PROPERTIES & CHARACTERISATION OF THE HALOCHROMIC CMC-PEG HYDROGEL FILM.

MASSARA BINTI SAMSUL BAHARIN

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by

MASSARA BINTI SAMSUL BAHARIN

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Tg Glass transition temperature

Tm Melting temperature

Mw Average molar mass

% Percentage

Ws Weights of the dry

Wd Weights of swollen

ΔE Total of colour change

g Gram

W/W weight per weight

LIST OF ABBREVIATIONS

CMC	Carboxymethyl Cellulose
PEG	Polyethylene glycol
CPR	Chlorophenol red
CA	Citric Acid
DI	Deionized water
OH	Hydroxyl Group
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
USM	Universiti Sains Malaysia

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Thesis Title'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: **MASSARA BINTI SAMSUL BAHARIN** Signature:
Date: 15 JULY 2022

Witness by Supervisor: **DR. KU MARSILLA BINTI KU ISHAK** Signature: marsilla
Date: 15 JULY 2022

Dr. Ku Marsilla Ku Ishak
Program Kejuruteraan Polimer
Pusat Pengajian Kejuruteraan Bahan & Sumber Mineral
Universiti Sains Malaysia
14300 Nibong Tebal, Pulau Pinang
Tel: 04-5995266
Email: ku_marsilla@usm.my

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SIFAT & KARAKTERISTIK FILEM HIDROGEL HALOKROMIK CMC-PEG

ABSTRAK

Matlamat kajian ini adalah untuk mengarang sifat dan pencirian filem hidrogel CMC-PEG halokromik. Kerja ini menerangkan penghasilan filem karbosimitilselulosa (CMC) – polietelin glikol (PEG) menggunakan asid sitrik sebagai komponen bukan toksik dan semula jadi yang bertindak sebagai agen silang dan khlorofenol merah (CPR) sebagai pewarna yang memantau variasi pH melalui perubahan warna dan sifat-sifat halokromik. Filem hidrogel komposit telah dibuat dengan menggunakan teknik tuangan larutan. Analisis fisiokimia, morfologi dan mekanikal telah dijalankan untuk menganalisis permukaan bahan sebelum dan selepas bersilang. Pendekatan ini akan membantu menentukan sama ada kesan rawatan kimia ke atas hidrogel selulosa meningkatkan sifat hidrofilik, kekasaran, dan reologi filem hidrogel selepas sintesisnya, semua filem kemudiannya dicirikan melalui Ujian Ketindakbalasan Halokromik, Analisis warna, Ujian Tegangan, Ujian Kebengkaan, Spektroskopi Inframerah Fourier Transformasi (FTIR), and Mikroskop Mengimbas Elektron (SEM). Analisis instrumen ini membolehkan penilaian sifat mekanikal, suhu peralihan kaca, suhu lebur dan kebolehan berundur halochromic filem hidrogel ini. Oleh itu, parameter seperti kepekatan asid sitrik, masa tindak balas dan nilai pH yang berbeza diubah secara individu untuk menganalisis kesannya terhadap sifat filem hidrokimia halokromik dan penciriannya menggunakan teknik instrumental yang relevan. Penemuan ini menunjukkan hasil sampel, berjaya menukar warna dari kuning (pH 4) menjadi ungu (pH 6). Selain itu, sifat dan ciri filem CMC-PEG pernghubung-silang ditemui.

PROPERTIES & CHARACTERIZATION OF THE HALOCHROMIC CMC-PEG HYDROGEL FILM

ABSTRACT

The aim of this study is to fabricate the properties and characterization of the halochromic CMC-PEG hydrogel film. The present work describes the production of carboxymethylcellulose (CMC) - polyethylene glycol (PEG) films using citric acid as a non-toxic and natural component which acts as a crosslinking agent and chlorophenol red (CPR) as a dye that monitors pH-variations through a colour change of halochromic behaviour. The solution-casting process was used to create the composite hydrogel films. The material's surface was analysed before and after crosslinking using physiochemical, morphological, and mechanical methods. This method would assist in determining whether the hydrophilicity, roughness, and rheological properties of the hydrogel films are improved by the chemical treatment of the cellulose hydrogel. After their synthesis, all films were then characterized through Halochromic Responsive Test, Colour Analysis, Tensile Test, Swelling Test, Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). This instrument analysis allows evaluation of the mechanical properties, glass transition temperature, melting temperature and reversible halochromic behaviour of these hydrogel films. Hence, the parameters such as concentrations of citric acid, reaction time and different pH values were varied individually to analyse their impact on the halochromic hydrogel film properties and their characterization using relevant instrumental techniques. This finding shows the results of the sample, successfully changing colour from yellow (pH 4) to violet (pH 6). Besides, the properties and characterization of crosslinker CMC-PEG films were discovered.

CHAPTER 1

INTRODUCTION

1.1 Background Study

Chromism is the phenomena of a substance's reversible colour change, which has change in the development of new smart materials. The colour changes phenomena can be differentiated based on types of an external stimuli such as thermochromic (colour change caused by heat), photochromic (colour change caused by light), magnetochromic (colour change caused by magnetic field), and halochromic (colour change caused by pH) (Jia Yam *et al.*, 2021). Fundamental research has a fascination with chromism because colour changes based on wavelength changes in absorption, emission, or reflection correlate with stimuli-responsive structural shifts of materials on the subnanometer to micrometre scale (Mutai *et al.*, 2020). Recently, in the light of stimuli-responsive polymeric materials a growing interest is indicated in the development of colour-changing materials such as pH-sensitive textile materials (de Meyer *et al.*, 2016a).

Halochromic is defined as reversible colour change arising from a pH change. Herein, chlorophenol red (CPR) dye one of the sulfonphthaleine dyes which was applied in this research. CPR is commonly used as a pH indicator because it shows a colour shift from yellow to voilet in the pH range 4.8 to 6.7. The presence of dye able to determine acidity and alkalinity of chemicals or environments. Thus, halochromic can be developed in a broad range of applications such as a textile pH sensor which integrated into protective equipment, for instance, might signal the presence of acid gases in a working environment. Another good example, a pH-sensitive wound dressing could hence aid to the follow-up of the wound healing, without having to remove the gauze (van der Schueren and de Clerck, 2012c).

In this article, we propose a method for creating hydrogel films in aqueous polymer solutions. However, to form a good properties of hydrogel film, the selection of material is essential. The use of biodegradable polymer has various issues with performance and processing, such as brittleness and heat distortion temperature, respectively, their usage has been restricted. Thus, among several substitutes of natural polymers, cellulose and its derivatives have been mostly used as a natural source for creating of hydrogels and composites in several fields including biomedical, textile medical, food packaging and pharmaceutical. Carboxymethyl cellulose (CMC), is an anionic linear polysaccharide derived and semi-synthetic derivative of cellulose that is produced by partial substitution of the 2, 3, and 6 hydroxyl groups of cellulose by carboxymethyl groups (Yadav *et al.*, 2013a). Besides, CMC is mainly used since it has high viscosity, is non-toxic, and is non-allergenic. The frequent hydroxyl and carboxylic groups in CMC allow water binding and moisture sorption properties, and thus CMC hydrogels show a high-water content, good biodegradability, and a large range of applications due to its low cost (Nie *et al.*, 2004; Yadav *et al.*, 2013b). The advantage of CMC is film formulation and the ability to blend with other polymers such as poly(ethylene glycol) (PEG), which is biocompatible, less toxic, and hydrophilic (Cheng *et al.*, 2006).

Polyethylene glycol (PEG) has been applied in some biotechnical fields because of its favourable biocompatibility, resistance to protein adsorption and low immunogenicity (Zhang *et al.*, 2002). CMC has poor mechanical properties therefore by adding PEG which act as a plasticizer, able to overcome and improves the properties of polysaccharide-based films. Before casting and drying processes, plasticizers are typically added to the film-forming solution as a way to combat the brittleness of the films. In contrast, plasticizers commonly enhance hydrophilicity of the film which in turn promotes water vapor permeability (Krochta and de Mulder-Johnston, 1997; Müller, Yamashita and Laurindo, 2008). PEG is a polyether that is soluble in various organic solvents as well as water and is amphiphilic. Additionally, it is freely presented in a broad range of molecular weights, and it has been seen to be nontoxic (Capanema *et al.*, 2018a).

Furthermore, crosslinking is an effective technique for enhancing the properties of biopolymer-based hydrogel films. In this studies, citric acid crosslinked of CMC-PEG hydrogel films were prepared by esterification-crosslinking method. It provides greater stability and mechanical strength, causing in a fixed matrix with swelling capacity, good mechanical properties, thermal stability, and better resistance to dissolution in water (Tavera-Quiroz, Feria Díaz and Pinotti, 2018). According to Ramaraj (2007), the mechanical properties and dissolution of the blend films exhibited significant development compared to the non-cross-linked films (Kim and Lee, 2002; Ramaraj, 2007). Further investigation has characterized the hydrogel films using FTIR, SEM, thermal analysis and evaluated them for swelling ratio. Not to forget, the reversible halochromic material was described using pH indicator testing and colour analyzation which able to identify the colour changes of the hydrogel films.

The objective of this study was to fabricate the properties and characterization of the halochromic CMC-PEG hydrogel films when citric acid and PEG was added in the CMC-based films. It has been investigated how different concentrations of citric acid and PEG affect the mechanical characteristics of the film as well as morphological and structural alterations.

1.2 Problem Statement

In this research, the properties and characterization to fabricate halochromic CMC-PEG films were identified by using biocompatible and eco-friendly crosslinkers throughout this process. The hydrogel films were fabricate using the solution-casting technique, and their physicochemical, thermal, and mechanical characteristics were assessed. Since, it is difficult to fabricate hydrogels with superior structures and properties using nontoxic and desirable simple cross-linking methods. Several researchers have prepared CMC-based hydrogels using physical or chemical crosslinking (Chang *et al.*, 2010; Ghorpade *et al.*, 2018a).

However, the hydrogels obtained through physical crosslinking are believed to be weak (Sannino, Demitri and Madaghiele, 2009) and may not be permanent in nature. Although physical hydrogels can absorb water, defects in the network or inhomogeneities might occur because of unattached chain ends or loops. Meanwhile, chemically crosslinked hydrogels can indeed have some disadvantages, such as the low water solubility of polymer precursors and the inherent cytotoxicity of popular chemical crosslinkers due to the possibility of unreacted species in the system. Consequently, using chemically modified polymer derivatives, such as carboxymethyl cellulose (CMC) able to overcome the problem by maintain its water-solubility and the use of biocompatible and eco-friendly crosslinkers (e.g., citric acid) all through the whole process may improve the film properties (Demitri et al., 2008; Reza and Nicoll, 2010; Capanema et al., 2018b).

Thus, in this study CMC was used. CMC is a cellulose derivative with some carboxymethyl groups on its backbone. Moreover, CMC is a water soluble polyanionic cellulose derivative with broad applications in biomedical and pharmaceutical field (S.Kamel *et al.*, 2008) which consist of biocompatibility, biodegradability, water solubility, and low cost. Besides, with the presence of citric acid which is a non-toxic crosslinker and the PEG as a network modifier may improve the morphological traits alongside with the physicochemical and nanomechanical properties.

A better hydrogel with suitable transmittance, mechanical properties, simple preparation process and biocompatibility is still a challenge (Li *et al.*, 2019). Therefore, we have prepared the halochromic CMC-PEG blend films with crosslinked citric acid hydrogel film to identify the properties and characterization of this formulation. Furthermore, by converting the current hydrogel film into a smart material film by way of explored the pH-sensitivities of the hydrogels, able to significantly improve and enhance the application.

1.3 Research Objective

The objectives for this research are to study and fabricate the properties and characterization of the halochromic CMC-PEG hydrogel film. The specific research objectives are as follows:

i. To investigate the effect of dye to the efficiency of halochromic behaviours.
ii. To fabricate halochromic of CMC-PEG hydrogel film that can change colour at different pH-variation.
iii. To investigate the effect of citric acid concentration to the efficiency of hydrogel film properties.
iv. To investigate the effect by adding PEG into the composite formulation of hydrogel film properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Smart Materials

Smart materials respond to stimuli by changing their properties, adapting to their surroundings, and, in reaction to a specific input, giving a predictable and reproducible result (output). In other words, they are classifying as materials that have the potential to think and adjust to the surrounding environment with the aim to fulfil the required need. Smart materials are fundamentally different from ordinary materials due to their changing qualities. Common materials are certainly used most often as a medium to provide an item fixed feature, and a change in those attributes or behaviour with respect to their environment is frequently considered as a challenge that must be traded with rather than an opportunity to add new functionality. In this scenario, these characteristics are flexible, and the material will react on its own to a certain environmental event, and at the same time give information, interact with, and entertain the user (Esther et al., 2014).

Newly developed materials known as "smart materials" surpass traditional structural and functional materials. Smart materials are divided into two groups which are active and passive. According to Fairweather (1998), he described active smart materials as those materials which acquire the capability to change their geometric or material properties in the application of electric, thermal, or magnetic fields, thereby acquiring an inherent capacity to transduce energy (Kaushal, Vardhan and Rawat, 2016). Meanwhile, passive smart materials are those that do not naturally possess the ability to convert energy. A good example of passive smart material is fibre optics (Damodharan and Sreedharan, 2018). In addition, smart material can be classified as shape memory, magnetorestrictive, thermoresponsive, self-healing, piezoelectric and chromic. In addition, they have some features that make them to be distinguished from the other materials, such as (Sadeghi, Masudifar and Faizi, no date; Song, Wei and Qu, 2011):

a) Transiency: they can respond to different stimuli and can be situated in varies states.
b) Immediacy: they response to the external effects without wasting time.
c) Self-actuation (intelligence): this ability is inside the mater.
d) Selectivity: the response is distinguished and predictable.
e) Directness: both act and react are accrued in the same place.

2.1.1 Classification of Chromic

In the fields of displays, switches, and sensors, stimuli-responsive chromic materials have gotten a lot of attention. In this study, chromic materials have incredibly outstanding property to change their colour once exposed to external stimulus (pH, temperature, lights, electric field. The suffix "chromism" denotes a reversible change in colour and, consequently, a reversible change in other physical characteristics. Chromic materials are also known as "chameleon materials" due to their ability to change colour (Talvenmaa, 2006a). Based on several forms of an external stimulus, such as thermochromic, photochromic, halochromic, electrochromic, and more, colour change phenomena can be classified. In this project, we are concentrating on halochromic which is capable to change colour from varying pH values.

Due to their superior mechanical qualities, these materials are being used more and more frequently in fields including automotive, aerospace, mini actuators, micro electromechanical systems (MEMS), and biomedicine. Chromic materials can be classified as mentioned below:

(a) Thermochromic : Changing of temperature

(b) Photochromic : Absorbing electromagnetic light
(c) Halochromic : Changing of pH-value
(d) Magnetochromic : Appling magnetic field
(e) Piezochromic : Mechanical loading
(f) Electrochromic : Appling electric field
(g) Solvatochromic : Contact with some liquid

2.1.1(a) Thermochromic Material

The colour shift that can be seen in chromic materials as a result of temperature changes is known as thermochromism. In thermochromic, the only characteristic used to cause a colour shift is the activation temperature. The thermochromic transition the change in colour that happens at a specific temperature describes this process. The colour can differ with the change of temperature in a certain temperature range, due to the obvious absorption spectrum of discoloration compounds or mixtures changed while heated or cooled (Zhu and Wu, 2005; Cheng *et al.*, 2018). Thermochromic materials have widely important application areas like security printing (Chowdhury, Joshi and Butola, 2014), plastic strip thermometers, food packaging, medical thermography, the non-destructive testing of engineered articles, electronic circuitry (Christie and Bryant, 2005) and pharmaceutical industry (Kantola *et al.*, 2013).

There are three main categories of thermochromic materials: inorganic, organic, and liquid crystal. It is generally known that inorganic substances exhibit thermochromic behaviour both as solids and in solutions. This compound provides outstanding temperature resistance, durability, light resistance, and processability, among other advantages. As for organic compounds the mechanism in charge for thermochromism changes with molecular structure due to an equilibrium between two molecular species (acid-base) (Talvenmaa, 2006a). This compound which has the pros of optional and flexible colours, low discoloration temperature, high sensitivity of discoloration and low cost. Meanwhile, thermochromic liquid crystals exhibit a range of colours at varying temperatures as a result of their structure's selective reflection of specific light wavelengths. Thermochromic liquid crystals have the benefit that they express a lightly coloured look, but they have the drawback of high cost and low colour density (Talvenmaa, 2006a).

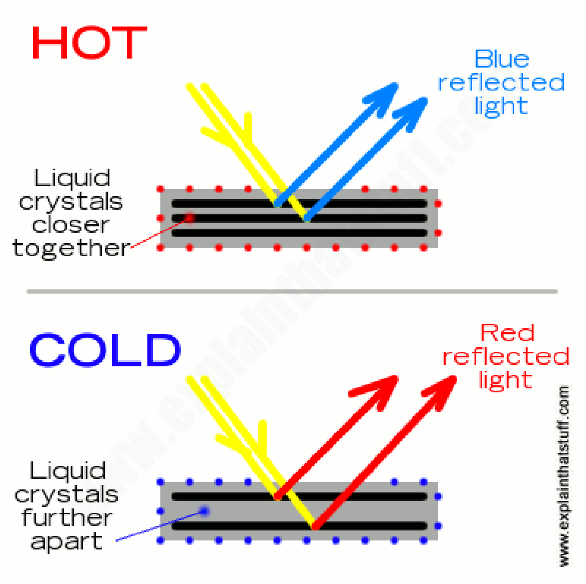


Figure 2.1 Top: To create a certain colour of light, incoming light rays interfere with one another as they pass through layers of liquid crystals (black lines) by either adding to or removing from one another. Here, blue is obtained by a process known as Bragg diffraction (Bragg scattering). Depending on how densely the crystal layers are packed together, the colour of the reflected light changes. Bottom: In this hypothetical example, chilling the liquid crystals causes them to migrate farther apart, altering how the emitted light waves interfere, and intensifying the colour of the reflected light.(Chris Woodford, 2021).

2.1.1(b) Photochromic Material

Photochromism is typically referred to as a reversible colour changing phenomenon via alternating visible light irradiation and another stimulus such as heat, and ultraviolet light (Brown and Zweig, 1973). Particularly, there are transparent materials which show better light absorption when they exposed to light. The phenomenon is well known both in optical glasses (Werner, Klimant and Wolfbeis, 1995a) or plastic material or other materials. Photochromic responses are generally based on cis-trans isomerization, electrocyclization, redox, and light-induced proton transfer mechanisms. The difference between the molecular structure before and after light irradiation results in a remarkable variation in the absorption or photoluminescence (PL) spectra (Ma *et al.*, 2021). Moreover, both organic and inorganic substances, including their hybrid materials, show photochromism. Spirooxazine compounds, which have strong light fatigue resistance, have been used in experiments with a range of organic photochromic materials. Spirooxazine is an important class of organic photochromic materials (Bouas-Laurent and Dürr, 2001; Lokshin, Samat and Metelitsa, 2002) because of their potential in photochromic materials, the behaviour of these dye molecules has attracted the interest of many new technology applications. Applications of these materials include security markings, ions and solvents probing, optical shutters, photo-switchable molecular devices, topographical change materials, and optical memory storage systems (Klajn, 2014).

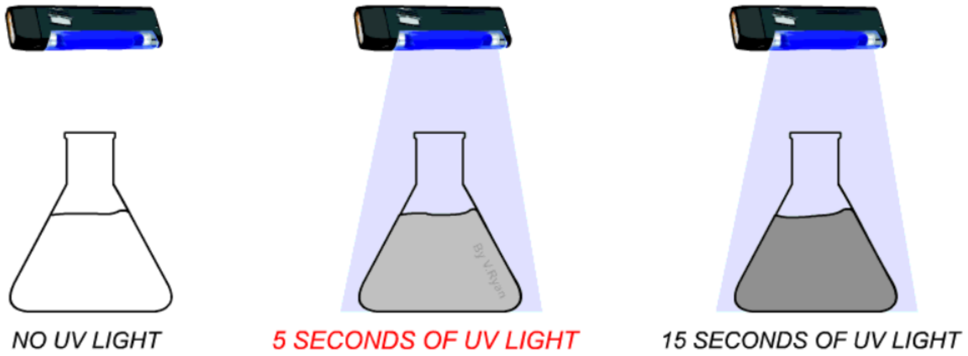


Figure 2.2: A special UV torch shining ultraviolet light on a test tube filled with photochromic ink. (V.Ryan, 2011)

2.1.1(c) Pieozochromic Material

Piezochromism is the phenomenon where crystals experience a main change of colour or luminescence reversibly in response to mechanical stimuli (grinding, stretching or hydrostatic pressure) (Xie *et al.*, 2021). The generated colour returns to the original colour as soon as the fractured crystals are kept in the dark or dissolved in an organic solvent (Bouas-Laurent and Dürr, 2001). Besides, piezochromic materials also may alter certain physical characteristics, such as absorbability, emissivity, reflectivity, or transparency, by applying a specific pressure and by bathochromic shift. Most frequently, two types of external forces are used to research the piezochromic behaviours of organic materials which are anisotropic forces generated by mechanical grinding and the isotropic hydrostatic pressure, this could cause different piezochromic effects (Nagura et al., 2013; Gong et al., 2020). For example, uMoO4 molecule need 2.5 kbar to change its colour from green to red, while Palladium (Pd) need a pressure more than 1.4 GPa (Rodríguez, Hernández and Garcia-Jaca, 2000).

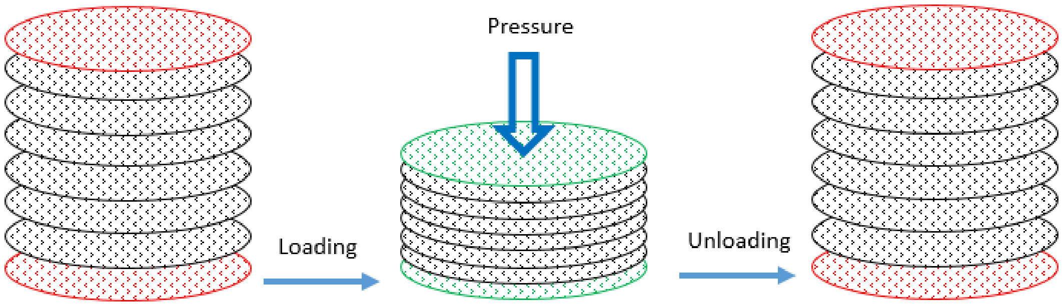


Figure 2.3: A typical piezochromic material, which its color is changed under an external load. (Seeboth, Loetzsch and Ruhmann, 2012)

2.1.1(d) Salvatochromic Material

Solvatechromism is the phenomenon, where colour changes caused by a change in solvent polarity of the surrounding environment (Reichardt, 1994) or when it contacts with a liquid, for example, water. Additionally, the shift in the absorption maximum's significance is shown by the colour change, which occurs as a result of differences between the solvation energy of the initial and excited state in various solvents (Rijavec and Bračko, 2007). A difference in the solvent polarity will cause different stabilization of the ground and excited states (He and Chen, 2018). The effect of this can be seen in π→π* transitions, according to Rijavec, T. (2007), the excited state, which is more polar than the initial state, is more stable in more polar solvents, thus it called as positive solvatechromism since lower energy is required to produce bathochromic shift of the absorption spectrum. Because of this, specific markers of the interactions between the molecules of the solute and solvent can be found in changes to the location, intensity, and shape of the absorption spectrum. Due of its high utility in applications, the solvatochromic material has gained a lot of attention such as fluorescent probe, indicator, chromogenic reagent, molecular recognition field and so on (Marini et al., 2010; Cabot and Hunter, 2012).

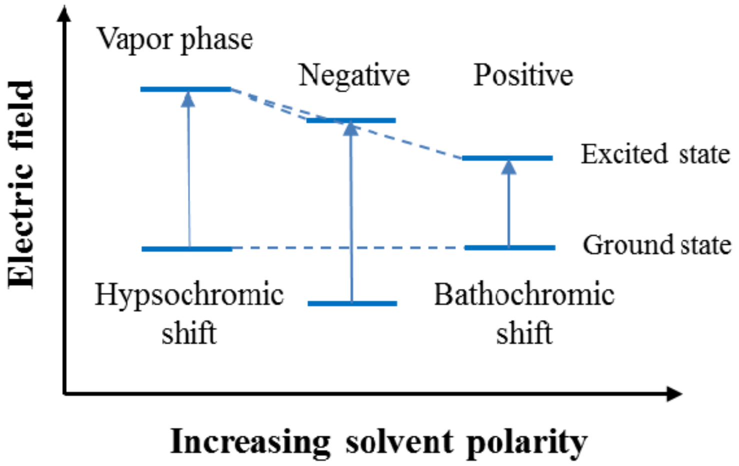


Figure 2.4: Schematic diagram of interaction in solvatochromism material. (Lee *et al.*, 2014)

2.1.1(e) Electrochromic Material

Reversible transmittance or reflectance changes are seen by electrochromic materials in visible and infrared (IR) range upon electric or electrochemical stimulus (Xu *et al.*, 2016; Wang *et al.*, 2020). Electrochromic systems have been utilised effectively in mirrors and windows for anti-glare and anti-reflective (Talvenmaa, 2006), auto dimming rear-view mirrors, E-paper (Casini, 2018; Granqvist *et al.*, 2018), camouflage materials, chameleonic fabrics, and more applications. The colour shift typically occurs between two coloured states or between a transparent (or "bleached") state and a coloured one. When more than two redox states are electrochemically available, the electrochromic material may show some colours and may be labeled as polyelectrochromic or possess multicolour-electrochromism (Somani and Radhakrishnan, 2002). Using a simple categorization system established from that of (Chang, Gilbert and Sun, 1975) electrochromic materials contain of three simple types on the basis of the solubility of each redox state (Gladfelter, 1996). Type I substances that are soluble in both the reduced and oxidised states are present in every electrolyte solution. Type II materials that create a solid coating on the surface of an electrode after electron transfer but are soluble in one redox state. In type III electrochromic materials that are solid in both or all redox states (Mortimer, 2011).

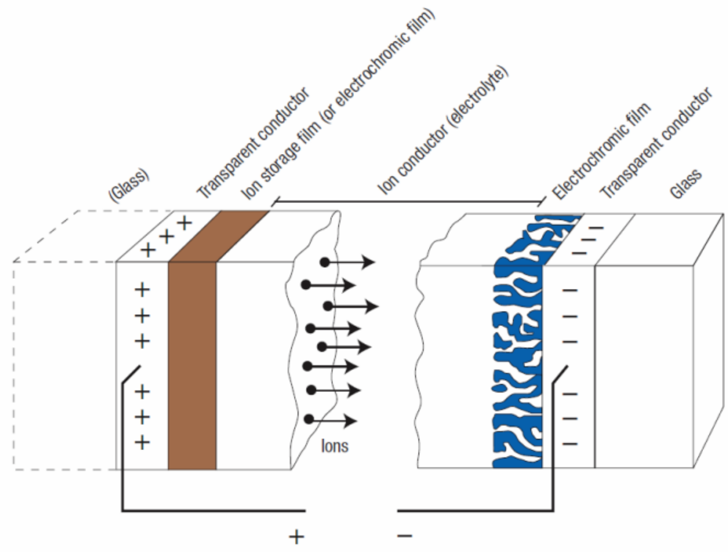


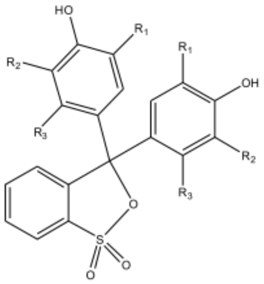
Figure 2.5: Schematic illustration of a layered electrochromic device showing the movement of ions/electrons under an externally applied electric field. (Granqvist, 2006)

2.2 Halochromism

“Chromic” is the term for colour change of halochromic materials in response to pH changes which usually caused by a reversible proton exchange via the acid-base reaction. Halochromic compounds are well suited for usage in situations where pH changes occur regularly or when significant pH variations occur. Such materials have been broadly applied as colorimetric indicators, chemical sensors, biosensors, and optoelectronic devices (van der Schueren and de Clerck, 2012a; Yao *et al.*, 2013; Tang *et al.*, 2017). Halochromic materials were filled with pH-indicator dyes for monitoring pH variations in various liquids (Bazbouz and Tronci, 2019). For instance, bromothymol blue (BTB) produces either a green or blue coloration when dissolved in an alkaline environment, whereas it produces a yellow colour when dissolved at a pH lower than 6.0. (de Meyer *et al.*, 2014a). The development of the halochromic material has numerous benefits, including its potential to be applied to large surfaces and to provide a local signal. For instance, a colour change will be immediately apparent to everyone, thus it can be used as a first, non-destructive warning signal. Additionally, a textile pH sensor might, for instance, reveal the presence of acid fumes at a workplace.

2.2.1(a) pH-sensitive Dyes

When dyes are exposed to substances that modify the physical and chemical properties of molecules, such as acids, alkalis, sunlight, water, mechanical stress, and electricity, their colour may change. Despite being a relatively small dye class, sulfonphthaleine dyes are frequently utilised as acid-base indicators because they exhibit a distinct colour change as a function of pH. In this chapter, the dyes that change colour in response to pH variations and then revert to their original colour once normal conditions are restored. The usual use of pH indicators has but significantly reduced because of the expansion of more accurate measuring systems (Liu *et al.*, 2014). Consequently, a lot of effort has gone into the research and development of new halochromic dyes to comprehend their behaviour and meet the strict criteria for this high-value use of pH-sensitive dyes. For instance, Griffiths and Cox discovered that the azo dye derived from 10-methyl-9-methylene-9,10- dihydroacridine typically displays a positive halochromism, but changes to a negative halochromism in the occurrence of an exceptionally powerful acceptor and/or donor substituent (Griffiths and Cox, 2000). The future and potential for use in pH-sensitive dyes for a particular application should eventually be made possible by studies of these systems.



	R_1	R_2	R_3	pK_a
(1) Phenol Red	H	H	H	8.0
(2) Cresol Red	CH_3	H	H	8.3
(3) m-Cresol Purple	H	H	CH_3	8.5
(4) Xylenol Blue	CH_3	H	CH_3	9.1
(5) Thymol Blue	i-Pr	H	CH_3	8.9
(6) Chlorophenol Red	Cl	H	H	6.7
(7) Bromophenol Blue	Br	Br	H	4.1
(8) Bromocresol Purple	Br	CH_3	H	6.3
(9) Bromocresol Green	Br	Br	CH_3	4.8
(10) Bromothymol Blue	i-Pr	Br	CH_3	7.4

Figure 2.6 Basic structure of sulfonphthaleine dyes and substituents of all studied molecules
(de Meyer *et al.*, 2016b)

2.2.1(b) Mechanism of Colour Change Properties in Halochromic Behaviour

In this context, changes in pH levels are crucial dye stimuli. Here, we concentrate on the halochromic (pH-sensitive) sulfonphthaleine dyes such as chlorophenol red as a representative example. It is still unclear how exactly this colour change occurs, and in particular, what influence the environment plays. In order to forecast the characteristics of additional dyes in aquatic environments, we want to develop a theoretical technique that may be used to comprehend the structural changes at the molecular level that lead to halochromism.

Due to the shift in absorption spectra caused by the protonation/deprotonation of their phenol groups, sulfonephthalein dyes, a class of halochromic indicators, can change colour. Figure 1 illustrates how the structure of chlorophenol red dyes varies in both acidic and alkaline environments. These dyes are sensitive to varied pH ranges and exhibit a spectrum of colours due to various aromatic substituents.

It is clear from looking at the sulfonphthaleine dyes' fundamental structure in Figure 2.7 that they will act as acids when in neutral state. Deprotonation allows for a rearrangement of the internal bonds when solvated (1). This deprotonation is driven by two factors: first, an internal rearrangement produces a bigger conjugated system and second, the formation of a SO3 group (1a). This might be more advantageous energetically because it permits a high level of contact with the surrounding water molecules (de Meyer *et al.*, 2014b). In addition, the deprotonation of a single anion (1a) into a double anion (1b) that is resonance stabilised is caused by pKa values (de Meyer *et al.*, 2016c). It is evident from Fig. 2.6, which shows the deprotonation process from 1a to 1b, that the substituents have a significant impact on the pH range in which this reaction takes place.

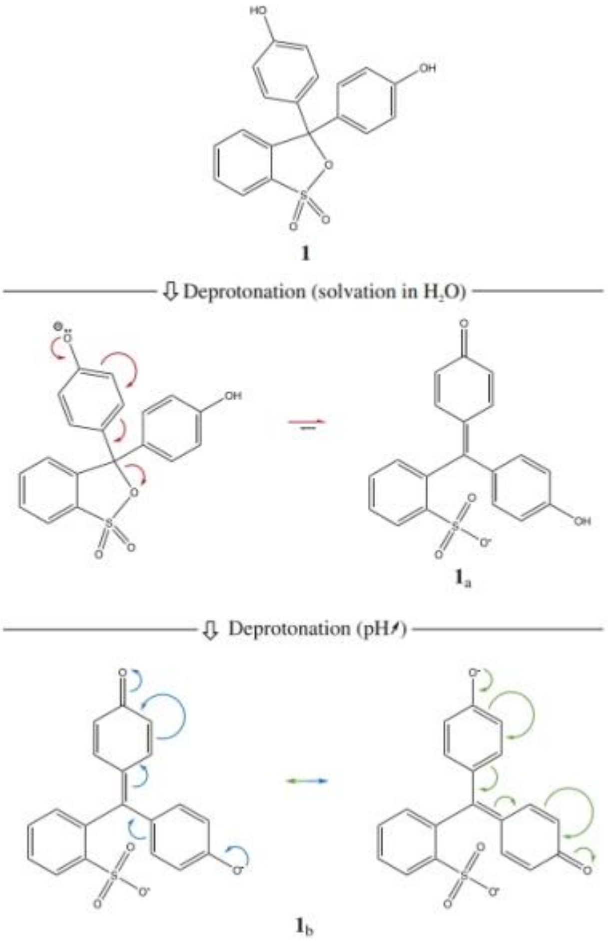


Figure 2.7 In aqueous solution, 1 act as an acid and the molecule loses a proton, which results in a rearrangement of the internal bonds (1a). When going to more alkaline media (above pH 6), a deprotonation results in the resonance stabilized form 1b (de Meyer et al., 2014)

2.2.2 Method of Synthesis of Halochromic

2.2.2(a) Solution-Casting

The solution casting method is being widely used to prepared hydrogel film by casting method. This technique consists of solubilization, casting, and drying. This procedure involves dissolving the polymer along with all other components to create a homogenous solution in a common solvent, then casting that solution onto a flat glass plate or Petri dish, as shown in Figure 2.7. To put it another way, prepolymer and polymer are combined evenly and made soluble in the appropriate solution. The nanoparticles dispersed in the same solution or a different solution and became mixed with the polymer, which was the matrix phase, making the polymer more easily soluble in the solution (Das, Pattanayak and Swain, 2018). The polymer must be soluble in the selected solvent in a correct concentration which is rigorously related to final application (Galiano, 2014). Other than that, solution casting is usually used to produce a thin film which capable to change film extrusion to deliver high-quality films with superior optical, mechanical, and physical film properties (Maria Koomen, 2015). Even with a small thickness, the solution casting technique can efficiently produce a polymer film with high quality surfaces and optical properties

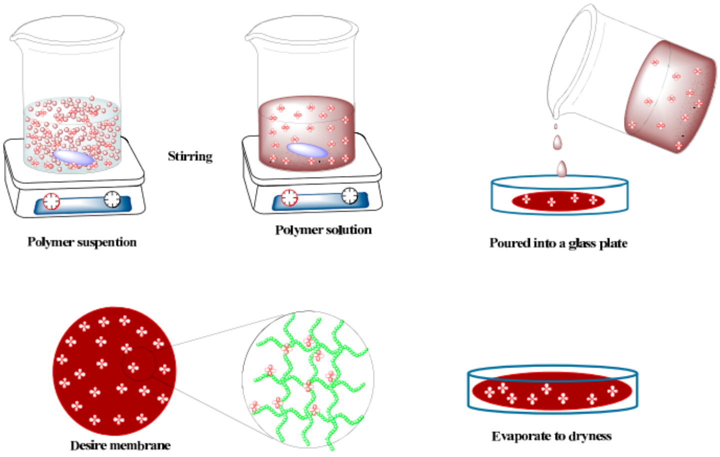


Figure 2.8: Preparation of Nanocomposite Membrane (NCM) by solution casting method. (Roy and Singha, 2017)

2.2.2(b) Melt Mixing

A process known as "melt mixing" involves combining a polymer melt with a solid filler in a high-shear mixer, which mechanically forces the filler into the polymer matrix. (Dunlop and Bissessur, 2020). The deterioration of the polymer will depend on the temperature and pressure. By mechanically shearing the nanoparticles in the molten polymer matrix, the melt mixing process disperses them. Since it is based on traditional polymer processing techniques, this technology provides increased preparation convenience. In comparison to other processes, melt mixing is the most popular and practical way to create thermoplastic nanocomposites since it is easy, economical, and ecologically friendly. Yanjuan Ren et at, investigated by using the melt mixing procedure as indicated in Figure 2.8, it was tested how well thermoplastic composites filled with nanofiller conduct heat.

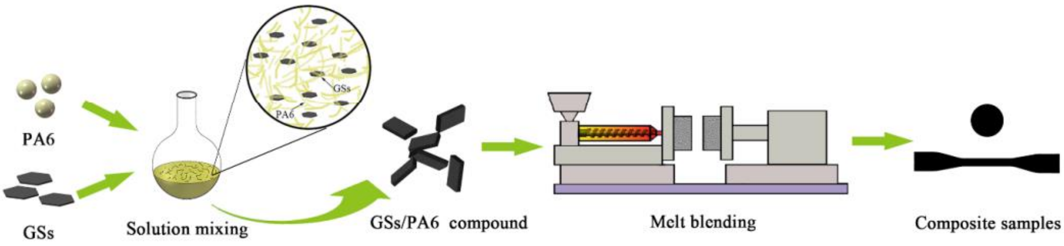


Figure 2.9 Schematic diagram of fabrication process of GSs/PA6 composites. (Ren *et al.*, 2019)

2.2.2(c) Extrusion

Extrusion processing enables the continuous production of exceptionally homogeneous goods by precisely controlling the processing conditions to physicochemically transform powder into a molten or wet mass. Recently, it was intended for the halochromic thermoplastic polymer to be processed using extrusion technology and moulded into films and injection-molded plastic items. The mixtures of polymer and prepolymer were used to prepare the halochromic polymer filament by extrusion processes. In Figure 2.9, it shows the types contain in extruder. Single-screw extrusion (SSE) is a mechanically simple and low-cost processing option, twin-screw extrusion (TSE) has been used widely for mixing, compounding, or agglomerating a variety of ingredients to create a wider range of products (Chen *et al.*, 2017a). Twin-screw extruder played an important role in manufacturing, especially for mixing and compounding diverse materials according to their respective applications (Chen *et al.*, 2017b). Additionally, the filament feeding system has gained popularity as a technology for use in material extrusion procedures because of its mechanical simplicity, reliability, and continuous feeding capacity (Volpato *et al.*, 2015).

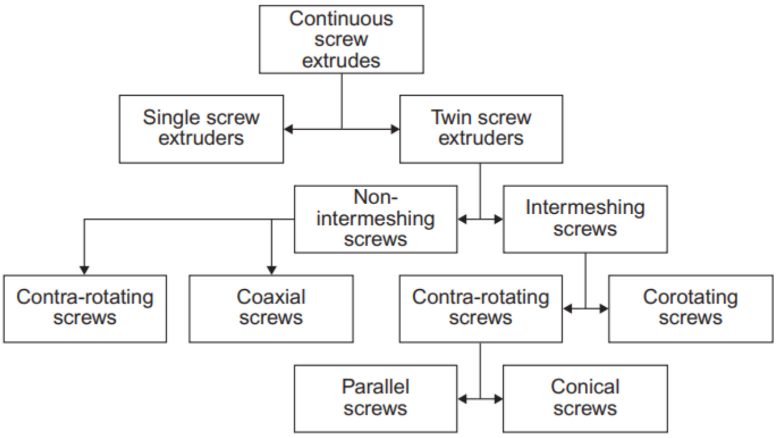


Figure 2.10: Type of extruders. (Chen *et al.*, 2017a)

2.2.2(d) 3D Printing

3D printing technologies have drawn interest because of their capability to design and generate polymeric specimen with controlled. The 3D printing process starts with the concept of a 3D model of the product with the help Computer Aided Design (CAD) software (Parashar and Sharma, 2016). 3D printing based on material extrusion, generally well-known in industry as Fused Deposition Modeling (FDM) or among additive manufacturing enthusiasts as Fused Filament Fabrication (FFF) is a well continued additive manufacturing technology at the moment. For example, a thermochromic membrane which responds to temperature, was fabricated with the selected method used for 3D printing is Fused Deposition Modelling (FDM). FDM method are generally versatile in applications, varying from quick and inexpensive rapid prototyping to tough and rigid parts suitable for end-use (Najmon, Raeisi and Tovar, 2019). Compared to 3D printing, the FDM approach has a number of advantages, including the absence of unbound loose powder and the absence of solvent removal, it requires flexibility to the material in processing and handling (de Mulder, Buma and Hannink, 2009). Figure 2.10 shows the process in FDM method step-by-step.

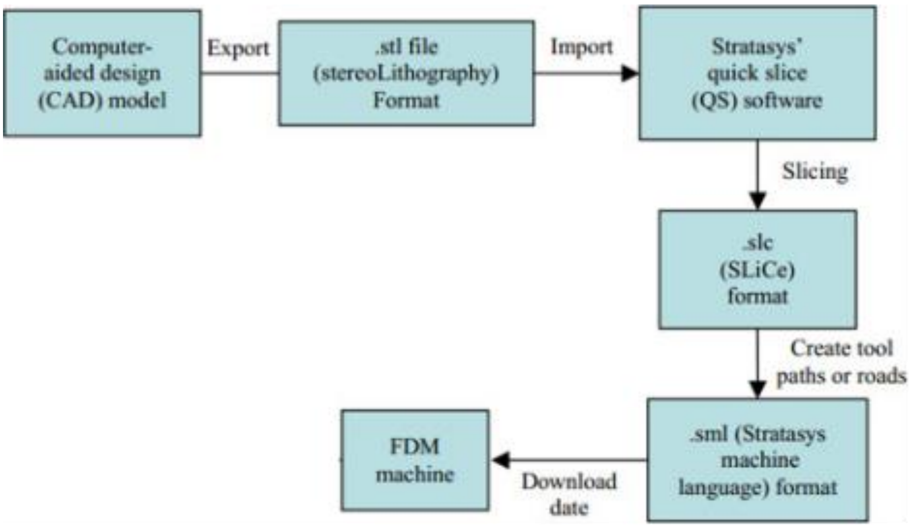


Figure 2.11: Data processing in FDM (Owida *et al.*, 2011)

2.3 Application of Halochromic

Since pH detection will be the initial hazard identification at every event, it can have a significant impact on protecting human life. Newly, new researchers produced wound dressing (Musa and Razak, no date; Steyaert *et al.*, 2015) and protective clothing can detect infection and toxic acidic and harmful environment in real-time at the workplace (de Meyer *et al.*, 2016d). Moreover, according to Lien Van der Schueren and Karen De Clerck, (2011), fabricated wound bandage that shifts colour upon infection where a healed wound appear yellow colour (slightly acidic) and turn to purple if an infection is present. Therefore, several alternatives of natural polymer such as cellulose have been widely utilised as natural resources to create hydrogel and composites in a variety of industries, including would dressing, drug delivery and tissue engineering (Shin et al., 2020).

2.3.1 Smart Textile

The non-destructive display of an easily visible signal by a color-changing textile makes it possible to employ it as a sensing system. A textile sensor also exhibits considerable flexibility, which it is a significant benefit over the commonly used sensor systems (Lien Van der Schueren and Karen De Clerck, 2011). A halochromic fabric could be used in a variety of applications, such as protective clothing, camouflage design, textile printing pastes and others. Due to CMC's durability to acids and alkalis within the pH range of these pastes and its ability to be utilised with a variety of dyes, it has been effectively used as a thickener to manufacture textile printing pastes (Feddersen and Thorp, 1993). Caldara et al. (2016), developed a smart fabric using sol-gel for optical sweat pH monitoring utilising the halochromic dye litmus. Monitoring the acidity of sweat, urine, nasal discharge, etc. using a halochromic textile is therefore valuable (Curto *et al.*, no date; van der Schueren and de Clerck, 2012b).

2.3.2 Food Packaging

A packaging system that can monitor food quality in real time and warn consumers about food safety problems by way of an electronic signal is referred to as smart food packaging (pH, optical, chemical, electric, etc.) in response to changes in the packaging environment and food quality in real-time (Biji *et al.*, 2015; Balbinot-Alfaro *et al.*, 2019; Rai *et al.*, 2019). Smart packaging built on biodegradable films and natural colours has become a popular substitute for utilising in food packaging due to their low or nontoxicity, eco-friendly, easy preparation, biodegradability and more (Choi *et al.*, 2017; Balbinot-Alfaro *et al.*, 2019). These natural colourants contained in the biopolymeric film matrix tend to change colour as the physiological circumstances of food change over spoilage. In addition, even spoilage sensors show reversible colour change, their indication of the actual quality of food highly uncertain (Werner, Klimant