DEVELOPMENT OF SMART POLYBUTYLENE ADIPATE TEREPHTHALATE (PBAT) BLENDING FOR PLANT POT APPLICATION

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by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Development of Smart Polybutylene Adipate Terephthalate (PBAT) Blending for Plant Pot Application”. I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body of University.

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Date:

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LIST OF SYMBOLS

ΔE	Delta Energy
˚C	Degree Celsius
T_d	End decomposition temperature
g	Gram
g/mol	Gram per mol
T_{onset}	Initial decomposition temperature
L*	Lightness
MPa	Mega Pascal
T_m	Melting temperature
mm	Millimeter
T_{max}	Peak temperature at maximum decomposition rate
%	Percent
cm^{-1}	Per centimeter
pH	Potential gydrogen
a*	Redness to greenness
b*	Yellowness to blueness

LIST OF ABBREVIATIONS

ASTM	America Society for Testing and Material
BCP	Bromocresol purple
CA	Cellulose acetate
FTIR	Fourier Transform Infrared spectroscopy
PAN	Polyacrylonitrile
PA-6	Polyamide-6
PBAT	Polybutylene co-adipate terephthalate
PEG	Polyethylene glycol
PLA	Polylactic acid
PEG	Poly ethelene glycol
SEM	Scanning Electron Microscope

PEMBUATAN PASU TANAMAN PBAT PINTAR

ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan PBAT/Kanji/PEG dan pewarna yang mempunyai sifat halochromic melalui mesin pengiling bergulung dua dan teknik pengacuan tekanan. Campuran pewarna timol biru dan metil merah digunakan sebagai pewarna pH dan kanji PBAT diplastiskan dengan polietilena glikol (PEG) menggunakan mesin pengiling bergulung dua yang dipanaskan. Sifat halochromic bagi sampel PBAT/kanji/PEG/Pewarna dicirikan oleh tindak balas visual di mana analisis warna dilakukan menggunakan model ruang warna CIE L*a*b*. Perubahan warna sampel halochromic telah diuji pada larutan pH yang berbeza seperti asid hidroklorik, asid borik, dan larutan natrium hidroksida. Di samping itu, sifat keterbalikan halochromic juga disiasat. Didapati sampel bertukar warna daripada jingga kepada hijau apabila terdedah kepada persekitaran beralkali manakala ia bertukar jingga kepada jingga gelap dalam persekitaran asid. Perubahan adalah pantas, dalam masa 1 minit selepas pendedahan. Walau bagaimanapun, kebolehbalikannya telah diuji dengan sampel rendam selama 30 minit. Dapat diperhatikan bahawa dengan menggunakan mata kasar, selepas 30 minit mencelup air suling, sampel yang dicelup ke dalam HCl dan asid borik berjaya bertukar menjadi warna jingga muda. Walau bagaimanapun, bagi sampel yang direndam dalam larutan NaOH tiada perubahan warna yang jelas diperhatikan. Morfologi PBAT/kanji/PEG/Pewarna dianalisis dengan mengimbas mikroskop elektron (SEM). Dapat disimpulkan bahawa zarah kanji dalam PBAT/Kanji/PEG/Pewarna menjadi kecil apabila jumlah PEG meningkat. Sifat PBAT/Kanji/PEG/Pewarna pada sifat tegangan telah dikaji. Jumlah PEG yang

semakin meningkat telah meningkatkan sifat mekanikal seperti kekuatan tegangan, pemanjangan semasa putus dan modulus tegangan.

DEVELOPMENT OF SMART PBAT PLANT POT

ABSTRACT

The objective of this research was to fabricate PBAT/Starch/PEG and dye that has halochromic properties via two roll mill and compression moulding techniques. The mixing of thymol blue and methyl red was used as pH dye and PBAT-starch was plasticized with polyethylene glycol (PEG) using heated two-roll mill. The halochromic properties of the PBAT/starch/PEG/Dye samples were characterized by visual response where the colour analysis was performed using CIE L*a*b* colour space model. The colour changes of halochromic sample were tested at different pH solution such as hydrochloric acid, boric acid, and sodium hydroxide solution. In addition, its reversibility halochromic properties were also investigated. It was found that sample change colour from orange to green when exposed to alkaline environment while it turns orange to dark orange in acid environment. The changes were rapid, within 1 minutes after exposure. However, its reversibility was tested with immerse sample for 30 min. It can be observed that by using naked eye, after 30 minutes dipping distilled water, the sample that was dipped into HCl and boric acid are successfully turn into light orange colour. However, for sample that was immersed in NaOH solution there is no obvious colour changes observed. Morphology of PBAT/starch/PEG/Dye were analysed by scanning electron microscopy (SEM). It can be concluded that the starch particle in PBAT/Starch/PEG/Dye became small when the amount of PEG increases. The properties of PBAT/Starch/PEG/Dye on the tensile properties were studied. The increasing amount of PEG has improved the mechanical properties such as tensile strength, elongation at break and tensile modulus.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Chemical and physical degradation are resistant to the majority of petroleum-based polymers used in manufacturing and consumer goods. When a product's usefulness expires, the disposal of plastic waste becomes a major concern. Biodegradation is an alternate method of disposal, particularly for agricultural plastic wastes. Biodegradation concerns specially designed so-called biodegradable polymers (Kyrikou and Briassoulis, 2007). Various plastics items such as containers, trays, pots, packaging, crop row and mulch films are available in bioplastic and widely used in agriculture nowadays (Brodhagen *et al.*, 2014). It takes three to six months for such products to completely degrade. Within six months in a regulated composting setting, at least 90% of the weight of the bioplastic should disintegrate (Folino *et al.*, 2020). As a result, biodegradable polymers are created to decay when disposed of by living creatures. In biological oxidation and hydrolysis systems, they will breakdown into biomass, carbon dioxide (CO_2), and methane (CH_4) by the activity of living organisms. As a result, to replace synthetic polymer could be an efficient way to address these concerning problems by designing and developing environmentally friendly biodegradable polymer (Wei *et al*., 2019).

The most promising and popular aliphatic-aromatic co-polyester with great development potential in a wide variety of applications is poly (butylene adipate-co-terephthalate) (PBAT), which is generated by poly-condensation between butanediol (BDO), adipic acid (AA), and terephthalic acid (TA) (PTA). It has shown to be the most suitable combination in terms of outstanding characteristics and biodegradability. Polyesters in general are synthesized by polycondensation from combinations of diols and dicarboxylic acids (Marcin R *et al*., 2007). PBAT, in particular, may be made using normal polyester manufacturing technique and equipment by poly condensing BDO, PAT, and AA, as shown in Figure 1.1 (Jian, J.,2020).

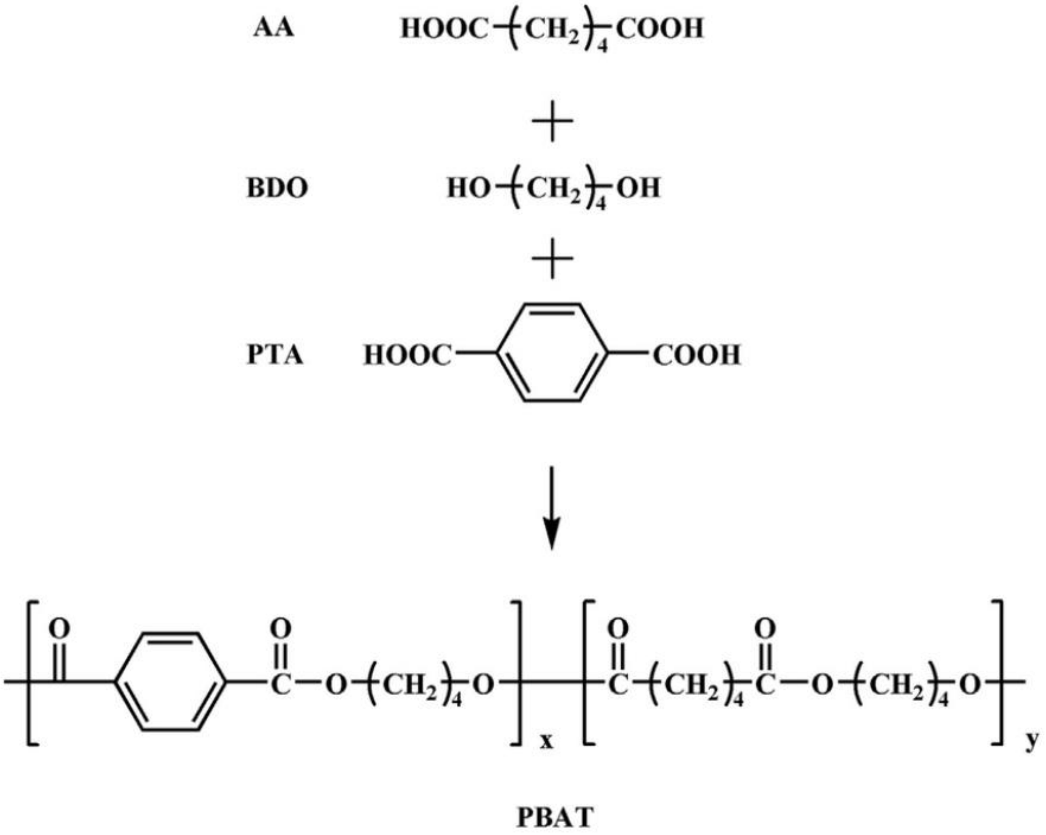


Figure 1.1: Schematic diagram of synthesis of PBAT. 17.(Jian, J., 2020)

As polycondensation catalysts, organometallic compounds based on zinc, tin, and titanium can be employed. Pre-mixing, pre-polymerization, and final-polymerization processes are used in the synthesis of PBAT. The preparation of PBAT necessitates a long reaction time, a high vacuum, and a temperature of at least 190 C. These conditions are required to favour condensation reactions and remove the lighter molecules (water) as a product (Staneva D. *et al.*, 2007). To optimize PBAT crystallization behaviour and avoid tack, nucleating agents can be employed in the final polymerization process of PBAT manufacturing. The most appropriate nucleating agents are often inorganic compounds, such as talc, chalk, mica, or silicon oxides. Phosphorous substances such as phosphoric acid and phosphorous acid can be used as colour stabilizers in the pre- or post-polymerization process, however this reduces the condensation rate.

Chromism has become a booming research field in various scientific domains (Bamfield P *et al.,* 2001). In the world of textiles, chromic materials also have a lot of promise. Besides the well-known thermo-chromism and photochromism, the less exploited halochromism(or pH-sensitivity) may be of great value for various textile applications such as wound dressings, protective clothing etc. (Van der schueren & de clerk et *al.,* 2012). These textile pH-sensors function effectively than previously used sensor materials due to their comfort, flexibility, and potential for a vast coverage area. Thus, research has focused on the correlation between the chemical structure of newly developed dyes and their halochromic behavior in solution rather than on their behavior in a textile material (Thirumurgan P *et al.,* 2019). It is indeed generally recognized that a changing microenvironment affects the halochromic behavior of dyes (Ertekkin K *et al.,* 2003).

pH is an important parameter in many fields that may be utilized in a variety of ways. The colour of halochromic material varies when the acidity of the surrounding medium changes. This properties of halochromic material enables it to be used in a broad range of application such as intelligent packaging for food freshness, textile industry, medical sector, pH paper etc (Prietto *et. al,* 2018). Halochromic material can be integrated into food packaging to measure food quality and freshness. Extrusion, calendaring, injection moulding, transfer moulding, compression moulding, and solution casting are examples of well-known polymer processing processes that may be used to incorporate halochromic dyes into polymeric materials. Adsorption of dyes into polymers or polymer dispersion by coating are the mechanisms involved.

Conventional dyeing, sol-gel technique, and electrospinning has been used to obtain pH sensitive materials (Van der Schueren & Clerck, 2012).

In the present work, the effect of different dye in PBAT/Starch/PEG blending will be assess. Starch will act as a plasticizer in PBAT plant pot fabrication. Methyl red and thymol blue is use in this study due to its colour response from brownish yellow to reddish violet (phenol red) and yellow to blue (bromothymol blue) when exposing to different pH. Phenol red is responsive in range of 6.5-8.0 while bromothymol blue is responsive in the range of 6.0-7.6 providing significant value in various plant. Another formulation of adding Polyethylene Glycol (PEG) with fixed composition were assessed. Moreover, this thesis also highlights the mechanical properties of the PBAT film using tensile testing by following ASTM D882 standard and thermal analysis using thermogravimetric analysis. For the halochromic properties, some characterization methods will be used such as visual observations, colour analysis, and Fourier transform infrared (FTIR) to study the halochromic behavior of the PBAT film.

1.2 Problem Statement

In general, a variety of halochromic materials have been investigated in terms of their physical, chemical, and mechanical characteristics. The majority of the fabrics were made from textiles, nanofibers, and synthetic polymers, but not many of them were made from biodegradable polymers. Furthermore, most synthetic dyes are damaging to the environment and are linked to allergic, poisonous, and other negative reactions (Devarayan and Kim, 2015). As a result, biodegradable polymer PBAT is employed as a raw material in this study to create halochromic material.

Among the bioplastics, poly (butylene adipate-co-terephthalate) is a biodegradable random copolymer with aromatic and aliphatic chains, specifically a co-polyester of adipic acid, 1,4-butanediol, and terephthalic acid. It is a synthetic semicrystalline thermoplastic polyester, with mechanical and thermal properties similar to those of some polyethylene's (U. Witt *et. al* 1996). PBAT is a totally biodegradable polymer that may be used as a replacement to low-density polyethylene and has comparable desirable characteristics, such as flexibility, as compared to PLA, which is brittle. By mixing PBAT with other polymer, the characteristics of PBAT may be changed by changing the monomer unit composition. The use of starch as a dye carrier and plasticizer is intended to provide PBAT additional flexibility. However, just a few studies on the plasticization of starch into PBAT have been published.

For creating smart PBAT with enough acceptable colour shifts, the impact compositions of halochromic dye, bromothymol blue, and phenol red concentration are crucial. To ensure good mechanical characteristics, the appearance of the films, and the high mobility of the dye incorporated into the films, fixed composition starch and PEG were used.

Currently, the halochromic plastic blend was not used for agriculture application. Developing a smart PBAT plant pot using poly (butylene adipate-co-terephthalate), starch, polyethylene glycol (PEG) and halochromic dye is seen as a potential research and challenge. The target of the sample materials was to have optimum and clear colour change at acidic and alkaline region at the same time to have optimum mechanical properties.

1.3 Research Objective

The research objectives of my Final Year Project are as follow:

1. To fabricate smart PBAT plant pot that has halochromic properties.
2. To assess the effect of different amount of PEG toward PBAT/Starch/PEG blending in mechanical, thermal properties and halochromic responsive.

1.4 Expected Outcome

From this research, it was expected that the PBAT-pH sensors can be produced. It was postulated visible colour change will occur towards acid and alkaline due to the presence of thymol blue and methyl red dye as the dye interact with the pH stimulus. Orange colour were expected to be observed at acidic and green colour were expected in alkaline conditions. It was expected that higher polyethylene glycol composition leads to higher colour variation of the sensors.

1.5 Thesis Outline

Chapter 1 introduces the smart material, halochromic material, pH sensitive dye and PBAT. Polymers utilised to make halochromic material, pH sensitive dyes that have been added into halochromic material in the last year, and PBAT characteristics are all discussed. This chapter also contains the problem statement, objective, research study scope, and thesis outline.

Chapter 2 discusses the literature review of the study. Smart material, halochromic material, type of smart material, mechanism of colour change properties in halochromic materials, type of polymer used as halochromic, and their application are discussed in detailed in this chapter.

Chapter 3 provides the information about the material and the procedure in this study. The general description of the material such as PBAT, tapioca starch, PEG, thymol blue and methyl red are given in this chapter. Characterization techniques such as SEM, FTIR, tensile properties, TGA, UV-Visible, accelerated QUV, colour change by visual inspection and real-life plan application are included as well.

Chapter 4 discuss the experimental result, findings, and discussion. A more detailed elaboration and explanation about the molecular structure, tensile, thermal, and morphological properties, colour change and real-life plan application are provided in this chapter.

Chapter 5 summarizes the significant findings in this study. Recommendations and suggestion for future study are also provided as well

CHAPTER 2
LITERATURE REVIEW

2.1 Smart material

In the last two decades, smart materials research has attracted a lot of attention. In response to external stimuli, these materials will change their colour, size, solubility, and form, among other things. Alloys, composites, gels, and polymers have all been explored for a number of uses ranging from aerospace to medical technology. Smart materials may be designed with a range of reactions and actuation methods, depending on the demands of the application.

Smart materials are materials that can be altered to respond in a reversible and controlled way to external stimuli, changing some of their characteristics. Pressure, temperature, electric and magnetic forces, chemicals, hydrostatic pressure, and radioactive radiation might all be stimuli. According to (Kamila et al., 2017), The associated changeable physical properties could be shape, stiffness, colour, optical or thermal changes.

With technical advances in engineered materials, sensors, actuators, and image processing, the subject of smart materials and structures is quickly evolving. The self-adaptability, self-sensing, memory, and numerous capabilities of a smart material or structure are used to define its smartness. These properties make these materials and structures suitable for a wide range of applications in aircraft, industrial, civil infrastructure systems, and biomechanics. This characteristic can be utilized to activate the smart material embedded in the host material in a proper way to compensate for the fault (Voyiadjis & Ph, 2003).

2.1.1 Classification of smart material

Todays, there are numerous types of smart material available which are piezoelectric, thermo-responsive materials, magneto strictive materials, polymer gels and chromogenic materials (Kamila, 2013). However, many of these technologies are still in the research stage and have yet to be commercialized. According to Arvind Kaushal (2016), smart or intelligent material can be active or passive, Table 2.1.

Table 2.1: Classification of Smart Materials (Kaushal, 2016).

Smart materials	**Examples**	**Definition**
Active	Piezoelectric	When piezoelectric material is exposed to an electric charge or a change in voltage, it will alter mechanically, and vice versa. The direct and converse impacts are the terms used to describe these events.
	Magneto Strictive	This material will experience induced mechanical strain when exposed to a magnetic field, and vice versa (direct and reverse effects). As a result, it can function as sensors and/or actuators.
Passive	Fiber Optics	Fibres that use intensity, phase, frequency, or polarization of modulation to measure strain, temperature, electrical/magnetic fields, pressure, and other measurable quantities. They are excellent sensors.

2.1.2 Chromic material

Chromic materials are materials that modify, radiate, or erase colour. As a suffix, chromism denotes a reversible change in colour, as well as a reversible change in other physical attributes. Chromic materials are also known as chameleon materials because of their ability to change colour. This colour changing phenomenon is caused by the external stimulus and chromic materials can be classified depending on the external stimulus of induction (P.Talvenmaa, 2006) as shown in Table 2.2:

Table 2.2: Classification of Chromic Materials and Their External Stimulus (P.Talvenmaa, 2006).

Classification of chromic materials	External Stimulus
Photochromic	Light
Thermochromic	Heat
Electrochromic	Electricity
Piezochromic	Pressure
Solvatechromic	Liquid
Carsolchromic	Electron beam
Halochromic	pH value

2.1.2(a) Photochromic material

Photochromic materials change their colour by light and these materials are both organic and inorganic, but the most studied are organic photochromic materials. There are also photochromic materials called heliochromic compounds, which are activated by unfiltered sunlight and deactivated under diffuse daylight conditions. Therefore, they are suitable for sun lens applications (Bouas-Laurent, H., & Dürr, H., 2016).

With variations in light intensity, photochromic materials change colour reversibly. In a dark environment, they are usually colourless, but when exposed to sunshine or UV-radiation, the material's molecular structure changes and it takes on colour. The colour vanishes when the appropriate light source is removed. Changes from one colour to another colour are possible by mixing photochromic colours with base colours (Lukkassen, 2016).

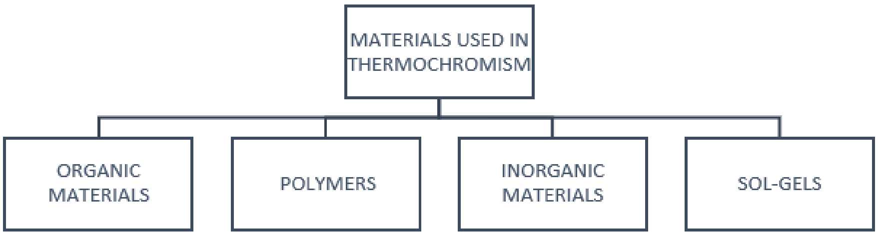
When photochromic pigments are exposed to sunshine or UV radiation, their structure changes, resulting in a colour shift. The reversible transition might be from colourless to colour or from one colour to another using a mix of photochromic conventional dyes. For industrial or construction applications, the lifespan of these compounds is quite limited.

Photochromic materials are used in lenses, paints, inks and mixed to mould or cast materials for different application (Lukkassen, 2016). In textiles, photochromic compounds are mostly utilized for ornamental effects in jacquard fabrics, embroideries, and printing on various clothing.

2.1.2(b) Thermochromic material

Thermochromic materials change colour as a result of heat reaction, particularly when thermochromic dyes whose colours change at specific temperatures are used. Two types of thermochromic systems have been used successfully in textiles, the liquid crystal type, and the molecular rearrangement type (P.Talvenmaa, 2006).

Thermochromic materials change colour in response to temperature changes in a reversible way. Semiconductor compounds, liquid crystals, and metal compounds can all be used to make the materials. The thermochromic transition happens when the colour changes at a particular temperature. In the 1970s, encapsulated dyes were used to create thermochromic materials. Japanese businesses patented the technology, which was then mostly used to the textile and novelty industries. Textiles and novelty items, toys, and baby spoons are just a few examples of commercial products that employ thermochromic materials.



There are different mechanisms according to which materials are used. The following four materials used in thermochromism, as shown in Figure 2.1.

Figure 2.1: Materials Used in Thermochromism

2.1.2(c) Electrochromic material

Electrochromic material undergoes a permanent but reversible colour shift as a result of an electrochemical reaction, a process known as electrochromic. The reversible and apparent change in transmittance and/or reflectance associated with an electrochemically driven oxidation-reduction process is known as electrochromic. It is caused by the production of various visible area electronic absorption bands when redox states are switched. The colour transition is usually between a transparent ('bleached') and a coloured state, or between two coloured states. When an electrochromic material has more than two redox states available electrochemically, it can display several colours and is referred to as poly-electrochromic or multicolor-electrochromic. This optical change is affected by a small electric current at a low d.c. potential of the order of a fraction of a volt to a few volts (Carl M. Lampert, 2004)

Electrochromic materials, which change their optical properties in response to an electric field and can be returned to their original state by a field reversal, have major advantages (Carl M. Lampert, 2004) such as a small switching voltage (1–5 V), they show specular reflection, they possess a grey scale, they require power only during switching and they exhibit adjustable memory, up to 12–48 hours.

Electrochromic devices are commonly used in large area switching devices. They are being developed for various applications such as building and vehicle windows, mirrors, and electronic books. Many chromic materials can be fabricated on plastic substrates, which is an advantage for future display applications (P.R. Somani, 2003). One example of an electrochromic display is a paper-thin one that's controlled by a printed circuit. The display can be powered by a rechargeable battery or a photovoltaic cell.

2.2 Halochromism

Chromism refers to a colour change, which is characterized by an irreversible (remains in the new state after reaction) or a reversible (returns to its nearly original state after reaction) colour changing process (Bilgin, 2021). Halochromic substances have the functionality of pH indicators (acid/base) to determine pH changes in combination with a colour shift (Peters and Freeman, 1995), which may be used to measure the progress of a chemical reaction or describe the condition of a chemical system.

A change in colour is caused by a different protonation state of the compound–different charge states at different pH values (Schwartz, 2002). It uses chemical indicators that measure the difference between a pH range of 1-14. A halochromic material can also be used to make paints that change colour when the water in contact with them changes. The term pH refers to how acidic or basic a material is in relation to its hydrogen ion concentration. A subgroup of chromotropic materials is halochromic materials. They are sensitive to a property change in the environment (influencing factor) and respond to an external stimulus with a reversible or irreversible reaction, which in this case is pH fluctuations.

2.2.1 Halochromic dye

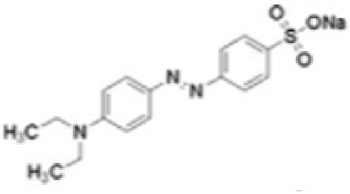
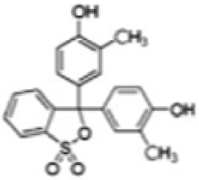
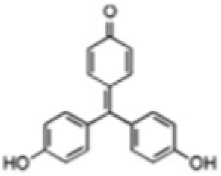
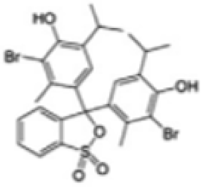
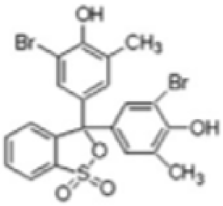
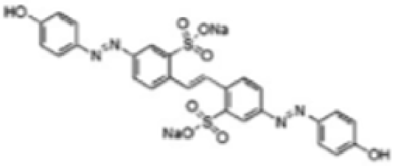
Generally, pH indicator is a halochromic chemical compound that causes the color of the solution to change depending on the value of pH (A. Agarwal *et al.*, 2012). The pH is a very important characteristic of solutions of many substances. For example, pH–dependent electrical potential variations inside glass electrodes16 or photometrically determined changes in the vis–absorption17 and fluorescence18 of suitable indicator–dye molecules are established ways for determining it. Acid–base indicators are the most often used indicator dyes in spectrophotometry units. A weak acid or a weak base serve as an acid–base indicator. The colour of an indicator does not shift from pure acid to pure base at a precise hydrogen ion concentration, but rather throughout a wide range of concentrations. The colour change interval, which is stated as a pH–range, is the name given to this range. Table 2.3 shows the pH ranges and colour changes of different pH indicator dyes in aqueous solution (A. Agarwal *et al.*, 2012).

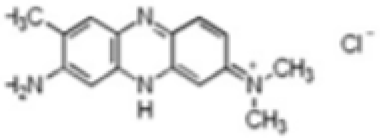
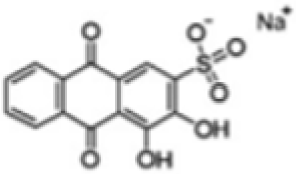
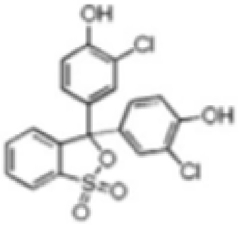
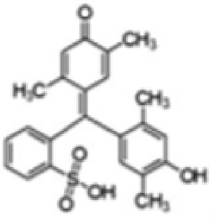
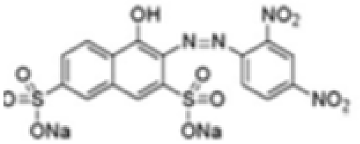
Table 2.3: pH ranges and colour changes of different pH indicator dyes in aqueous solution (A. Agarwal *et al.*, 2012).

pH Indicators	***pH range***	***Colour change***
Methyl Red	4.4–6.2	Red to yellow
Bromocresol Green	3.8–5.4	Yellow to blue
Bromothymol Blue	6.0–7.6	Yellow to blue
Phenol Red	1.2–3.0	Brownish orange to yellow
	6.5–8.0	Brownish yellow to reddish violet
Phenolphthalein	8.3–10	Colourless to fuchsia

2.2.2 Mechanism of colour change properties in halochromic materials

Table 2.2: The molecular structure of pH-indicator dyes

pH-indicator dyes	Molecular structure
Ethyl Orange	
Cresol Red	
p-Rosolic Acid	
Bromothymol Blue	
Bromocresol Purple	
Brilliant Yellow	

Neutral Red	
Alizarin Red	
Chlorophenol Red	
Xylenol Blue	
Nitrazine Yellow	

When deprotonated, most halochromic dyes display a bathochromic or hypsochromic shift of the absorption peak and are classed as positive or negative halochromic dyes. Bathochromic and hypsochromic shift is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength. Ring opening mechanism involved upon the deprotonation of the halochromic dyes which the ring opening in the molecule of halochromic dye or on a tautomerism, as tautomers have different colours and tinctorial strengths, which contribute to the colour change properties of the dye (Van der Schueren

& de Clerck, 2012). It is based on the phenomena, which generate the change of the electron density of substances, especially π- or d-electron state, or the change in the arrangement of the substance supramolecular structure (Rijavec & Bračko, 2007). Figure 2.3 shows the ring opening upon deprotonation of phenolphthalein halochromic dye.

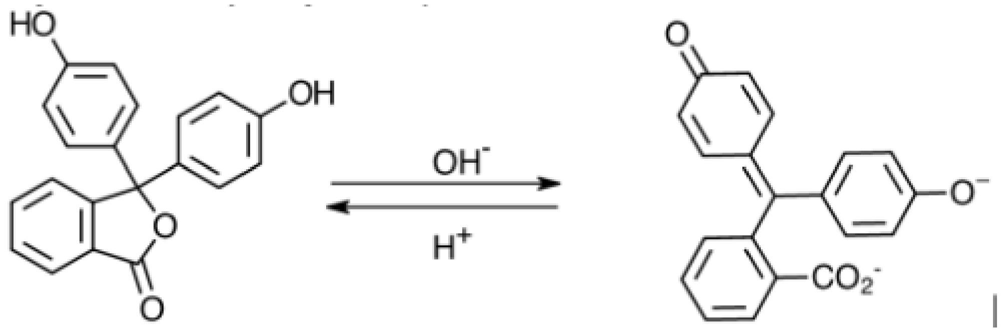


Figure 2.2: Ring opening upon deprotonation of phenolphthalein halochromic dye left (colourless) to right (red colour) (Van der Schueren & de Clerck, 2012).

Another kind of chain-growth polymerization is ring opening mechanism (ROP), in which the terminal end group of a polymer chain functions as a reactive centre where additional cyclic monomers can react by ring-opening and adding to the broken bond to build a longer polymer chain. Coordination, covalent, ionic (anionic or cationic), metathetic, radical, and enzymatic are some of the most common terms used. Active chain - end or activated monomer processes can be separated based on the position of the active species. Cyclic monomers that have been polymerized via ring - opening encompass a variety of structures, such as alkanes, alkenes, compounds containing heteroatoms in the ring: oxygen, sulfur, nitrogen, phosphorus, or silicon (Duda & Kowalski, 2009).

2.3 Type of polymer used as halochromic

There are many types of polymers that have used as base materials in halochromic materials such as cellulose acetate (CA), polystyrene (PS), poly (acrylonitrile) (PAN) and Polybutylene co-adipate terephthalate (PBAT).

2.3.1 Cellulose Acetate (CA)

(Derayan et al., 2019) have been reported halochromic thin film sensors for monitoring the degree of spoilage of packed seer fish. In this research, they have been prepared three halochromic thin film sensors by combining cellulose acetate, starch/potato dextrose agar, polyvinyl alcohol, and BCG as halochromic dye. Fourier-transform infrared spectroscopy was used as for characterization.

Image processing and colour measurement such as CIE Lab and RGB value determination was used to evaluate the response of halochromic thin film sensors. Good halochromic sensing properties was obtained for real-time monitoring spoilage of packed seer fish at room temperature. Under moisture condition, the stability of BCG/CA was further evaluated for spoilage monitoring at 4˚C and 2˚C. The BCG/CA thin film sensor showed excellent obviously identifiable colour shifts from yellowish red to greenish blue to dark blue in proportion to packed fish rotting, according to the findings.

2.3.2 Poly (lactic acid) (PLA)

In the research that have reported by (Jia Yam et al., 2020), they have reported the ability of polylactic acid blends with polyethylene glycol (PEG) and bromocresol purple (BCP) dye as an innovative for pH sensing. They found that the e halochromic PLA-BCP pH film has a clear color response from yellow to purple at pH 3–11 with a rapid response time within a minute. The interactions between PLA, PEG, and dye were due to entrapment of dye within PLA. In comparison to changing dye compositions, the results demonstrated that modifying PEG concentration had a substantial influence of halochromic responsive on reaction time. In terms of film strength, the combination of PEG and dye increased the PLA film's flexibility while also giving it a halochromic property.

2.3.3 Polystyrene (PS)

Polystyrene nanofibrous mats (PSNF) containing the bromothymol blue (BTB) indicator was reported by (Miranda et al., 2020) and it were obtained by solution blow spinning technique for the pH sensing of wine sample. The smart PS nanofibers that were created were visually sensitive to changes in pH in both aqueous and vapour mediums. The addition of BTB to PS fibres did not result in significant morphological changes to the nanofibers, but it did result in the production of beads that helped the dye to be encapsulated.

As a consequence of this research, the PS nanofibrous mat's halochromic potential was linked to a quick chromatic reaction to red wine vapour, causing a change in the nanofibers' colour owing to the presence of volatile acids in the beverage. They indicated that the PSNF/BTB-0.2 nanofibrous mats might be employed as a nanomaterial sensor for a variety of applications involving direct or indirect surface contact.

2.3.4 Poly (Acrylonitrile) (PAN)

(Noshirvani Sharifabad & Bahrami, 2016) reported that Nanofibers from PAN and PAN/phenolphthalein were prepared in research study. Electrospinning was used to make PAN/phenolphthalein nanofibers in this study, and it produced nanofibers with a smaller diameter than a PAN solution of same concentration under the same electrospinning circumstances. The viscosity of PAN was lowered by adding phenolphthalein to the solution, and pH sensitive halochromic nanofiber webs were utilised in the pH range of 8-13.

When these nanofibers come into touch with basic solutions, they change colour, and the nanofibers with smaller diameters show better colour change due to the larger surface contact area. The dye release of these webs was investigated, and it was discovered that webs with a larger nanofiber diameter release less dye. The results for halochromic nano sensor reusability and reversibility reveal that under these conditions, nanoweb may be used more than 200 times with no trace of colour change. It's also been noted that increasing the diameter of the nanofiber reduces dye release. This might be attributed to PAN shrinkage in this solution, and the web's colour stability could be linked to a putative interaction between PAN and phenolphthalein.

2.3.5 Polyamide-6

In the research done by (De Meyer et al., 2016), they showed that the application of pH-sensitive dye molecules onto textile materials is a promising method for the development of sensor materials. They incorporated ten commonly used pH-indicators, namely sulfonphthaleine dyes, onto polyamide 6 using two distinct methods which is conventional dyeing of fabrics and dye-doping of nanofibers.

Using conventional dyeing, a large influence of the substituents was found both on the leaching properties and the halochromic ability. A linear trend between the molecular weight of each dye and the amount of dye leached was found. It was also observed that only dyes with halogen substituents still exhibited pH-sensitive behaviour. Hydrogen bonds are possible for each dye molecule and, with the aid of molecular modelling, it was seen that the hydrogen bond interaction energy is about the same for each dye. Dyes with halogen substituents can also show halogen bonding, which was proposed to be an important contribution to the overall interaction. In conclusion, the substituents have both an indirect effect (molecular weight) and direct effect (halogen bonding) on the possible interactions with PA-6.

For the dye-doped nanofibrous non-woven, most dyes are in the neutral state during electrospinning form a formic acid/acetic acid mixture, meaning they have little to no tendency to interact with the polyamide chains. Moreover, the dye solubility will be enhanced when placed into an aqueous environment. When adding a polycationic complexing agent, however, it was seen that the leaching properties of two dye molecules with four bromine substituents greatly improved. From result in UV-Visible spectroscopy, it was seen that these dyes are still mostly in the anionic form, allowing for interaction with the positively charged complexing agent. This could be understood from the high electron withdrawing effect of bromine. The substituents have therefore an indirect effect on the interaction with PA-6 nanofibers, namely the (de)protonation state of the molecule in the electrospinning solution.

2.4 Application of smart materials

Halochromic materials have the capacity to change colour when subjected to diverse external stimuli such as pH, and the changes are plainly visible, therefore they have a wide range of applications. Table 2.4 show the application of smart material.

Table 2.4: The application of smart materials.

Halochromic	**Application**	**Polymer**	**Colour change**	**References**
Nitrazine Yellow	Smart textile	Glycidyl methacrylate	Yellow to blue	[34]
Black carrot	Wound healing	SA/PVA	Red to black-green	[24]

Lycium ruthenicum Murr	Smart food Packaging	κ-carrageenan films	Depending on the degree of spoilage of packaged shrimp	[28]
Halochromic dye		CA//PVA/starch	Light blue to dark blue	[9]

2.4.1 Smart textile

Halochromic materials can be applied in smart textile application. The study shown by (Trovato V. *et al.*, 2021) was focused on the development of a Nitrazine yellow-glycidyl (NY) methacrylate coating onto cotton fabric through thermal-induced radical polymerization reactions: a simple approach towards wearable pH sensors applications. In this paper, the bifunctional monomer glycidyl methacrylate (GMA) was employed in a simple two-step synthetic strategy with the aim of developing a Nitrazine Yellow-based pH-meter wearable sensor. Both reactions have been confirmed by Nuclear Magnetic Resonance Spectroscopy and by Infrared Spectroscopy, respectively. Furthermore, the morphology of the treated cotton samples was studied by means of Scanning Electron Microscopy. Figure 2.4 and 2.5 shows the graphic abstract and solutions after 1 and 5 washing cycles and images relative to pH-dependant colour variation of samples after different laundry cycles.

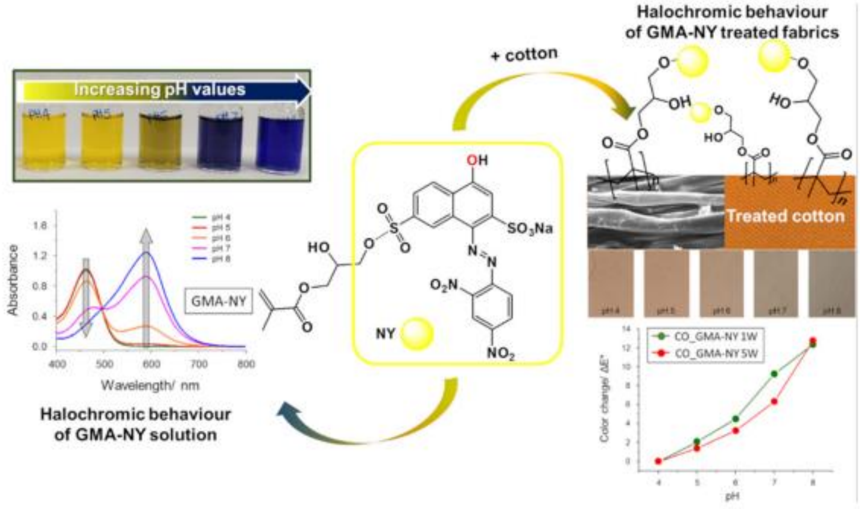


Figure 2.3 : Graphic Abstract (Trovato V. *et al.*, 2021)

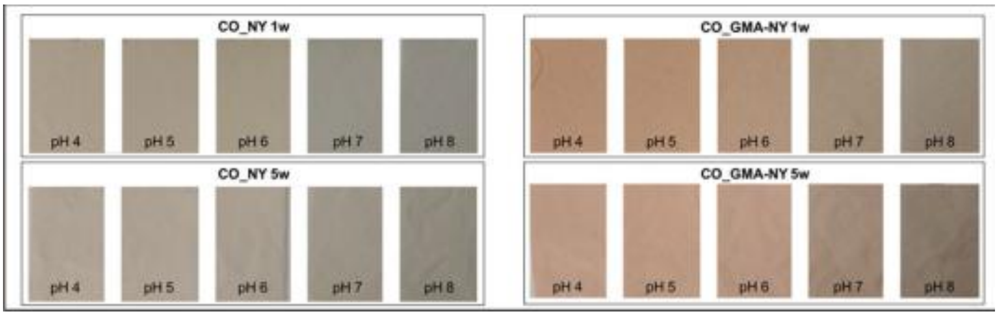


Figure 2.4: Solutions after 1 and 5 washing cycles and images relative to pH-dependant colour variation of samples after different laundry cycles (Trovato V. *et al.*, 2021)

The pH halochromic behaviour of the functionalized NY molecule was studied both in solution and onto the fabrics, by means of UV–Vis Spectroscopy, UV–Vis reflectance measurements and CIELAB colour changes. All experimental findings confirmed that the immobilized NY dyestuff still pertains consistent and typical halochromic properties in the pH range 6.0–7.0. The novel functional fabric developed in this work paves the way to non-disposable and reversible wearable pH sensors in smart textiles.

2.4.2 Wound healing

The study by (Ayben Pakolpakçl *et al.*, 2019) shown that halochromic materials can be applied in wound healing application and they were focused on the development and characterization of a wound dressing for pH monitoring based on a sodium alginate (SA) and polyvinyl alcohol (PVA) nanofibrous mat including anthocyanins extracted from black carrot (BC). PVA/SA-based halochromic nanofibrous mat for wound healing monitoring was prepared using the electrospinning process. The crosslinking of the nanofibrous mat was carried out using glutaraldehyde (GA). The visual colour change of PVA/SA/BC electrospinning solutions and crosslinked PVA/SA/BC nanofibrous mats are presented in Figure 2.6.

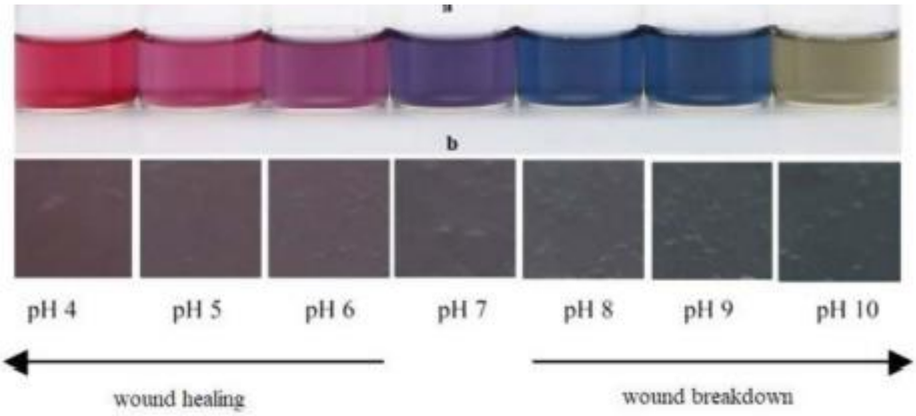


Figure 2.5: The colour schemes at pH4.0–10.0, (a) PVA/SA/BC electrospinning solutions, (b) crosslinked PVA/SA/BC nanofibrous mats (Ayben Pakolpakçl *et al.*, 2019).

For halochromic behaviour, the PVA/SA/BC nanofibrous mats exhibited halochromic behaviours exactly same to PVA/SA/BC electrospinning solutions, demonstrating that natural pH-indicator anthocyanins (extracted from BC) were successfully integrated into the nanofibrous mats. The halochromic PVA/SA/BC nanofibrous mat with a short response time presented visibly distinguishable colours, especially at pH of 4.0–6.0 and 8.0–10.0, which are consistent with the pH changes in