WAX-BASED EMULSIFIERS FOR WAX EMULSIONS FOR USE IN ENGINEERED WOOD PRODUCTS

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Abstract

In this study new value-added products were developed from four commercially available refined waxes for use as commercial emulsifiers via the technique of maleation. This research was performed in collaboration with an industrial partner with the hope of developing a wax emulsifier product that could replace commercially used wax emulsifiers in engineered wood product emulsions at a cost reduction by beginning with the design of a cost effective process that could be incorporated into an existing factory production line. Through the investigation and subsequent optimization of this process, a highly maleated product was achieved using 6 different quick and simple approaches. A standardized experimental design was applied to the parameters of the experiment: reaction time, peroxide, starting wax, maleic anhydride concentration, and temperature to observe and understand the individual effects of each on the resultant final product. Three organic peroxide initiators were evaluated; di-*tert*-butyl peroxide, di-*tert*-butyl peroxybenzoate and benzoyl peroxide, as well as a thermally initiated approach. The resultant waxes were then identified by their acid number and drop melt point; and from this, the overall efficiency of the combined parameter levels was calculated as a function the initial maleic anhydride amount versus that of the final. The maleated wax emulsifiers were incorporated into emulsions and applied to engineered wood products. Emulsifiers made via the thermally initiated approach showed statistically significant improvements in the desired properties, water absorbance and thickness swell, of the engineered wood products as compared to a commercial control formulation.

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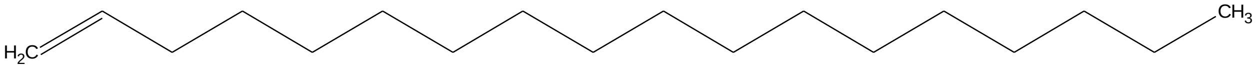

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ACE – Acetone Wash Technique

AN – Acid Number

BA – Bulk Addition

Bmill – Ball Milling

BPO – Benzoyl Peroxide

DG – Degree of Grafting

EWP – Engineered Wood Products

Exp Wax – Wax Emulsifier

FTIR – Fourier Transform Infrared Spectroscopy

G.Z. – Grafting Efficiency

KOH – Potassium Hydroxide

MAH – Maleic Anhydride

MEA – Monoethanolamine

Melt Temp – Drop Point Melting Temperature

M.W. – Molecular Weight

PA – Pulse Addition

PBlend AN – Preblend Acid Number

PE – Polyethylene

PI – Peroxide Initiated

PP – Polypropylene

PPu – Peroxide Pumping

RPW – Refined Paraffin Wax

RTime – Reaction Time

Solids (%) – Solids Content

TBP – Di-*tert*-butyl peroxide

TBPB – *tert*-butylperoxybenzoate

Temp – Temperature

TI – Thermally Initiated

Visc – Viscosity

VW – Vacuum Oven Technique

wt % - Weight Percent

WW – Water Wash Technique

List of Symbols

ν – Kinematic viscosity

ρ – Density

η – Dynamic viscosity

V_{KOH} – Volume of Standard KOH solution added to titration

MW_{KOH} – Molar mass of KOH

C_{KOH} – Concentration of Standard KOH Solution

mg_{KOH} – milligrams of KOH

$t_{1/2}$ – Half-life

N_2- Nitrogen Gas

AN – Acid Number

MW_{MAH} – Molar mass of Maleic Anhydride

wt $\%_{MAH}$ – Weight percent of maleic anhydride charged to reactor

m_E – Mass of emulsifier added

AN_E – Acid number of emulsifier

m_S – Mass of slack wax

AN_P – Acid number of pre-blend

Chapter 1: Introduction, Research Background and Objectives

1.1 Introduction to Waxes and Their Production Technologies

Waxes are comprised of polyethylene and/or polypropylene polymers having molecular weights less than 10,000 Mn [1]. Waxes are typically thermoplastic, insoluble in water and soluble in xylene at room temperature with melting points ranging from 90-200 degrees Celsius [1]. In 2003, the global demand for polyolefin waxes was estimated at 288 million pounds, this market has seen solid growth since then reaching an estimated 9200 million pounds demand in 2010 [2]. This growth has arisen primarily from the development of new applications for the wax due in part to the development of further modified, value-added versions of the polyolefin waxes [2].

The composition and structure of waxes can be easily tailored during production , in post-production modification or through the modification of such things as the wax molecular weight, branching or functional groups, allowing innovators of the wax industry to produce different products with unique and useful properties [3]. Consequently many commercial applications have been found for wax derived products [2]. In response to this increasing demand, new processes for the development of said waxes such as Fischer-Tropsch synthesis [4], Metallocene catalyzed wax production [5] and wax derivation from vegetables oils [6] have been developed and expanded.

Currently, the primary demand for waxes is for use in candles [2]. However, waxes and wax emulsions are also incorporated into a wide variety of other commercial products. Some examples of the commercial applications of polyolefin waxes are listed in Table 1, along with a brief description of the properties attributed to the addition the wax into the commercial product.

Table 1 Example commercial applications of polyolefin waxes

Commercial Application	Benefits of added wax components
Building Products (i.e. drywall, particle board, engineered wood products)	Water repellency, insulation [7]
Chlorinated paraffin	Plasticizing properties and lubricating properties [8]
Coatings	Oxygen permeability, water impermeability [9]
Inks	Improve brightness and sliding while preventing scratching [10]
Rubbers (i.e. tires)	Protective barrier from atmosphere (i.e. ozone) [11]

Waxes can be defined into many subclasses of wax corresponding to the processing approach of said waxes [1]. Some of the primary differences amongst these subclasses of polyolefin waxes include their chemical structure, homogeneity and oil content [1]. Table 2 lists some of the common commercial wax subclasses. For the purposes of this study, only three types: slack, refined paraffin and synthetic alpha-olefin waxes will be examined, presented in bold font in Table 2.

Table 2 wax subclasses [1]

Type	Examples
1. Natural Waxes	
1.1 Animal Waxes	Beeswax, Lanolin, Tallow
1.2 Vegetable Waxes	Carnauba, Candelilla, Soy
1.3 Mineral Waxes	
1.3.1 Fossil or Earth	Ceresin, Montan
1.3.2 Petroleum	
1.3.2.1 Paraffin	**Slack**, Scale Wax, **Refined Paraffin**
1.3.2.2 Microcrystalline	
1.3.2.3 Petrolatum	
2. Synthetic Waxes	
2.1 Ethylene polymers	Polyethylene, polyol ether-esters
2.2 Chlorinated napthalenes	

2.3 Hydrocarbon	Fischer Tropsch, Metallocene, **Synthetic Alpha-olefin**

1.1.1 Slack Wax

Slack wax is considered a subclass of paraffin wax although the term slack wax refers to a mixture of oil and wax (with oil contents between 3% and 50%) that is a side product derived from crude oil refining for the production of lubricating oil [1]. Slack wax was first refined in Canada in 1949 and initial production for that year was 5 million pounds per year, since then production has grown to 150 million pounds per year [12]. Slack wax usually consists of a range of hydrocarbon chains of varying lengths, degrees of saturation, branching and stereochemistry [13]. The degree of variability in each of these properties is a result of the crystallization, recovery and filtration processes used in refining the wax [14]. Minimizing the oil content of slack wax is important for improving the purity of the wax, promoting consistency in the desired properties of the wax and also because the lubricating oil is a valuable product [15]. High levels of lubricating oil in slack wax also renders the wax unsafe for use in food products [16].

A typical process used to separate slack wax involves the chilling and precipitation or crystallization of the wax from the wax oil mix followed by the addition of an oil solvent [17]. The rate of crystallization and amount of solvent added has a direct effect on the variety of structures present in the recovered wax. This is because differently structure hydrocarbon chains will crystallize at different rates and also interact with the solvent differently [14]. This means that modification of the crystallization and solvent addition processes can be used as a means of tailoring the properties of the final slack wax product [1][3]. The next step in purification involves filtering the wax from the solvent and oil in a separation zone [17]. The oil can then be recovered from the solvent [15]. The recovered wax further purified by repeating the process; however, each improvement in the purification process presents an additional economic concern that must be compared against the final return in order to justify it [17]. In some cases a further decolorizing or deodorizing step is added depending on the final desired properties for the slack wax [3].

Structurally, the majority of the hydrocarbon chains present in slack wax (between 80-90% of the wax content) are consistent with the unbranched "straight" fully saturated carbon chain structure known as paraffin structure and typically are between 20-30 carbons in length [1]. This structure is demonstrated in Figure 1.

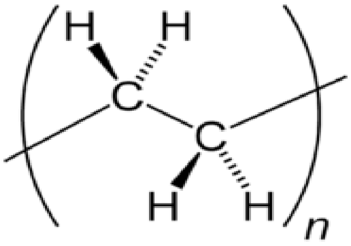
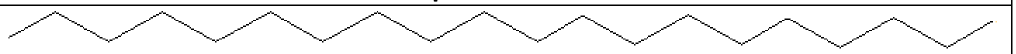


Figure 1 Paraffin hydrocarbon Chain General Structure[1]

The remaining portion of the slack wax may contain unsaturated hydrocarbon chains, branched hydrocarbon chains, known as iso-paraffins, hydrocarbon chains with cyclic carbon rings present within their structure, known as cycloparaffins and/or molecules with combinations of unsaturated, iso-paraffinic and/or cycloparaffinic structures [18]. These structures are demonstrated in Figure 2.

Chemical Composition	$H_3C\text{-}(CH_2)_n\text{-}CH_3$ n≈20-30
Name	**Example of Structure**
Paraffin	

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[1] Figure source: Polyethylene-repeat-2D.svg (Image is public domain)

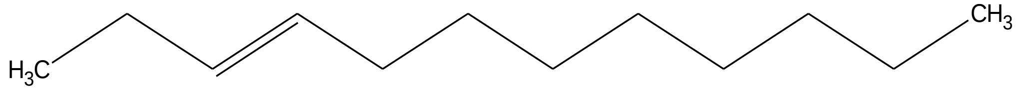
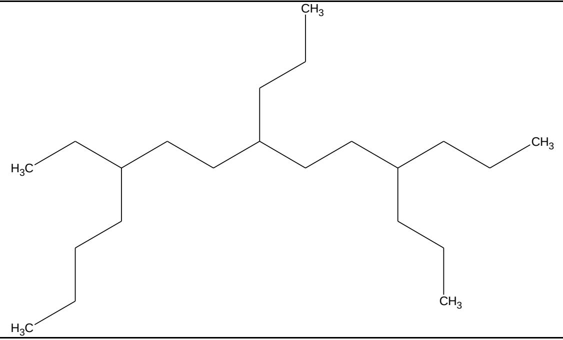
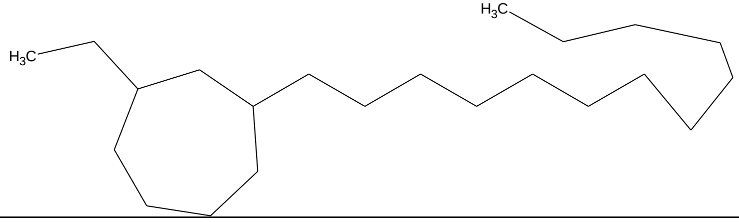
Unsaturated	
Iso-paraffin	
Cycloparaffin	

Figure 2 Examples of paraffin type structures present in slack wax [17]

Properties which govern the possible industrial applications of a slack wax such as melt point, penetration, viscosity, oil content and colour reflect the homogeneity and purity of said wax as well as the differing ratios of structurally different hydrocarbons and the interacting forces between these structures [1].

1.1.2 Refined Paraffin Wax

Refined Paraffin waxes, have a higher degree of purity than slack waxes as well as lower oil content (below 0.5%) [19]. Waxy parraffins were first identified by Carl Riechenbach in 1830 [20] and first produced in 1867 [21]. They can be derived from the same process in which slack waxes are derived following a more intensive separation process [16]. The improved purity and homogeneity seen in refined paraffin waxes results in enhancement of certain properties such as decreased toxicity, reactivity, color and combustion by-products [19]. Refined waxes also have a less variable melting point range which is typically between 100 and 160 degrees Celsius [1]. Refined Paraffin waxes are typically soluble in ether and benzene [19].

Refined Paraffin can also be produced synthetically by processes such as the Fischer-Tropsch reaction which involves the production of hydrocarbon chains from the catalyzed reaction of carbon monoxide and hydrogen [4].

1.1.3 Synthetic Alpha-Olefin wax

Synthetic alpha-olefin waxes are similar in structure to ``straight`` paraffin hydrocarbon chain waxes except that there is a unsaturated double bond present between the 1st and 2nd carbon, the alpha position, at the beginning of the hydrocarbon chain [22].

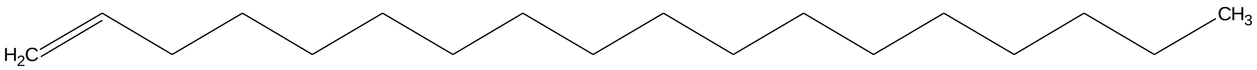


Figure 3 Example Synthetic n-Alpha-Olefin Structure [22]

These hydrocarbons have chain lengths ranging between 18-30 carbons and are prepared synthetically via the polymerization of ethylene [23] or by cracking paraffinic hydrocarbons [24]. The presence of the alpha unsaturated bond on the terminus of the synthetic alpha-olefin wax hydrocarbon chain enhances the reactivity of the molecule; because of this, unlike true fully saturated paraffin wax hydrocarbons, synthetic alpha-olefin waxes are not completely insoluble to water and are more sensitive to environmental contaminants including oxygen [23]. Synthetic alpha-olefins can react with oxygen to form peroxides, which in turn can react to form alcohols or carbonyls [23].

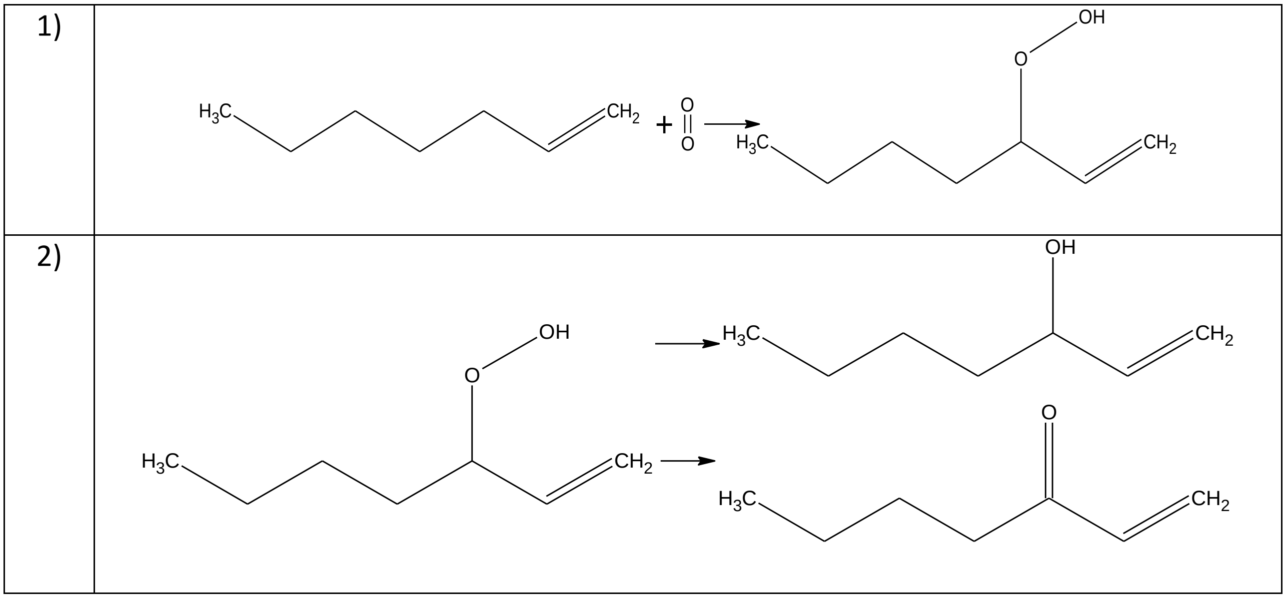


Figure 4 Synthetic Alpha-Olefin reactions caused by Oxygen Contamination

In the presence of drying agents, synthetic alpha-olefins may isomerize into less reactive internal olefins [23]. The presence of the unsaturated bond also affects the crystallization of the synthetic alpha-olefin leading to a less compacted product as compared to fully saturated hydrocarbon chains of the same length [23].

1.2 Wax Testing

Industrial waxes are tested in accordance with ASTM international standards [25]. Common tests include those for viscosity, color, drop melt point, needle penetration, oil content and density [25]. Gas chromatography and calorimetry are also used to measure wax properties [25]. These tests are further defined and described in chapters 1.2.1, 1.2.2, 1.2.3, 1.2.4, 1.2.5, 1.2.6, 1.2.7 and 1.2.8.

1.2.1 Viscosity

The work required to pump a wax or a composition containing wax depends upon its viscosity as does the utility of said composition as a lubricant [26]. The kinematic viscosity, v, is measured on a viscometer and then the dynamic or absolute viscosity, η, can be determined by multiplying the density, ρ, of the liquid by its kinematic viscosity as demonstrated in Equation 1 [26].

$$v * \rho = \eta$$

Equation 1 Dynamic viscosity equation

For the purposes of this study a rotational bob or Searle viscometer was used to measure viscosity. This device comprises a bob placed into the sample. The device then measures the torque that is required in order to maintain the bob rotating at a constant rate against the viscous resistance of the surrounding liquid, from this an estimate of the fluids viscosity is calculated [27].

1.2.2 Color

Color can be an important property of the developed wax because of its impact on the aesthetic of the final product in which it will be incorporated [28]. Color can also often be used as a simple indicator of the overall refinement or the presence of contamination within the wax product [28]. There are three common industrial color ranges used in measuring the color of petroleum products, the Saybolt, Gardner and Rosin Color scales [28]. For the purposes of this study wax products were compared against the Saybolt and Gardner color scales which examine colors ranging from white to red [28]. When color is an important property it is often described by having a upper Gardner or Saybolt limit at which point the color of the wax will negatively impact the aesthetic of the product in which it will be incorporated [28].

1.2.3 Drop Melt Point

The drop melt point of a wax is a common industrial term that describes the temperature at which a wax becomes significantly fluid so as to drop from a glass or metal rod or thermometer onto which it has been previously coated[28]. This method provides a less accurate discrete temperature point rather than a temperature range as seen in other melt point determination techniques. This level of accuracy is often sufficient for the temperature quantifications needed when examining a wax specifically when making energy requirement estimations for processing [29]. In cases where a more sensitive measurement of temperature is needed, such as when the final purpose of the wax will involve its use as an insulator, a more accurate melt point temperature reading must be taken or calorimetry may be used [28].

1.2.4 Needle Point Penetration

Needle Point Penetration is a common industrial term that describes the hardness of wax sample. Needle point penetration measures the penetration of a needle in a wax sample at a specific temperature, force and time [30]. It is performed when the wax sample is at either 25 or 40˚C. The needle point penetration distance is inversely related to the hardness of the wax, so hard waxes will have low needle point penetrations, while soft waxes will have high needle penetration numbers [30]. Needle point penetrations are typically standardized to a range from 1 to 25 [30].

1.2.5 Oil Content

The oil content of a wax can have a significant impact upon many of the wax properties including strength, hardness, flexibility, friction, expansion, melting point and straining [26]. The

ASTM standard for determining the oil content of a wax involves dissolving the oil-wax composition in methyl ethyl ketone and then precipitating the wax out of the solution at a lower temperature over a period of 2 hours, similar to the process through which waxes are refined [28]. New techniques are being developed to incorporate the use of NMR techniques to provide a safer and more rapid alternative for determining the oil content of a wax [31].

1.2.6 Gas Chromatography

Gas Chromatography is used to determine the carbon number distribution of a wax sample it is also used as a means of determining the ratio of straight chain hydrocarbons compared to non-straight chain hydrocarbons [32]. Results from the gas chromatography of waxes are compared against industry standards as a means of estimating the nature of the carbon number distribution and prevalence of non-straight chain hydrocarbons [28]. In cases where a more detailed understanding of the carbon number distribution is needed, mass spectrometry is used; however, this is not an industry standard [32].

1.2.7 Calorimetry

Differential Scanning Calorimetry is often used as the accurate way of measuring a waxes behavior over different temperature ranges [33]. This information can be used for determining the properties of a wax and also in the estimating the cost, energy and work requirements necessary in the processing of a wax [25]. There are two primary transitions that are measured through differential scanning calorimetry, one is the solid-liquid transition which is referred to as the complete melting transition. The other transition is the solid-solid transition which can provide useful information about the hardness of the wax and it's blocking temperature [33]. The blocking temperature is defined as the point in which a wax when placed between two sheets of paper will evenly adhere to both sheets of paper [25]. This is an important property because it demonstrates the temperature at which a wax can damage adjacent surfaces such as those of products it is meant to insulate [25].

1.2.8 Additional Tests for Maleation

Maleation refers to the grafting of maleic anhydride to a polymer chain. Additional tests that measure maleation are not typically industry standard, but they are important for the nature of this project. They extend into the realm of wax functionalization, In this case post processing. The ASTM standard for determining the maleation of a wax, i.e. the percent of grafted maleic anhydride to the wax, is achieved via the titration of the wax against a standardized potassium hydroxide solution in heated toluene (to ensure that the wax product is dissolved) with phenolphthalien as a visual indicator [25]. The volumetric quantity of the standardized potassium hydroxide solution needed to neutralize the solution and the mass of the wax dissolved in the toluene can be used to calculate the acid number of the wax [25]. The acid number is the milligrams of potassium hydroxide needed to neutralize the wax per gram of wax and is determined using Equation 2 [25].

$$Acid\ Number = \frac{V_{KOH} * MW_{KOH} * C_{KOH}}{m_{gw}} = \frac{mg_{KOH}}{g\ of\ grafted\ wax}$$

Equation 2 Acid Number Equation

Correcting for any acidity that may be contributed by the wax prior to its maleation, one can attribute the found acid number to the maleic anhydride groups grafted to the wax chains by assuming that it requires two moles of potassium hydroxide to neutralize one mole of maleic anhydride [34]. It is also possible to confirm grafting of Maleic anhydride on a wax using Fourier Transform Infrared Spectroscopy (FTIR) by the presence of specific peaks such as one at 1715 cm^{-1} which will be explained in detail further in chapter 2 [35].

1.3 Wax Modification

1.3.1 Introduction

Chemical modification techniques used to produce modified and/or functionalized large chain polymeric materials have been applied to the shorter chain wax analogs as a means of producing new value added products from wax precursors [36]. The techniques and understanding used to modify long chain polymeric materials can often be successfully applied to shorter chain wax materials of similar structure. Reasonable predictions can be made about the effectiveness of the technique and the properties of the final product [36]. A major difference between the measured properties of waxes and long chain polymers results from the length of the chain causing the wax material to be at a different phase then its long chain polymer counterpart under the same processing conditions [3].

Chemical techniques such as grafting, cross linking and chain scission, have found applications in the growing wax modification industry and are often used in conjunction with copolymerization [3]. It has been also shown that modified larger chain polymers can be degraded through pyrolysis or thermal degradation as another means of producing modified waxes [37]. The development of these new waxes and wax precursor products has led to increased applications for and demand on the global wax supply [2]. Modification by grafting has produced many commercially important functionalized waxes including those with altered polarities such as maleic anhydride grafted wax, a major focus of this thesis [36].

1.3.2 Maleic Anhydride for Wax Modification

Maleic anhydride (*cis*--butenedioic anhydride, toxilic anhydride, 2,5-dioxofuran*cis*-butenedioic anhydride, toxilic anhydride or 2,5-dioxofuran) and similar isostructural compounds and their derivatives; including, maleic, fumaric, citraconic, itaconic acids, amides, imides esters and nitriles, have been used as an effective modifying agents for both high and low molecular weight polymers including waxes [36]. This is due to their polyfunctionality, reactivity and availability [36].

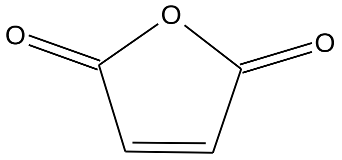
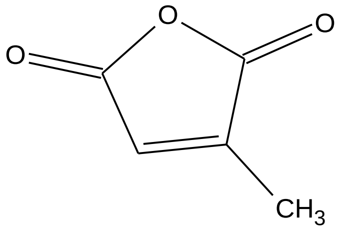
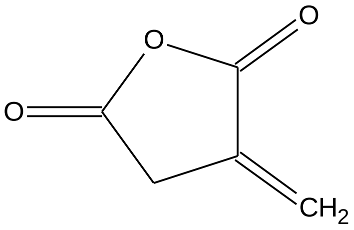
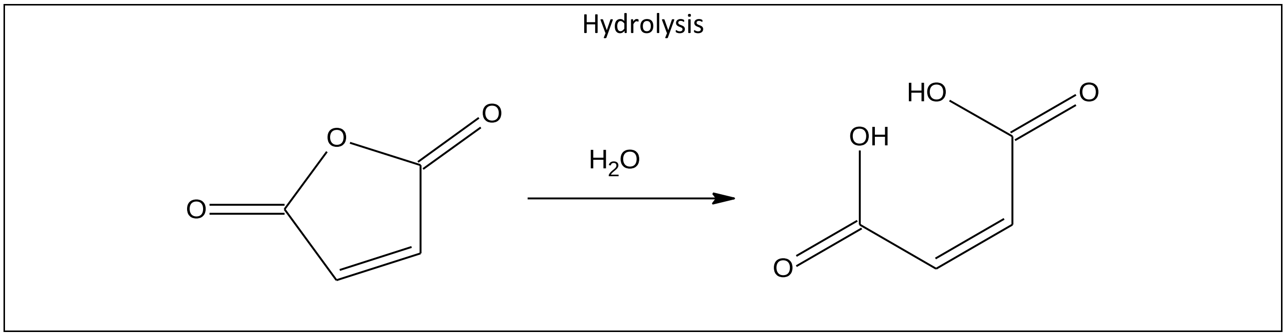
Maleic Anhydride	Citraconic Anhydride	Itaconic Anhydride
		

Figure 5 Structure of Maleic Anhydride and Isostructural Anhydrides [36]

The unsaturated double bond present maleic anhydride and its isostructural analogs makes these molecules effective modifying agents of carbon chain polymers allowing for an array of functional groups to be incorporated into a polymers structure [36]. The double bond often allows for these isostructural compounds and their derivatives to be substituted with each other in processes used to modify polymers with similar but not identical efficiencies and grafting results [36].

Maleic anhydride is manufactured via the oxidation of benzene or n-butane or as a side product in the production of phthalic anhydride [38]. Production is currently shifting away from the use of benzene as a starting product due to concerns over safety and rising cost. The global production of Maleic anhydride is expected to reach 2 million metric tons by 2012 [39]. The primary demand for Maleic anhydride comes from its use in the production of unsaturated resins with growth in the industry being stimulated by increased consumption as well as the development of new applications [39]. Maleic anhydride is a soluble white crystal solid at room temperature with a melting point of 52.8 °C and a boiling point of 202 °C. It has been shown to sublime at temperatures higher than 80 °C [38]. Maleic anhydride is an eye, skin and respiratory irritant and is harmful if ingested [40].

Wax polymers modified with Maleic anhydride can be further modified in most reactions which modify Maleic anhydride including acid chloride formation, reduction, saponification with alkalies, hydrolyzation, amidation, esterification [36]. They also can be further polymerized or crosslinked through mechanism such as reaction with glycols or epoxides to produce polyesters [36]. Maleic anhydride will hydrolyze to maleic acid on contact with water, will produce a half ester or diester when reacted with an alcohol and will produce a half amide, maleamic acid, or a diamide when reacted with ammonia [36].


Hydrolysis

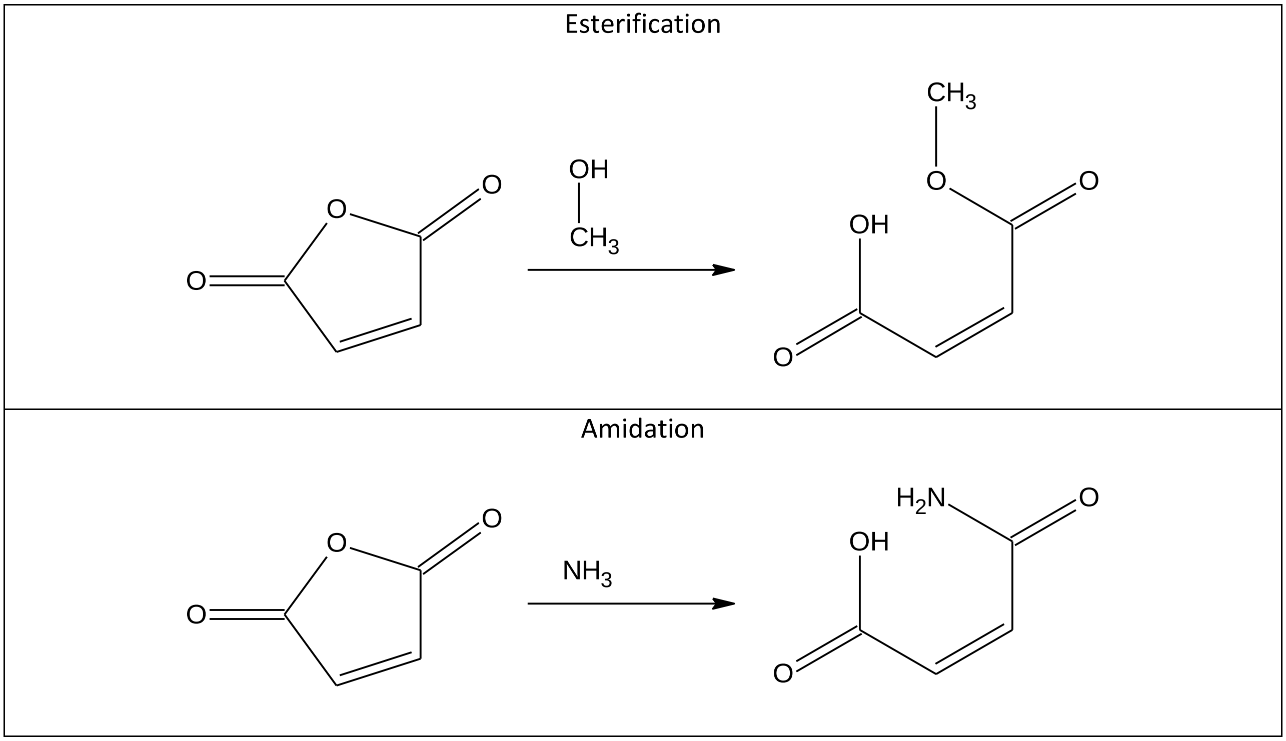


Figure 6 Examples of Maleic Anhydride Reactions [36]

1.3.3 Functionalization by Grafting

Grafting refers to the bonding via chemical reaction of a molecule that is structurally different from the wax chain structure either in its components or arrangement to the main chain of the wax [41]. This modification is achieved with higher efficiency and with more regularity when sites containing unsaturated double bonds or other functional group containing similarly reactive protons are present on both the wax chain and the molecule; however, this is not a requirement of the process [42]. Free radical initiator additives are often used to expedite the grafting process when then wax and grafting molecule are not sufficiently reactive on their own [43].

The functionalization of polymers of low to high molecular weights through the technique of grafting is an art that has long held the focus of both industrial development and polymer research [41]. Grafting can be an effective means of not only functionalizing a polymer material with new properties but can also serve as a means of improving the compatibility of a polymer with an otherwise incompatible material, such as water for example [42]. Maleation, the grafting of maleic anhydride to a polymer material for the purposes of functionalization, is a popular example of polymer grafting present in both research and industrial production [36]. Maleation is commonly used to functionalize high molecular weight polymers for a variety of purposes, such as the compatibilization of bio-materials with polypropylenes [36].

In the past, the processes developed to maleate waxes require the use of either one or a combination of the following in order to achieve a highly maleated wax: (a) an inert atmosphere, such as one of nitrogen gas to protect the grafting reaction for reactions with oxygen, and as a means of expelling unreacted maleic anhydride radicals; (b) radical initiators such as DI-*tert*-butyl peroxide or tert-butyl peroxybenzoate; (c) solvents, as a means of delivery of the maleic anhydride monomer or as a means of purification of the final product; and (d) the delivery of molten maleic anhydride to the reaction vessel [36]. All of these requirements contribute a significant increase in the cost, environmental impact, safety risk and complexity to the wax maleation process.

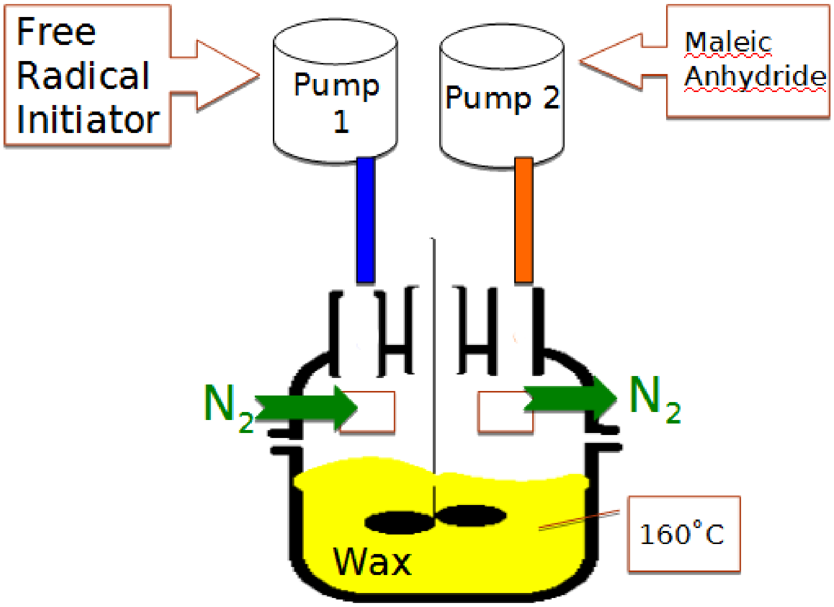


Figure 7 Example of Wax Maleation Process [44]

Wax maleation processes which reduce or eliminate the requirement of any of the factors contributing to cost, complexity, danger and environmental impact while still producing a highly maleated product, would result in a significant increase in the cost savings, simplicity and safety of said process as compared to prior art, thereby serving a vital need in the wax maleation and wax emulsion industries. Furthermore, the added option of the recovery of any unreacted maleic anhydride from the reaction process, would add to the cost effectiveness of the process while also reducing the environmental impact. In order to address these issues some new methods of maleation have been explored including photo-irradiation [45], ultrasonic initiation [46], microwave assisted radical grafting [47], copolymerization with styrene [48] and ball milling [49].

1.4 Wax Dispersions and Emulsions

As a means of effective delivery, processing and application wax particles are often dispersed in aqueous solutions in the form of wax emulsions [50]. In reality, an emulsion is defined as the mixture of two immiscible liquids; and as such, the term wax emulsion is only accurate during the period in which the wax moiety is in liquid form [51]. Once the mixture cools to the point where the wax solidifies within the mixture it is technically a dispersion. It is common practice within industry to refer to these products as wax emulsions nonetheless [50]. In industry, these wax emulsions are defined by containing average wax particle sizes within the emulsion of 1 micrometer or less [51]. These particles can be stabilized within the aqueous solution via an electrostatic or steric mechanism or a combination of the two [50]. This is achieved by the addition of wax emulsifiers to the solution [50]. To effectively promote compatibility, wax emulsifiers must contain a hydrophilic portion which can be either ionic or non-ionic and a portion compatible with the wax component [50]. They can be produced through other means such as copolymerization [52].

Maleation is also used as a means of functionalizing smaller molecular weight polymers such as waxes to, among other things, promote hydrophilicity [36]. Maleated waxes that are self-emulsible constitute an important part of many industries that use emulsions as a means of incorporating the properties of waxes into commercial products [44], such as cosmetics, floor polish and wallboards. This is typically achieved by using a wax emulsifier derived from the same wax intended to be used within the emulsion [52]. A polymer with a high degree of grafted maleic anhydride, because of the functional group's polar nature, will typically show a higher degree of compatibility with water and therefore make a more stable emulsion [44]. As a consequence, one focus of both research and industrial development has been the production of highly maleated waxes for the use in emulsions [44].

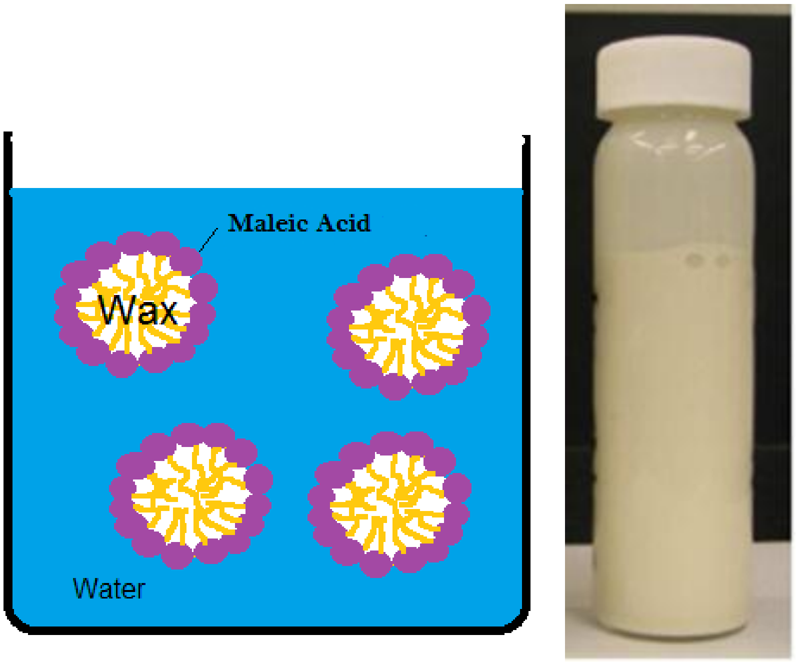


Figure 8 (Left)-Theoretical Cross Section of Wax Emulsion **(Right)**-Photo of Wax Emulsion

1.5 Engineered Wood Products

The term, engineered wood products, refers to materials prepared via the binding of smaller wood pieces together with an adhesive resin to make a product of a desired shape, strength and density [53]. Engineered wood products are further sub-classified depending on the size and shape of the wood material used; for example, particle board, medium density fibre board or plywood [53]. Engineered wood products can be further sub-classified if the wood materials are oriented in a specific fashion so as to provide unique properties to the final product; i.e., oriented strand board [53]. The wood materials used in the production of engineered wood products are often by-products of the timber processing industry process, such as sawdust and woodchips [53]. As a result, they are of low cost and considered an environmentally friendly use of what would most likely otherwise be a waste product [53]. In comparison to processed timber products, engineered wood products are cheaper and have greater overall uniformity, strength and quality [53]. In some cases where a decrease in strength of the material is acceptable, engineered wood products have been used as a cheaper alternative to steel [53]. The North American demand for engineered wood products is driven primarily by the demand for particle board, medium density fibreboard and plywood which are used to make structural panels. This demand is expected to grow to 28 billion square feet by 2012 with production rising to meet this demand [54]. North American production of other forms of engineered wood products such as Glulam lumber, i-joists and laminated veneer lumber are also expected to grow between 4 and 11% from the previous demand in 2011 [54].

Engineered wood products are prepared by coating or tossing the wood starting materials with an adhesive resin and then subjecting the materials to high temperature and pressure to mold them into the designed final product dimensions [53]. Prior to pressing the boards the particles are sometimes spray coated with melted paraffin wax or a wax emulsion which is used to impart properties including water repellency, dimensional stability, an anti-dust effect, and a smoother and softer feel to the final product.

The use of a wax emulsion as opposed melted paraffin wax to impart this products is preferred because a wax emulsion allows for a smaller particle size which improves wax penetration into the engineered product resulting in a more uniform enhancement of properties such as water repellency [55]. Wax emulsions also allow for a lower temperature of application, pumping and storage when compared with melted paraffin [55]. Wax emulsions are also less flammable than melted paraffin wax and have been shown to reduce the amount of adhesive resin needed in the production of engineered wood products when compared with melted paraffin wax or products manufactured without a wax component [55]. A wax emulsion must be able to withstand the high shear conditions of the spraying process without fallout which can cause clogging of the spray nozzle and subsequent damage to the apparatus [56].

1.6 Thesis Research Objectives and Outlines

This project aims to develop a new process for the synthesis of maleated wax emulsifiers for use as wax emulsifiers in wax emulsions used as a component in the production of commercial engineered wood products. Work was completed towards formulating a new emulsifier that will act as a more suitable and cost effective alternative to commercially available equivalents. The scope of the project and specific milestones regarding the completion of the project were set out by parties involved both at McMaster University and at Norjohn Emulsions Ltd., the industrial supporter of the project.

The primary objective of this project was to develop a process for modifying hydrophobic waxy materials and/or polymers to produce new products for use as emulsifiers with desirable properties for creating stable wax/water emulsions via their modification by maleation to be used as an additive for the creation of engineered wood products. This process would be developed so as to be realistically incorporated into an existing industrial production line currently using wax emulsifiers as a component in the finalized commercial engineered wood product. The parameters set forth to outline the accomplishment this task were as follows: The development of a new wax emulsifier product and process for producing the same that show potential for industrial application and/or its incorporation into the pre-existing commercial market.

This potential was examined by comparing standardized industrial measurements of some of the waxes physical properties which can be used to infer its potential commercial viability, its subsequent incorporation into an emulsion followed by further testing to once again access potential commercial viability and finally the incorporation of this emulsion into a engineered wood product to compare its effect on the properties of said product with other emulsions presently in commercial use. For the purposes of this project, wax properties included; Acid number, drop point temperature, relative purity and observed emulsification. The emulsion properties included; viscosity, high shear stability, 24 hour stability and storage stability. Finally the engineered wood product properties evaluated were water absorption and thickness swell. These properties were then compared against the projected cost of production and return of investment of a scaled-up incorporation of the process into a pre-existing industrial process as a means of computing the commercial viability of the developed process.

Further requirements of the product and process included that it must be synthesized using normal paraffins, slack waxes or synthetic hydrocarbon waxes exemplary of actual products available for purchase in industry. Similarly, the use of industrial grade peroxides and maleic anhydride was also a requirement again to maintain consistency with options available for purchase in industry. The industrial price estimates of the industrial versions of all products were used a means of estimating projected product scale up costs. Both the maleated wax product and its wax precursors must exhibit a melt point of no more than 110 °C so as to ensure ease of process-ability and transport at temperatures of operation consistent with similar industrial practices.

Considerations regarding the environmental impact and safety of the process were not only considered intrinsic to the measured success of the project but certain baseline requirements were made with these factors involved. First, the process must be achieved without the use of any solvent. Second, the use of hazardous materials, inert gasses and high pressures must be minimized or avoided when possible. If used, safety precautions and proper disposal must be implemented as part of the cost estimate and allotted time for completion of the process. These considerations would further serve alongside the final products physical properties as factors used to determine the optimal process.

Chapter 2: Wax Maleation

2.1 Objective and Scope

The purpose of this chapter is to compare 6 different processes developed to graft maleic anhydride onto 4 different waxes, a slack wax a fully refined paraffin wax and 2 differing alpha olefin waxes. 5 of the methods explore the use of a peroxide initiated grafting mechanism while 1 method explores the use of a thermally initiated grafting mechanism. The end goal of the experiments was to develop a robust, efficient and repeatable method of producing a maleic anhydride grafted wax emulsifier capable of replacing current commercial emulsifiers. The methods were developed and evaluated against practices commonly used in industry to determine which approach would be the most appropriate for incorporation into a wax emulsion production line designed to produce commercial wax emulsions for incorporation into the production of engineered wood products. Whenever possible, experimental parameters were standardized between the different approaches. Each approach was evaluated in terms of its grafting efficiency, robustness, purity of product, safety, environmental impact and ease of scale up incorporation.

2.2 Introduction to Peroxide Initiated Wax Maleation

As mentioned earlier, the maleation of most waxes requires the addition of a peroxide to the reaction vessel as a means of increasing the reactivity of the two other components, particularly the wax [36]. While maleation can be achievable without the use of peroxides, it usually requires very high temperatures and reaction times, and so the incorporation of a peroxide, which increases the efficiency of the reaction, is useful despite the increase in cost, contamination and possible safety concerns [36]. In this subchapter, the development and evaluation of 5 different methods that all rely on the use of peroxide initiators to enhance the maleic anhydride grafting reaction are detailed.

2.2.1 Peroxides Used for Chemical Modification of Waxes

Organic peroxides are often used in a variety of methods of polymer synthesis and modification, including the production of waxes and functionalized waxes [57]. The typical structure of an organic peroxide is demonstrated below in Figure 9.

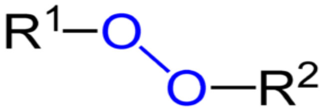


Figure 9 Typical Peroxide Structure[2]

This type of compound is often used because of its ability to consistently generate free radicals at rates proportional to certain temperatures by homolysis of its oxygen to oxygen bond [57]. This ability is quantified in industry through the designation of a discreet time period half-life temperature corresponding to the temperature of the system at which 50% of the organic peroxide present within the reaction system undergoes homolysis within that designated time frame [57]. Specific organic peroxide half-life temperatures are frequently reported for 10 hours, 1 hour and 1 minute. For the purposes of this study the peroxides were characterized by their 1 hour half-lives. The 1 hour half-life temperature refers to the temperature at which half of the moles of peroxide added to a reaction will undergo bond homolysis in an hour [57].

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[2] Figure source: Peroxide group v.2.png (Image is public domain)

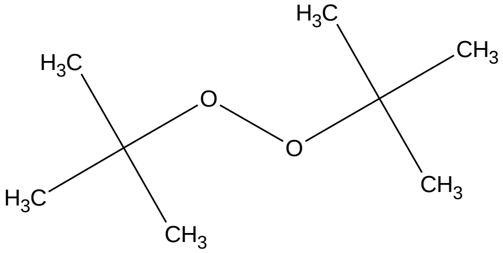
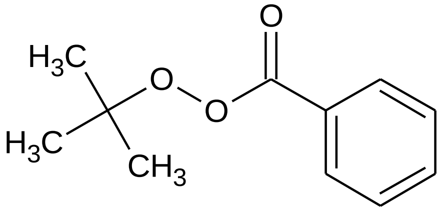
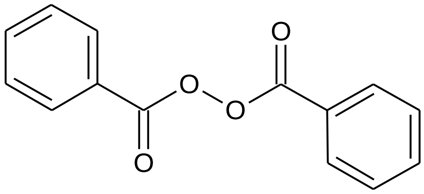
Despite being an effective initiator for wax modification reactions by free radical grafting, such as wax maleation, the use of peroxides is not without some undesirable complications [57]. Peroxides, especially those with lower half-life temperatures, can be explosive [57]. This requires an increased focus on safe peroxide handling, storage and delivery when they are used in reactions [58]. Peroxides are typically safely stored at temperatures well below room temperature and must be kept away from open flames, static charges and other heat sources whenever possible [58]. In terms of safety, it is preferential to have a peroxide with 1 hour half-life temperature well above room temperature thereby making explosions less likely [58]. However, choosing a peroxide with a high 1 hour half-life temperature will increase the temperature required for an effective modification reaction, directly impacting the cost of the process. Furthermore, Any Industrial processes using peroxides in chemical reactions operating at temperatures above their appropriate storage temperatures should be designed in such a way so as to eliminate the chance of heat conduction from the reaction vessel back to the peroxide storage vessel [58].

Another complication that can arrive from peroxide use in wax modification chemical reactions is the generation of side products formed after the molecule undergoes bond hemolysis [57]. Depending on the nature of the side groups, the new molecules formed from the split of the peroxide molecule may evaporate out of the system, potentially causing issues of collection and disposal, or may remain in the system, potentially contaminating the product and inhibiting the desirable properties of the final product which would require an additional step of product purification. The complications can potentially further contribute to the environmental impact, safety concerns and cost of the free radical grafting process when implemented in a real world industrial scale.

Finally, the phase of the peroxide will also have an impact on the development of the process. Peroxides which are solid at room temperature will require different handling and addition to those that are liquid [58]. Liquid phase peroxides are more easily pumped than solid peroxides which will require either vacuum pumps or solvents in order to be introduced to a reaction continuously.

The use of three distinct peroxides with distinct structures and half-life temperatures were examined for the purposed of this study. Those chosen were Di-*tert*-Butyl Peroxide, Tert-Butyl Peroxybenzoate and Benzoyl Peroxide. Their structures are compared below in Table 3.

Table 3 Structure of Peroxides Used [59]

Name	Structure
Tert-Butyl Peroxide	
Tert-Butyl Peroxybenzoate	
Benzoyl Peroxide	

An important prediction that can be made from the comparison of the structures of each organic peroxide is the by-products that will be produced following the bond homolysis reaction. Di-*tert*-butyl peroxide can produce *tert*-butanol, Benzoyl peroxide can produce benzoic acid and *tert*-Butyl Peroxybenzoate can produce both *tert*-butanol and benzoic acid. These by-products become increasingly significant in their asserted effects on the properties of the final product with an increased proportion of organic peroxide added to the reaction particularly *tert*-butanol which is highly flammable and has a camphoric odor which may affect the applicability of the final product. Additionally these differing yet related structures of the organic peroxides result in differing phases at room temperature as well as different half-life temperatures. The properties of the three different peroxides are compared below in Table 4 [59].

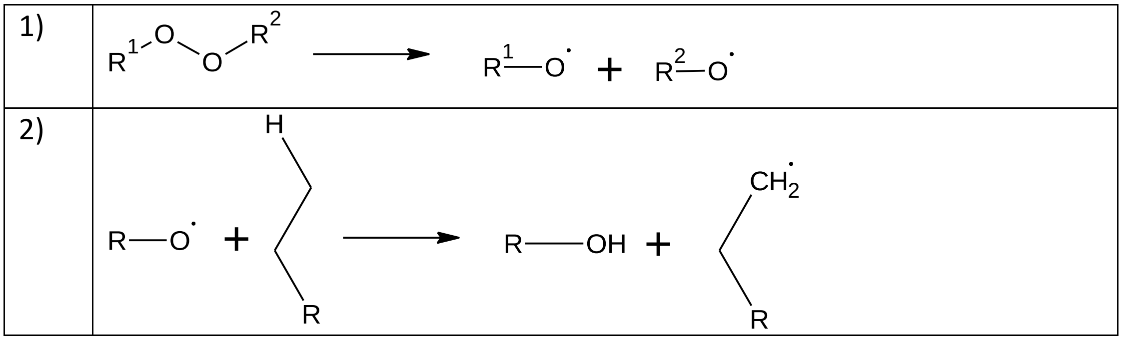
Table 4 Comparison of Peroxides [59]

Name	Phase at 25˚C	M.W.	1 Hour Half-Life Temperature (˚C)	Flash Point (˚C)	Autoignition Temperature (˚C)
Di-*tert*-butyl Peroxide	Liquid	146.23 g/mol	149	1	N/A possible
tert-butyl Peroxybenzoate	Liquid	194.2 g/mol	122	93	N/A possible
Benzoyl Peroxide	Solid	242.23 g/mol	92	N/A	80

In terms of storage safety it is clear from the above table that the *tert*-butyl peroxybenzoate is the best choice because it has the highest flash point. The data for the autoignition for *tert*-butyl peroxybenzoate and Di-*tert*-butyl peroxide is currently unavailable, however; this does not mean that autoignition is not possible. The above peroxides are often not available for purchase in their pure forms because of their flammability and hazardous decomposition which may also contribute impurities to the final products when they are incorporated into a reaction.

2.2.2 Peroxide Initiated Methods: Reaction Mechanism

The reaction mechanism associated with the grafting of maleic anhydride to paraffin wax in the presence of an organic peroxide is generally well known and defined [36]. An illustrated mechanism for the reaction series towards creating the desired maleated wax product is seen below in Figure 10. The initiator in the system, which in the case of these reactions is organic peroxide, undergoes bond homolysis at high temperature to create two peroxyl radicals. In the desired reaction, a peroxyl radical will abstract a hydrogen atom from the wax backbone which creates a grafting site for the addition of maleic anhydride. The radical site on the wax backbone will attack the double bond in maleic anhydride, resulting in the addition or grafting of the maleic anhydride to the wax backbone and the formation of a new radical site on the grafted maleic anhydride [36]. Ideally, this radical will go on to abstract a hydrogen from another wax molecule, giving a molecule of the desired grafted wax product and a new wax radical to carry on the reaction [36].



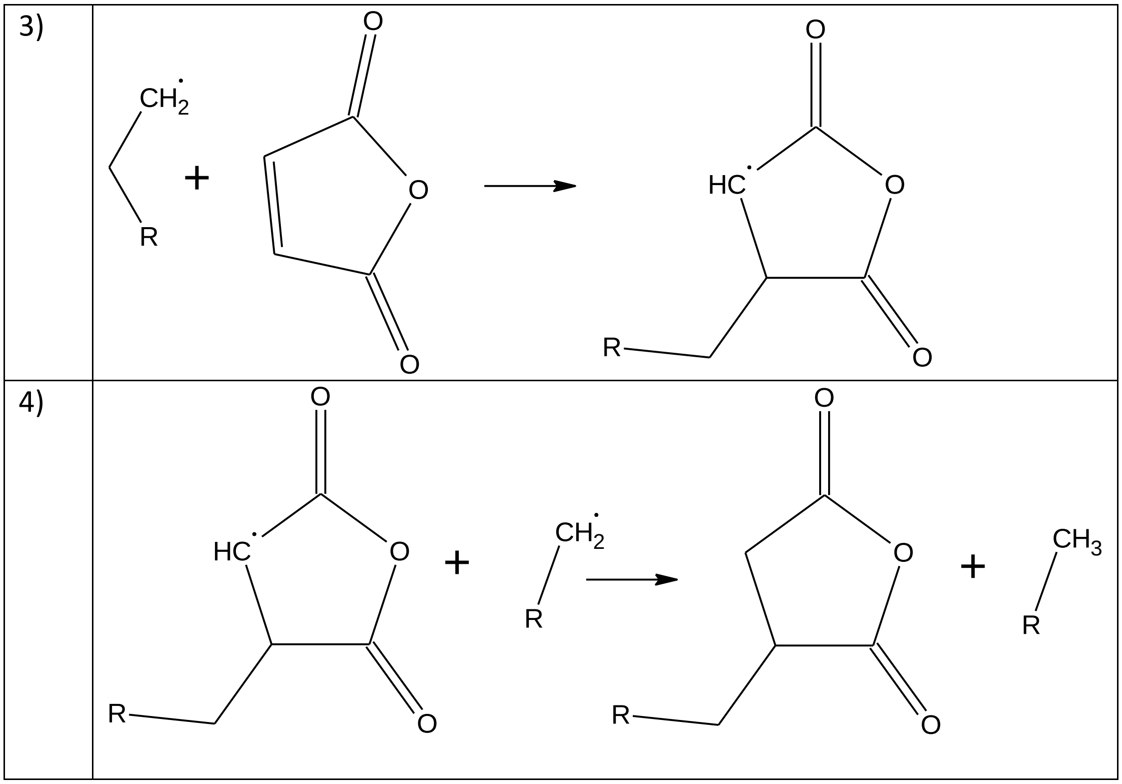


Figure 10 Proposed Reaction Mechanism

Possible undesired side reactions may occur from the radical attacking other moieties present in the reaction vessel [36]. These side reactions include crosslinking between two wax radicals, bridging reactions involving maleic anhydride and homopolymerization reactions involving maleic anhydride [36]. Products of these reactions can be seen in Figure 11. Peroxide radical can be sensitive to contaminants as well as oxygen in an open atmosphere laboratory environment [57]. Process optimization was used in order to find conditions where these side products are largely avoided.

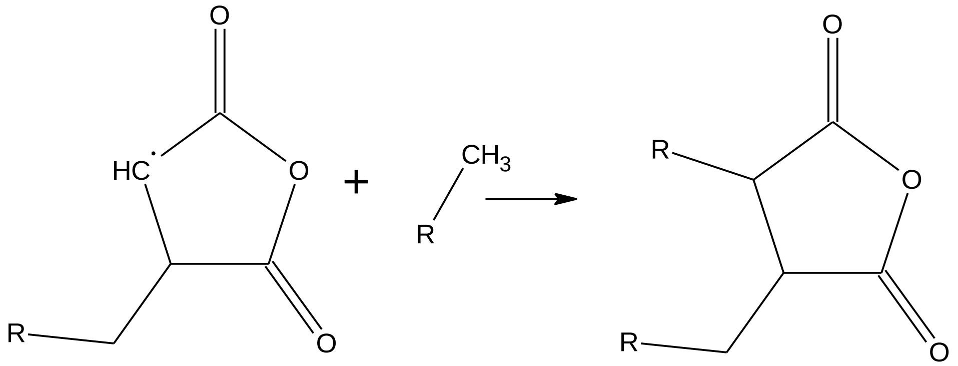
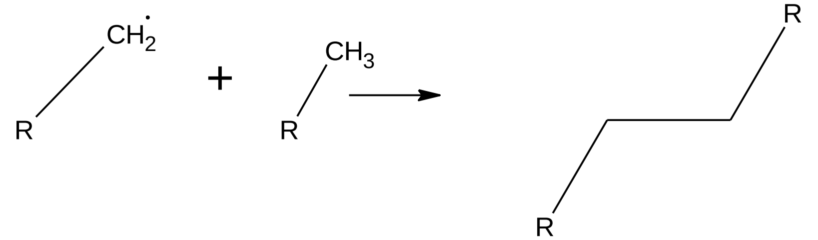
1s)	
2s)	

Figure 11 Possible Side Reactions

2.2.3 Waxes used in peroxide initiated grafting methods

Three different waxes were examined as starting materials for the peroxide initiated grafting methods; IGI 1212u, a fully refined paraffin wax; ProWax 563, a commercial slack wax; and AlphaPlus® C30+ a synthetic n-alpha-olefin wax. The technical properties of each wax are detailed below in Table 5.

Table 5 Comparison of Waxes used in Peroxide Initiated Methods [60][61][23]

Wax	**Linear Chain (wt. %)**	**Branched Chain (wt.%)**
IGI 1212u Paraffin wax	77.62	22.38
ProWax 563 Slack wax	30	70
AlphaPlus® C30+	71.4 (n-alpha-olefin) 2.9 (linear internal olefin)	24.7 (branched olefin)

Wax	**Viscosity (cSt) @99°C**	**Color**	**Melt Point (°C)**	**Needle Point Penetration 0.10mm, @25°C**	**Oil Content (%)**	**Average Molecular Weight (g/mol)**
IGI 1212u Paraffin wax	3.8	+28 min ASTM (pale yellow)	45-76	15	<0.5	403
ProWax 563 Slack	7.03	<1.5 min ASTM	61.9	75	13.0	534

wax		(pale yellow)				
AlphaPlus® C30+	6.78	Saybolt 52 (opague white)	71.5	13	1.9	419

Of the three waxes, the alpha-olefin wax has the most specifically defined chemistry, and of particular importance within that chemistry is the 71.4% weight contribution of n-alpha-olefin chains [23], which theoretically provide a defined terminal unsaturated double bond ideal for grafting of the maleic anhydride via peroxide initiation [36] and possibly thermal initiation which will be further discussed later in this chapter. It is therefore expected that the alpha-olefin wax would produce a higher proportion of similarly structured maleic anhydride grafted carbon chains than either the refined paraffin wax or the slack wax.

The slack wax, as detailed earlier in the introduction has the least regular chemistry with only a 30% weight contribution of linear carbon chains [61]; however, despite this increased irregularity, the slack wax was evaluated as a possible starting material partly because it composes the unmodified wax component of the engineered wood product commercial emulsion [56]. As such, there existed a possibility that the emulsifiers produced from a maleic anhydride grafted slack wax may show the greatest degree of compatibility with the unmodified wax proportion of the emulsion [56]. Using the slack wax as a starting material for the maleation process would also provide the easiest means of incorporating this process into an existing EWP emulsion factory line due to the fact that the entire emulsion wax component could be subjected to a low level grafting process before its emulsification.

The refined paraffin wax was chosen because it is readily available in industry and because it has a high proportion of linear carbon chains ideal for producing wax emulsifiers. The refined paraffin wax is also a common component of many wax emulsions and as such a wax emulsifier derived from a refined paraffin source could be potentially incorporated into a variety of existing commercial emulsion; and as such, in those emulsions it would not require a separate production stream similar to the slack wax in the EWP emulsions [53].

2.3 Introduction to Thermally Initiated Wax Maleation

Research has shown that it is also possible to graft maleic anhydride onto an polymer using a thermal initiated approach that operates using the ene-reaction or Alder-ene reaction mechanism due to the ability of maleic ahydride to act as a potent enophile [23]. This reaction has been applied in industry to large chain polymer and in research to shorter chain polymers such as waxes and vegetable oil triglycerides [62]. This pericyclic group transfer reaction is facilitated by the terminal unsaturated bond on the end of the carbon chain of the wax and typical requires a high operating temperature for application in the grafting of polymers, between 160-240˚C [36].

Despite the increase in temperature this mechanism provides many advantages over the peroxide initiated mechanism, stemming primarily from the elimination of the organic peroxide as a reaction component [62]. These advantages include improved safety of the process and an purer final product [23]. Removing the organic peroxide from the reaction also eliminates the need for an inert atmosphere. This mechanism could also work in concert with the peroxide initiated mechanism provided there is an appropriate ene and enophile for the mechanism to take place [63].

2.3.1 Thermal Initiation Method: Reaction Mechanism

The thermal Initiation method as understood is presented below in Figure 12 [36]. Here, the enophile maleic anhydride unsaturated double bond migrates to form a σ-bond with the terminal carbon of the wax chain causing a 1,5 hydrogen migration from the alpha position. In this case the two electron withdrawing carbonyl bonds of the maleic anhydride molecule make it a potent enophile [36]. It is possible for this reaction to happen on an internal unsaturated bond of a wax polymer chain; however, steric hindrance typically makes this form of the ene reaction unfavorable [36].

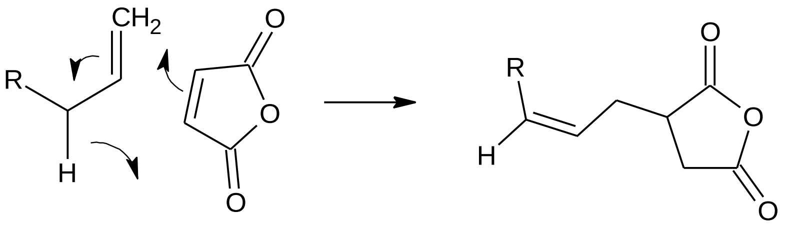


Figure 12 Thermal Addition Reaction Mechanism

2.3.2 Waxes used in thermally initiated grafting methods

Two different waxes were examined as starting materials for the thermal initiated grafting metho, AlphaPlus® C30+ and AlphaPlus® C30+ HA two synthetic n-alpha-olefin waxes. The technical properties of each wax are detailed below in Table 6.

Table 6 Comparison of Waxes used in Thermally Initiated Methods [23]

Wax	**Linear Chain (wt. %)**	**Branched Chain (wt.%)**
AlphaPlus® C30+	71.4 (n-alpha-olefin) 2.9 (linear internal olefin)	24.7 (branched olefin)
AlphaPlus® C30+ HA	75.4 (n-alpha-olefin) 4.2 (linear internal olefin)	19.4 (branched olefin)

Wax	**Viscosity (cSt)**	**Color**	**Melt Point**	**Needle Point Penetration**	**Oil Content (%)**	**Average Molecular Weight (g/mol)**

	@99°C		**(°C)**	**0.10mm, @25°C**		
AlphaPlus® C30+	6.78	Saybolt 52 (opague white)	71.5	13	1.9	419
AlphaPlus® C30+ HA	6.73	Saybolt 49.6 (opague white)	66.9	15	1.9	419

As can be seen from the technical data of both waxes the AlphaPlus® C30+ HA has a higher proportion of n-alpha-olefin chains present in its composition and overall a higher linear chain composition [23] which theoretically should result in a higher probability of success thermally initiation grafting reactions between the maleic anhydride and the AlphaPlus® C30+ HA wax as compared to the AlphaPlus® C30+ wax. The AlphaPlus® C30+HA wax also has a lower melting point and viscosity which also make it more favorable when considering the processing of each wax [23].

2.4 Experimental for Peroxide Initiated Methods

A free-radical grafting approach was taken in order to functionalize the paraffin and slack waxes with maleic anhydride. Several different experimental approaches were developed and tested in order to determine the best method of peroxide intiated grafting. A design of experiments was carried out in order to optimize reaction conditions. The parameters to be optimized were chosen based on results from literature and acceptable operating limits as laid out by Norjohn Limited. The following parameters were used for all experiments:

- Between 1-12 hours per run;
- A Reaction temperature of between 80-160˚C, in general the temperature was chosen to correspond with the chosen peroxide one hour half-life, although some side experiments

were performed to see how differing temperature affected the peroxide performances. In general:

  - A temperature of 160˚C was chosen for experiments with Di-*tert*-butyl peroxide as an initiator
  - A temperature of 130˚C was chosen for experiments with *tert*-butyl peroxybenzoate as an initiator
  - A temperature of 80˚C was chosen for experiments with benzoyl peroxide as an initiator

- Between 2-20 weight % maleic anhydride by weight of wax was charged to the reactor;
- Between 0.6-10 weight % peroxide by weight of wax was charged to the reactor. In each case the molar ratio of peroxide to maleic anhydride was calculated bearing in mind that each mole of peroxide is capable of producing two moles of radicals capable of grafting initiation.
- Stirring was held constant throughout all experiments of the same scale.
- Experiments were initially performed in batch sizes of 100 grams in a round bottom flask and experiments that produced adequate results at this scale were then increased to 500 grams in a glass reaction vessel.
- Experiments conducted in a round bottom flask were stirred with a magnetic stir bar and heated in an oil bath, while those conducted in a larger glass reaction vessel were stirred with an IKA dual-range mixer and heated with a heating mantle attached to a Love Instruments bench-top temperature controller with temperature being recorded using a J-type thermocouple.

- In any method where the vessel was sealed to the atmosphere, an outlet tube was run from the vessel into a vial of silicone oil to allow volatiles to escape from the system without allowing oxygen from the air to enter the system.
- Upon completion of the reaction, the wax product was removed from heat and tested for an initial acid number titration and then purified by one of several washing techniques to be discussed later and then the acid number was retested. The acid number of the product was also tested several days after being stored in a oven above the melting point of the wax to determine the thermal stability of the product.

The various methods used are detailed below in subchapters 2.4.2 through 2.4.6 in increasing order of the complexity of the process.

2.4.1 Materials

- IGI 1212U fully refined paraffin wax, purchased from The International Group, Inc.
- Prowax 563 Slack Wax, purchased from Imperial Oil.
- 99.5% Pure Maleic Anhydride (M0625), purchased from Bartek
- 98% Pure Di-*tert*-Butyl Peroxide (Luperox® DI 168521), purchased from Sigma Aldrich
- 98% Pure *tert*-Butyl Peroxybenzoate (Luperox® P 159042), purchased from Sigma Aldrich
- 97% Pure Benzoyl Peroxide (Fluka 33581), purchased from Sigma Aldrich
- 90% Pure reagent grade Potassium Hydroxide (484016), purchased from Sigma Aldrich
- Reagent grade acetone, ethanol, methanol, and xylene purchased from Caledon

2.4.2 Method 1: Bulk Addition

In this approach, the reactionvessel was filled with the desired amount of wax, maleic anhydride and peroxide at room temperature prior to heating or stirring. In some runs of the experiment, the reaction vessel was sealed and degassed to determine the effect of oxygen contamination on the experiment while under constant stirring for beginning an hour before heating the reaction. Experiments were performed in nitrogen, argon and normal air atmospheres, however it was noted that degassing with an inert atmosphere was not absolutely necessary as successful maleated products were produced from a process using an open air atmosphere. After degassing, the reaction mixture was brought up to the appropriate temperature and allowed to react for the desired amount of time. An example apparatus used in this bulk addition method can be seen in Figure 13.

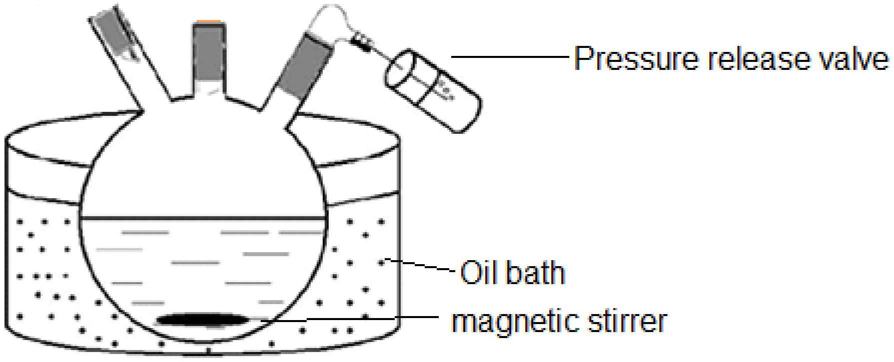


Figure 13 Bulk Addition Method

2.4.3 Method 2: Ball Milling

In this approach, a planetary ball mill was used as an alternative apparatus and an example setup can be seen in Figure 14. Ball-milling is typically used a form of grinding substances however; inspiration for exploring this method came from recent research purporting the successful maleation of high molecular weight polymers such as polypropylene using a ball-milling technique [49]. This method is more energy efficient than its counterparts [49]. For this method, small stainless steel reaction vessels of approximately 100 mL volume were filled with the desired amount of wax and maleic anhydride. Several small stainless steel ball bearings were added to each vessel and the vessels were sealed. Samples were not degassed during the reaction and as such the reaction was performed under open atmosphere.

After the vessels were sealed, they were heated to the appropriate temperature and then placed inside the ball mill apparatus, which then spun them to promote mixing on 1 hour cycles and internal heating via friction caused by the ball bearings within the vessels. The planetary ball mill housed two separate reaction vessels which were both mass balanced equally. Each planetary ball mill cycle lasted 1 hour and maleation experiments were subjected to multiple cycles. The temperature of the reaction mixture was checked frequently and adjusted accordingly if the mixture began to cool below the desired operating temperature. After the reaction had been run for the desired amount of time, the product was purified by one of the washing techniques detailed in subchapter 2.7. Samples from both reaction vessels were tested for each experiment.

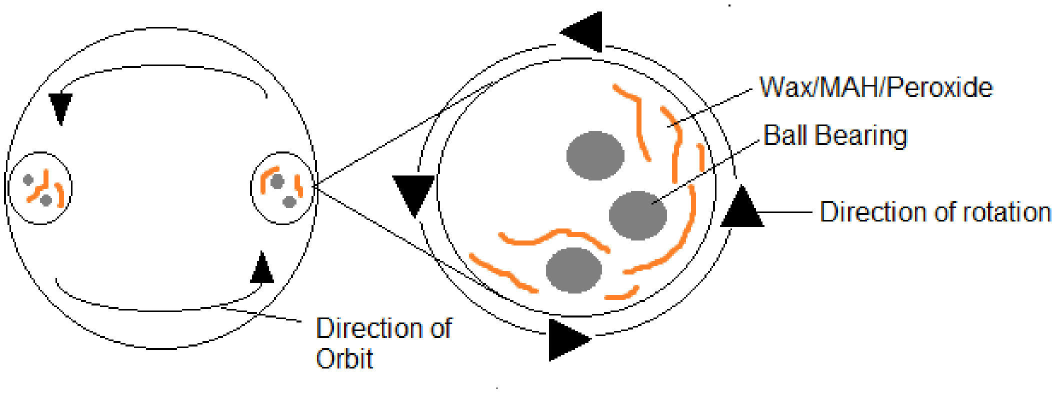


Figure 14 Ball Milling Top View representation

2.4.4 Method 3: Peroxide Pulse Addition

In this approach, a slightly modified apparatus was adopted, which can be seen in Figure 15. A separatory funnel was attached and sealed to one neck of a round bottom flask which allowed for peroxide to be added into the system in quick discreet pulses different from that which would be possible through the use of a pump. Initially, the reaction vessel was filled with the desired amount of wax and maleic anhydride and stirred. The vessel was sealed and brought up to the desired reaction temperature. The wax mixture was degassed for between 30 minutes and one hour with an inert atmosphere consisting of either argon or nitrogen gas. The reaction vessel was sealed so as to maintain an inert atmosphere throughout the reaction. After degassing, peroxide was added into the reaction mixture at specific intervals of time over the course of the reaction. To ensure an efficient use of peroxide all the pulses were added within the first hour of the reaction. Some experiments were performed in which peroxide pulses were charged to the reaction throughout the entire process, to examine the effect on the grafting process. Upon completion of the reaction, the mixture was removed from heat and purified by one of several washing techniques.

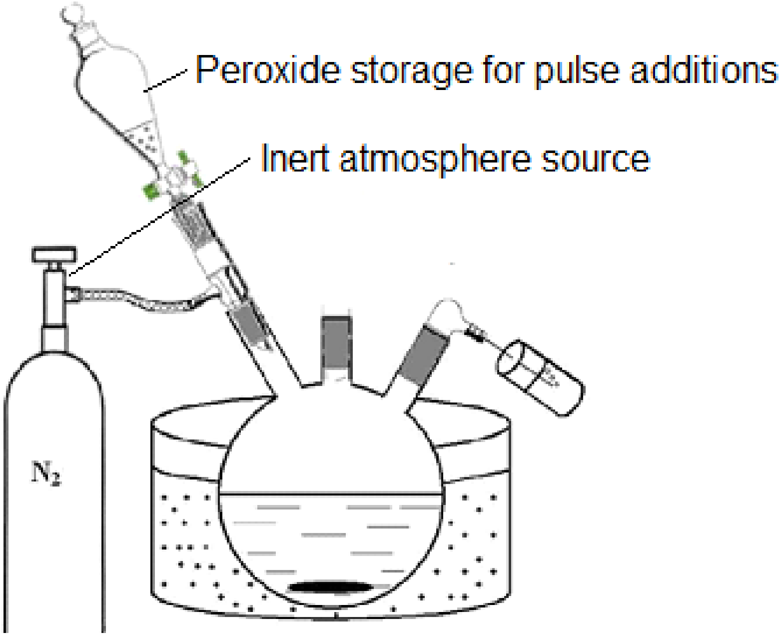


Figure 15 Peroxide Pulse Addition Method

2.4.5 Method 4: Peroxide Pumping

For this method, a Cole-Parmer peristaltic pump was calibrated using a mass/time technique to ensure that pump readings were accurate. The apparatus used is similar to that of the bulk addition method, as seen in Figure 16. The reaction vessel was filled with the desired amount of wax and maleic anhydride and then subjected to constant stirring. The reaction mixture was brought up to the desired temperature and then degassed for between 30 minutes and one hour. The reaction was then maintained under an inert atmosphere for the entirety of the reaction.

After degassing, peroxide was pumped into the reaction vessel at a constant rate depending on the volume of peroxide used and the desired reaction time. The reaction was considered completed after all the peroxide had been pumped into the reaction vessel. At this point the mixture was removed from heat and purified by one of several washing techniques detailed in subchapter 2.7. In an early version of this approach, maleic anhydride was also pumped into the reaction vessel over time. This required the use of either a solvent or for the maleic anhydride to be heated to beyond its melting point. This initial approach was not compatible with current industrial requirements for this process because of the use of solvents or the added safety and process complications of the maleic anhydride pumping components despite acceptable final product results and was not explored further.

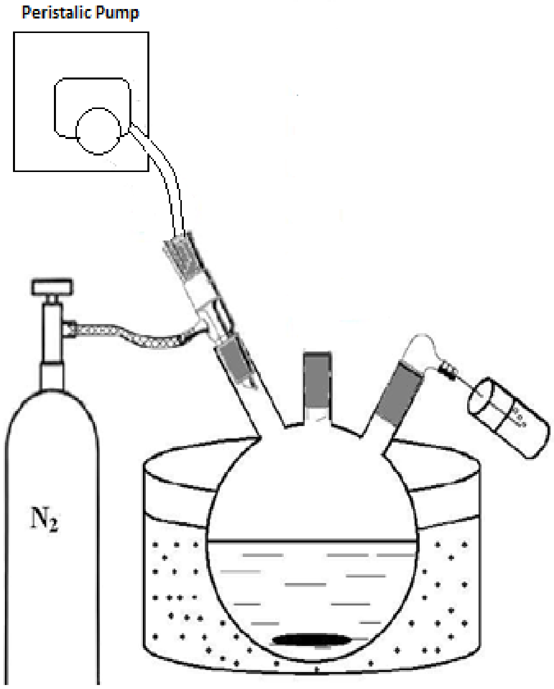


Figure 16 Peroxide Pumping Method

2.4.6 Method 5: Maleic Anhydride Addition

For this method, the apparatus used is the same as that of the bulk addition method, as seen in Figure 17. Wax and the desired amount of peroxide were added to the reaction vessel and then the vessel was brought up to the desired temperature and stirred constantly. The mixture was not degassed and was left open to the atmosphere. The mixture was allowed to stir at the desired temperature for half an hour to allow for some initial decomposition of the initiator in the system and then the desired amount of maleic anhydride was added in solid form to the mixture slowly over the next hour.

After addition of the maleic anhydride, the reaction was allowed to progress for the desired amount of time. Upon completion, the reaction mixture was removed from heat and purified by one of several washing techniques. This method was developed to address the problem of homopolymerization of the maleic anhydride occurring in the other methods aside from the ball-milling method. Homopolymerizatin refers to the unwanted reaction of maleic anhydride molecules within the reaction creating a solid cross-linked product.

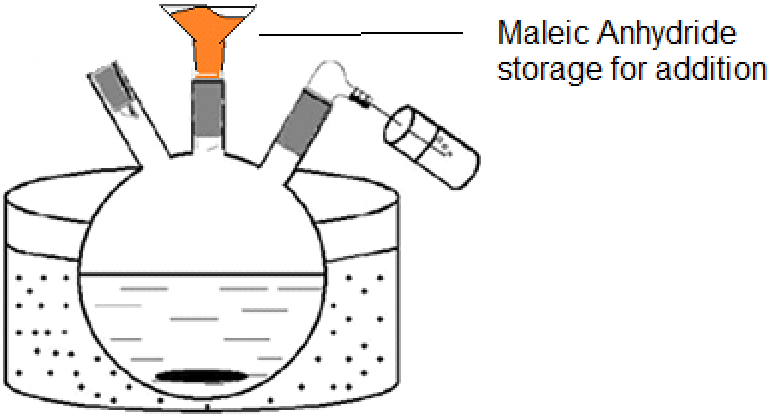


Figure 17 Maleic Anhydride Addition Method

2.5 Experimental For Method 6: Thermally Initiated Maleation

Experiments were conducted in this method based on the mechanism outlined in subchapter 2.3. The following parameters were used for all thermally initiated experiments:

- Between 1-8 hours per run
- A reaction temperature of between 200˚C
- Between 2-20 weight % maleic anhydride by weight of wax was charged to the reactor;

- Stirring was held constant throughout all experiments of the same scale.
- Experiments were initially performed in batch sizes of 100 grams in a round bottom flask and experiments that produced adequate results at this scale were then increased to 500 grams in a glass reaction vessel.
- Experiments conducted in a round bottom flask were stirred with a magnetic stir bar and heated in an oil bath, while those conducted in a larger glass reaction vessel were stirred with an IKA dual-range mixer and heated with a heating mantle attached to a Love Instruments bench-top temperature controller with temperature being recorded using a J-type thermocouple.
- All experiments were conducted in open atmosphere.
- Upon completion of the reaction, the wax product was removed from heat and tested for an initial acid number titration and then purified by one of several washing techniques to be discussed later and then the acid number was retested. The acid number of the product was also tested several days after being stored in a oven above the melting point of the wax to determine the thermal stability of the product.
- The setup for this method was most similar to the bulk addition method approach which is detailed in Figure 13; although in this case a organic peroxide initiator was not used.

2.5.1 Materials

- 99.5% Pure Maleic Anhydride (M0625), purchased from Bartek
- AlphaPlus© C30+ Alpha Olefin wax purchased from Chevron Phillips
- AlphaPlus© C30+ HA Alpha Olefin wax purchased from Chevron Phillips
- Reagent grade acetone, ethanol, methanol, and xylene purchased from Caledon

2.5.2 Maleic Anhydride Recovery

In the thermally initiated reactions, It was noted that maleic anhydride was sublimating out of the reaction mixture and condensing on the upper portion of the reaction vessel. The crystallization of this maleic anhydride was recovered after the reaction and weighed.

2.6 Acid Number Titration

1 gram wax samples of the final maleated wax products from all peroxide and thermally initiated method were dissolved by heating in xylene and titrated colourimetrically against a standardized 0.100 molar KOH solution and phenolphtalein indicator as per ASTM D 974. Acid number titrations were performed a minimum of 3 times for each wax sample and average was taken of the 3 results to determine the acid number of the grafted wax product. The acid number of each titration was determined using Equation 2.

2.7 Measurement of Clarity and Relative Purity of Wax Products

Final product maleated wax samples of all methods both peroxide and thermally initiated were visually inspected for changes in color and clarity following the reaction, the final color was compared to the color of the initial starting wax. Notes were taken on any odor given off by wax if present. At the end of each experiment form every method, samples were purified using 3 techniques in an attempt to remove unreacted maleic anhydride. The 3 techniques are:

1. Vacuum oven Technique:

Samples were placed in glass beakers in a vacuum oven at a temperature 100 ˚C for repeated periods of 24 hours. The acid number of these samples was retested once they were removed.

2. Water wash Technique:

Samples were added into 90˚C temperature water then stirred together for a period of 20 minutes the wax was then allowed to harden and was then separated from the water via a separatory funnel. This process was repeated 3 times before the acid number of the wax was retested. Some wax was lost during this process due to emulsification with the water.

3. Acetone wash Technique:

The wax was melted and then washed with room temperature acetone through a vacuum filter. Following this the newly solidified wax was re-melted while allowing for any trapped acetone to evaporate from the wax. The wax was then rewashed 2 more times with acetone in a vacuum filter before the acid number was retested.

Of the three purification methods, the acetone wash technique was the best at removing unreacted maleic anhydride from the reaction. Unfortunately the use of acetone was not compatible with industrial requirements of this project. Results from samples purified from the acetone wash technique were used as a baseline measurement to evaluate the purity of the final product produced from each method as compared to the results from the untreated equivalent maleated wax product.

Results from products that were purified via either the vacuum oven technique or the water wash technique were evaluated against the acetone wash technique to determine if these techniques could be added to the industrial process of any of the above mentioned maleation methods that may require purification before their commercial or industrial use.

2.8 Observed Emulsification of Wax Products

Samples of the final maleated wax products were mixed with water and the evaluated visually so as to see if the product themselves would emulsify with water. Products that did not emulsify were not subjected to further testing.

2.9 FTIR Characterization of Maleation

Wax samples were applied onto a sodium chloride disk, then using a Nicolet 510 FTIR spectrometer, FTIR spectra were recorded in a range of 4000 to 560 cm^{-1} with 4 cm^{-1} resolution and 24 scans. Evidence of grafting was supported with the presence of the following: asymmetric carbonyl (C=0) stretching peaks between 1860 to 1880 cm^{-1}, symmetric carbonyl stretching peaks visible between 1700 to 1790 cm^{-1}, an asymmetric di-ester line stretch (=C-O-C=) present near 1220 cm^{-1}, a symmetric di-ester line stretch (=C-O-C=) near 1050 cm^{-1}, a saturated cyclic five membered anhydride ring stretch near 910 cm^{-1} and the absence of double carbon-carbon bond (C=C) sharp bands normally seen near 860 cm^{-1} and 890 cm^{-1}.

2.10 Drop Point Temperature Characterization

The drop melt point technique is an Industrial standard practiced at Norjohn Emulsions Ltd. and was used to evaluate the melting temperature of samples. This technique was performed by coating a thermometer bulb with the melted maleated wax sample. The maleated wax was then allowed to cool and solidify around bulb. Following this, the thermometer was suspended in an Erlenmeyer flask and placed on a laboratory scale electric heating pad. The temperature of the system was then raised until the point where the wax sample falls or drops from the thermometer. The temperature is the read at this point from the thermometer. The temperature at which this occurs is considered the drop melt temperature and reported in Celsius. A representation of this process is illustrated in Figure 18.

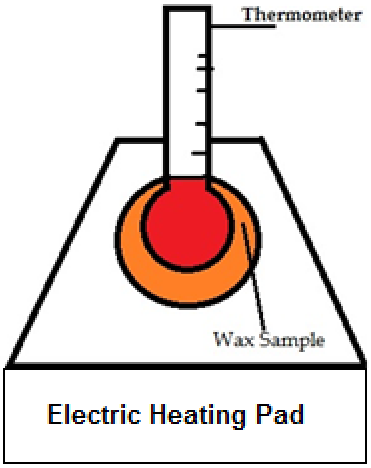


Figure 18 Drop Melt Point Technique

2.11 Degree of Grafting and Grafting Efficiency

Two final parameters were calculated to evaluate the success of each experiment using the results of the acid number titrations, the degree of grafting and the grafting efficiency. The degree of grafting was calculated using Equation 3 detailed below

$$Degree\ of\ Grafting = \frac{AN * MW_{MAH} * g * 1mol_{MAH}}{2mols_{KOH} * 1000mg * MW_{KOH}} * 100\%$$

Equation 3 Degree of Grafting Equation

The purpose of the degree of grafting is to provide a better sense of the amount of maleic anhydride that has been successfully grafted in proportion to the wax sample. It corrects for the fact that 1 mol of maleic anhydride is capable of neutralizing 2 moles of potassium hydroxide. More importantly, the degree of grafting can also be used to determine the grafting efficiency as related to the maleic anhydride charged to the reaction as detailed in Equation 4.

$$Grafting\ Efficiency = \frac{DG}{wt\%_{MAH}} * 100\%$$

Equation 4 Grafting Efficiency Equation

2.12 Results and Discussion

For this chapter wax emulsifier samples were labeled according to the method, peroxide and wax used. A number designation was used for the method between 1-6 corresponding to each method number (i.e. Bulk Addition =1, Ball Milling =2, Pulse Addition= 3, Peroxide pumping= 4, Maleic Anhydride Addition= 5 and Thermal Initiation=6). This followed by a letter for the peroxide (i.e. A=Benzoyl Peroxide, B= *tert*-Butyl Peroxybenzoate, C= Di-*tert*-Butyl Peroxide and X=no peroxide used) and finally a number was used to designated the type of starting wax used (i.e. 1=IGI 1212U fully refined paraffin wax, 2= Prowax 563 Slack Wax, 3= AlphaPlus© C30+ Alpha Olefin wax, and 4= AlphaPlus© C30+ HA Alpha Olefin wax). An example designation then would be 1-A-1 which would refer to a wax sample produced by Bulk Addition using Benzoyl Peroxide with IGI 1212U fully refined paraffin wax.

2.12.1 FTIR Characterization of Maleated Wax Product

The FTIR spectra taken of the maleated wax samples presented significant evidence in support of successful maleic anhydride grafting onto both the refined paraffin and olefin wax chains. The composition of those maleated waxes created by grafting onto the ProWax 563 slack wax had compositions that were too irregular to produce a sharp and identifiable spectra and set of recognizable peaks. A sample spectrum taken of a maleated refined paraffin wax sample prepared using the maleic anhydride addition method is seen below in Figure 19. The sample was prepared by charging 20g of maleic anhydride to the reactor along with 100g of IGI1212U wax and 29.8g of Di-*tert*-butyl peroxide for 10 hours at 160˚C.

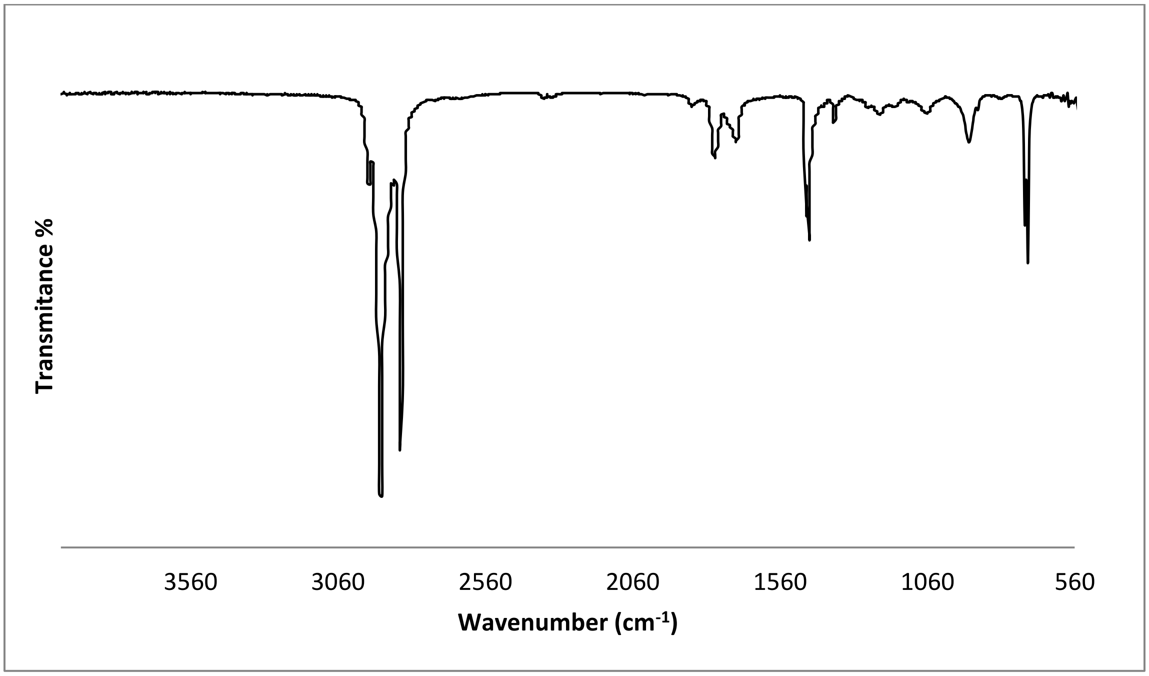


Figure 19 FTIR Sample Spectra of 5-C-1 Sample (20% MAH, 160°C)

Relevant peaks that were identified in the above spectrum in Figure 19 are presented in Table 7. Peaks corresponding to the structure of the refined paraffin wax are also identified. Consistent spectra and peaks were seen in all spectra readings performed for maleated products made from the IGI1212U refined paraffin wax starting material. Peaks supporting the grafting of maleic anhydride were less pronounced in products with lower acid number as would be expected.

Table 7 Peak Assignment for Figure 14 FTIR spectrum

Identified Peak (cm^{-1})	**Assignment**
Missing Peaks at 867 and 892	Absence of double carbon-carbon bond (C=C) sharp bands
919	Saturated cyclic five membered anhydride ring stretch
1051	Symmetric di-ester line stretch (=C-O-C=)
1224	Asymmetric di-ester line stretch (=C-O-C=)
1786-1784	Symmetric carbonyl (C=O) stretch
1864-1860	Asymmetric carbonyl (C=O) stretch
2959,2920,2851	Paraffin Wax Peaks

A sample spectrum taken of a maleated n-alpha-olefin wax sample prepared using the thermal addition method is seen below in Figure 20. The sample was prepared by charging 20g of maleic anhydride to the reactor along with 100g of alphaplus© 30+HA wax for 8 hours at 160˚C.

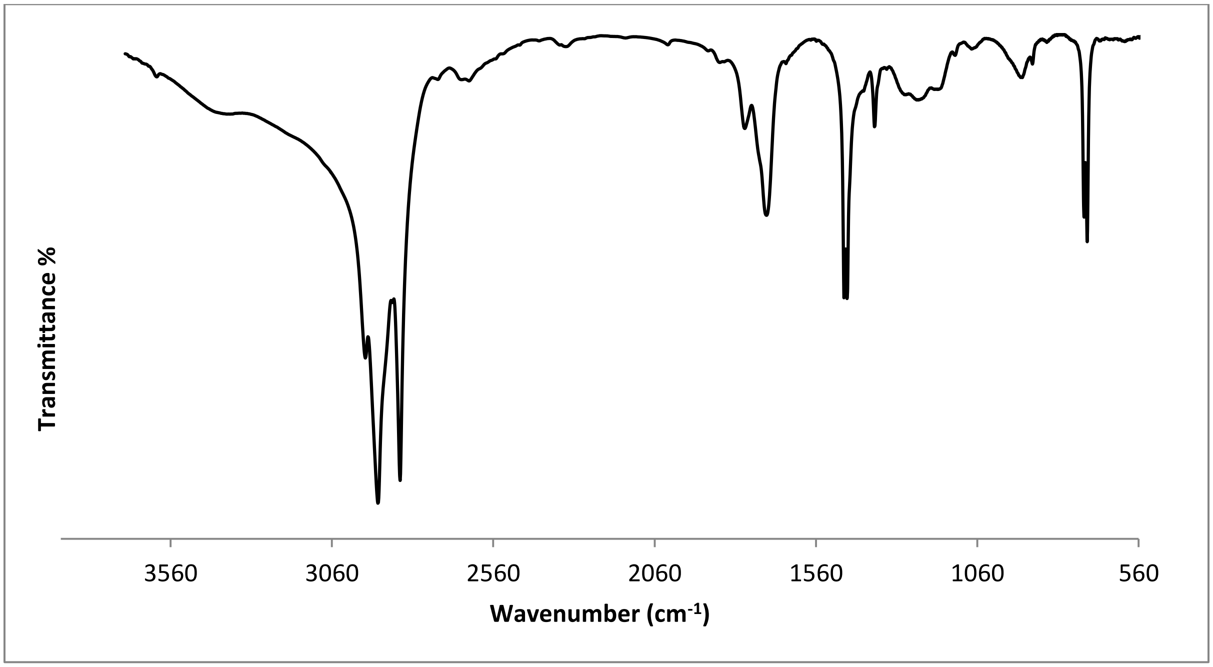


Figure 20 FTIR Sample Spectra of 6-X-4 Sample (20% MAH 200°C)

Relevant peaks that were identified in the above spectrum in Figure 20 are presented in Table 8. Peaks corresponding to the structure of the alpha olefin wax are also identified.

Similar to the results of the maleated refined paraffin wax, consistent spectra and peaks were seen in all spectra readings performed for maleated products made from the alphaplus© 30+ and 30+HA wax starting material. Peaks supporting the grafting of maleic anhydride were also less pronounced in products with lower acid numbers.

Table 8 Peak Assignment for Figure 15 FTIR spectrum

Identified Peak (cm^{-1})	**Assignment**
914	Saturated cyclic five membered anhydride ring stretch
1046	Symmetric di-ester line stretch (=C-O-C=)
1220	Asymmetric di-ester line stretch (=C-O-C=)
1472	(CH_2) Bend, Olefin Wax Peak
1642	(C=C) stretch, Olefin Wax Peak
1784-1782	Symmetric carbonyl (C=O) stretch
1863-1859	Asymmetric carbonyl (C=O) stretch
2918,2851	Sp^3 (C-H) stretch, Olefin Wax Peak

2.12.2 Effects of Peroxide Type on Final Product

Of the three peroxides, peroxide initiated maleated products produced using Di-*tert*-butyl peroxide showed the highest average acid number and grafting efficiency as can be seen in Figure 21 when compared in results from the bulk addition method. Special considerations should be made for the fact that experiments performed with Di-*tert*-butyl peroxide where performed at a higher temperature of 160˚C as compared to 130˚C for *tert*-butyl peroxybenzoate experiments and 80˚C for benzoyl peroxide experiments. Additionally it should be noted that the source of benzoyl peroxide was 1% less pure than either the Di-*tert*-butyl peroxide source or the *tert*-butyl peroxybenzoate which may account for some of the difference in the average acid number.

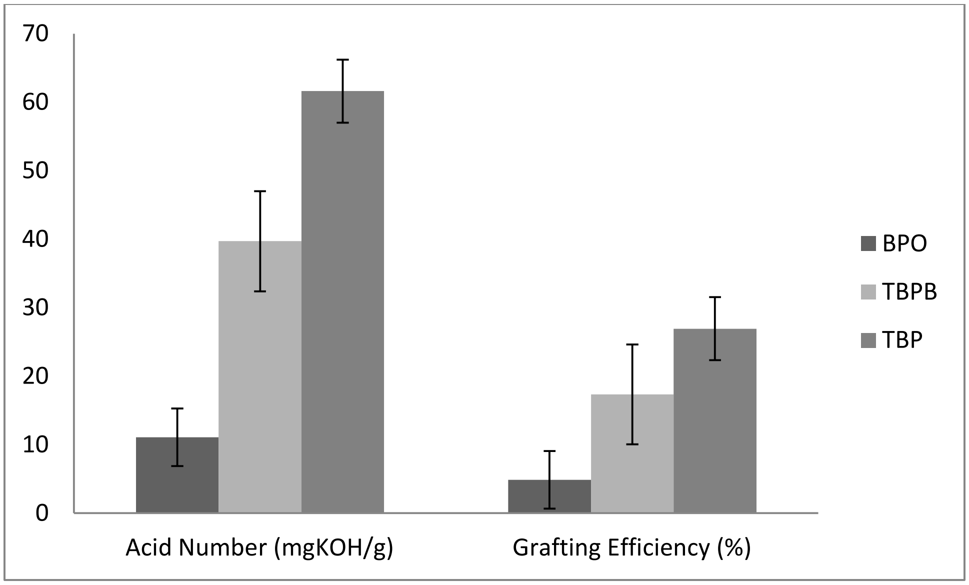


Figure 21 Average Acid Number and Grafting Efficiency of Products from Each Peroxide using the Bulk addition method

Due to the fact that benzoyl peroxide is a solid it was impossible to use it as a peroxide initiator in the pumping or pulse methods without the incorporation of a solvent which was against the industrial specifications of this project as mentioned previously.

2.12.3 Effect of Peroxide Concentration on Grafting Efficiency and Acid Number

The amount of peroxide used in relation to the amount of maleic anhydride charged to the reactor had a noticeable effect for all peroxide initiated methods and for all types of peroxide used as evidenced by Figure 22**,** Figure 23**,** Figure 24**,** Figure 25 and Figure 26 which show acid number results for standardized experiments with decreasing amounts of peroxide initiator added in terms of molar ratio to the amount of moles of maleic anhydride charged to the reactor. It is clear from the nature of the 5 figures that an increase in the proportion of peroxide compared to the maleic anhydride resulted in an increase in acid number of the final product. This effect is most pronounced in the bulk addition, ball-milling, and peroxide pulse, experiments, as can be seen in Figure 22, Figure 23 and Figure 24 respectively.

One possible explanation for these results is that the bulk addition, ball-milling and peroxide pulse experiments by their nature resulted in a longer exposure of these high concentrations of peroxide to the complete experimental quantity of maleic anhydride charged to the reactor. Conversely, in the peroxide pumping method the peroxide is pumped in over the entirety of the experiment and as such will likely not have such a pronounced effect, an examination of the efficient use of peroxide in each of the 5 peroxide initiated method is discussed further later in subchapter 2.12.5.

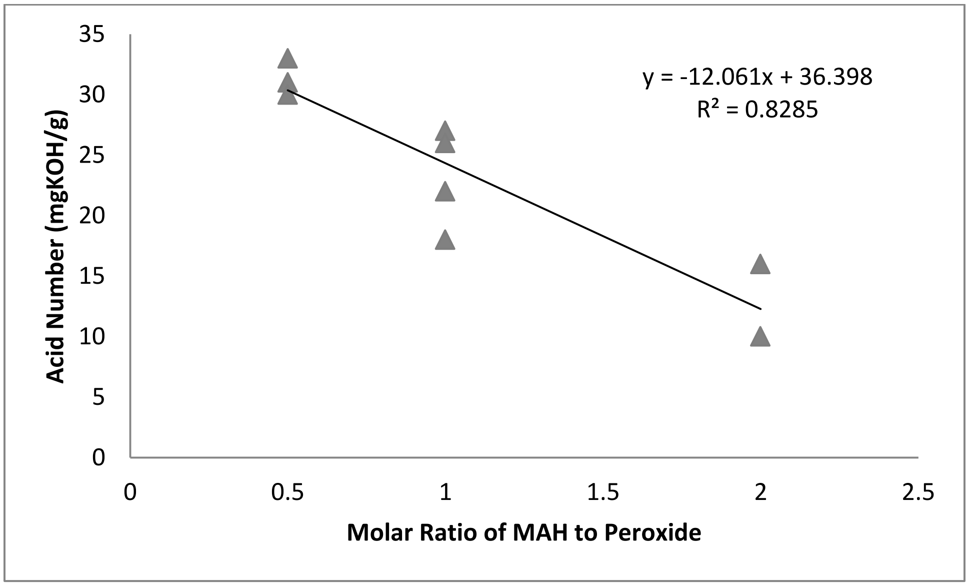


Figure 22 Graph depicting Molar Ratio of Maleic Anhydride to Peroxide with relation to Acid Number for 1-C-1 sample (10 Hours, 160˚C)

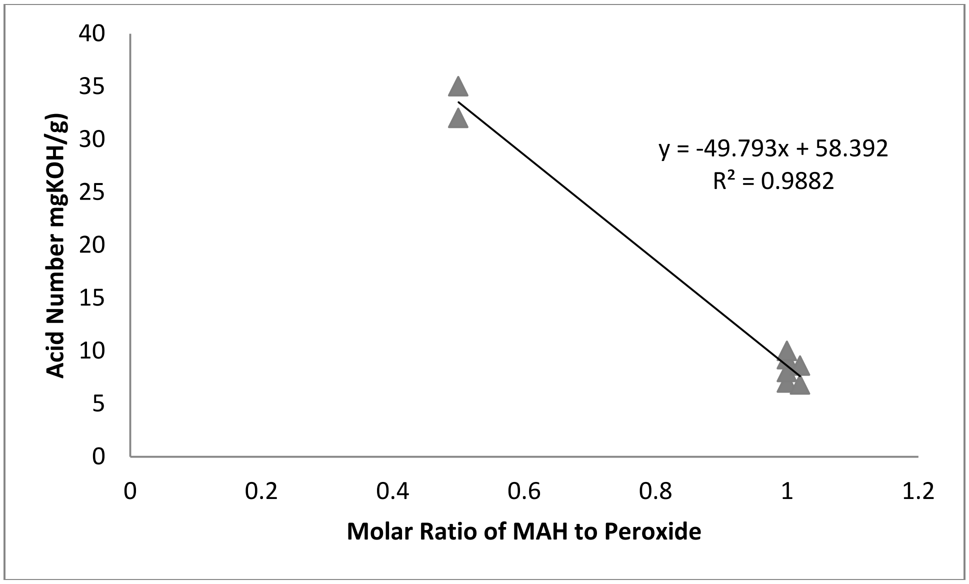


Figure 23 Graph depicting Molar Ratio of Maleic Anhydride to Peroxide with relation to Acid Number for 2-A-1 sample (6 hours, BP0, 80˚C)

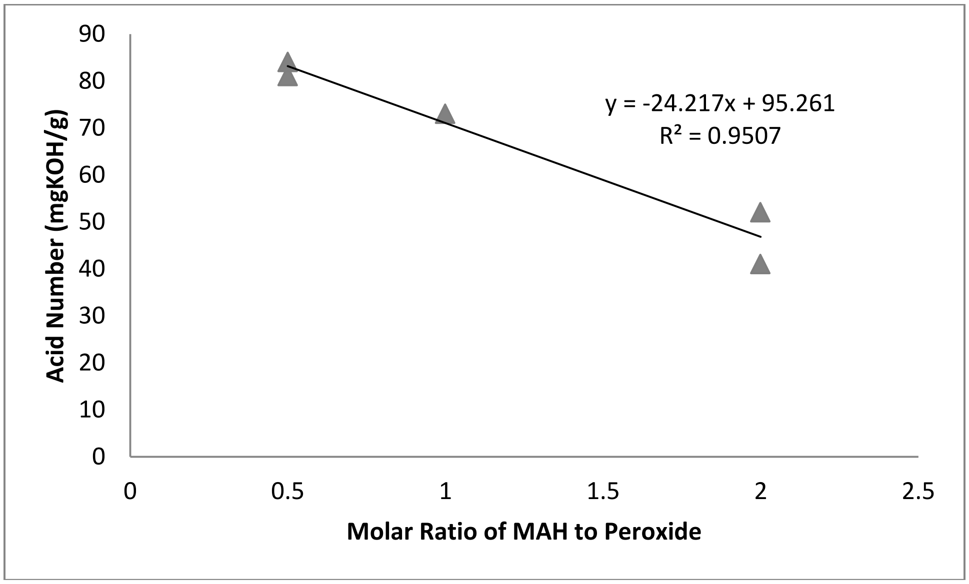


Figure 24 Graph depicting Molar Ratio of Maleic Anhydride to Peroxide with relation to Acid Number for 3-C-1 sample (10 Hours, 160˚C)

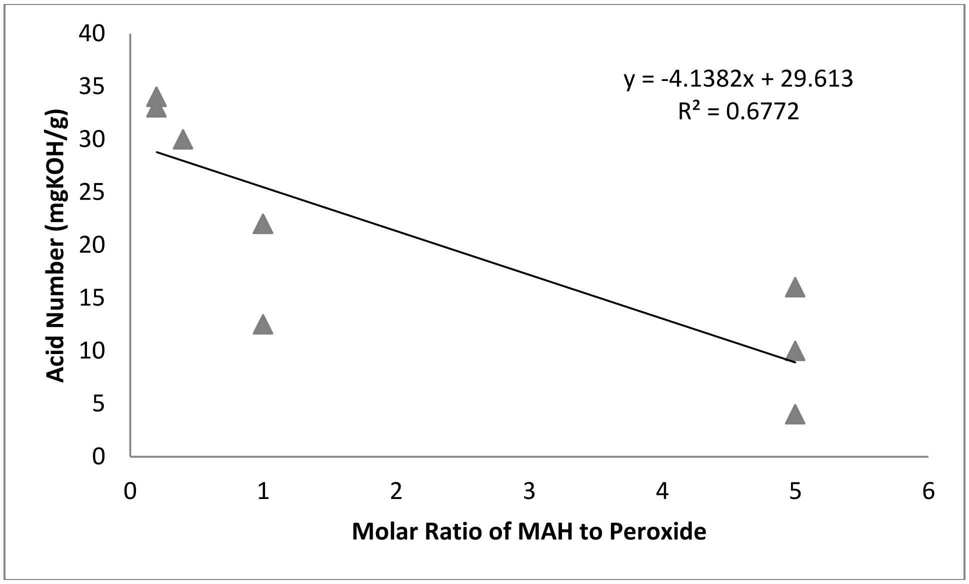


Figure 25 Graph depicting Molar Ratio of Maleic Anhydride to Peroxide with relation to Acid Number for 4-C-1 (0.5 Hours, 160˚C)

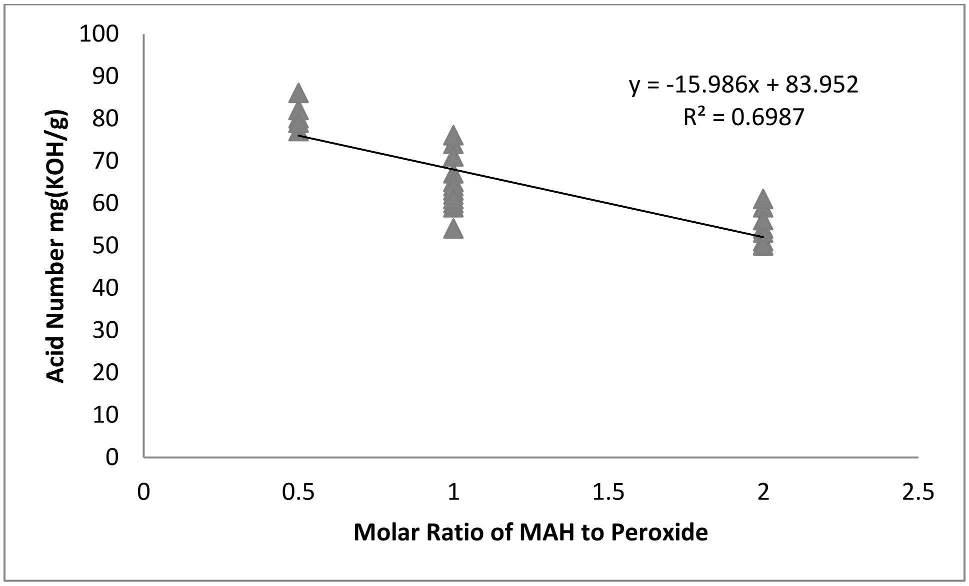


Figure 26 Graph depicting Molar Ratio of Maleic Anhydride to Peroxide with relation to Acid Number for 5-C-1 sample (10 Hours, TBP, 160˚C)

2.12.4 Differences between waxes as Starting Material

Of the 3 different waxes examined as starting materials for the peroxide initiated experiments. The alphaplus© C30+ alpha olefin wax had the best grafting efficiency and acid number as evidenced in Figure 27.

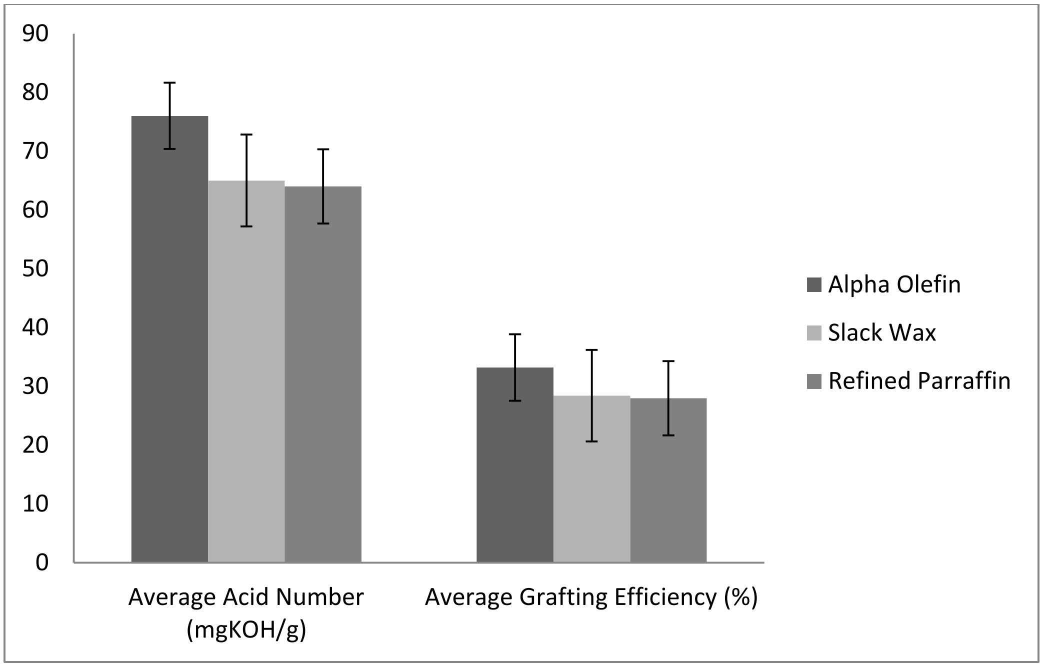


Figure 27 Comparison of Average Acid Number and Grafting Efficiency of Maleic Anhydride Addition Experiments with relation to starting wax

Figure 27 compares the wax starting materials using a standardized approach following the maleic anhydride addition method. The samples were prepared by charging 100g of wax and 29.8g of Di-*tert*-butyl peroxide to the reactor for 10 hours at 160˚C while adding a total 20g of maleic anhydride to the reactor over the first hour. These results demonstrated above in Figure 27 are as would be expected due to the higher proportion of linear carbon chains of the alpha olefin wax relative to the slack and refined paraffin waxes as well as the higher proportion of unsaturated double bonds present on the alpha olefin wax chains which serve as a ideal grafting site due in part to the possibility of the ene-reaction. Another important difference between in the results of products derived from the 3 starting waxes is that while the alpha-olefin and refined paraffin wax produced maleated products that were yellow in color, the slack wax produced maleated products that were noticeably darker in color than that of either the refined paraffin or alpha-olefin.

Of the 2 different olefin waxes examined as starting materials for the thermally initiated experiments. The alphaplus© C30+ HA alpha olefin wax had the best grafting efficiency and acid number as evidenced in Figure 28.

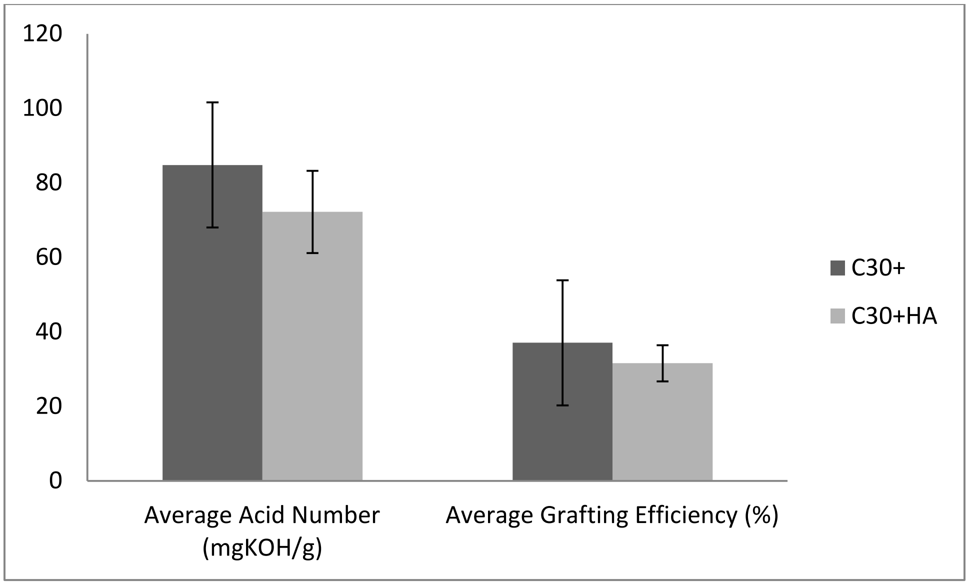


Figure 28 Comparison of Average Acid Number and Grafting Efficiency of Thermally Initiated Experiments with relation to starting Wax

Figure 28 compares the wax starting materials using a standardized approach following the thermally initiated grafting method. The samples were prepared by charging 100g of wax and 20g of maleic anhydride to the reactor for 8 hours at 200˚C. The results demonstrated above in Figure 28 are also as would be expected for similar reasons as those of Figure 27. This is most likely due to the higher proportion of linear carbon chains of the alphaplus© C30+ HA wax relative to the alphaplus© C30+ wax as well as the higher proportion of unsaturated double bonds present in the alphaplus© C30+ HA composition which serve as a ideal grafting sites for the ene-reaction.

Average melt points of the maleated wax products from each of the 4 starting wax materials were measured and the results showed a consistent melting temperature very similar to that of the wax starting material as demonstrated below in Figure 29. The alphaplus© 30+ olefin wax consistently produce maleated products with the highest melting point which reflects the fact that it was the wax with the highest starting material.

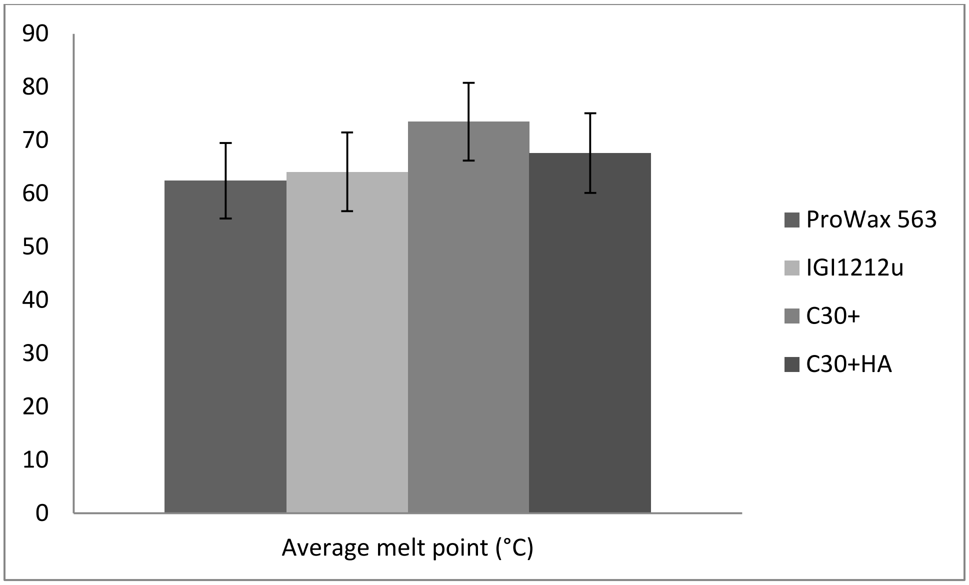


Figure 29 Average Melt Point of Maleated Wax products of different starting wax materials

2.12.5 Comparison of Methods

Selected results from experimental runs are demonstrated in Table 9, Table 10, Table 11, Table 12, Table 13 and Table 14 as an example of runs performed for each process. This collection of results is meant of a means of showing the range and typical results of the various different methods.

Table 9 Selected Bulk Addition Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (°C)	RTime (hours)	Acid Number (mg_{KOH}/g)	Grafting Efficiency (%)	Final Color
1-C-2	20	2	160	10	41	18	Dark Orange-Brown
1-C-1	20	0.5	160	12	84	37	Yellow

1-C-2	10	0.5	160	12	33	29	Dark Orange-Brown
1-C-1	10	1	160	11	26	23	Yellow
1-C-1	5	1	160	10	9	16	Yellow
1-C-1	5	1	160	10	11	19	Yellow

Experiments performed using the Bulk Addition method of wax maleation required an inert atmosphere as it appeared that experiment performed under open atmosphere or those in which the inert atmosphere had been contaminated would often result in homopolymerization of the maleic anhydride, which would cross-link, harden and render the final products irretrievable and therefore not successful. Homopolymerization of the maleic anhydride was commonly seen in the bulk, peroxide pumping and pulse processes as well, particularly when they too had been exposed to open atmosphere. Due to the fact that the homopolymerization rendered the final maleated wax products useless for the purposes of this project, experiment which showed evidence of homopolymerization of maleic anhydride were deemed failed experiments.

Table 10 Selected Ball Milling Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (°C)	RTime (hours)	Acid Number (mg$_{KOH}$/g)	Grafting Efficiency (%)	Final Color
2-A-1	5	1	80	1	7	12	Yellow
2-A-1	5	1	80	2	8	14	Yellow
2-A-1	2.5	1.02	80	6	6.8	24	Yellow
2-A-1	2.5	1.02	80	6	8.6	30	Yellow
2-A-1	20	0.5	80	6	32	14	Yellow
2-A-1	20	0.5	80	6	35	15	Yellow

Experiments performed using the Ball Milling method of wax maleation produced consistent and robust results that were under open atmosphere. A high acid number wax was not achievable using the ball milling method. None of the ball milling experiments produced any signs of homopolymerization of the maleic anhydride. Due to the limitations of the planetary ball mill apparatus all ball milling experiments were done on a small scale. Despite being one of the more robust processes the ball milling approach was not best suited to meet the goals of this project because of the added complication of a scale-up incorporation of the ball mill apparatus as well as the inability of the process to produce a high acid number wax.

Table 11 Selected Pulse Addition Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (°C)	RTime (hours)	Acid Number (mg_{KOH}/g)	Grafting Efficiency (%)	Final Color
3-C-1	20	1	160	10	76	33	Yellow
3-C-2	20	1	160	10	29	13	Dark Orange-Brown
3-C-2	10	1	160	10	13	11	Dark Orange-Brown
3-C-1	10	1	160	10	13	11	Yellow
3-C-1	5	1	160	10	9	16	Yellow
3-C-1	5	1	160	10	11	19	Yellow

The pulse addition method had similar results to the peroxide pumping method. A small proportion of the pulse addition experiments failed due to homopolymerization. A higher acid number wax was achievable using the peroxide pumping maleation method than the pulse addition method. The peroxide pumping and pulse addition methods were a less efficient use of the peroxide initiator. This is because as opposed to the other methods the peroxide initiator in the pumping and pulse methods is not exposed to the reaction at high temperature for the same amount of time as it is in the other methods when performed for the equivalent amount of time. This is exemplified in Equation 5 when you take into account the constant pumping as the concentration, x, increases over the period of one hour.

$$\int [1 - 0.5^{(1-x)}]$$

Equation 5 Peroxide Efficiency of Use Equation

Using Equation 5 it is evident that ideally when 1 mol is pumped in over the period of one half-life roughly 27.9% is converted which is equal .558 usable moles of radical as compared to 2 moles of radical for the other 3 peroxide initiated methods. One other concern about the peroxide pumping method was that it would be unsafe to have a pumping line connecting the active reaction back to a peroxide reservoir which would be necessary with the industrial scale up of the peroxide initiated method.

Table 12 Selected Peroxide Pumping Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (°C)	RTime (hours)	Acid Number (mg_{KOH}/g)	Grafting Efficiency (%)	Final Color
4-C-1	25	3	160	10.5	33	12	Yellow
4-C-2	20	5	70	10	11	5	Yellow
4-C-1	10	1	160	0.5	9	7.8	Yellow
4-C-1	10	0.2	160	0.5	40	34	Yellow
4-C-1	5	0.4	160	0.5	30	52	Yellow
4-C-2	5	1	70	10	7	12	Yellow

Of the 5 peroxide initiated methods, the Maleic Anhydride Addition method consistently produced the highest average acid number. Of all the methods it had the highest grafting efficiency. It was also much less likely to produce homopolymerization of the maleic anhydride than the other peroxide methods to the point where it was possible to perform this method without the need for an inert atmosphere.

Table 13 Selected Maleic Anhydride Addition Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (°C)	RTime (hours)	Acid Number (mg_{KOH}/g)	Grafting Efficiency (%)	Final Color
5-C-3	10	1	160	4	45	39	Yellow
5-C-3	15	1	160	10	80	47	Yellow
5-C-2	20	1	160	10	80	33	Dark Orange-Brown
5-C-2	20	1	160	10	71	31	Dark Orange-Brown
5-C-1	20	1	160	10	64	28	Yellow
5-B-1	20	0.5	130	10	79	34	Yellow

The results of the thermal initiated method outperformed all of the peroxide initiated methods in terms of acid number of final product wax and purity of product. The thermally initiated method was also capable of being performed without the need for an inert atmosphere and produced better results in a shorter period of 8 hours which is preferable for an industrial setting. The thermally initiated method required a higher operating temperature. Recovery of the maleic anhydride that sublimated out of the reaction may be possible with the design of a condensing mechanism in the lid of the reaction vessel.

Table 14 Selected Thermally Initiated Wax Maleation Results

Wax Sample	Maleic Anhydride Initially Charged (wt %)	Temp (°C)	RTime (hours)	Acid Number (mg_{KOH}/g)	Grafting Efficiency (%)	Final Color
6-X-3	23	200	8	82	29	Yellow
6-X-3	15	200	8	72	42	Yellow
6-X-3	23	200	8	79	30	Yellow
6-X-4	11.5	200	8	49	37	Yellow
6-X-4	23	200	8	72	27	Yellow
6-X-4	23	200	8	77	29	Yellow

The average acid number of each method are presented below in Figure 30**.** As can be seen from the chart the thermal initiation and maleic anhydride addition method on average had the best and 2nd best results respectively. The other four methods produced similar results. One possible explanation is that the homopolymerization of maleic anhydride was more favourable in these methods.

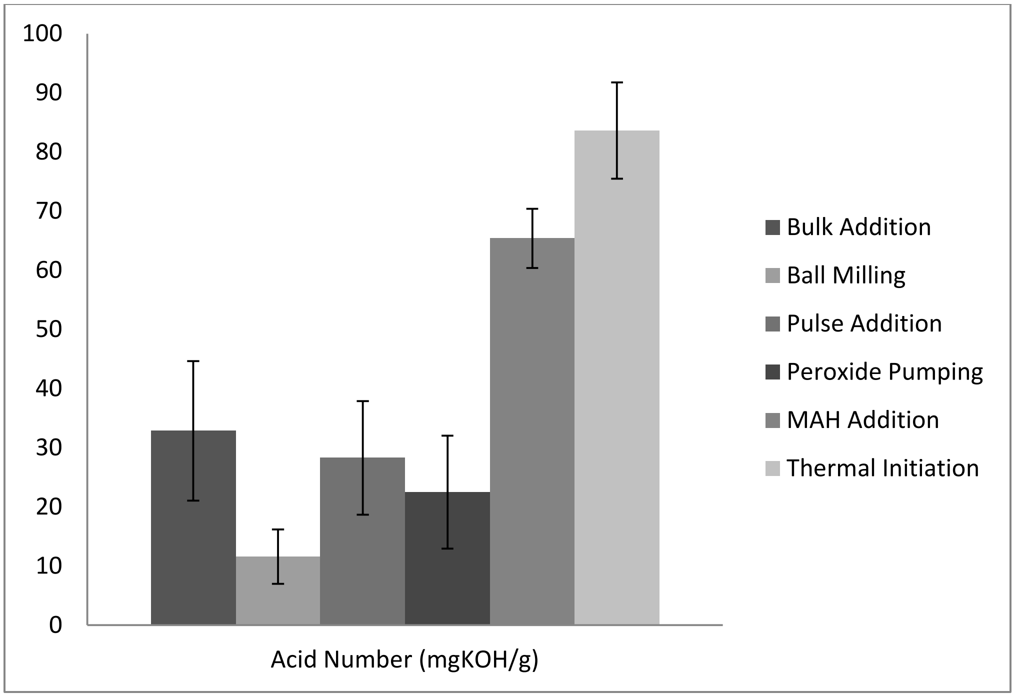


Figure 30 Comparison of Average Acid Number of Products of Maleation Methods

Using the C30+ Alpha Olefin Wax as a standard. The grafting efficiencies of the methods that produced the two highest are presented in Figure 31. Due to the incorporation of a peroxide initiator the average grafting efficiency with the Maleic Anhydride Addition method was higher.

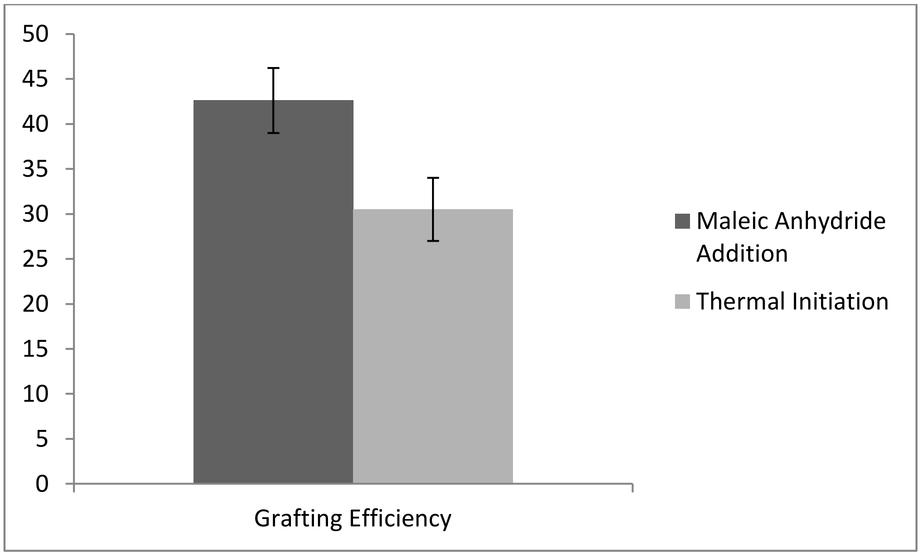


Figure 31 Grafting Efficiency of Maleic Anhydride Addition and Thermal Initiation methods with AlphaPlus C30+ Wax

The success rates of the sum of the experiments of each of the 6 methods are presented in Figure 32. This result reflect the robustness of each method and a consistent production of a viable maleated wax product. There were no cases of failure due to homopolymerization in either the Ball Milling or Thermal Initiation methods. All other methods demonstrated the possibility of producing homopolymerized maleic anhydride rather than a maleated wax product. This production of homopolymerized maleic anhydride may have been caused by contamination or machine error such as a pause in stirring.

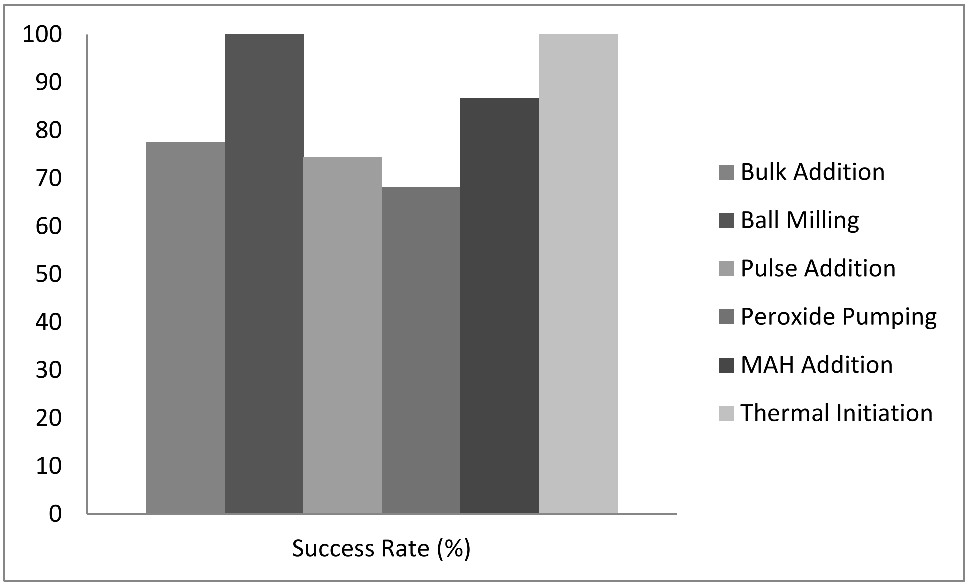


Figure 32 Comparison of Success Rate of Maleation Methods

2.12.6 Effect of Grafting Method on Melt Point of Wax Product

All 6 methods of grafting used in this project produced statistically indistinct average melting temperatures for their successfully maleated products ranging from 60-73˚C for the as demonstrated in Figure 33. There was no significant change in the temperature of the final product compared to the starting wax material depending on the method of grafting. All successfully maleated waxes from all grafting methods had melt points that were acceptable within the industrial product confines put forth for this project.

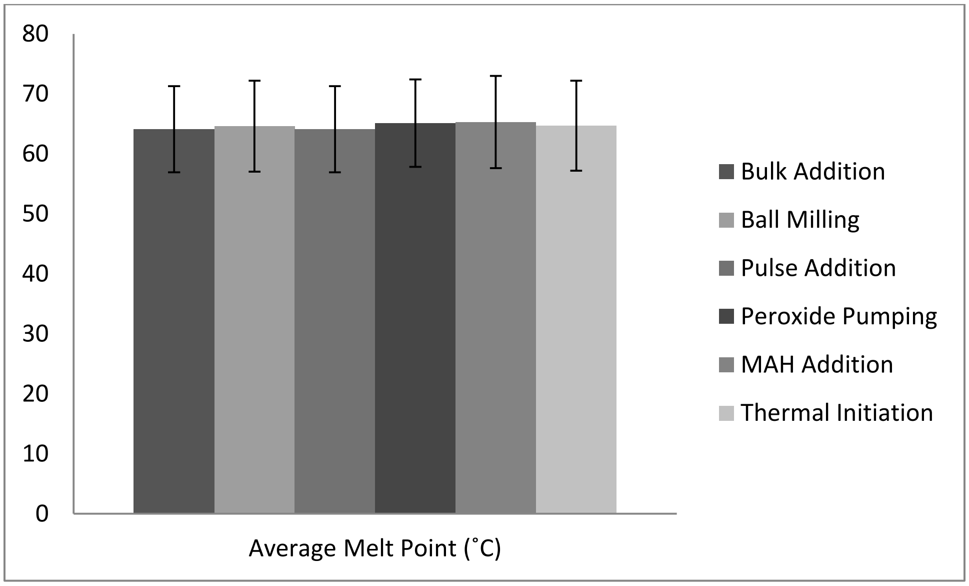


Figure 33 Average Melt Point of Grafting Method Products

2.12.7 Purity of Samples

Following each experiment the acid number of the maleated wax sample was tested and then a portion of the maleated wax sample was washed using the acetone washing method. The acid number readings for the prewash and post wash samples were compared and the change in acid number was noted. This average change in acid number for each was then evaluated as a percent of the average acid number for each of the 6 methods. This calculation was viewed as a means of quantifying the purity of the final product of each method prior to washing to examine the possibility of not needing a washing component for the maleation method when produced on an industrial scale. The results are summarized in Figure 34. Once again the maleic anhydride method and thermal initiation method demonstrated the best results, this is again possibly a product of the fact that both methods were performed in open atmosphere and that in each case the maleic anhydride was able to sublimated out of the reaction and condense on the lid of the reaction vessel more easily than in the other methods possibly because it was less favourable for the maleic anhydride to homopolymerize in these methods. It was also apparent that higher temperature reactions particularly those run at 160˚C or above produced purer products. This is as would be expected because the sublimation of maleic anhydride would be promoted at higher temperatures.

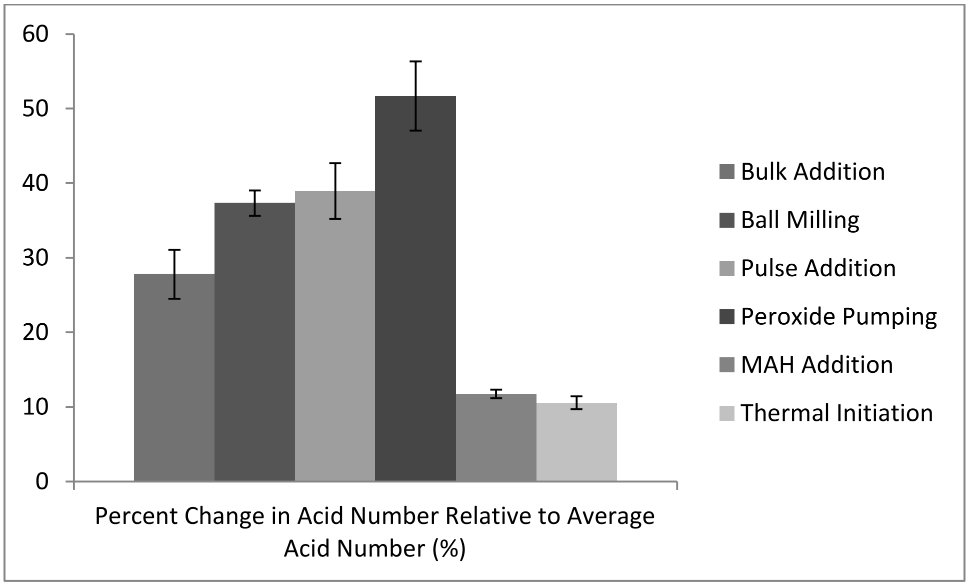


Figure 34 Comparison of The Average Change in Acid Number reported as a percent of Average Acid Number Following Acetone Wash of Products of Maleation Methods

2.12.8 Effect of Reaction Time on Acid Number and Grafting Efficiency

Experiments to measure the effect of the time of the reaction on the acid number of the final product were performed for each of the 6 grafting methods as demonstrated below in Figure 35**,** Figure 36**,** Figure 37**,** Figure 38**,** Figure 39**,** and Figure 40. It became clear from these experiments that in general the majority of grafting occurs in the 5 hours of the experiment. This factor may explain differences seen in the effects of the molar ratio of peroxide to maleic anhydride in each of the 5 peroxide initiated grafting methods. These experiments also allowed for predictions of the acid number that would be generated by each method given a certain operating time, which would be useful in scale up considerations for each method because of the imposed constraints of the typical industrial working shift of around 8 hours or less.

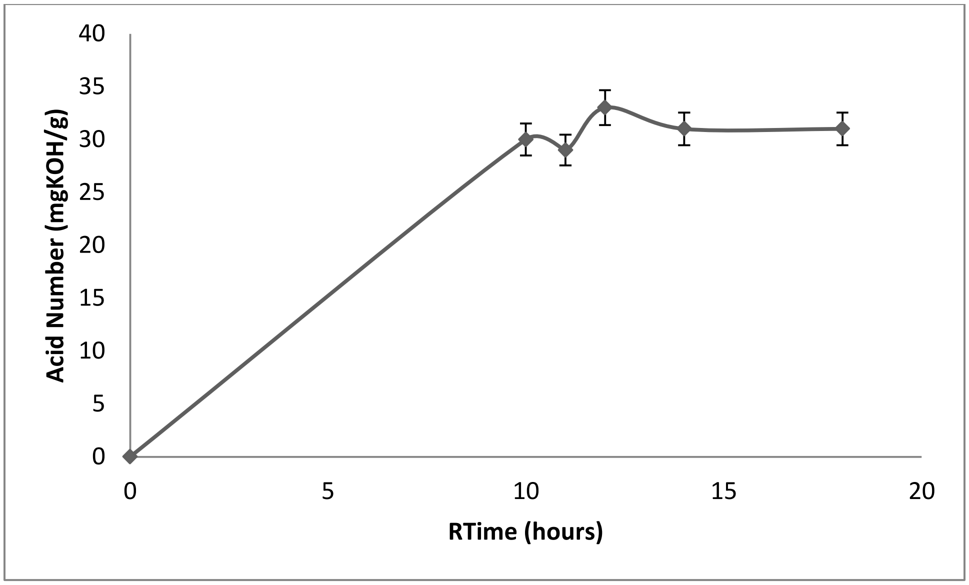


Figure 35 Plot of Reaction time vs. Acid Number for Bulk addition sample (10% MAH, 7.4%TBP, 160˚C)

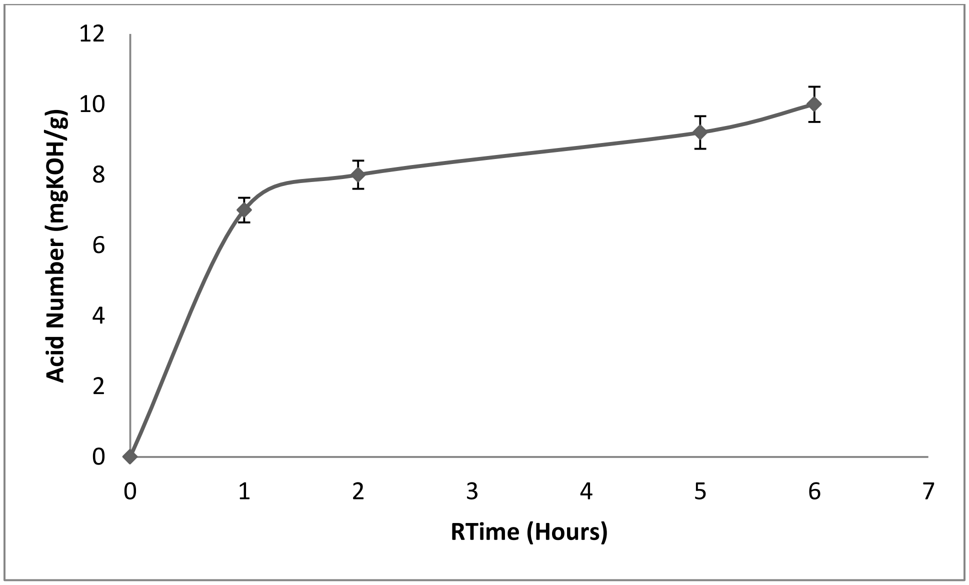


Figure 36 Plot of Reaction time vs. Acid Number for Ball milling sample (5% MAH, 12.4%BPO, 80˚C)

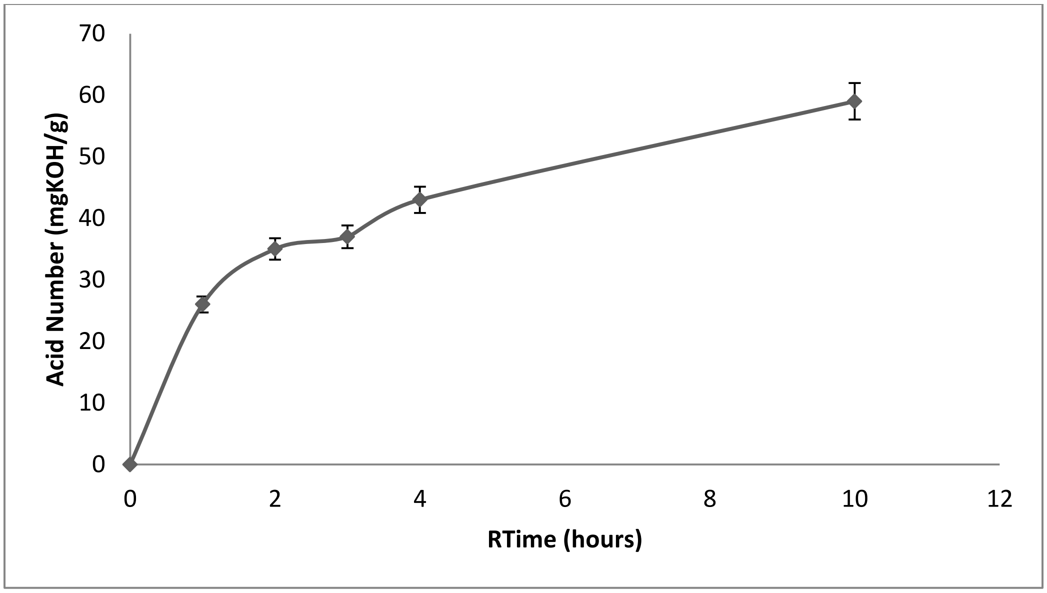


Figure 37 Plot of Reaction time vs. Acid Number for pulse addition sample (20% MAH, 30%TBP, 160˚C)

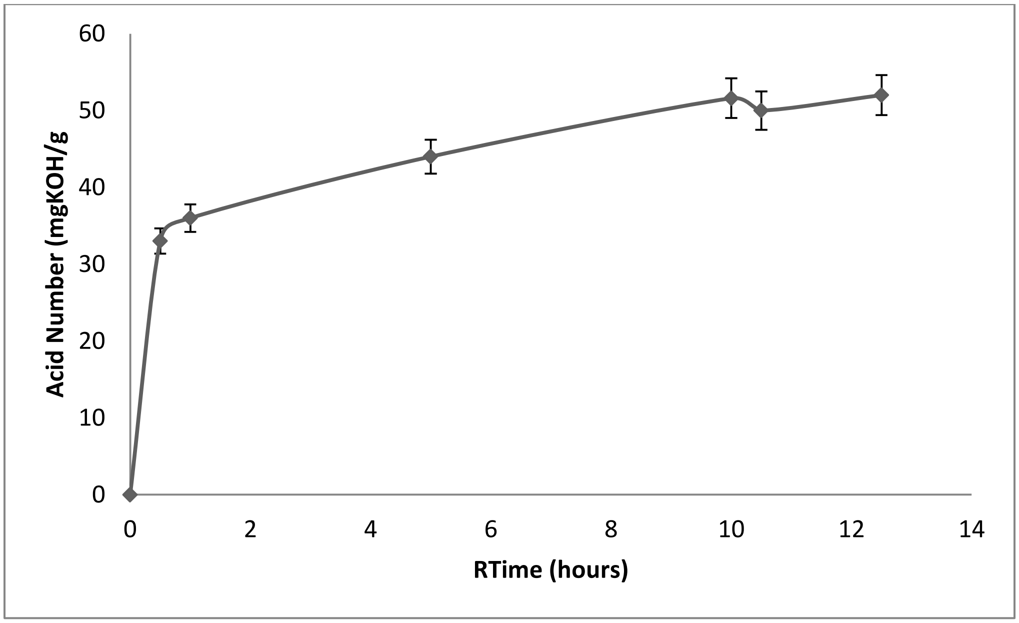


Figure 38 Plot of Reaction time vs. Acid Number for peroxide pumping sample (20% MAH, 30%TBP, 160˚C)

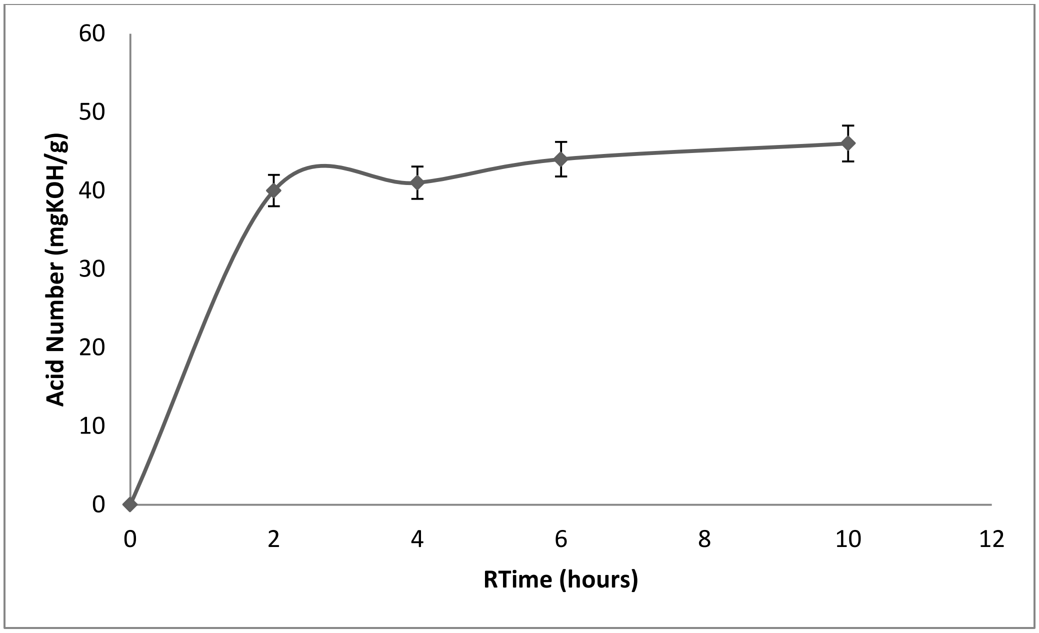


Figure 39 Plot of Reaction time vs. Acid Number for Maleic anhydride addition sample (10% MAH, 15%TBP, 160˚C)

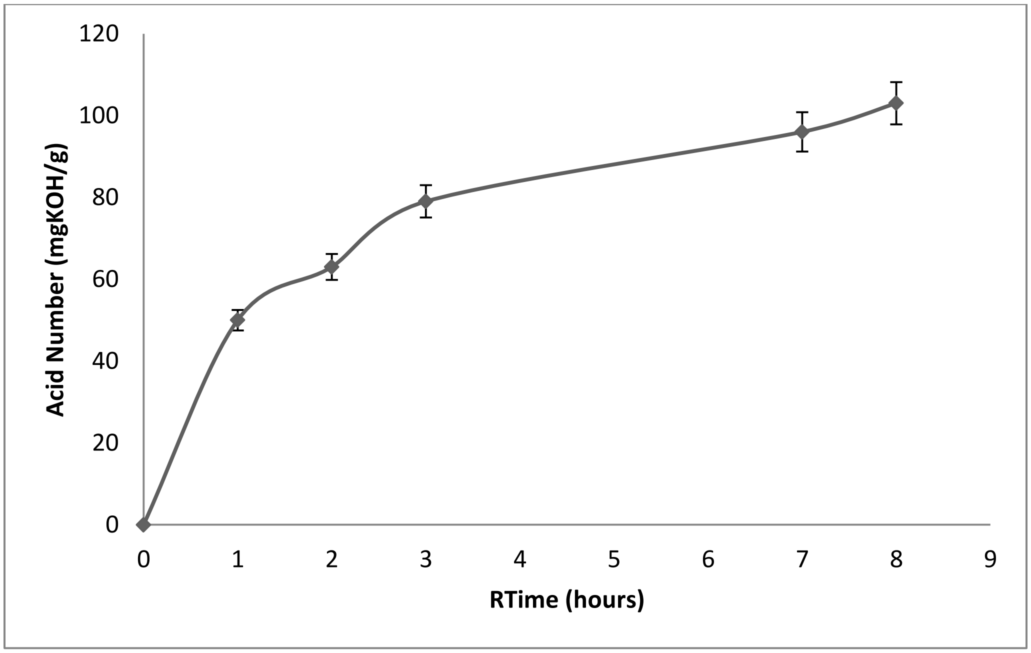


Figure 40 Plot of Reaction time vs. Acid Number for Thermal Initiation Sample (10% MAH, 200˚C)

2.12.9 Effectiveness of Washing Techniques

In cases where the purity of the maleated product may be an issue with the application of said product possible techniques were examined as a means of further purify this product as explained in subchapter 2.7. Of the three techniques the acetone washing technique showed the greatest decrease in acid number post washing which would suggest that it was the best means of purifying a wax sample, however due to the use of the solvent acetone it was not viewed as an acceptable scale up possibility. The water wash technique showed the next largest decrease in acid number post wash of the sample, but the samples would self-emulsify in the water causing either a loss of water or an added separation step. The vacuum oven technique showed similar results to storing the wax in an oven at room pressure which would translate to a simple storage tank in the industrial scale up equivalent.

2.13 Conclusion

The Experimental Methods that were designed so as to be performed under open atmosphere, Maleic Anhydride Addition, Ball-Milling and Thermal Initiation were the most robust and consistent in their results. Due to the consistency with which it was able to produce a high acid number wax 60+, the robustness of the method, grafting efficiency and purity of final product; the Maleic Anhydride Addition method appeared to be the best peroxide initiated choice. The Thermally Initiated method appeared to be the best grafting method overall for incorporation into the Industrial setting due to the consistency with which it was able to produce a high acid number wax 70+, the robustness of the method, purity of final product, length of experiment and lack of peroxide initiator.

Chapter 3: Emulsion formulations for use in Engineered Wood Products

3.1 Objective and Scope

The purpose of this chapter is to examine the waxes produced using the methods detailed in chapter 2 to examine their effectiveness as replacement emulsifiers in a commercial emulsion used to instill hydrophobicity and dimensional stability, as well as other beneficial properties, to engineered wood products. In this case a method for constructing particle boards is used to represent the typical incorporation of wax emulsions into engineered wood product manufacturing. The newly developed maleated waxes were investigated as replacement emulsifiers to Pristerine™, a fatty acid based emulsifier produced by Croda, in a commercial emulsion for incorporation into engineered wood products produced commercially by Norjohn Limited.

3.2 Experimental

3.2.1 Materials

- Monoethanolamine supplied by Norjohn Emulsions Inc.
- Pristerine™ purchase from Croda
- Undistilled water
- Prowax 563 Slack Wax, purchased from Imperial Oil
- Successfully Maleated Waxes developed from the processes of chapters 2
- A phenol-formaldehyde resin supplied by Norjon Emulsions Inc.
- Wood particle chips purchased from Panolam Industries.

3.2.2 Preparation of Emulsions

Emulsions for use in particle board engineered wood products are prepared to test a possible commercial application for the maleated waxes prepared in the previous two chapters, 2, prior to the incorporation into boards and subsequent board testing. The standard emulsion formulation is as follows: An aqueous mixture of water and monoethanolamine (MEA) was prepared and heated to 95 ˚C while stirring to ensure that all MEA has dissolved. At the same time a mixture of the Imperial Oil slack wax and a sample of the one of the maleated waxes from produced in chapter 2 was prepared and heated to 110 ˚C while stirring to ensure homogeneity.

It is important to note that the entire source of slack wax must be heated to well past its melting point and mixed before a portion is added. This is due to the oil content of slack wax which means that in a slack wax sample the oil content will melt first and a sample will not appropriately reflect an industrial scale sample unless it is fully melted and mixed homogenously. Initially, the ratio of experimental emulsifying wax content in relation to slack wax content was chosen so as to produce a preblend acid number similar to that of the control sample that was prepared with Pristerine^{TM}. The preblend acid number was calculated using Equation 6. An acid number titration of the Prowax 563 Slack Wax revealed that it had an acid number of 0.

$$\frac{m_E * AN_E}{m_S + m_E} = AN_p$$

Equation 6 Pre-blend Acid Number Calculation

In the next step the aqeuous mixture was then mixed in a Silverson laboratory disperser while the wax mixture was added slowly to create the initial oil-water emulsion. Once the wax mixture had been fully added the emulsion was subjected to high shear mixing for several minutes to promote homogeneity. Subjecting an emulsion to high shear has been shown to reduce particle size and improve emulsion stability [51]. As mentioned previously smaller wax particles have been shown to greater improve the desired properties when applied to engineered wood products [55]. At the same time, a high shearing speed must reflect methods that are feasible on an industrial scale [51]. As such, the emulsion is processed through a homogenizer to further reduce the wax particle size and to simulate industrial mixing conditions, once again for several minutes so as to ensure several passes of the emulsion through the homogenizer [51]. In this case the emulsion is homogenized at high pressure by a piston which forces the emulsion through a valve as picture below in Figure 41.

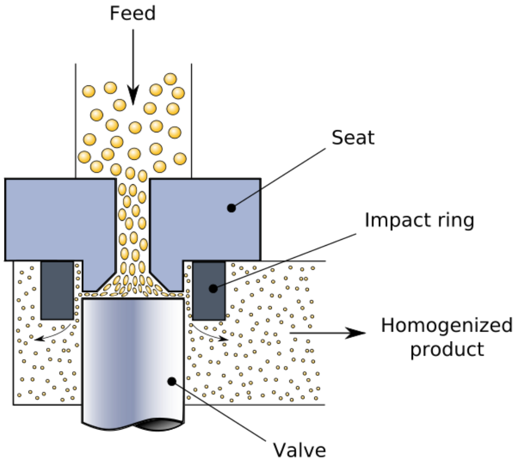


Figure 41 Homogenizer Example Schematic[3]

The emulsion is then cooled to room temperature in a water bath whilst under constant stirring so as to prevent fallout.

Once it has reached room temperature, the emulsion is examined to determine if it has become overly viscous or thick which may suggest instability or insufficient water to oil ratio in the mixing process. The emulsion is also examined for large particles, grains or grit which may also suggest instability and can cause significant issues in the particle board process because they can clog the spraying nozzle used to apply the emulsion [51]. The emulsion is then tested for pH and viscosity [51]. A sample of the emulsion is removed to examine the solids content of the emulsion primarily to ensure there were no errors in its preparation. Part of the emulsion is then tested a high shear at room temperature in the same Silverson labarotory disperser used to mix it to ensure that the emulsion will be able to withstand the shear forces present in the spraying nozzle and in pumping the emulsion during processing and transport. Finally the

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[3] File Source Valvola_omogeneizzatrice.svg Attribution: By Aushulz (Own work) [GFDL (http://www.gnu.org/copyleft/fdl.html) or CC-BY-SA-3.0-2.5-2.0-1.0 (http://creativecommons.org/licenses/by-sa/3.0)], via Wikimedia Commons (licensed under Creative Commons, GNU Free Documentation License) http://commons.wikimedia.org/wiki/Commons:GNU_Free_Documentation_License_1.2 http://creativecommons.org/licenses/by-sa/3.0/deed.en

emulsion is revaluated for storage stability over a period of more than 24 hours and then a period more than 2 weeks, at this time the emulsion is subjected to a final shear test to examine changes in the emulsion stability over time [51].

Repeated formulations were made with all successfully maleated waxes from chapter 2 to determine the ideal ratio of maleated wax emulsifier to slack wax in the formulation for each unique wax while making an effort to maintain the same solids content.

3.2.3 Evaluation of Emulsions

Emulsions are evaluated as appropriate for testing in engineered wood products primarily by the results of testing for solids content, shear stability and storage stability and additionally by tests measuring viscosity and pH. As mentioned previously, solids content is an excellent test to evaluate that the final emulsion matches the formulation ratios of wax component to water component and as such is an effective way of double checking for errors in the formulation process. It can also be a useful tool for predicting emulsion stability and viscosity [51]. Solids content is measured by weighing a sample of the emulsion and then slowly heating said sample so as to only evaporate the liquid portion off of the sample. The mass is then measured of the dehydrated sample. The solids content is reported as the percent of solid mass in relation to the total mass of the emulsion [51].

$$\frac{Solid\ Dehydrated\ Mass}{Emulsion\ total\ Mass} * \%100 = Solids\ Content\ (\%)$$

Equation 7 Solids Content Calculation

The shear stability of an emulsion is measured once after the emulsion has been cooled down to room temperature and again once is has been stored at room temperature for 48 hours or more [51]. Shear stability was measured by subjecting a sample of the emulsion to the highest setting of a Silverson laboratory disperser. Prior to the testing a threshold value of 3 minutes was determined in which the sample must survive without any visible signs of fallout, i.e. graininess, clumping or thickening [51]. Samples that showed signs of fallout below the 3 minute threshold were deemed not viable for further testing. Samples were examined by stirring following each shear test to ensure that no signs of fallout were missed during the test.

At the same time the emulsion is evaluated for stability over time, also referred to as storage stability. This is done visually and repeatedly over a minimum of a 1 month storage period. Once again the emulsion is evaluated for any signs of fallout that include: phase separation, graininess, thickening, coagulation and clumping. Wax emulsions with poor stability will, on occasion, develop a thick and viscous creamy layer on the top possibly indicative of a separate water-oil phase [51]. Emulsions that present any early signs of fallout are not acceptable for further testing and incorporation into engineered wood products; however, those that present minimal signs fallout such as minor phase separation can be deemed acceptable provided they re-emulsify following minimal stirring. The emulsions are also evaluated for visually signs of phase separation and discoloration at the same time.

The emulsions are also tested to determine their pH and viscosity. In the case of pH a simple laboratory pH meter was used to calculate pH. As with wax testing a rotating bob or Searle viscometer was used to quantify the kinematic viscosity of the sample which was then converted to a dynamic viscosity value. The data obtained from the pH and viscosity tests did not carry the same “pass/fail” importance as the solids content, shear and storage stability tests, and as such there was a greater range of tolerance for both the viscosity and pH results of an emulsion that may be tested or used in engineered wood product formation [51]. Nonetheless, grossly atypical results in either pH or viscosity testing are still indicative of an emulsion that is not viable for commercial use [51].

3.2.4 Incorporation of Emulsion into Engineered Wood Products

Particle Board samples were prepared following standard procedures set forth by Norjohn Emulsions Inc. The materials used included wooden chip particles, the formulated wax emulsion and a proprietary phenol-formaldehyde resin. Wooden chips were spray coated with the emulsion while being tossed in a tumbling apparatus. Following the application of the emulsion the wooden chips were sprayed coated with resin and once again tossed in the tumbling apparatus. The wooden chips were then heated pressed in a special mold press of a designated volume for a specified set of time. Following this the boards were allowed to cool before being transferred to a drying oven for four hours or more. The boards were then allowed to cool to room temperature before being tested with a moisture sensor. If the boards showed signs of continued moisture they were replaced in the drying oven until they we acceptably dry [51].

The boards were then measured by length and width and then weighed. After this the boards were soaked in a water bath for 2 hours. The boards were then reweighed in order to determine water absorption by comparing the post water bath mass to the pre water bath mass. The boards were also measured again after the water bath in order to determine the thickness swell of the boards. Results of each experimental emulsion was compared against a standard emulsion prepared the same day so as to account for any environmental changes in the laboratory setting as well as changes in the calibration of the equipment, specifically the moisture sensor [51].

3.3 Results and Discussion

Wax emulsions were formulated using maleated waxes developed using the bulk addition, pulse addition, peroxide pumping and maleic anhydride addition methods. Sample emulsions and results are displayed in Table 15**,** Table 16**,** Table 17 and Table 18. Emulsions which passed the Shear and Storage stability were created with waxes from each of the 5 chosen methods; however, reproducing consistent results with any of the peroxide initiated grafting methods proved difficult as is evident in Table 15**,** Table 16**,** Table 17 and Table 18. Typically emulsions that were created with higher pre blend acid numbers were more likely to pass although some emulsions were made with acid numbers as low as 5.46 that did pass, see Table 17.

Table 15 Selected Bulk Addition Sample Emulsion results

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pre-blend AN (mg_{KOH}/g)	Solids (%)	Visc (cp)	pH	Signs of Fallout	Shear test (min)	Storage stability
49.49	7.00	42.51	1.00	8.79	56.63	163.5	10.5	No	2:30	Pass
48.14	8.35	42.51	1.00	10.04	54.15	136.9	10.36	No	2:45	Pass
45.99	10.50	42.65	0.86	8.92	54.8	83.4	10.15	Yes	0:00	Fail
43.49	13.00	42.65	0.86	8.97	55.1	102.6	10.47	Yes	0:00	Fail
49.49	7.00	42.87	0.64	5.70	53.7	126.3	10.11	Yes	0:00	Fail
49.99	6.50	42.37	1.14	8.05	51.96	114.7	10.86	No	3:00	Pass

Table 16 Selected Pulse Addition Sample Emulsion results

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pre-blend AN (mg$_{KOH}$/g)	Solids (%)	Visc (cp)	pH	Signs of Fallout	Shear test (min)	Storage stability
49.49	7.00	42.58	0.93	5.70	51.02	122.2	8.46	Yes	0:00	Fail
50.49	6.00	42.58	0.93	5.31	53.05	582.1	10.43	Yes	0:15	Fail
46.19	10.30	42.87	0.64	9.11	53.68	115.5	8.46	No	2:30	Pass
46.19	10.30	42.87	0.64	8.93	48.67	145.7	8.33	Yes	0:00	Fail
46.19	10.30	42.87	0.64	9.11	58.58	189.6	8.93	No	2:30	Pass
42.20	14.29	42.87	0.64	8.85	40.71	168.2	9.5	Yes	1:15	Fail

Table 17 Selected Peroxide Pumping Sample Emulsion results

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pre-blend AN (mg$_{KOH}$/g)	Solids (%)	Visc (cp)	pH	Signs of Fallout	Shear test (min)	Storage stability
52.53	3.96	42.87	0.64	5.46	57.10	199.5	9.85	No	3:00	Pass
48.45	8.05	42.87	0.64	5.69	51.96	30.0	9.98	No	3:00	Pass
47.03	9.47	42.87	0.64	5.69	54.79	40.5	10.48	Yes	2:00	Fail
47.03	9.47	42.87	0.64	5.69	55.67	45.3	10.14	Yes	0:54	Fail
36.37	20.13	42.87	0.64	5.70	55.52	32.7	10.18	Yes	0:15	Fail
49.49	7.00	42.87	0.64	8.92	54.15	194.1	8.15	Yes	1:00	Fail

Table 18 Selected Maleic Anhydride Addition Sample Emulsion results

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pre-blend AN (mg$_{KOH}$/g)	Solids (%)	Visc (cp)	pH	Signs of Fallout	Shear test (min)	Storage stability
52.53	3.96	42.87	0.64	5.60	54.93	175.5	10.26	Yes	0:30	Fail
50.49	6.00	42.87	0.64	8.49	55.48	157.0	10.11	No	3:00	Pass
51.49	5.00	42.87	1.00	7.08	57.14	573.0	10.48	Yes	0:05	Fail
51.09	5.40	42.87	0.64	7.16	41.95	2.4	9.45	Yes	1:00	Fail
48.00	2.00	49.00	1.00	4.00	50.00	42.0	10.11	No	3:00	Pass
49.49	7.00	42.65	0.86	8.92	55.76	220.2	9.54	No	2:30	Pass

Of the emulsions that were created using peroxide initiated grafting methods those that had waxes grafted with Di-*tert*-butyl peroxide were much more successful than those that were grafted using *tert*-butyl peroxybenzoate as demonstrated in Figure 42. Waxes grafted with benzoyl peroxide as an initiator were not tested in emulsions because they did not maleate waxes of high acid number consistently. One possibility for the fact that greater success was found with the Di-*tert*-butyl peroxide initiated waxes is the side products generated from the peroxide may have been more compatible with the phases of the emulsion as compared to those generated from *tert*-butyl peroxybenzoate. Another possibility is that because the experiments using TBP as an initiator were performed at typically higher temperatures than those performed using TBPB as an initiator. The final products may have been more pure, even after washing. This contamination could have also caused fallout and failure in the emulsions.

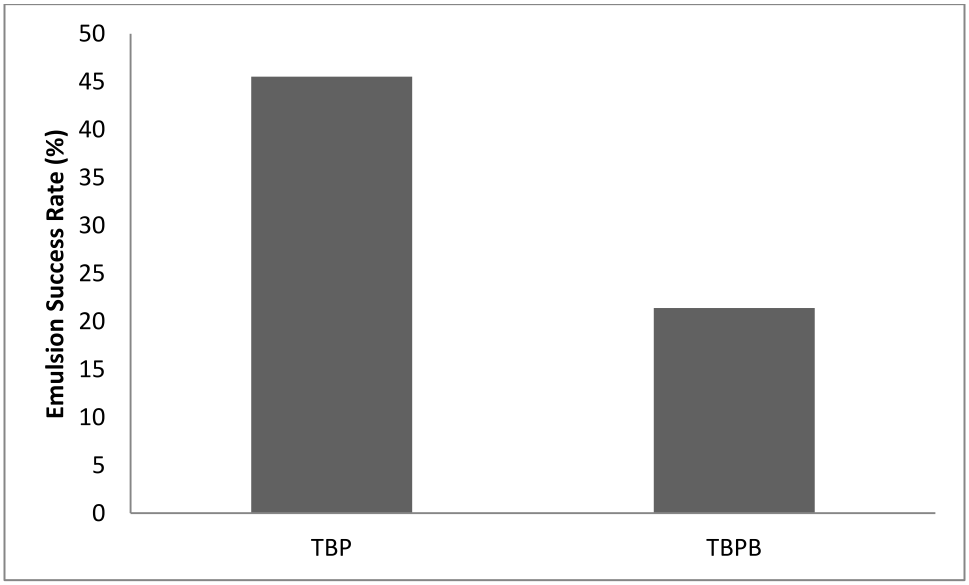

Figure 42 Comparison of Peroxide Effect on Emulsion Success Rate

Several emulsions were also created using maleated waxes produced from the thermally initiated grafting method as represented below in Table 19.

Table 19 Selected 6-X-3 Sample Emulsion results

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pre-blend AN (mg_{KOH}/g)	Solids (%)	Visc (cp)	pH	Signs of Fallout	Shear test (min)	Storage stability
52.49	4.00	42.87	0.64	5.62	55.96	141.3	9.56	No	3:00	Pass

52.99	3.50	42.87	0.64	4.55	55.72	138.9	9.55	No	3:00	Pass
53.49	3.00	42.87	0.64	3.90	57.1	140.7	10.62	No	3:00	Pass
53.99	2.50	42.87	0.64	3.25	56.8	156.7	10.21	No	3:00	Pass
54.49	2.00	42.87	0.64	2.60	56.82	140.3	10.17	No	3:00	Pass
54.79	1.70	42.87	0.64	2.21	56.46	108.3	10.14	No	3:00	Pass

The emulsions created using maleated waxes from the thermally initiated method had a significantly higher success rate as well as a tolerance for a much lower pre blend acid number. The emulsion success rates of each of the waxes from the different maleation methods are displayed below in Figure 43. Of the peroxide initiated methods the maleic anhydride grafting method had the highest success rate, but; the peroxide initiated methods all had success rates below 50% which was unacceptable to consider them as potential maleation methods for producing acceptable emulsifiers for this emulsion. At this stage, the waxes produced via the thermally initiated method were the only ones which showed true potential.

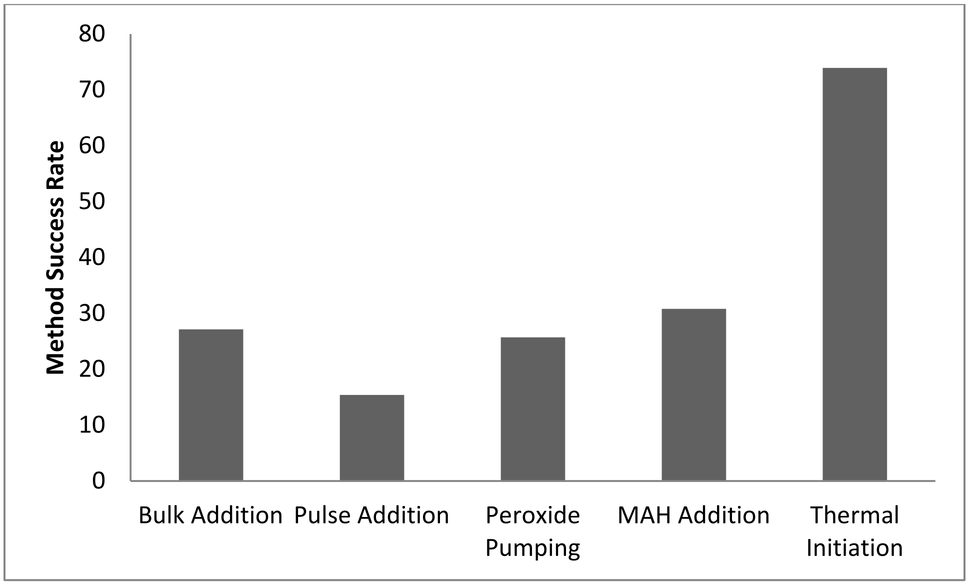

Figure 43 Comparison of Grafting Methods effect on emulsion Success Rate

3.3.1 Results of Engineered Wood Product Application

Any emulsion created that passed the shear and storage stability tests was tested in the creation of particle board engineered wood products. Due to the fact that boards were tested for both water absorbance and thickness swell which can be affected by environmental effects such as humidity a commercial standard was prepared using a commercial emulsion currently used in the production of engineered wood products which uses the product Pristerine as an emulsifier as stated previously. Average water absorbance and average thickness swell of the experimental emulsions created using the experimental waxes were compared to the water absorbance and thickness swell average of the control prepared on the same day. Table 20 compares selected results of the prepared boards. The emulsifier type, referring to the experimental maleated wax is classified as either peroxide initiated, PI, or thermally initiated, TI.

Table 20 Selected EWP Particle Board Results

Emulsifier Type	Emulsifier Content (wt.%)	Slack Wax Content (wt.%)	Shear Stability (min)	Water Absorbance (z-score)	Thickness Swell (z-score)
Pristerine (Control)	1.70	54.79	2:30		
PI	4.00	52.49	3:00	1.04	0.15
PI	4.00	52.49	3:00	**-1.48**	**-0.52**
PI	4.00	52.49	3:00	0.09	**-0.07**
PI	3.96	52.53	3:00	2.13	0.65
PI	8.05	48.44	3:00	1.26	0.23
PI	6.00	50.49	3:00	0.63	0.00
PI	7.00	49.49	2:30	**-2.01**	**-0.41**
TI	4.00	54.99	3:00	**-0.21**	**-0.10**
TI	4.00	54.99	3:00	**-0.78**	**-0.15**
TI	4.00	54.99	3:00	**-3.37**	**-1.42**
TI	4.00	54.99	3:00	**-1.45**	**-0.56**
TI	4.00	54.99	3:00	**-0.97**	**-0.23**
TI	4.00	54.99	3:00	1.40	0.77

TI	4.00	54.99	3:00	**-4.30**	**-1.70**
TI	4.00	54.99	3:00	**-1.29**	**-0.39**
TI	1.50	54.99	3:00	**-0.74**	**-0.20**
TI	1.50	54.99	3:00	**-0.78**	**-0.08**
TI	1.50	54.99	3:00	**-3.13**	**-1.14**
TI	1.50	54.99	3:00	**-1.55**	**-0.47**

In Table 20**,** the results of some of the emulsions are demonstrated with a calculated z-score to evaluated the difference between the experimental board and that of the standard. Each row in Table 20 represents a different particle board made on a different day. Those formulations that follow the same component ratios reflect the consistency of that specific formulation. Normality of data was tested using the Shapiro-Wilk test with a p value of 0.01, in all cases the null hypothesis was accepted. An example of the z-score equation designed to evaluate the results of each experimental board is demonstrated below in Equation 8.

$$\frac{(\boldsymbol{Average\ of Sample}) - (\boldsymbol{Average\ of\ Control})}{(\boldsymbol{Standard\ Deviation\ of\ Control})} = \boldsymbol{z - score}$$

Equation 8 Z-score calculation for boards

A water absorbance and thickness swell below that of the control is ideal because it represents an increase in the desired properties. Therefore, one can see from Table 20 that the thermally initiated waxes produced the best and most significant results. Water absorbencies measured for the sample boards produced ranged from 30-60 wt.% change and thickness swell ranged from 17-27 % change in the width of the boards.

3.4 Additional Applications

In collaboration with my colleague, Mark Rattle, research was also done into the use of these emulsifiers in emulsion formulations for use in gypsum wall board. It was determined experimentally that the emulsifiers made using the peroxide initiated grafting methods; the reduction in water absorption that was conferred to the wall boards was not statistically significant as compared to the currently used commercial gypsum emulsion. Emulsions were also made using the thermally initiation method of grafting. These emulsions produced a reduction in water absorption was equivalent or better at 1% emulsifier loading than in control samples at 1.29% emulsifier loading.

3.5 Conclusion

The emulsions produced from the waxes that were maleated using peroxide initiator methods did not show an adequate rate of success nor did they impart the desired properties to the particle board engineered wood products in a fashion that was significantly better than that of the control. The emulsions produced using the thermally Initiated method produced using the thermally initiated method of grafting were the best for using in the existing industrial setting because of the rate of success of the emulsions produced and the consistent and significant values is water absorbance and thickness swell as compared to that of the control.

Chapter 4: Significant Research Contributions and Recommendation for Future Developments

4.1 Significant Research Contributions of Thesis Work

The presented research is part of the body of work known as polyolefin modification, more specifically; this thesis concentrates on the grafting of the monomer, maleic anhydride onto three distinct types of wax commonly in use in industry. This thesis explores the use of peroxide initiated methods as well as thermally initiated methods of grafting. In order to meet the goals set forth for this project, new processes were developed with a realistic outlook on how these processes may be implemented into an operating industrial emulsion production line. A number of significant contributions to the polyolefin wax research field and industry have been made by this thesis work; these contributions are detailed as follows.

The processes developed in this project present a significant improvement in the environmental impact and the safety as compared to processes currently incorporated in industry. The emulsions in this project developed from these processes impart an improvement in properties to both engineered wood products and gypsum board products as compared to those prepared with other commercial emulsifiers currently in use. This project was handled in such a way so that the developed process may be incorporated into existing formulations as a replacement for these commercial emulsifiers at a cost savings.

4.2 Recommendations for Future Research

4.2.1 Development of Industrial Scale production of Wax Emulsifiers

Now that there is significant evidence as presented in this thesis to support the replacement of current commercial emulsifiers with those developed in this thesis. There exists a strong incentive to develop an industrial scale process based on the methods describe within this project. Ideally such a process would be developed so that it may be incorporated into a existing industrial production line which produces emulsions used in building projects such as engineered wood products and gypsum boards. As mentioned previously the wax emulsifiers developed from this project could then be incorporated into existing formulations as substitutes for commercial wax emulsifiers that are more expensive.

4.2.2 Process for the Recovery of Unused Maleic Anhydride

As mentioned earlier in this thesis it was noted that maleic anhydride was sublimating throughout the course of the thermally initiated process. Development of a means of recovering this sublimated maleic anhydride would most likely provide a significant cost saving and environmental benefit when incorporated into and industrial scale up of the grafting process. This could potentially be achieved simply through the means of a modified lid on the reactor that has an attachment fitting which could be used to maintain the maleic anhydride in a volatile form until is it transferred to a collection vessel where it may then be condensed.

4.2.3 Incorporation of Products Made from Renewable Sources

Three distinct waxes were examined as potential starting products for wax maleation. These waxes are all developed from petroleum products and as such are connected to the petroleum industry. Further research could examine the potential for waxes derived from renewable sources, such as those detailed in the introduction of this thesis, to be grafted with maleic anhydride and use as emulsifiers as well using the methods detailed in this thesis. Similarly one could examine if the emulsions developed in this project would also provide beneficial properties to engineered wood product particle board analogs such as those made with bamboo particles.

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Appendix A: Additional Wax and Emulsion Data

The following appendix lists additional data not listed in the body of the thesis of the experiments performed to provide a broader sampling of experiments performed.

A.1. Additional Wax Data

Table 21 Additional Bulk Addition Method Data

Initiator Used	MAH Charged (wt %)	Molar ratio of MAH to Initiator	Temp (° C)	Time (hours)	Acid Number (mg(KOH)/g)	Melt Point (° C)	Grafting Efficiency (%)
T-Butylperoxide	20	2	160	10	41	67	18
T-Butylperoxide	20	2	160	10	52	64	23
T-Butylperoxide	20	1	160	10	73	63	32
T-Butylperoxide	20	0.5	160	10	81	61	35
T-Butylperoxide	20	0.5	160	12	84	64	37
T-Butylperoxide	10	0.5	160	12	33	62	29
T-Butylperoxide	10	0.5	160	10	30	69	26
T-Butylperoxide	10	2	160	10	10	60	9
T-Butylperoxide	10	2	160	11	16	59	14
T-Butylperoxide	10	1	160	11	26	66	23
T-Butylperoxide	5	1	160	10	9	62	16
T-Butylperoxide	5	1	160	10	11	64	19
t-butylperoxybenzoate	20	0.5	160	10	34	68	15
t-butylperoxybenzoate	20	0.5	160	14	31	57	14
t-butylperoxybenzoate	20	1	160	14	22	63	10
t-butylperoxybenzoate	20	1	160	10	18	64	8
t-butylperoxybenzoate	20	1	160	18	27	69	12
t-butylperoxybenzoate	10	1	160	18	13	70	11
t-butylperoxybenzoate	10	1	160	10	13	60	11

Table 22 Additional Ball-Milling Method Data

Initiator Used	MAH Charged (wt %)	Molar Ratio of MAH to Initiator	Temp (° C)	Time (hour)	Acid Number (mg(KOH)/g)	Melt Point (° C)	Grafting Efficiency (%)
Benzoyl	5	1	80	1	7	63	12

Peroxide							
Benzoyl Peroxide	5	1	80	2	8	67	14
Benzoyl Peroxide	5	1	80	5	9.2	71	32
Benzoyl Peroxide	5	1	80	6	10	64	17
Benzoyl Peroxide	2.5	1.02	80	6	6.8	65	24
Benzoyl Peroxide	2.5	1.02	80	6	8.6	63	30
Benzoyl Peroxide	20	0.5	80	6	32	66	14
Benzoyl Peroxide	20	0.5	80	6	35	62	15

Table 23 Additional Pulse Addition Method Data

Initiator Used	MAH Charged (wt %)	Molar ratio of MAH to Initiator	Temp (° C)	Time (hour)	Acid Number mg(KOH)/g)	Melt Point (° C)	Grafting Efficiency (%)
T-Butylperoxide	5	1	160	10	7	67	12
T-Butylperoxide	20	1	160	10	61	64	27
T-Butylperoxide	20	1	160	10	31	63	14
T-Butylperoxide	20	1	160	10	64	61	28
T-Butylperoxide	20	1	160	10	20	64	9
T-Butylperoxide	20	1	160	10	33	62	14
T-Butylperoxide	20	1	160	10	18	69	8
T-Butylperoxide	20	1	160	10	21	60	9
T-Butylperoxide	20	1	160	10	76	59	33
T-Butylperoxide	20	1	160	10	29	66	13
T-Butylperoxide	5	1	160	10	9	62	16
T-Butylperoxide	5	1	160	10	11	64	19
t-butylperoxybenzoate	20	1	160	10	34	68	15
t-butylperoxybenzoate	20	1	160	10	31	57	14
t-butylperoxybenzoate	20	1	160	10	22	66	10
t-butylperoxybenzoate	20	1	160	10	18	64	8
t-butylperoxybenzoate	20	1	160	10	27	69	12
t-butylperoxybenzoate	10	1	160	10	13	70	11
t-butylperoxybenzoate	10	1	160	10	13	62	11

Table 24 Additional Peroxide Pumping Method Data

Initiator Used	MAH Charged (wt %)	Molar ratio of MAH to Initiator	Temp (° C)	Time (hour)	Acid Number (mg(KOH)/g)	Melt Point (° C)	Grafting Efficiency (%)
T-Butylperoxide	5	5	160	0.5	10	63	18
T-Butylperoxide	5	1	160	10	25	67	45
T-Butylperoxide	20	5	70	0.5	11	63	5
T-Butylperoxide	20	1	70	0.5	13	64	6
T-Butylperoxide	20	5	160	10	78	76	35
T-Butylperoxide	20	1	160	0.5	32	69	14
T-Butylperoxide	5	5	70	0.5	4	58	5
T-Butylperoxide	5	5	70	10	7	59	12
T-Butylperoxide	5	1	160	0.5	22	66	39
T-Butylperoxide	20	5	70	10	11	62	5
T-Butylperoxide	20	1	70	10	16	64	7
T-Butylperoxide	20	5	160	0.5	28	68	13
T-Butylperoxide	5	1	70	0.5	5	57	9
T-Butylperoxide	5	5	160	10	16	64	29
T-Butylperoxide	5	0.2	160	0.5	33	69	59
T-Butylperoxide	10	0.2	160	0.5	40	70	36
T-Butylperoxide	5	0.2	160	1	36	70	64
T-Butylperoxide	5	0.4	160	0.5	30	68	54
T-Butylperoxide	5	1	160	0.5	22	66	39
T-Butylperoxide	5	0.2	160	0.5	34	64	60.6
T-Butylperoxide	5	0.2	160	0.5	34	64	60.6
T-Butylperoxide	5	1	160	5	16	62	27.4
T-Butylperoxide	5	1	160	10	12	63	20.8
T-Butylperoxide	25	3	160	10.5	32.6	65	19.1
T-Butylperoxide	5	1	160	0.5	12.5	65	22.7
T-Butylperoxide	2.5	1	160	0.5	5	63	18.7
T-Butylperoxide	7.5	1	160	0.5	5	64.5	6.1
T-Butylperoxide	10	1	160	0.5	9	68	8.2
T-Butylperoxide	20	1	120	10	6.7	63	2.9
Tert-Butyl peroxy benzoate	20	0.5	100	10	24.9	65	10.9
Tert-Butyl peroxy benzoate	20	1	100	10	9.6	72	4.19
Tert-Butyl peroxy benzoate	20	1	130	0.5	22.7	62	9.9
Tert-Butyl peroxy benzoate	20	1	120	0.5	17.4	62	7.6
Benzoyl Peroxide	5	2	90	1	11.1	64	19.4

Table 25 Additional Maleic Anhydride Addition Method Data

Initiator Used	MAH Charged (wt %)	Molar ratio of MAH to Initiator	Temp (° C)	Time (hour)	Acid Number (mg(KOH)/g)	Melt Point (° C)	Grafting Efficiency (%)
T-Butylperoxide	20	0.5	160	10	82	35	35.83298
T-Butylperoxide	20	0.5	160	10	79	67	34.52201
T-Butylperoxide	20	0.5	160	10	80	63	34.959
T-Butylperoxide	20	0.5	160	10	77	68	33.64804
T-Butylperoxide	20	0.5	160	10	82	64	35.83298
T-Butylperoxide	20	0.5	160	10	79	76	34.52201
T-Butylperoxide	20	1	160	10	74	69	32.33708
T-Butylperoxide	20	1	160	10	71	58	31.02611
T-Butylperoxide	20	1	160	10	67	59	29.27816
T-Butylperoxide	20	1	160	10	76	66	33.21105
T-Butylperoxide	10	1	160	10	64	62	55.9344
T-Butylperoxide	10	1	160	10	61	64	53.31248
T-Butylperoxide	10	1	160	10	59	68	51.56453
T-Butylperoxide	10	1	160	10	63	64	55.06043
T-Butylperoxide	10	1	160	10	62	65	54.18645
T-Butylperoxide	10	1	160	10	54		47.19465
T-Butylperoxide	10	1	160	10	65	69	56.80838
T-Butylperoxide	10	1	160	10	61	70	53.31248
T-Butylperoxide	10	1	160	10	60		52.4385
T-Butylperoxide	10	2	160	10	59	70	51.56453
T-Butylperoxide	10	2	160	10	50	63	43.69875
T-Butylperoxide	10	2	160	10	51	68	44.57273
T-Butylperoxide	10	2	160	10	54	66	47.19465
T-Butylperoxide	10	2	160	10	53	64	46.32068
T-Butylperoxide	10	2	160	10	50	64	43.69875
T-Butylperoxide	10	2	160	10	56	62	48.9426
T-Butylperoxide	10	2	160	10	61	63	53.31248
T-Butylperoxide	10	1	160	10	63	62	55.06043
T-Butylperoxide	10	1	160	10	65	66	56.80838
T-Butylperoxybenzoate	20	0.5	130	10	86	65	37.58093
T-Butylperoxybenzoate	20	0.5	130	10	79	67	34.52201
T-Butylperoxybenzoate	10	1	130	10	63	65	55.06043
T-Butylperoxybenzoate	10	1	130	10	64	63	55.9344
T-Butylperoxybenzoate	10	1	130	10	66	64.5	57.68235
T-Butylperoxybenzoate	10	1	130	10	61	71	53.31248

T-Butylperoxybenzoate	10	1	130	10	60	61	52.4385

A.1. Additional Emulsion Data

Table 26 Additional Emulsion Data

Slack Wax (wt %)	Exp Wax (wt%)	Water (wt%)	MEA (wt%)	Pblend AN	Solids (%)	Visc (cp)	pH	Stability test	shear test	Storage stability
52.53	3.96	42.87	0.64	5.47	57.1	199.5	9.85	Pass	3:00	Pass
48.45	8.05	42.87	0.64	5.70	51.96	30	9.98	Pass	3:00	Pass
47.03	9.47	42.87	0.64	5.70	54.79	40.5	10.48	Fail	2:00	Fail
47.03	9.47	42.87	0.64	5.70	55.67	45.3	10.14	Fail	0:54	Fail
36.37	20.13	42.87	0.64	5.70	55.52	32.7	10.18	Fail	0:15	Fail
48.00	2.00	49.00	1.00	4.00	50	42	10.11	Pass	3:00	Pass
52.53	3.96	42.87	0.64	5.61	54.93	175.5	10.26	Fail	0:30	Fail
50.49	6.00	42.87	0.64	8.50	55.48	157	10.11	Pass	3:00	Pass
51.49	5.00	42.87	1.00	7.08	57.14	573	10.48	Fail	0:05	Fail
51.09	5.40	42.87	0.64	7.17	41.95	2.4	9.45	Fail	1:00	Fail
49.49	7.00	42.87	0.64	8.92	54.15	194.1	8.15	Fail	1:00	Fail
49.49	7.00	42.65	0.86	8.92	55.76	220.2	9.54	Pass	2:30	Pass
49.49	7.00	42.51	1.00	8.80	56.63	163.5	10.5	Pass	2:30	Pass
48.14	8.35	42.51	1.00	5	54.15	136.9	10.36	Pass	2:45	Pass
45.99	10.50	42.65	0.86	8.92	54.8	83.4	10.15	Fail	0:00	Fail
43.49	13.00	42.65	0.86	8.98	55.1	102.6	10.47	Fail	0:00	Fail
49.49	7.00	42.87	0.64	5.70	F	F	F	Fail	0:00	Fail
50.49	6.00	42.87	0.64	5.31	55.7	175.5	9.97	Fail	0:15	Fail
49.49	7.00	42.58	0.93	5.70	F	F	F	Fail	0:00	Fail
50.49	6.00	42.58	0.93	5.31	53.05	high	10.43	Fail	0:15	Fail
46.19	10.30	42.87	0.64	9.12	53.68	115.55	8.46	Pass	2:30	Pass
46.19	10.30	42.87	0.64	8.93	F	F	F	Fail	0:00	Fail
46.19	10.30	42.87	0.64	9.12	58.58	189.6	8.93	Pass	2:30	Pass
42.20	14.29	42.87	0.64	8.85	40.71	168.2	9.5	Fail	1:15	Fail
51.49	5.00	42.87	0.64	6.20	51.06	127.7	10.06	Pass	3:00	Pass
51.49	5.00	42.87	0.64	6.28	50.32	129.7	10.26	Fail	1:00	Fail
51.49	5.00	42.65	0.86	6.20	53.27	122.5	10.93	Pass	3:00	Pass
51.49	5.00	42.37	1.14	6.20	54.92	146.1	10.96	Pass	3:00	Pass
49.99	6.50	42.37	1.14	8.05	51.96	114.7	10.86	Pass	3:00	Pass
52.49	4.00	42.87	0.64	4.96	53.42	117.3	10.24	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.10	56.45	134.1	10.26	Pass	3:00	Pass
53.49	3.50	42.87	0.64	4.42	53.46	114.9	10.91	Pass	3:00	Pass
53.49	3.00	42.87	0.64	3.82	55.52	135.9	10.45	Pass	3:00	Pass

53.99	2.50	42.87	0.64	3.19	54.18	125.4	10.35	Pass	2:30	Pass
52.49	4.00	42.87	0.64	5.10	56.51	156.9	10.28	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.62	56.34	136.8	9.48	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.62	56.81	162.9	9.52	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.20	55.3	132	10.3	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.20	54.77	125.7	10.32	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.40	55.62	148.2	10	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.17	56.96	159.3	10.06	Pass	3:00	Pass
52.49	4.00	42.87	0.64	5.62	55.96	141.3	9.56	Pass	3:00	Pass
52.99	3.50	42.87	0.64	4.55	55.72	138.9	9.55	Pass	3:00	Pass
53.49	3.00	42.87	0.64	3.90	57.1	140.7	10.62	Pass	3:00	Pass
53.99	2.50	42.87	0.64	3.25	56.8	156.7	10.21	Pass	3:00	Pass
54.49	2.00	42.87	0.64	2.60	56.82	140.3	10.17	Pass	3:00	Pass
54.79	1.70	42.87	0.64	2.21	56.46	108.3	10.14	Pass	3:00	Pass