inter-molecular interaction between the hydroxyl group of starch and the carboxyl group of CMC (Tongdeesoontorn, Mauer and Rachtanapun, 2011).

According to Ghanbarzadeh, Almasi and Entezami (2010), during the process of blending and drying the films, the hydrogen bond between starch molecules was replaced by the new hydrogen bonds formed between the hydroxyl groups in starch molecules and the carboxyl groups in CMC. Furthermore, other intermolecular interactions between corn starch and CMC including dipole-

dipole and charge effect resulted in a more compact molecular structure which causes an increased in TS (Li, Shoemaker and Zhong, 2008).

These results were consistent with cassava starch film (Tongdeesoontorn, Mauer and Rachtanapun, 2011), pea starch film (Ma, Chang and Yu, 2008) and corn starch films (Ghanbarzadeh, Almasi and Entezami, 2010) in which TS was improved as the concentration of CMC added in starch film formulation increased.

Besides, the flexibility of the films was also affected by the blending composition. As shown in Fig. 4.12, the elongation at break (EB) of the film increased as the CMC content in the corn starch film increased. These results could be related to structural modification of the starch network by water and CMC content, which causes a greater flexibility in polymer structure (Tongdeesoontorn, Mauer and Rachtanapun, 2011).

Aguirre-Cruz, et al. (2005) reported that CMC increased the viscosity of corn starch, which was due to the formation of three-dimensional network through CMC-starch association. Furthermore, Lee, Baek and Lim (2002) also reported the interaction between CMC and potato starch whereby the CMC associates with swollen starch or leached amylase chains. From the result obtained by Rachtanapun (2009) on blended films of CMC from papaya peel and corn starch, the EB increased as the amount of CMC increased in blended films.

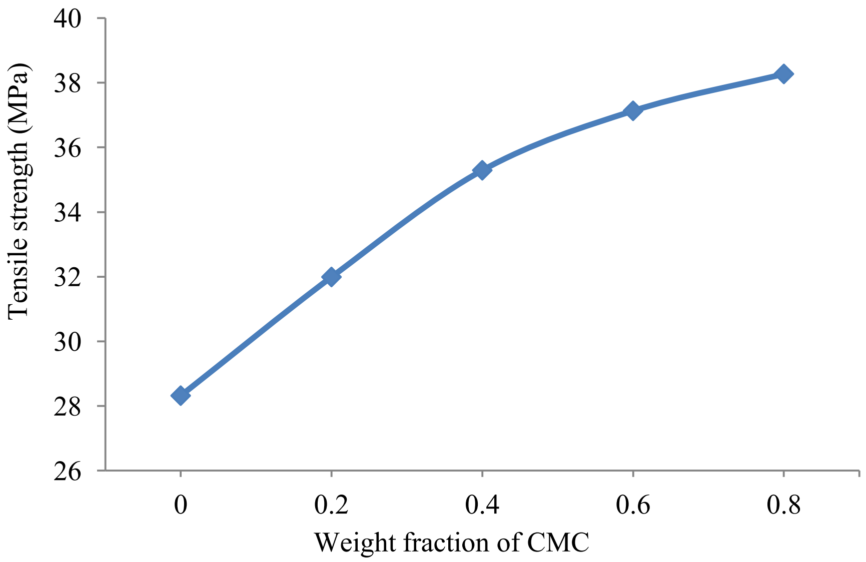

Fig. 4.11: Tensile strength of the corn starch films as function of weight fraction of CMC

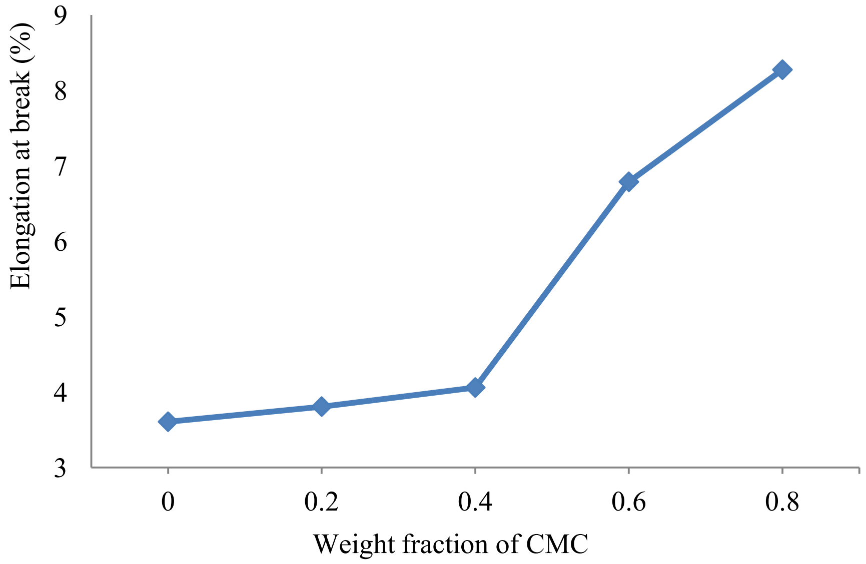

Fig. 4.12: Percent elongation at break of the corn starch films as function of weight fraction of CMC

4.6 Thermal properties

4.6.1 Differential scanning calorimetry (DSC) analysis

The melting point of SCB, Na-cellulose and cellulose were determined according to the temperature program mentioned in section 3.3.4.1. Table 4.5 shows the fusion process of SCB occur over a wide range of temperature, which is from 94.4 ºC to 150.2 ºC. This is because raw SCB contain varying proportions of non-cellulosic constituents such as hemicellulose, lignin and pectin besides cellulose (Mandal and Chakrabarty, 2011).

On the treatment of SCB with NaOH, a large proportion of non-cellulosic materials were lost as reported in FTIR spectrum. In this process, the cellulose crystals rearranged leading to a more compact crystal structure and cause a higher onset of crystalline melting temperature as well as a narrower endotherm width of cellulose (134.53 – 150.50 ºC) (Mandal and Chakrabarty, 2011).

Furthermore, subsequent hydrolysis of cellulose in the nitric acid mediums increased the interlayer spacing of cellulose due to relatively bulky nitrate groups substituted on the hydroxyl groups present in the alkali treated cellulose (Mandal and Chakrabarty, 2011). Therefore, the changes in orientation and simultaneous breakdown in molecular weight leads to an earlier onset value of cellulose as compared to Na-cellulose. The width of the fusion endotherm of cellulose was narrower with respect to Na-cellulose as the proportion of the amorphous region increased due to the effect of acid hydrolysis (Mandal and Chakrabarty, 2011).

Table 4.5: Melting temperature (T_m) and heat of fusion (ΔH_f) of SCB, Na-cellulose and cellulose

Type of compound	**Onset (ºC)**	**Endset (ºC)**	**T_m (ºC)**	**ΔH_f (J g^{-1})**
Grounded SCB	94.39	150.24	119.36	208.03
Na-cellulose	134.53	150.50	136.67	198.64
Cellulose	133.45	136.78	132.76	180.18

4.6.1.1 The effect of CMC content on thermal properties of CMC/corn starch blend films

All the CMC/corn starch blend films exhibited sharp endothermic peaks since corn starch is a semi-crystalline polymer (Ghanbarzadeh, Almasi and Entezami, 2010). Fig. 4.13 shows a decrease in the melting temperature as CMC content increased up to 40 % (w/w) CMC. The CMC content at lower level act as a lubricant agent which decreases the intermolecular interaction and association in corn starch film matrix, thus, decrease the degree of crystallinity and also T_m (Ghanbarzadeh, Almasi and Entezami, 2010).

However, higher than 40 % (w/w) CMC content, the melting temperature increased with CMC content. This indicates that, higher CMC content favor the formation of larger crystal domains and lower the mobility of amylopectin which in turn increased the T_m (Mondragon, Arroyo and Romero-Garcia, 2008). No glass transition was observed in the thermograms of blended films due to low heat capacity change at the glass transition which is difficult to be determined by DSC analysis (Ghanbarzadeh, Almasi and Entezami, 2010).

The total heat of fusion is determined from the area under the endothermic peak (Rachtanapun, Selke and Matuana, 2004). As shown in Table 4.6, the total heat of fusion decreased with increasing CMC content in corn starch films up to 40 % (w/w) CMC. This is due to greater interaction of hydrocolloids and starch retained more water molecules, which cause a higher mobility during heating (Gimeno, Moraru and Kokini, 2004). The increase in mobility of molecules indicates a higher kinetic energy and thus decreases the enthalpy value. However, the enthalpy increases when higher than 40 % (w/w) CMC is added. This is due to the effect of higher crystallization as CMC has a higher degree of crystallinity (Gimeno, Moraru and Kokini, 2004).

Table 4.6: Melting temperature (T_m) and heat of fusion (ΔH_f) of CMC/corn starch blend films

Weight fraction of CMC	**Onset (°C)**	**Endset (°C)**	**T_m (°C)**	**ΔH_f (J g^{-1})**
0.0	130.99	159.86	144.67	289.29
0.2	114.60	158.93	144.26	284.38
0.4	139.66	161.75	142.03	283.82
0.6	142.57	171.46	147.92	319.24
0.8	141.89	168.12	153.29	360.23
1.0	150.11	172.14	152.07	318.13

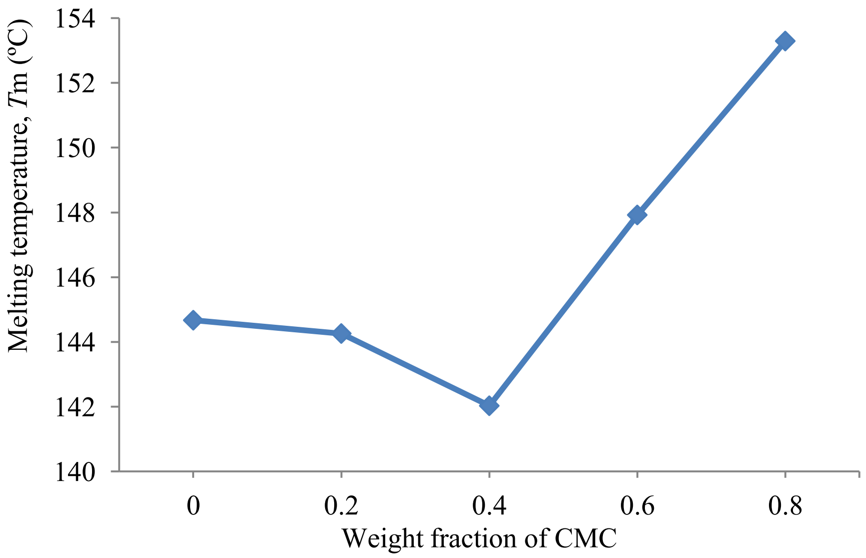

Fig. 4.13: T_m of the corn starch films as function of weight fraction of CMC

4.6.2 Thermogravimetric analysis (TGA)

TGA is a method used to determine the thermal stability of materials through the measure of weight change with temperature. The initial degradation temperature (T_d) of grounded SCB, Na-cellulose and cellulose is lower than 100 ºC attributes for the loss of moisture due to evaporation (Mandal and Chakrabarty, 2011).

Table 4.7 shows an early onset of degradation temperature of SCB due to the presence of non-cellulosic constituents which decomposed at a lower temperature (Mandal and Chakrabarty, 2011). Alkali treated cellulose removed a large amount of non-cellulosic materials provides a denser and compact structure and hence has a higher onset temperature of degradation. This was agreed with Mandal & Chakrabarty (2011) finding.

Acid hydrolyzed cellulose has a lower onset temperature of degradation as compared to the cellulose obtained from alkali treatment, which corresponds to a reduction in molecular weight of cellulose (Mandal & Chakrabarty 2011). Furthermore, introduction of the nitrate group into the crystals of cellulose in the nitric acid hydrolysis process reduces the thermal stability of the cellulose (Kim, Wada and Kuga, 2001).

Alkali treated cellulose has a lesser residue left than SCB due to the loss of low degrading non-cellulosic constituents (Mandal and Chakrabarty, 2011). In case of cellulose, an increase in the amount of residue remained as the nitrated amorphous and crystalline region of cellulose is intrinsically flame resistant (Maren and William, 2004).

Table 4.7: Degradation temperature (T_d) of SCB, Na-cellulose and cellulose

Type of compound	**Left limit (ºC)**	**Right limit (ºC)**	**T_d (ºC)**	**Residue (%)**
Grounded SCB	201.57	459.07	377.94	21.9275
Na-cellulose	205.56	461.18	365.12	16.5319
Cellulose	201.80	459.17	372.78	23.8436

4.6.2.1 The effect of NaOH concentrations on thermal degradation of CMC

The conversion of cellulose to CMC through chemical reaction affects both the molecular structure and bonding energy of the material result in different thermal behavior of CMC (Rosnah, et al., 2006). The derivatograms of synthesized CMC with various NaOH shows the decomposition in a two-stage process as shown in Fig. 4.14. The initial weight loss is attributed to the presence of a small amount of moisture whereas the second weight loss is due to the loss of carbon dioxide from carboxymethyl groups of CMC (Su, Huang and Li, 2010).

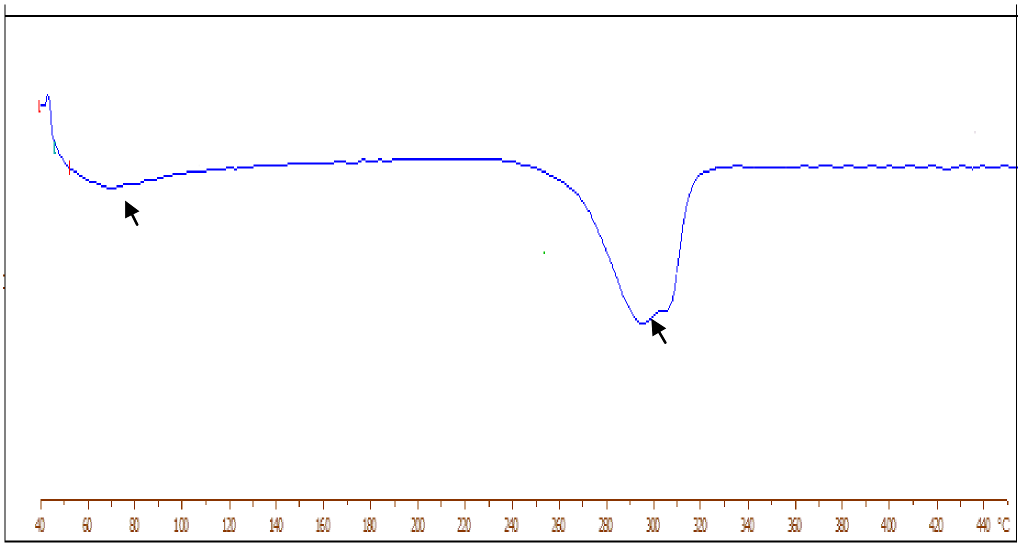

Fig. 4.14: Derivatogram of 20 % NaOH-CMC

The degradation temperature of CMC decreased as the level of NaOH concentration increased. This is caused by the interference with crystalinity as the presence of random irregularities produced by the relatively bulky side groups of carboxymethyl substituted on the cellulose backbone (Selke, Culter and Hernandez, 2004). The T_d was interrelated with DS_{abs}, as higher the DS_{abs} of CMC lower the degradation temperature of CMC.

Furthermore, migration of Na^+ into the cellulose lattice planes disrupts the hydrogen bonded crystalline region and thus weakens the energy bonding of the cellulose (Rosnah, et al., 2006). Replacing of the hydroxyl group of cellulose by ONa enlarge the molecule which then increased its reactivity toward alkylating agents to form CMC. Therefore, increased with the concentration of NaOH in the synthesis of CMC, increased the disruption of the cellulose crystalline region and affects the energy bonding of its derivatives, which results in less stable CMC to heat (Rosnah, et al., 2006).

Table 4.8: Degradation temperature (T_d) of CMC synthesized with various NaOH concentrations

Type of compound	Left limit (ºC)	Right limit (ºC)	T_d (ºC)	Residue (%)
10% NaOH - CMC	203.52	447.59	331.86	39.5264
15% NaOH - CMC	201.10	444.09	311.21	42.2220
20% NaOH - CMC	201.06	444.72	298.37	53.6843
25% NaOH - CMC	200.97	443.64	296.78	65.6591
30% NaOH - CMC	204.13	446.89	301.32	56.8360

4.6.2.2 The effect of CMC content on thermal degradation of CMC/corn starch blend films

All the blended films showed a small mass lost for first degradation (< 100 ºC) and more significant mass loss for second degradation (200-400 ºC). The first step degradation was due to evaporation of bound water while the second decomposition step was attributed to the degradation of side chains and the loss of carbon dioxide from CMC (El-Sayed, et al., 2011). The addition of CMC to corn starch caused a decrease in degradation temperature, which was attributed to the poor stability of CMC. This is in good agreement with the results reported by Ma, Chang and Yu (2008) for pea starch/CMC blends.

Table 4.9: Degradation temperature (T_d) of CMC/corn starch blend films

Weight fraction of CMC	Left limit (°C)	Right limit (°C)	T_d (°C)	Residue (%)
0.0	224.27	377.27	326.94	26.9097
0.2	223.03	376.57	303.57	41.3781
0.4	223.86	377.27	301.80	42.9301
0.6	224.38	377.74	302.47	44.1798
0.8	223.62	376.80	302.99	45.2466
1.0	201.06	444.72	298.37	53.6843

4.7 Water vapor permeability (WVP)

4.7.1 The effect of NaOH concentrations on WVP of CMC films

The relationship between changes in concentration of NaOH and alkalization on the water vapor permeability of CMC films was investigated. WVP is a property that directly associated to the hydrophilic nature of the film whereby more hydrophilic films will have greater WVP values, which mean lower water vapor barrier.

The WVTR (g h^{-1} m^{-2}) was defined as the slope of weight gain and time divided by the transfer area as shown in Eq. (4.10). After the permeation tests, film thickness was measured and WVP (g Pa^{-1} h^{-1} m^{-1}) was calculated from Eq. (4.11).

$$\mathrm{WVTR} = \frac{\text{weight gained (g)}}{\text{time (hour) x area of film sample } (\mathrm{m}^2)} \tag{4.10}$$

$$\mathrm{WVP} = \frac{\mathrm{WVTR\ x}\ L}{\Delta p} \tag{4.11}$$

where L is the mean thickness of the film (m), and Δp is the partial water vapor pressure difference (Pa) between two sides of the film specimen.

The partial water vapor pressures difference (Δp) across the film specimen was calculated by using the Eq. (4.12):

$$\Delta p = Ps\,\frac{(\mathrm{RH}_1 - \mathrm{RH}_2)}{100} \tag{4.12}$$

where Ps is the saturated water vapor pressure at 25 ± 1 ºC, RH_1 is the relative humidity in the desiccators, and RH_2 is the relative humidity in the permeation cell.

The WVP of the CMC films increased when NaOH concentration increased as shown in Fig. 4.15. This is due to the increase in the polarity of the cellulose when being converted to CMC (Rachtanapun and Rattanapanone, 2011). The film synthesized with 25 % NaOH concentration gave the highest WVP value. Furthermore, the DS_{abs} and WVP increased with NaOH concentration in carboxymethylation synthesis up to 25 % NaOH concentration. This is because of the hydrophilic nature of the CMC films increases with increasing carboxymethyl groups substituted on cellulose structure (Rachtanapun, Luangkamin and Suriyatem, 2012). However, beyond 25 % NaOH concentration, the WVP of CMC film decreases as the degree of substitution decreased and thus the film became a better barrier to water vapor.

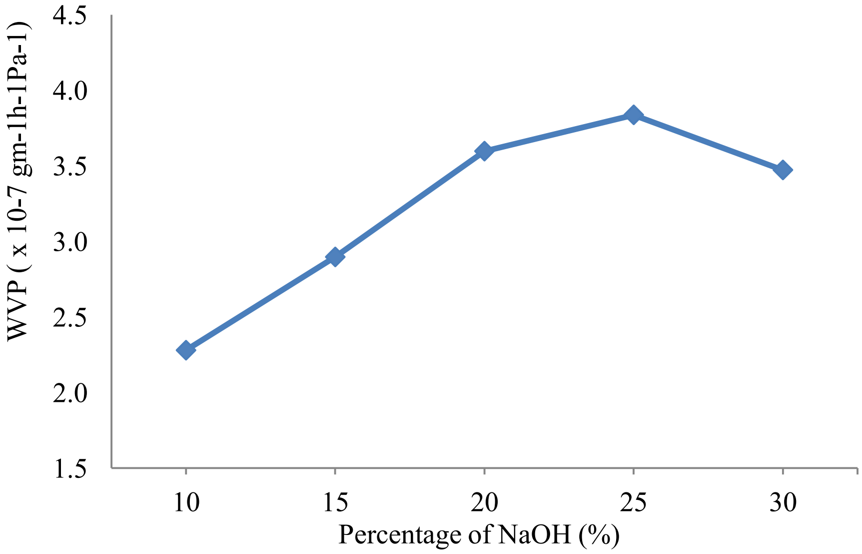

Fig. 4.15: WVP of CMC films synthesized with various NaOH concentrations

4.7.2 The effect of CMC content on WVP of CMC/corn starch blend films

The effect of CMC content on the WVP of CMC/corn starch blend films was investigated. Film for food packaging is often required to have at least moisture transfer between the food and the surrounding atmosphere, thus WVP should be as low as possible (Ma, Chang and Yu, 2008). The WVP for the corn starch film was the highest with a value of 3.6826 x 10^{-7} g Pa^{-1} h^{-1} m^{-1}, thus signify that water vapor easily permeated the corn starch film.

The WVP of the CMC/corn starch blend films decreased with increasing of CMC content up to 40 % (w/w) of CMC content. This is because CMC acts as filler at low content, which disperse well in the corn starch matrix and blocked the water vapor transmission. According to Ma, Chang & Yu (2008), water resistance of CMC was better than starch biopolymer, which could be due to the highly crystalline and hydrophobic character of cellulose fibers in comparison to starch polymer.

The addition of higher CMC content could introduce an intricate path for water molecules to pass through (Kristo and Biliaderis, 2007). Conversely, when higher amount of CMC blended with corn starch, WVP increased. This is because excessive filler easily congregates which in turn decreased the effectiveness of CMC contents and eases the water vapor permeation (Ghanbarzadeh, Almasi and Entezami, 2010; Ma, Chang and Yu, 2008).

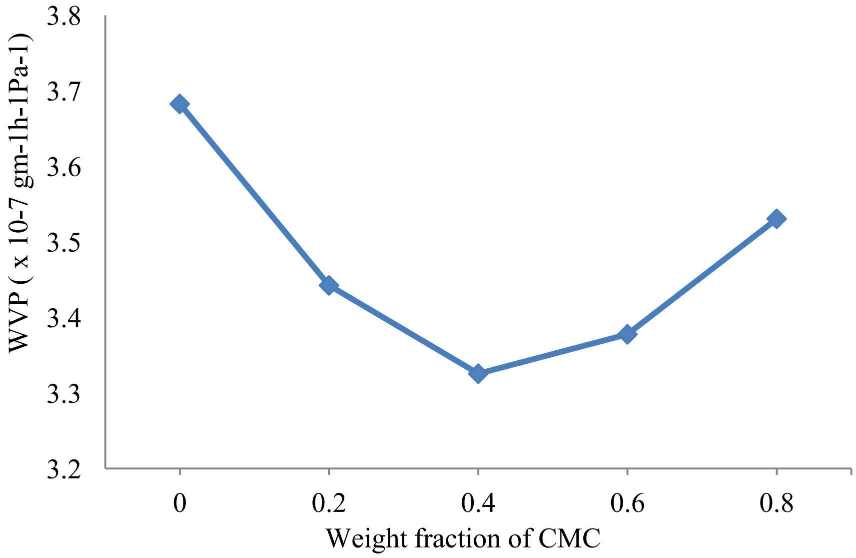

Fig. 4.16: WVP of the corn starch films as function of weight fraction of CMC

CHAPTER 5

CONCLUSIONS

Cellulose was successfully extracted from sugarcane bagasse through alkali treatment followed by the nitric acid hydrolyzed process. The two-step pretreatment recovered 38 % of cellulose. The cellulose was then converted to carboxymethyl cellulose (CMC) by mercization with various sodium hydroxide (NaOH) concentrations and subsequently etherified with monochloroacetic acid. The infrared radiation (IR) spectrum confirmed the change of cellulose to carboxymethyl cellulose by the presence of carboxyl, C=O group at wavenumber of 1606 – 1632 cm^{-1}.

The degree of substitution of carboxyl group in CMC can be determined from both infrared radiation spectra and potentiometric titration. The values obtained from infrared radiation spectra are the measurements of relative values of the degree of substitution (DS_{rel}), whereas values obtained from potentiometric titration correspond to the absolute values of the degree of substitution (DS_{abs}).

The DS_{abs} of CMC varied over the range from 0.4 to 0.6 depending on the amount of NaOH used in synthesis. The DS_{abs} increased with increasing NaOH concentration up to 25 % and then decreased at higher NaOH concentration. This is due to the crystalline region in cellulose become more amorphous with increasing NaOH concentration and thus enhanced substitution to occur. However, higher NaOH concentration will cause the degradation of cellulose polymer.

The molecular weight of CMC synthesized was determined using viscometry method. The viscosity average molecular weight (M_v) of CMC synthesized with various NaOH concentrations were in the range of 30,613 – 87,318 g mol^{-1}. It was categorized as low molecular weight since CMC with M_v of about 90,000 g mol^{-1} is considered a low molecular weight.

The tensile strength (TS) of the CMC films increased with increasing concentrations of NaOH up to 20 % (w/v) of NaOH and decreased at higher NaOH concentration. This is due to the increase in ionic character and intermolecular forces between the polymers chain as the substituted carboxymethyl group in anhydroglucopyranose unit increased. Nonetheless, above 20 % of NaOH concentration, the TS started to decrease due to polymer degradation. The tensile strength of corn starch films was improved with the increase of CMC content, which was due to the formation of inter-molecular interaction between the hydroxyl group of starch and the carboxyl group of CMC.

The various NaOH concentrations have no effect on the elongation at break (EB) of the CMC films. However, EB of the corn starch film increased as the CMC content increased. These results were due to the structural modification of starch network by water and CMC content, which causes a greater flexibility in polymer structure.

The melting temperature decreased as CMC content increased up to 40 % (w/w) of CMC. At lower level, CMC acts as a lubricant agent which decreases the intermolecular interaction and association in corn starch film matrix, thus, decrease the degree of crystallinity and also T_m. Whereas, higher CMC content favor the formation of larger crystal domains and lower the mobility of amylopectin which in turn increased the T_m.

The degradation temperature of CMC decreased as the level of NaOH concentration increased. This is caused by the interference with crystallinity as the presence of random irregularities produced by the relatively bulky side groups of carboxymethyl substituted on the cellulose backbone. The addition of CMC to corn starch caused a decrease in degradation temperature, which was attributed to the poor stability of CMC.

The water vapor permeability (WVP) of the CMC films increased when NaOH concentration increased up to 25 %. This is because of the hydrophilic nature of the CMC films increases with increasing carboxymethyl groups substituted on cellulose structure. The WVP of the CMC/corn starch blend films decreased with increasing of CMC content up to 40 % (w/w) of CMC content. This is because CMC acts as filler at low content, which disperse well in the corn starch matrix and blocked the water vapor transmission. However, excessive filler easily congregates which in turn decreased the effectiveness of CMC contents and eases the water vapor permeation.

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APPENDIX A

Table A.1: Percentage yield of cellulose

Sample	Weight of grounded SCB (g)	Weight of cellulose extracted (g)	Percentage yield (%)
1	25.0398	9.5109	37.98
2	25.0393	9.2651	37.00
3	25.0725	9.7765	38.99
4	25.0612	9.5984	38.30
5	25.0272	9.2551	36.98
6	25.0302	9.5686	38.23
7	25.0669	9.3651	37.36
8	25.0532	9.5933	38.29
9	25.0898	9.6301	38.38
10	25.0784	9.8302	39.20

Example of calculation for sample 1,

$$\text{Yield of cellulose (\%)} = \frac{\text{weight of cellulose obtained (g)}}{\text{weight of bagasse used (g)}} \text{ X } 100\%$$

$$= \frac{9.5109 \text{ g}}{25.0398 \text{ g}} \text{ X } 100\% = 37.98\%$$

A.2 Degree of substitution of CMC

Table A.2: Volume of HCl used in potentiometric back titration

% NaOH-CMC	Blank				Sample			
	Weight, m_0 (g)	V_i (cm^3)	V_f (cm^3)	V_0 (cm^3)	Weight, m (g)	V_i (cm^3)	V_f (cm^3)	V_n (cm^3)
10%	0.5006	0.05	25.05	25.00	0.5013	0.30	21.60	21.30
	0.5003	0.00	25.00	25.00	0.5035	0.25	21.70	21.45
15%	0.5034	0.15	25.05	24.90	0.5023	0.00	20.45	20.45
	0.5021	0.10	24.95	24.85	0.5030	0.00	20.40	20.40
20%	0.5028	0.20	25.30	25.10	0.5025	0.05	20.20	20.15
	0.5045	0.00	25.00	25.00	0.5038	0.10	20.20	20.10
25%	0.5032	0.00	25.00	25.00	0.5019	0.00	19.80	19.80
	0.5008	0.00	24.95	24.95	0.5003	0.15	20.05	19.90
30%	0.5009	0.05	25.20	25.15	0.5015	0.05	20.65	20.60
	0.5028	0.05	25.10	25.05	0.5028	0.20	20.80	20.60

Example of calculation for 10% NaOH - CMC,

$$V_0 = \frac{(25 + 25)\mathrm{cm}^3}{2} = 25\ \mathrm{cm}^3$$

$$V_\mathrm{n} = \frac{(21.3 + 21.45)\mathrm{cm}^3}{2} = 21.375\ \mathrm{cm}^3$$

$$m = \frac{(0.5013 + 0.5035)\mathrm{g}}{2} = 0.5024\ \mathrm{g}$$

$$M = 0.3\ \mathrm{mol\ dm}^{-3}$$

$$\text{Carboxymethyl content (\%CM)} = \frac{[(V_0 - V_\mathrm{n})M \text{ X } 0.059 \text{ X } 100]}{m}$$

$$= \frac{[(25 - 21.375)0.3 \text{ X } 0.059 \text{ X } 100]}{0.5024}$$

$$= 12.7712$$

$$\text{Degree of substitution } (\mathrm{DS_{abs}}) = \frac{162 \text{ X } \%\mathrm{CM}}{[5900 - (58 \text{ X } \%\mathrm{CM})]}$$

$$= \frac{162 \text{ X } 12.7712}{[5900 - (58 \text{ X } 12.7712)]}$$

$$= 0.4010$$

Table A.3: FTIR absorbance value of synthesized CMC

Type of powder	Absorbance at 1606 cm^{-1}	Absorbance at 2927 cm^{-1}
10% NaOH - CMC	0.28400	0.27572
15% NaOH - CMC	0.30980	0.28400
20% NaOH - CMC	0.38722	0.31876
25% NaOH - CMC	0.55284	0.43180
30% NaOH - CMC	0.28400	0.24413

Example of calculation for 10% NaOH - CMC,

$B = 0$

$$\text{Degree of substitution, } \mathrm{DS_{rel}} = \frac{A_{1606}}{A_{2927}} - B$$

$$= \frac{0.28400}{0.27572} - 0 = 1.03$$

A.3 Intrinsic viscosity and molecular weight of CMC

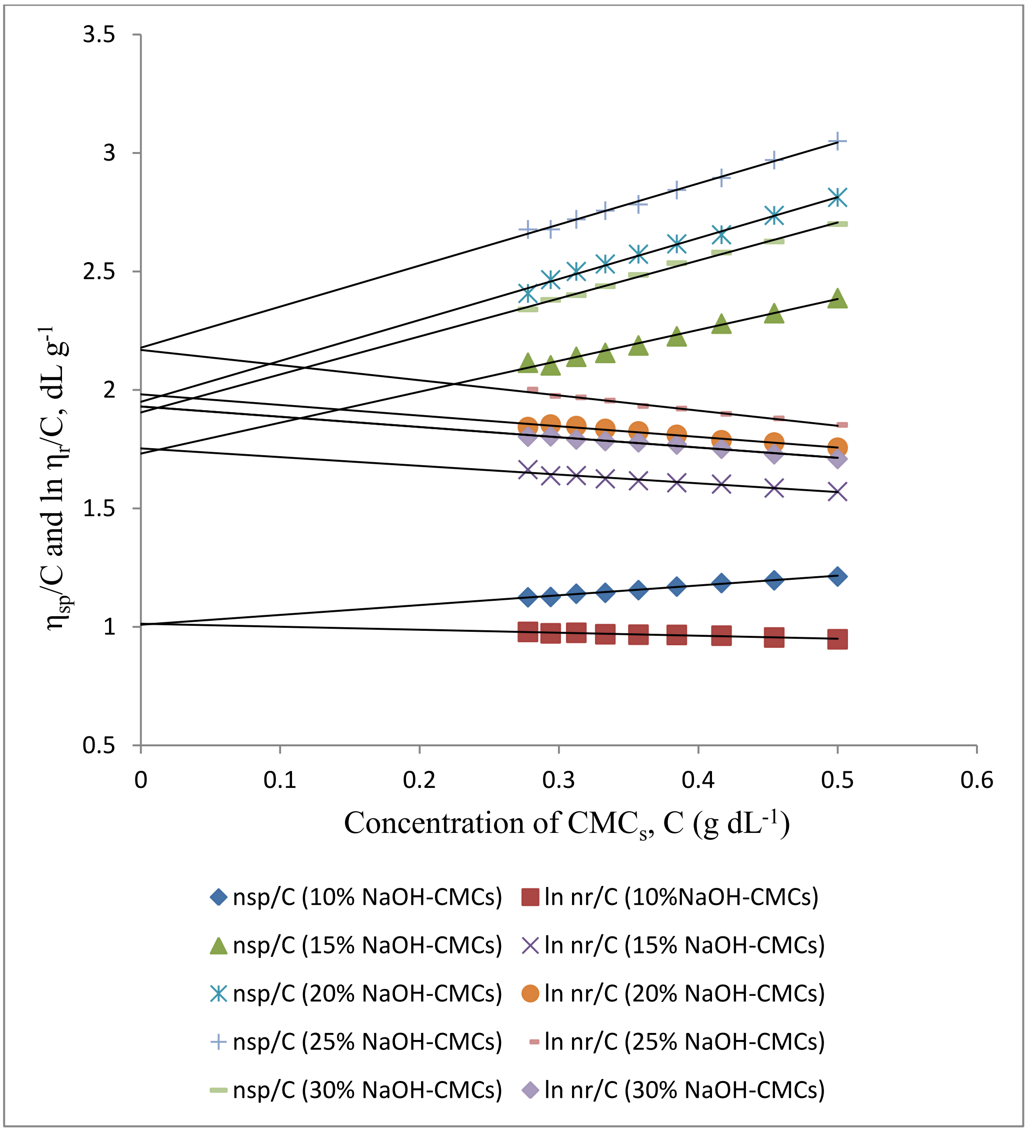

Fig. A.1: Determination of intrinsic viscosity of CMC synthesized with various NaOH concentrations using Huggins and Kramer equations

Example of calculation for 10% NaOH - CMC,

t_0 = flow time of 0.1M NaCl solvent = 160 s

t = flow time of CMC solution = 257 s

C = concentration of CMC solution = 0.5 g dL^{-1}

$$\text{Relative viscosity}, \eta_{\mathrm{r}} = \frac{t}{t_0} = \frac{257\ \mathrm{s}}{160\ \mathrm{s}} = 1.60625$$

$$\text{Specific viscosity}, \eta_{\mathrm{sp}} = \frac{t - t_0}{t_0} = \eta_{\mathrm{r}} - 1 = 1.60625 - 1 = 0.60625$$

$$\text{Reduced viscosity}, \eta_{\mathrm{red}} = \frac{\eta_{\mathrm{sp}}}{C} = \frac{0.60625}{0.5\ \mathrm{g\ dL^{-1}}} = 1.2125$$

$$\text{Inherent viscosity}, \eta_{\mathrm{inh}} = \frac{\ln \eta_{\mathrm{r}}}{C} = \frac{\ln 1.60625}{0.5\ \mathrm{g\ dL^{-1}}} = 0.947805$$

$$\text{Intrinsic viscosity}, [\eta] = KM_{\mathrm{v}}^{\alpha}$$

$$\text{Mark} - \text{Houwink constant}, K = 5.37 \text{ x } 10^{-4}\ \mathrm{dL\ g^{-1}}$$

$$\text{Mark} - \text{Houwink constant}, \alpha = 0.73$$

$$[\eta] \text{of } 10\% \text{ NaOH} - \text{CMC} = 1.01085\ \mathrm{dL\ g^{-1}}$$

$$\log[\eta] = \log K + \alpha \log M_{\mathrm{v}}$$

$$\log M_{\mathrm{v}} = \frac{\log[\eta] - \log K}{\alpha}$$

$$\log M_{\mathrm{v}} = \frac{\log(1.01085) - \log(5.37 \text{ x } 10^{-4})}{0.73}$$

$$\log M_{\mathrm{v}} = 4.4859$$

$$M_{\mathrm{v}} = 30{,}613\ \mathrm{g\ mol^{-1}}$$

A.4 Water vapor permeability

Example of calculation for 10% NaOH – CMC,

$$\text{WVP} = \frac{Ge}{tAS\,(\text{R}_1 - \text{R}_2)}$$

G = Weight gained (g)

e = film thickness (m)

t = time tested (h)

A = area of the test specimen sealed on the opening dish (m^2)

S = vapour saturation pressure (Pa)

R_1 = relative humidity in the desiccators = 0.7529

R_2 = relative humidity in the permeation cell = 0

G/t = slope of the graph = 0.0307 g h^{-1}

$A = \pi r^2 = \pi\ (0.0215\ \text{m})^2 = 1.4522 \times 10^{-3}\ \text{m}^2$

S = [(23.8 mmHg / 760 mmHg) x 101325 Pa x 0.7529]

= 2389 Pa

$e = 1.94 \times 10^{-5}$ m

$$\text{WVP} = \frac{(0.0307\ \text{g h}^{-1})(1.94 \text{ x } 10^{-5}\ \text{m})}{(1.4522 \text{ x } 10^{-3}\ \text{m}^2)(2389\ \text{Pa})(0.7529 - 0\ )}$$

$$\text{WVP} = 2.280 \text{ x } 10^{-7} \text{g Pa}^{-1}\text{h}^{-1}\text{m}^{-1}$$

Table A.4: Assignment of main absorption peaks of FTIR spectra.

Starting materials			Synthesized CMC					CMC_s/ corn starch blends					Assignment
SCB	Na-Cellulose	Cellulose	10% NaOH	15% NaOH	20% NaOH	25% NaOH	30% NaOH	0:100 %	20:80 %	40:60 %	60:40 %	80:20 %	
3411	3408	3422	3446	3432	3432	3432	3439	3285	3281	3270	3276	3276	OH stretching
2920	2899	2896	2923	2923	2927	2923	2927	2925	2924	2923	2920	2916	CH stretching
1730	-	-	-	-	-	-	-	-	-	-	-	-	C=O stretching
1622 & 1509	-	-	-	-	-	-	-	-	-	-	-	-	C=C stretching
-	1644	1644	-	-	-	-	-	1644	-	-	-	-	H_2O bending
-	-	-	1632	1615	1608	1606	1618	-	1589	1588	1587	1585	COO^- asymmetric
1447	1447	1447	1425	1421	1421	1421	1423	1409	1412	1415	1411	1411	CH_2 bending
1375	1375	1375	-	-	-	-	-	-	-	-	-	-	CH & C-O bonds
1321	1321	1321	1325	1325	1325	1325	1325	1359	1330	1325	1322	1320	OH in plane bending
1250	-	-	-	-	-	-	-	1205	1204	1202	1204	1202	C-O out of plane
1164	1164	1164	1162	1162	1162	1162	1162	1148	1148	1149	1150	1152	C-C ring breath
1111	1111	1111	1118	1118	1118	1118	1116	1076	1077	1077	1076	1076	C-O-C symmetry
1050	1055	1055	1052	1055	1048	1048	1048	993	994	994	996	993	C-O-C asymmetry
897	897	897	897	897	897	897	897	930	933	934	937	-	β-glycoside linkage

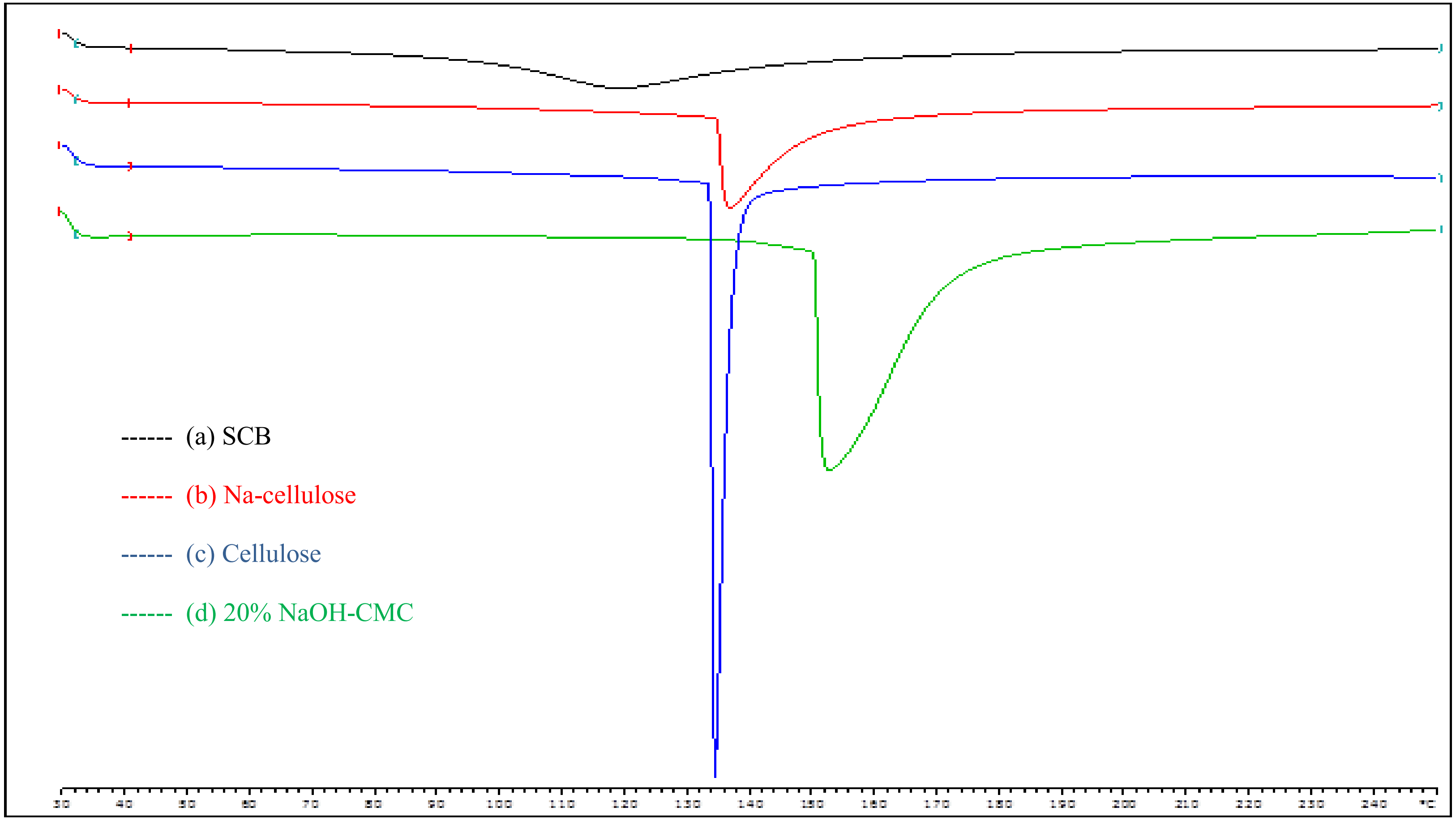

Fig. B.1: DSC thermogram of SCB (a), Na-cellulose (b), Cellulose (c) and 20% NaOH-CMC

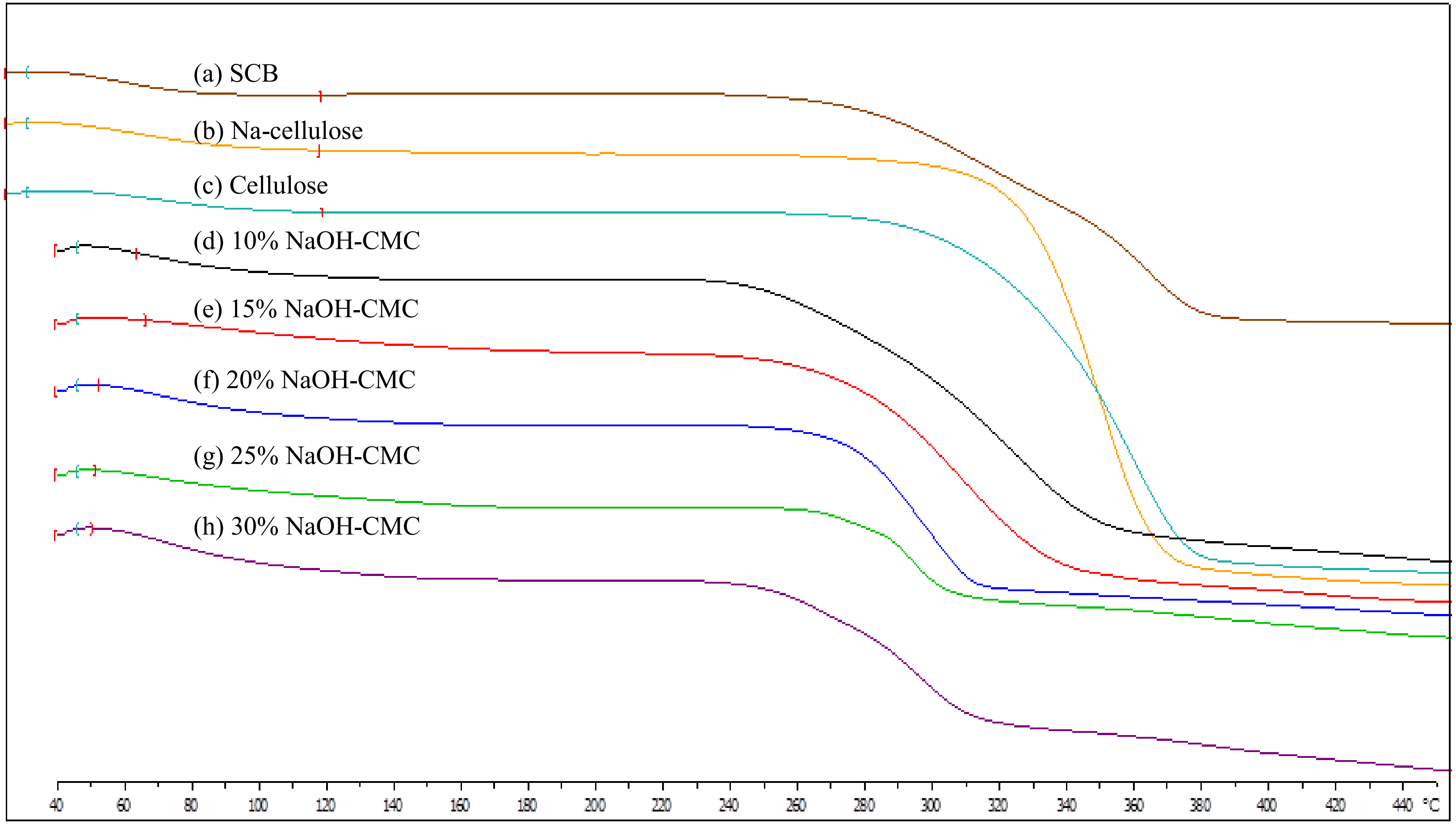

Fig. B.2: TGA thermogram of SCB (a), Na-cellulose (b), Cellulose (c) and 10-30% NaOH-CMC (d-h)

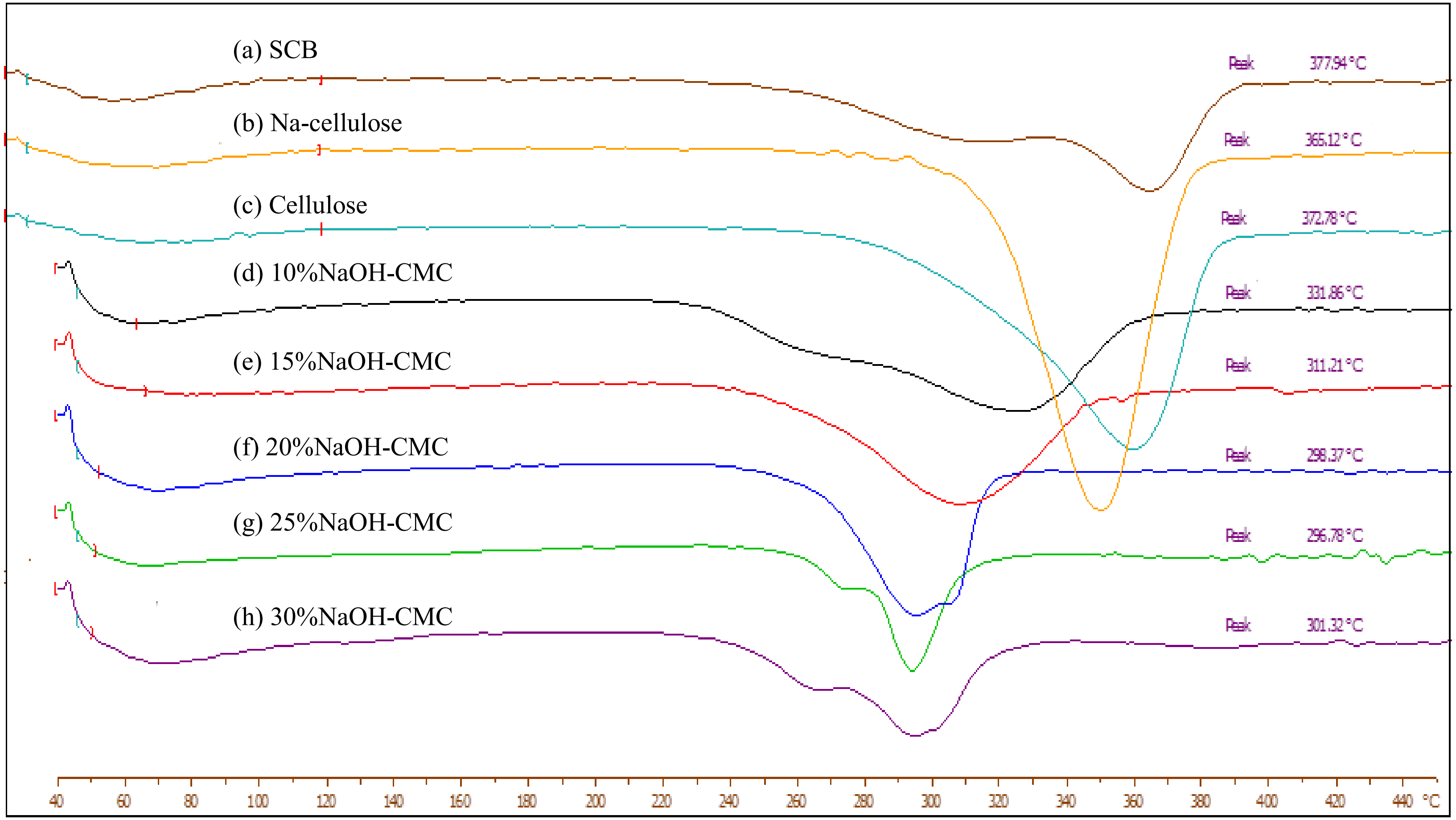

Fig. B.3: TGA derivatogram of SCB (a), Na-cellulose (b), Cellulose (c) and 10-30% NaOH-CMC (d-h)

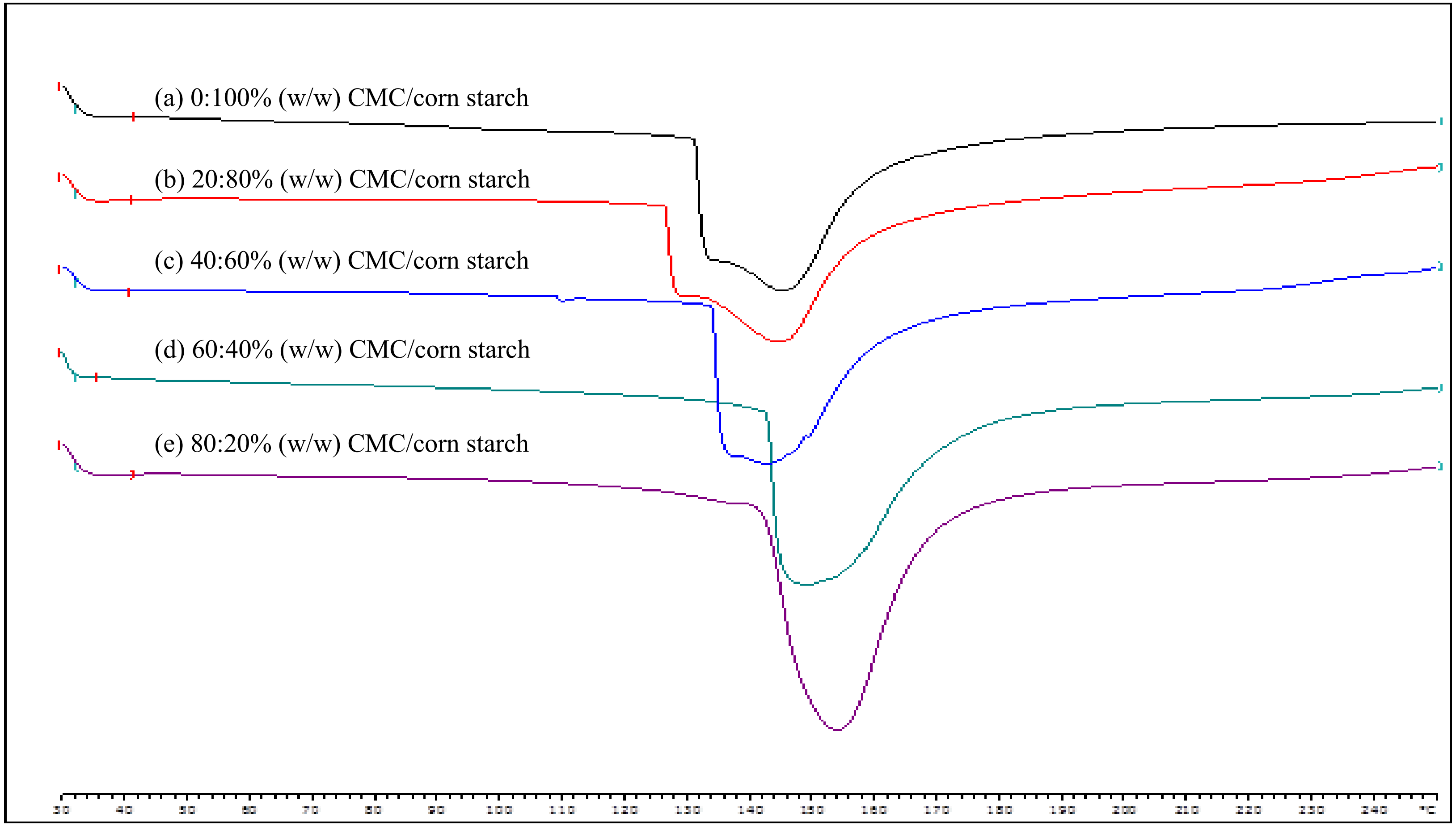

Fig. C.1: DSC thermogram of CMC/corn starch blend films

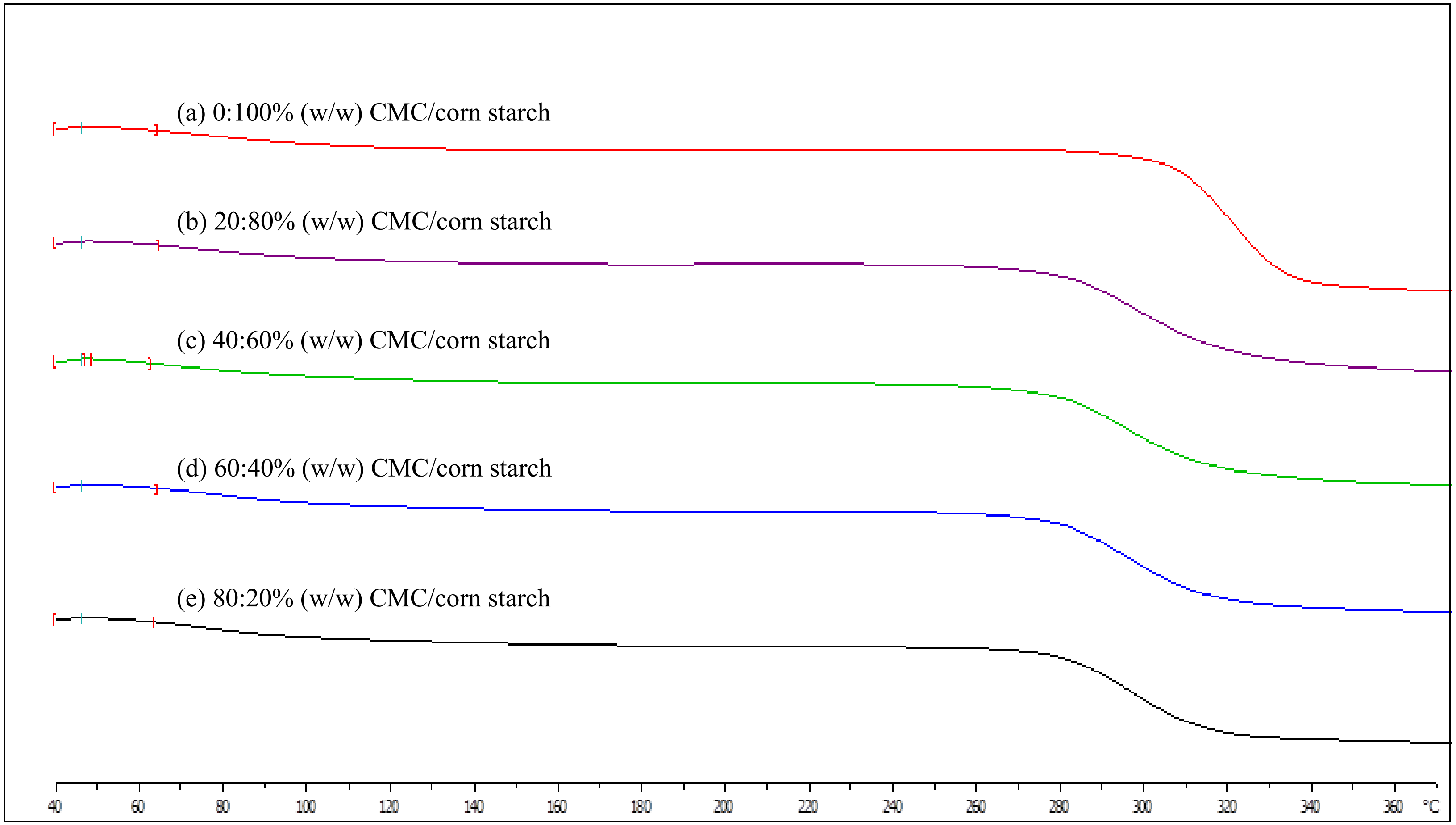

Fig. C.2: TGA thermogram of CMC/corn starch blend films

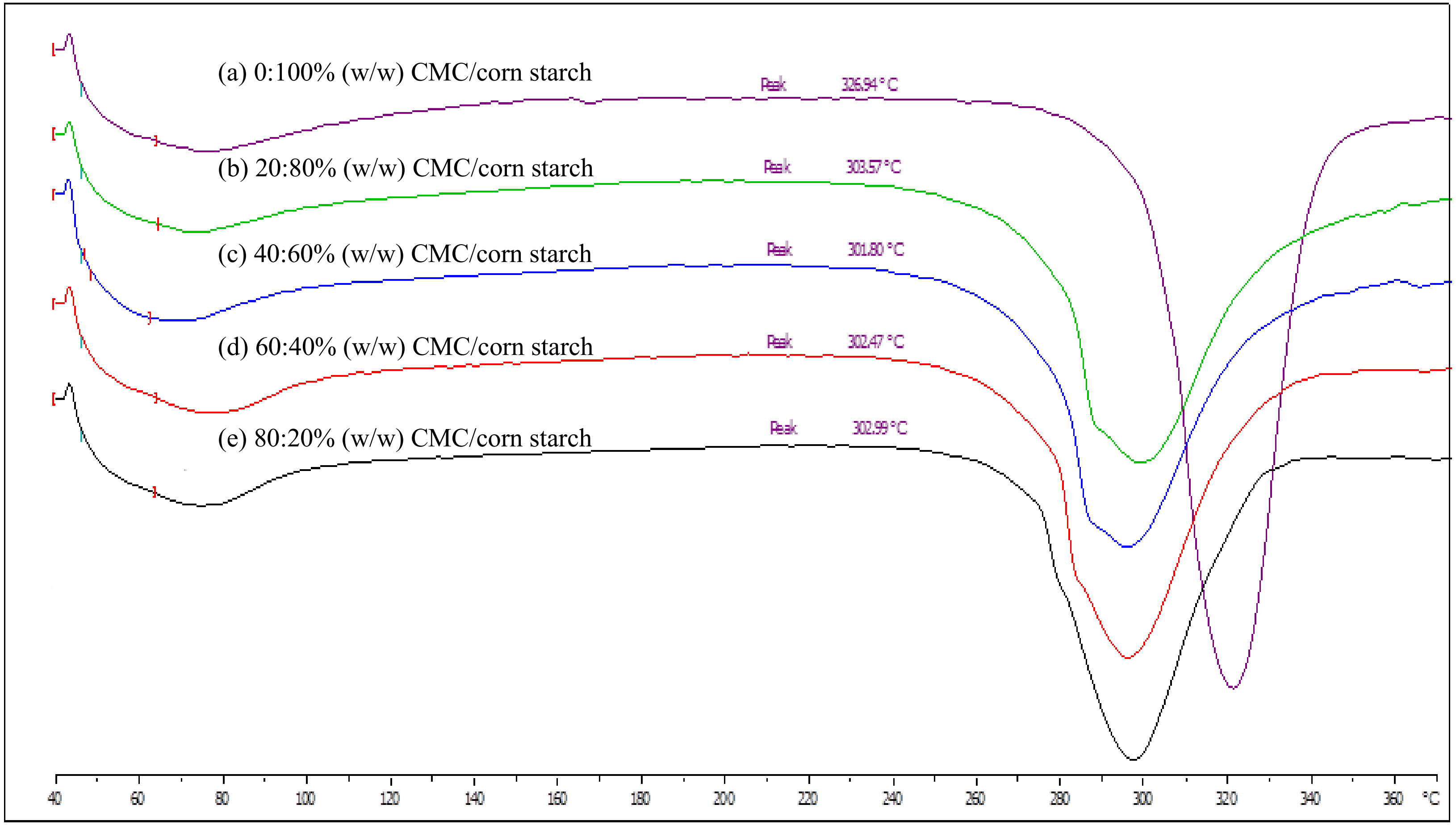

Fig. C.3: TGA derivatogram of CMC/corn starch blend films