STUDY ON HYDROLYSIS OF POLYVINYL ACETATE TO

POLYVINYL ALCOHOL

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STUDY ON HYDROLYSIS OF POLYVINYL ACETATE TO

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by

VINESSA MATHIVANAN

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LIST OF SYMBOLS

Symbol	Description	Units
Mv	Viscosity-Averaged Molecular Weight	g/mol
DH	Degree of Hydrolysis	%
S	Saponification value	-
V_2	Volume of HCl consumed by blank	ml
V_1	Volume of HCl consumed by sample	ml
M	Molarity of HCl solution	M
W	Weight of sample	g
E1	Experimental result 1	-
E2	Experimental result 2	-

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
EDX	Energy Dispersive X-Ray Analyzer
FDA	Food and Drug Administration
FP	Filter Paper
HCl	Hydrochloric Acid
MCC	Micro Crystalline Cellulose
NaOH	Sodium Hydroxide
PD	Petri Dish
PVA	Polyvinyl Alcohol
PVAc	Polyvinyl Acetate
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
VAc	Vinyl Acetate
VA	Vinyl Alcohol

KAJIAN HIDROLISIS POLYVINIL ASETAT KEPADA ALKOHOL POLYVINIL

ABSTRAK

Alkohol polivinil, PVA adalah polimer yang boleh dibiodegradasikan dan larut air dengan aplikasi yang luas dalam pelbagai industri. Kebelakangan ini, hidrogel dan campuran PVA telah menemui aplikasi luas dalam industri bioperubatan kerana sifat kelarutannya yang tinggi. Kelarutan PVA sangat dipengaruhi oleh tahap hidrolisis PVA. Tesis penyelidikan yang dibentangkan ini mengkaji kesan parameter yang berbeza seperti suhu tindak balas, masa tindak balas dan jenis pemangkin terhadap tahap hidrolisis PVA. Reaksi hidrolisis polivinil asetat, PVAc dilakukan dalam metanol pelarut dengan kehadiran pemangkin alkali, natrium hidroksida, NaOH pada suhu 40, 60 dan 80 ^{o}C dan masa tindak balas 30, 45 dan 60 minit. Untuk pemangkin asid, asid hidroklorik, HCl suhu dan masa tindak balas ditetapkan sebagai 60 ^{o}C dan 60 minit. Titrasi dengan asid atau alkali masing-masing dilakukan untuk menentukan tahap hidrolisis PVA. Kedua-dua parameter, suhu dan masa tindak balas adalah berkadar terus dengan tahap hidrolisis. Pemangkin alkali menghasilkan PVA yang lebih dihidrolisis berbanding pemangkin asid pada keadaan tindak balas yang sama. Kelarutan PVA meningkat dengan peningkatan tahap hidrolisis sehingga 91% dan kelarutan PVA menurun melebihi nilai hidrolisis itu. Pengimbasan Mikroskop Elektron, SEM digunakan untuk mengkaji morfologi permukaan PVA manakala Tenaga Dispersive X-Ray Analyzer, EDX digunakan untuk mengenal pasti komponen-komponen PVA. Berdasarkan analisis ANOVA, suhu optimum dan masa tindak balas untuk menghasilkan PVA tahap 97% hidrolisis adalah 79.93 ^{o}C dan 59.91 minit.

STUDY ON HYDROLYSIS OF POLYVINYL ACETATE TO POLYVINYL ALCOHOL

ABSTRACT

Polyvinyl alcohol, PVA is a biodegradable and water soluble polymer with vast application in various industries. In recent years, PVA hydrogels and blends have found wide application in the biomedical industry due to its high solubility property. The solubility of PVA is greatly affected by the degree of hydrolysis of the PVA. The presented research thesis studied the effect of different parameters such as reaction temperature, reaction time and the type of catalyst on the degree of hydrolysis of PVA. The hydrolysis reaction of polyvinyl acetate, PVAc was done with solvent methanol in the presence of alkali catalyst, sodium hydroxide, NaOH at temperatures 40, 60 and 80 ^{o}C and reaction times 30, 45 and 60 mins. For acid catalyst, hydrochloric acid, HCl the temperature and reaction time were set as 60 ^{o}C and 60 mins. Titration with acid or alkali respectively was done to determine the degree of hydrolysis of PVA. Both the temperature and reaction time were directly proportional to the degree of hydrolysis. Alkali catalyst produced more hydrolyzed PVA compared to acid catalyst at the same reaction conditions. The solubility of PVA increased with increasing degree of hydrolysis up to 91% hydrolysis and beyond that value the solubility decreased. Scanning Electron Microscope, SEM was used to study the surface morphology of PVA while Energy Dispersive X-Ray Analyzer, EDX was used to identify the components of PVA. From ANOVA analysis, the optimum temperature and reaction time to produce 97% hydrolyzed PVA is 79.93 ^{o}C and 59.91 mins.

CHAPTER ONE : INTRODUCTION

This chapter presents the overview and background of the research. It provides the introduction to PVA and its wide applications in the industry which led to the interest of many to do research on its properties. Chapter one is divided into four sections which are the research background, problem statement, research objectives and the scope of study.

1.1. Research Background

At present there is increasing interest in producing biodegradable polymers for various applications. One among those is PVA a synthetic biodegradable, water-soluble and polyhydroxy polymer with excellent mechanical properties. PVA is a versatile polymer, and it is a one of a kind synthesized polymer with a backbone that consists primarily of hydroxyl bonds that is biodegradable. PVA is available in the form of powders, fibers and films. PVA has a broad range of applications. PVA is widely used as a polymer in the production of adhesives, fibers, paper, membranes, drug release media, pharmaceutical and so on. It is tasteless, odorless and possesses good mechanical properties. It is also resistant to oil, grease and solvent. It has high ability to form films and a good compatibility in human tissues and fluids which makes it a good choice for drug deliveries. Figure 1.1 shows the vast market size of PVA films in the year 2013 and the prediction of its market size increase in the near future (Reporters, 2016).
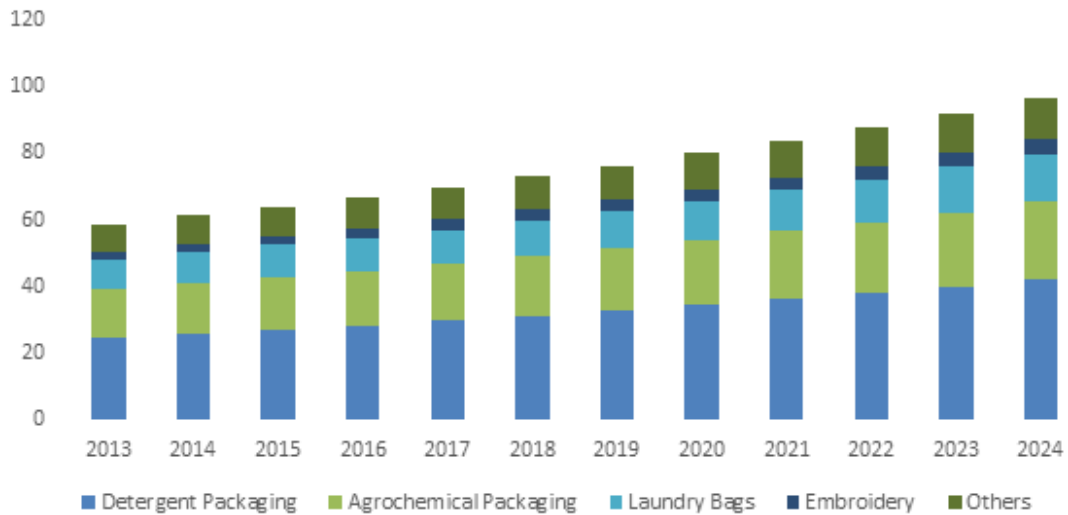
Figure 1.1 : US PVA film market size from 2013 to 2034 (Reporters, 2016).

The growing concern about health hazards from waste disposal has boosted the polyvinyl alcohol films market in recent years. Moreover, the stringent government regulations restricting the use of certain packaging materials have caused many packaging companies move towards the usage of polyvinyl alcohol films leading to the growing market size of PVA films.

PVA is very suitable and now has wide usage in pharmaceutical and biomedical industries since it is also not have mutagenic such that PVA-based microspheres were approved by the Food and Drug Administration (FDA) and other regulatory organizations for embolization. Depending on the type of additives they contain, PVA hydrogels are biocompatible in nature and possess non-irritating properties on soft tissues which makes them worthy for many biomedical applications. Some examples of PVA present in biomedical products are contact lenses and wound dressing (Chaouat et al., 2008). `

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1.2 Problem Statement

The production and use of PVA in many industries as mentioned earlier as grown throughout the years. In order to enhance the properties of PVA, they are usually treated with nature-based fillers such as chitosan, micro crystalline cellulose (MCC), and cotton fibers (Afghan, 2016). There is also addition of plasticizer agents to overcome film brittleness, one of its mechanical properties, caused by high intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chains, which improves the flexibility and extensibility of the film. Glycerol and polyethylene glycol are the most popular plasticizers used in film-making techniques, due to stability and compatibility with hydrophilic bio-polymeric packaging chain (Ismail and Zaaba, 2011).

Most of the literatures and studies conducted are on the additives and their influence on the properties of PVA at the end of the process. Cross-linking of PVA is also reported for property enhancements like compliance, elasticity and resistance to mechanical stress. The novel cross-linking is achieved by physical procedures (UV or gamma radiation) or by using chemical cross-linkers such as glutaraldehyde, formaldehydeor and epichlorohydrin (Chaouat et al., 2008). The solubility, mechanical properties and biodegradability of the PVA can also be obtained as desired by tweeting the degree of hydrolysis of PVAc, the raw material used to produce PVA. This approach will avoid the additional costs on the blending or cross linking-processes as well as reduces the possible toxicity of plasticizers. Therefore, this research is conducted to study the parameters which could affect the degree of hydrolysis of the PVAc to produce PVA.

1.3 Research Objectives

Following are the research objectives :

1. To study the effect of reaction temperature on the degree of hydrolysis of polyvinyl acetate to polyvinyl alcohol.

2. To study the effect of reaction time on the degree of hydrolysis of polyvinyl acetate to polyvinyl alcohol.

3. To study the effect of different type of catalyst used on the polyvinyl alcohol produced.

1.4 Scope of Study

This study focuses on the parameters affecting the hydrolysis of the PVAc to PVA. The polymerization of vinyl acetate (VAc) to PVAc are not studied rather, it is just described in the literature review for better understanding of the subsequent hydrolysis process. The parameters that were studied in this experiment are temperature of reaction, the time of reaction and the type of catalyst of hydrolysis reaction. The choice of catalysts was sodium hydroxide (NaOH) as the alkali catalyst and hydrochloric acid (HCl) as the acid catalyst. The temperatures of the reaction studied were 40, 60 and 80 ^{o}C while the reaction times chosen to be experimented were 30, 45 and 60 mins. The catalyst/PVAc mole ratio was set as 0.06 for all the sets of experimental runs. For alkali catalyst, experiments were conducted at different temperatures and time while for acid catalyst, the experiment was done only for one specified temperature and time as the purpose was to compare the performance of acid and alkali catalyst at constant temperature and reaction time. Eventually the product PVA was tested for its solubility in water structural morphology using Scanning Electron Microscope, SEM.

CHAPTER TWO : LITERATURE REVIEW

Chapter two presents the previous works and findings by other researches on PVA and its properties. The chapter works its way through the brief description on the monomers of PVA, the hydrolysis of PVAC to produce PVAc and finally the effect of different parameters like reaction temperature, reaction time and type of catalyst on the degree of hydrolysis of PVA. The relation between degree of hydrolysis and solubility of PVA is also presented in this chapter.

2.1 Production of Polyvinyl Alcohol

2.1.1   Vinyl Alcohol

PVA is not produced commercially by the direct polymerization of vinyl alcohol unlike any other polymers. The vinyl alcohol (VA) PVA's monomer, does not exist in a free state and is unstable in nature. VA happens to be the isomer of acetaldehyde. Hence, at normal conditions it tends to convert to acetaldehyde through a process called tautomerization. The acetaldehyde is more stable than vinyl alcohol. The conversion between acetaldehyde and VA is shown below in Figure 2.1.
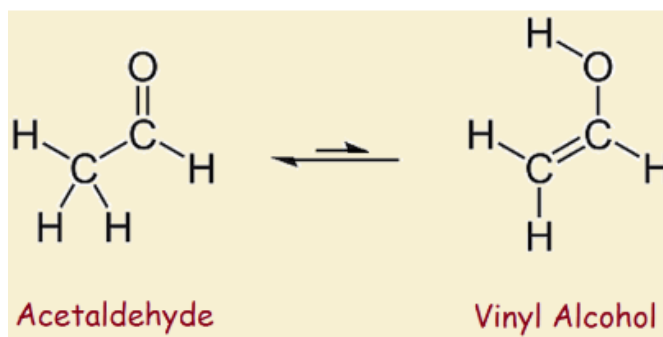
Figure 2.1 : Tautomerization of vinyl alcohol and acetaldehyde (Balcerak et al., 2012).

The double bond between the carbon atoms is easily rearranged to form the double bond in the carbonyl group of the acetaldehyde. The reaction requires low activation energy to rearrange into a much stable double bond which is the carbonyl group. It is such because the C=O is more polar as the oxygen atom is more electronegative in comparison to the C=C double bond. The basic chemistry says that a compound always tends to react until it reaches its at most stable form, in this case the acetaldehyde (Bouma et al., 1977).

2.1.2 Polymerization of Vinyl Acetate

The year 1926 saw the first major industrial use of PVAc where it was used as the intermediate in the production of PVA. The polymerization process was and is done by free radical solution polymerization in methanol but it has its own disadvantage. In order to produce higher molecular weight PVAc emulsion polymerization is preferred. Emulsion polymerization is a free radical polymerization in a heterogeneous reaction system whereas free radical solution polymerization occurs in a homogenous dispersion. The most widely used monomers are styrene, butadiene, vinyl chloride, various acrylates and vinyl esters where copolymerization is of these monomers are done to improve the resulting PVAc properties. The heterogeneous environment is commonly created by surfactant-stabilized oil-in-water solution (Bruyn, 1999). Figure 2.2 shows the simple mechanism of free-radical polymerization.
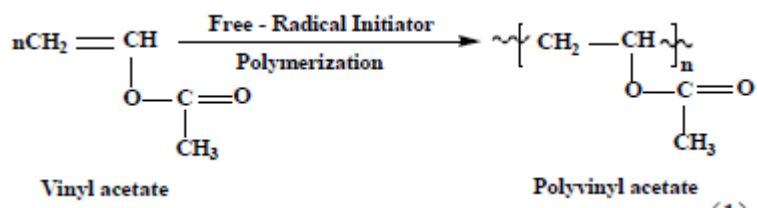
Figure 2.2 : Free-radical polymerization of VAc (Haweel and Ammar, 2008)

The emulsion polymerization occurs in three stages namely interval I, II and III. Interval I is defined as the period of particle formation where an emulsion of surfactant-stabilized monomer droplets in water is formed. A water-soluble initiator is added to this solution which eventually decomposes to produce the free radicals required to initiate polymerization. Interval II is the period of particle growth. The droplets act as monomer reservoirs leading to the particle's growth until all the droplet phase monomer is consumed. Interval III is the final stage, when the monomer droplets are exhausted. During this period, monomer concentration decreases which in turn decreases the polymerization rate. Figure 2.3 shows the simple illustration of the three phases of emulsion polymerization.
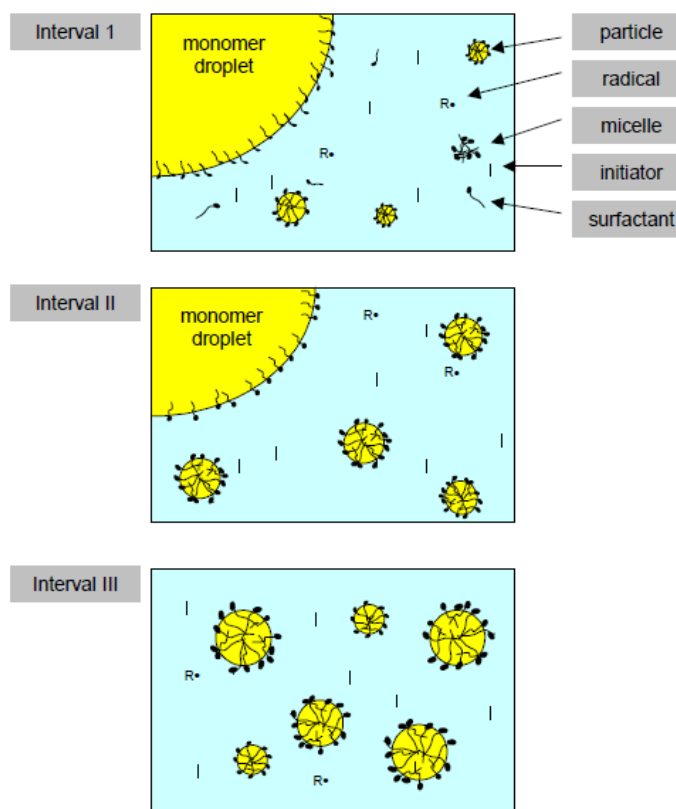
Figure 2.3 : The three stages of emulsion polymerization (Bruyn, 1999).

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2.1.3   Hydrolysis of Polyvinyl Acetate

The hydrolysis reaction of PVAc to produce PVA was first introduced by Herrman and Haehnel in 1924. The catalysts most often used for the hydrolysis reaction are alkali catalyst like sodium or potassium hydroxide, methoxide, or ethoxide. PVAc is produced in continuous mixed flow reactors. A special design of the mixing equipment is required to obtain PVA with a uniform and sustained degree of hydrolysis where it is also known as degree of saponification. The first step in the hydrolysis or saponification reaction is the attack on the carbonyl carbon atom of the acetate group by the anion from alcohol (CH_3O^-) (Alihemati and Navarchian, 2017). Unlike the methanol soluble PVAc, PVA is moderately soluble in methanol and thin white flakes of PVA are precipitated out during the hydrolysis process (Haweel and Ammar, 2008). The hydrolysis reaction can be halted at different reaction times to produced desired degree of hydrolysis of PVAc. Figure 2.4 show reaction pathway of the hydrolysis process where PVA is produced as the desired product and methyl acetate is produced as the undesired side product.
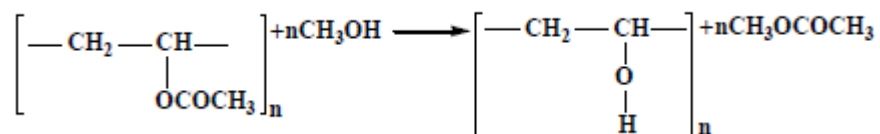
Figure 2.4 :Hydrolysis pathway of PVAc to produce PVA (Haweel and Ammar, 2008).

When PVAc is alcoholyzed with sodium hydroxide, NaOH as basic catalyst in methanol, a mixed polymer is formed containing both hydroxyl and acetyl groups. Starting as a homogeneous solution the solubility of the polymer ester in methanol decreases as increasing numbers of ester groups are converted to hydroxyl groups (Snyder et al., 1960). As a ratio of hydroxyl to acetyl groups increases, the solvent – solute relationship in the

reaction mixture changes, passing through a stage at which it is swollen and somewhat water – solubility. The increase in hydroxyl group contributes to the PVA solubility in water (Minsk et al., 1941).

The figure 2.5 shows the different side products produced from the hydrolysis of PVAc. In the presence of methanol the side product is methyl acetate and the process is widely known as alcoholysis. In the presence of water the side product is acetic acid and it is known as hydrolysis. The different types of solvent and their corresponding use of catalyst is described in detail in Section 2.2.3.
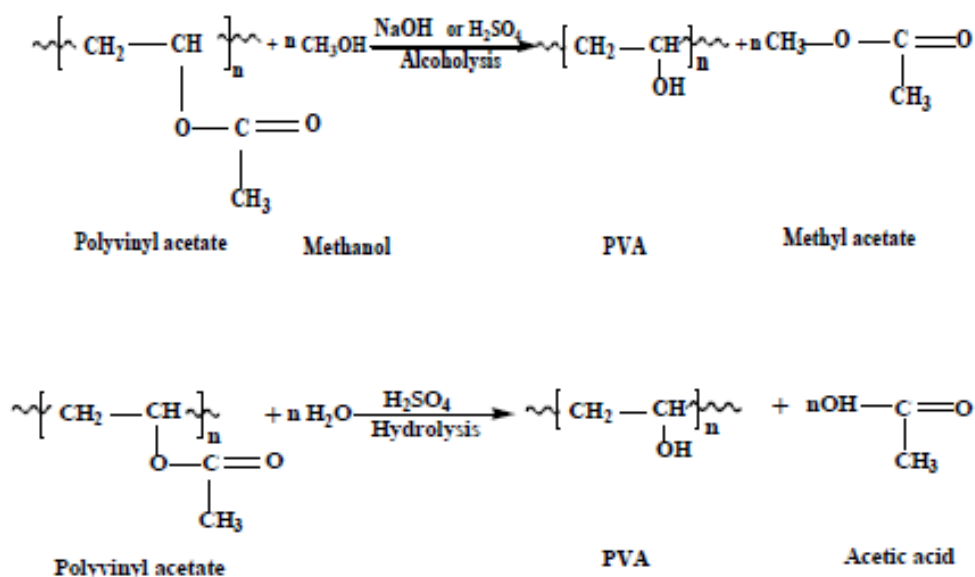
Figure 2.5 : Side products produced with different solvent (Haweel and Ammar, 2008).

2.1.4 Degree of Hydrolysis

An important aspect of PVA is that the degree of hydrolysis determines the mechanical properties that PVA possesses, like the tensile strength of 99% hydrolyzed PVA is 67-110 MPa and the tensile strength is lowered to 24-79 MPa for reduction of the hydrolysis degree by 10%. As this study concentrates on the solubility of PVA it was found that the water solubility of PVA is also strongly associated to the degree of hydrolysis (Haweel and Ammar, 2008). Fully hydrolyzed PVA has low water solubility compared to partially hydrolyzed PVA (Illanes, 2010). The reason behind this behavior is further explained in detail in Section 2.4.

The most common commercial grades classified by the degree of hydrolysis is as follows:

Fully hydrolyzed (1 – 2 mol% acetate groups)

Intermediate hydrolyzed (3 – 7 mol% acetate groups)

Partially hydrolyzed (10 – 15 mol% acetate groups)

Partially hydrolyzed PVA is also known as a copolymer of both VAc and VA as it contains both hydrophilic and hydrophobic parts in its structure.

The applications of PVA also differ based on the degree of hydrolysis of PVAc. Completely hydrolyzed PVAs are widely used in water-resistant adhesive where higher degree of wet tack is required. Partially hydrolyzed PVAs are used in making films for packages for bleaches, bath salts, insecticides, and disinfectants.
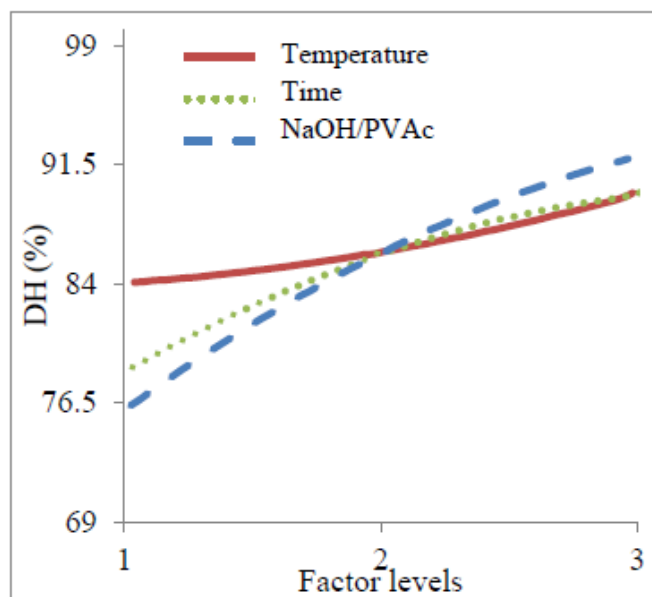
Figure 2.6 :Effect of different parameters on the degree of hydrolysis (Alihemati and Navarchian, 2017).

2.2 Operating Parameters in Hydrolysis of PVAc to PVA

Navarchian et al. (2009) and Lee et al. (2005) are among those who studied the effects of reaction time and temperature on degree of hydrolysis. They found that the higher degree of hydrolysis values were obtained for longer reaction times and higher temperatures (Navarchian et al., 2009, Lee et al., 2005). An obvious parameter that influences the degree of hydrolysis is the increase in catalyst concentration or ratio. High catalyst concentrations decrease the activation energy of this step in the hydrolysis reaction leading to higher reaction rate and therefore a greater degree of hydrolysis (Haweel and Ammar, 2008). The Figure 2.6 shows the effects of different parameters on the degree of hydrolysis. The degree of hydrolysis increases with all parameters.

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2.2.1 Temperature of Reaction

The usual temperature range for the reaction is 20 to 60 $^\circ$C. Beyond 60 $^\circ$C, there is a high tendency for the solvent to evaporate which leads to the usage of reflux system (Shibutani et al., 2010). Higher reaction temperatures lead to higher degree of hydrolysis because the rate of reaction increases with temperature especially in the presences of an alkali catalyst (Alihemati and Navarchian, 2017). High reaction temperatures though, has a risk of undesired reaction like in the presence of unconverted VAc monomers, it may react with the methanol to produce acetaldehyde and alkyl acetate. The alkyl acetate may eventually form metal acetate reacting with the alkali catalyst used. Figure 2.7 shows the results data of different reaction temperatures reported by Haweel and Ammar (2008) using alkali catalyst NaOH. At any reaction time and catalyst ratio the reaction temperature of 50 $^\circ$C has higher degree of hydrolysis compared to 25 ^{0}C.

Temp.($^\circ$C)	Time (min.)	Catalyst Ratio			
		0.01	0.02667	0.04334	0.06
25	20	56.6	58.34	65	73
	43.3	59	60.5	67	75.99
	66.6	67.71	76	82	87.9
	90	78.77	89.65	97.5	98.31
50	20	59	63	69.5	75.55
	43.3	61.99	68.8	72	79.46
	66.6	65.12	77.74	83.83	90
	90	79	90.69	97.25	99

Figure 2.7:Hydrolysis degree of PVA using NaOH (Haweel and Ammar, 2008).

2.2.2 Time of Reaction

Degree of hydrolysis increases with increasing reaction time because more amount of time leads to increase in number of hydroxyl groups in the polymer chain. The presence of autocatalytic effect enhances the reaction further. (Alihemati and Navarchian, 2017, Haweel and Ammar, 2008). When an acetate group of the PVAc hydrolyzes it produces acetic acid which functions as a catalyst on its own. This leads to further hydrolysis of other acetate groups of the polymer leading to the production of fully or partially hydrolyzed PVA. Increasing number of hydroxyl group in the polymer chain may also contribute to the hydrolysis where it exerts adjacent neighboring effect known as anchimeric effect (Jones et al., 2017).

2.2.3 Type of Catalyst

Sodium hydroxide, NaOH and hydrochloric acid, HCl are the common catalyst used in the industry for the hydrolysis reaction of PVAc. The base-catalyzed reaction has an advantage where it enables faster reaction to happen and the process is more economical. However, it is difficult to control the VAc :VA ratio. The remaining VAc monomers during partial hydrolysis are rather blocky. The acid-catalyzed reaction in the presence of water, on the other hand, is much slower, because water has a larger affinity for proton rather than the polymer. This advantage however is that it is easier to control the VAc : VA ratio, particularly when water-acetic acid is used as a solvent (Park and Yoon, 2005). The alkali catalyst is much more preferred compared to the acid catalyst in the industry due to its faster reaction rate. In the presence of an alkali catalyst the hydrolysis

reaction is endothermic where it requires energy to proceed with the reaction to produce PVA (Alihemati and Navarchian, 2017).

Referring to the Figure 2.5 provided in Section 2.1.3, the presence of acetic acid creates the autocatalytic effect. This implies that when the amount of acetic acid produced is controlled the hydrolysis can be controlled. One noticeable point here is that only acid catalyst is used when water is used as solvent. Such scenario has occurred because in the presence of water especially in higher amount along with alkali catalyst such as NaOH, the catalyst is consumed in the reaction. The side product acetic acid tends to react (acid-base reaction) with NaOH to produce acetate, a salt. Since acetic acid is a weak acid, the presence of high amounts of water will initiate the easy dissociation of it eventually react with the strong base. This undesired reaction dominates the PVAc hydrolysis reaction, leading to lesser amount of NaOH to remain in the solution. Thus, the rate of reaction is reduced (Sakurada, 1985). Hence, methanol is usually used as solvent in the presence of NaOH as the catalyst.

Other possible alkaline catalyst include potassium hydroxide, guanidine carbonate, sodium methyl carbonate and sodium ethoxide (Haweel and Ammar, 2008). Other acids that are useful as a catalyst to the reaction are sulfuric acid and perchloric acid. In comparison, in order to obtain the same degree of hydrolysis higher concentration of acid catalyst is required than alkali catalyst. The reaction rate of hydrolysis is dependent on the first power of the concentration of the alkali catalyst, and on the 1.22 power of the concentration of the acid catalyst (Minsk et al., 1941). Some of the disadvantages of acid catalyst faced by the industries are these acids are extremely corrosive to the usual materials of construction of the unit operations in the plant and the acid catalyst along with

their salts are non-volatile adding to the mass of PVA. The separation of these undesired substances in our end-product is very costly (Bristol and Lewiston, 1961).

2.3 Response Surface Methodology (RSM)

Most reports and experimental conducts use 'one-at-a-time' approach to study the parameters and their effects on the degree of hydrolysis. Alihemati and Navarchian (2017) have used the RSM method to optimize the response. It provides the smallest possible number of experimental runs to specify statistically the influences of the different parameters on the performance and determine the optimal conditions for the process, in this case the hydrolysis. Apart from degree of hydrolysis as the primary response, the article also reports on a secondary response which is viscosity-averaged molecular weight (M_v).

The Table 2.1 shows the experimental runs obtained from the use of Design Expert Software by the mentioned article.

Table 2.1 : Experimental runs based on Box-Behnken method using design expert (Alihemati and Navarchian, 2017).

Trial no.	Factors			Responses	
	A	B	C	DH (%)	M_v (g/mol)
1	50	40	0.06	85.90	35090
2	40	40	0.04	72.00	49000
3	60	20	0.06	83.33	38540
4	40	40	0.08	90.91	32400
5	60	60	0.06	90.60	33900
6	40	20	0.06	78.18	47000
7	50	40	0.06	86.60	35050
8	60	40	0.08	94.90	31400
9	50	40	0.06	85.30	36000
10	60	40	0.04	81.72	40540
11	50	60	0.04	79.00	44000
12	50	20	0.04	69.00	57000
13	50	60	0.08	99.80	30560
14	50	20	0.08	80.80	43570
15	40	60	0.06	87.50	34900

Alihemati and Navarchian (2017), has used the ANOVA analysis to study the effect of different parameters on the degree of hydrolysis. The F–ratio obtained from the analysis is useful to identify the extent of the parameters' impact towards the degree of hydrolysis. Higher F-ratios depict the higher influence of that particular parameter. The p-values on the other hand depict how significant the studied parameter is towards the response (degree of hydrolysis). Alihemati and Navarchian (2017) discovered in their experiment that the interactions of temperature of reaction, reaction time and catalyst ratio had minor effect on the response has compared to their individual effect. The R^2 value was about 0.97 to 0.98 referring that the model fits the empirical data.

Equations of polynomial models were developed to fit the experimental results. The second order polynomials that the article reports is as following.

$$\text{DH (\%)} = 85.93 + 2.74 \times A + 5.70 \times B + 8.09 \times C - 0.51 \times A \times B - 1.43 \times A \times C + 2.25 \times B \times C + 0.85 \times A^2 - 1.88 \times B^2 - 1.90 \times C^2 \qquad (2.1)$$

$$M_v \text{ (g/ml)} = 357967 - 2356.00 \times A - 5343.75 \times B - 6576.25 \times C + 1865.00 \times A \times B + 1865.00 \times A \times C - 2.50 \times B \times C - 1121.08 \times A^2 + 4326.42 \times B^2 + 4076.42 \qquad (2.2)$$

Where A is the factor reaction temperature, B is the factor reaction time and C is the factor of catalyst to polymer ratio. Table 2.2 shows the ANOVA analysis data obtained by the article. Since the p-values from the mentioned table are less than 0.005 both the regression models are able to describe the functional relationship between the experimental factors and the response variables.

Table 2.2 :ANOVA with F-ratio and p-value (Alihemati and Navarchian, 2017)

Factor	Degrees of freedom	Sum of squares	Mean square	F-Ratio	p-value
Temperature (A)	1	4.475 E+007	4.475E+007	19.49	0.0069
Time (B)	1	2.284E+008	2.284E+008	99.50	0.0002
NaOH/PVAc (C)	1	3.460E+008	3.460E+008	150.70	<0.0001
AB	1	1.391E+007	1.391E+007	6.06	0.0571
AC	1	1.391E+007	1.391E+007	6.06	0.0571
BC	1	25.00	25.00	1.089E-005	0.9975
A^2	1	4.461E+006	4.461E+006	2.02	0.2144
B^2	1	6.911E+007	6.911E+007	30.10	0.0027
C^2	1	6.136E+007	6.136E+007	26.72	0.0036
Model	9	7.792E+008	8.658E+007	37.71	0.0005
Pure error	2	5.780E+005	2.890E+005	–	–
Lack of fit	3	1.090E+007	3.634E+006	12.57	0.0746

2.4 Solubility of PVA in Water

The solubility of PVA in water depends on the degree of hydrolysis of it as well. The solubility increases for partially hydrolyzed PVA as the degree of hydrolysis increase up to 87-89% hydrolyzed. Beyond it and fully hydrolyzed PVAs find difficulties in dissolving in water due to its high tendency to form strong hydrogen bonds as well as it easily forms gels (Chaouat et al., 2008). Due to the hydrophilic property of the PVA it possesses excellent water-retention ability making it the primary choice to produce PVA-based hydrogels used as membranes to transport selective macromolecule.

PVA does have a good dissolving ability due to its polarity but at higher compositions of hydroxyl group like in fully hydrolyzed PVA, there are more number of hydrogen bonds between intra- and intermolecular hydroxyl group preventing the dissolution of PVA in water. When there are significant number of acetate groups present in the structure of PVA, its hydrophobic property weakens the strength of the hydrogen bond in the PVA leading to better solubility of partially hydrolyzed PVA in comparison to fully hydrolyzed PVA (Haweel and Ammar, 2008).

Huggins and Duda have discussed in their studies that the dissolution of PVA is a complex process where it is much dependent on temperature, concentration and polymer molecular weight. They have also mentioned the presence of hydrogen bonding in the PVA structure affecting its solubility (Huggins, 1964, Duda, 1985).

CHAPTER THREE : MATERIALS AND METHOD

This chapter provides the methodology and the materials required for the experiment to be conducted. The chapter begins with a list chemicals required for the experiment followed by the flow chart of the research approach and finally ends with the detailed methodology of the experiment.

3.1 Materials

Table 3.1 show the materials required to conduct the experiment along with their purity and suppliers.

Table 3.1 : Materials required for the experiment.

Material	Purity	Supplier	Usage
Sodium hydroxide	>97% purity	SYSTERM	Catalyst
Methanol	>97% purity	Fischer Scientific	Reactant
Polyvinyl Acetate	-	Fischer Scientific	Reactant
Hydrochloric Acid	Analytical grade	QReC	Catalyst
Sodium Hydroxide	(0.5 M)	SYSTERM	Titration agent
Hydrochloric Acid	(0.5 M)	QReC	Titration agent
Distilled water	-	-	Washing liquid
Phenolphthalein powder	-	Modern-Lab Chemicals	Titration indicator

3.2 Experimental Setup

3.2.1   Flow Chart

Figure 3.1 below show the flow chart constructed to depict the sequential approach to conduct the hydrolysis experiment.

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┌──────────────────────────────────────────────────────────────────┐
│      Purchasing of raw material, PVAc and other required chemicals.│
└──────────────────────────────────────────────────────────────────┘
                                    │
                                    ▼
┌──────────────────────────────────────────────────────────────────┐
│                      Hydrolysis reaction setup                     │
└──────────────────────────────────────────────────────────────────┘
                                    │
                                    ▼
┌──────────────────────────────────────────────────────────────────┐
│                           Experiment :                             │
│                   Effect of temperature of reaction                │
│                      Effect of time of reaction                    │
│                      Effect of type of catalyst                    │
└──────────────────────────────────────────────────────────────────┘
                                    │
                                    ▼
┌──────────────────────────────────────────────────────────────────┐
│                        Product Analysis :                          │
│                          Mass Recovery                             │
│                        Degree of Hydrolysis                        │
│                         Solubility in water                        │
│                         SEM and EDX analysis                       │
└──────────────────────────────────────────────────────────────────┘
                                    │
                                    ▼
┌──────────────────────────────────────────────────────────────────┐
│ ANOVA Analysis and Optimization using Response Surface Methodology (RSM) │
└──────────────────────────────────────────────────────────────────┘
```
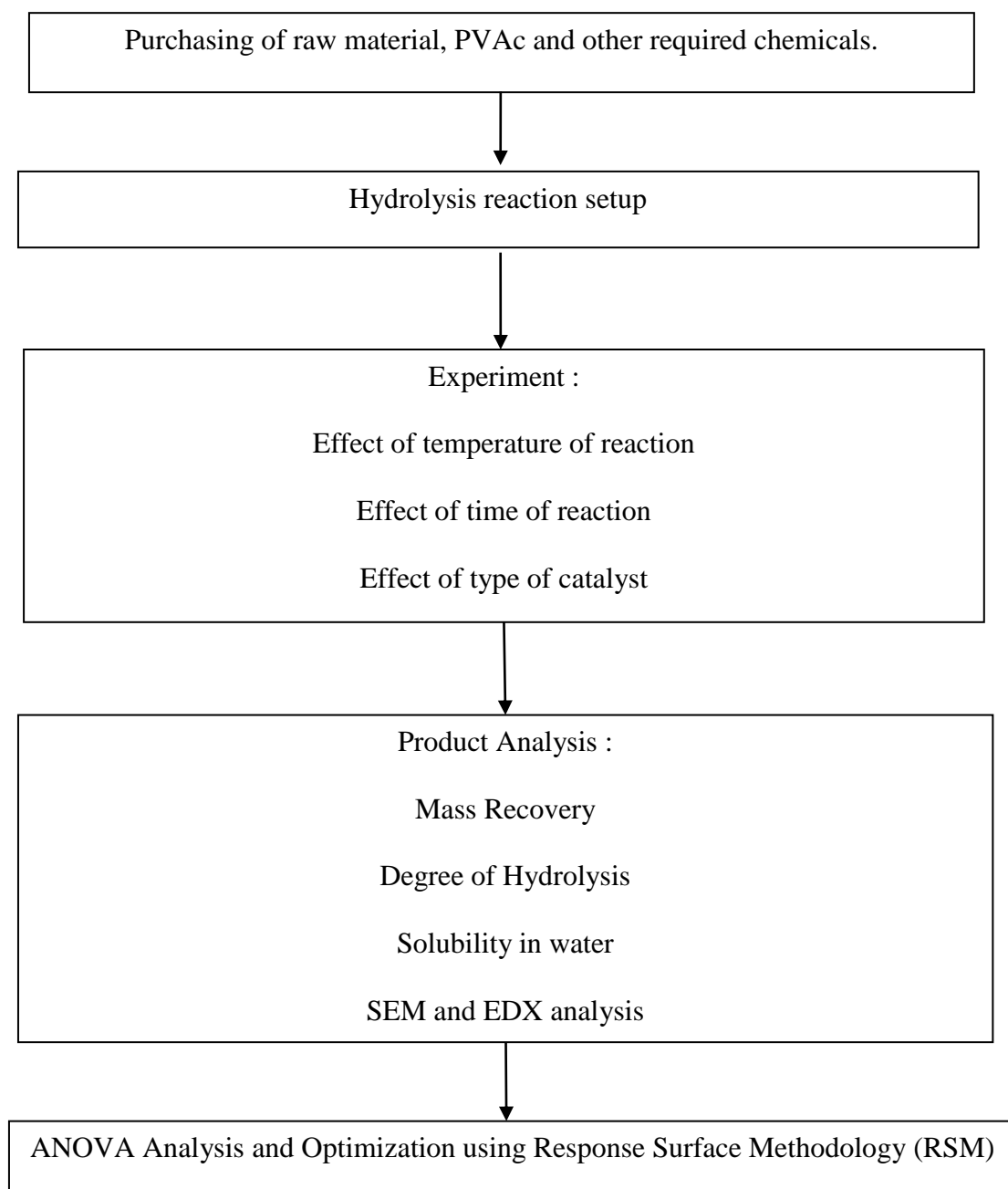
Figure 3.1 : The flow chart of conducting the hydrolysis PVAc to produce PVA.

3.2.2 Experimental Design

The experimental runs were designed using factorial design for parameters temperature and time of reaction in the presence of alkali catalyst, sodium hydroxide. In the presence of acid catalyst the temperature was set as 60 ^{o}C and time as 60 mins. This is to compare the PVA produced by acid and alkali catalyst at same reaction conditions. Table below show the experimental runs.

Table 3.2 : Experimental runs obtained from factorial design.

Alkali (Sodium Hydroxide)	
Temperature (^{o}C)	Reaction time (min)
40	30
60	30
80	30
40	45
60	45
80	45
40	60
60	60
80	60
Acid (Hydrochloric acid)	
60	60

3.3 Experimental Procedure

3.3.1 Hydrolysis

3g of PVAc was dissolved in 120 ml of methanol in the 250 ml round bottom flask. The polyvinyl acetate is purchased from Fischer Science. For all the experiments the concentration of the catalyst, NaOH or HCl was kept constant where the ratio of catalyst to polymer (PVAc) was 0.06. Then a solution of NaOH and methanol with 50:50 volume parts each was added to the PVAc solution. The hydrolysis reaction was allowed to occur at predetermined temperatures (40 ^{o}C, 60 ^{o}C, 80 ^{o}C) and time of reactions (30mins, 45mins, 60mins). The speed of stirring was set as 700 rpm. The mixing and heating was done under reflux system to avoid evaporation of solution especially methanol due to high reaction temperatures (Alihemati and Navarchian, 2017). The procedure was the same for the experiment conducted using HCl as the catalyst. Figure 3.2 shows the experimental setup for the hydrolysis reaction.

Figure 3.2 : Experimental setup of hydrolysis reaction with reflux system

3.3.2 Filtration and Drying

Once the hydrolysis reaction was done at predetermined temperatures and reaction time the solution was then filtered and washed with tap water using filter paper and filter funnel. The filtrate retained is scrapped of the filter paper and was put in a petri dish which is then dried in the oven at 60 ^{0}C overnight (Minsk et al., 1941). Figure 3.3 shows the oven utilized for the overnight drying of PVA while Figure 3.4 show the filtration process.

Figure 3.3: Filtration of product of hydrolysis reaction.

3.3.3 Titration and Degree of Hydrolysis

The titration was done to calculate the degree of hydrolysis of the polyvinyl acetate for given time and temperature of reaction. This titration procedure was adapted from the procedures prepared by 68[th] Joint FAO/WHO Expert Committee on Food Additives, JECFA. The dried sample was weighed first to obtain the mass recovery. 1g of the dried

sample was added to a 250 ml round bottom flask. Then 25ml of 0.5 M NaOH and 25ml of distilled water was added to the flask. The mixture was refluxed for 30 mins and 100 ^{0}C with a stirring speed of 500 rpm. After 30 mins the mixture is cooled to room temperature and immediately titrated using 0.5 M HCl. Two drops of phenolphthalein indicator was added for the titration. The indicator was prepared by dissolving 0.5g of phenolphthalein powder in 50 vol% of ethanol (50ml ethanol and 5ml water). The initial and final volume of HCl in the burette was recorded and the degree of hydrolysis was calculated using the following formula (Committee, 2007).

$$S = 39.997(V_2 - V_1) \times \frac{M}{W}$$

$$DH = 100 - \frac{(7.84 \times S)}{100 - (0.075 \times S)}$$

Where,

S = Saponification value

V_2 = Volume of HCl consumed by blank

V_1 = Volume of HCl consumed by sample

M = Molarity of HCl solution (0.5 M)

W = Weight of sample (1g)

DH = Degree of Hydrolysis