# BIOBASED PRODUCTS FROM STARCH USING EXTRUSION PROCESSING AND CHEMICAL MODIFICATIONS

By

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#### ABSTRACT

## BIOBASED PRODUCTS FROM STARCH USING EXTRUSION PROCESSING AND CHEMICAL MODIFICATIONS

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Biobased products from starch have shown great potential to replace petroleum based products and they are also environmentally friendly and biodegradable. Starch foams are one of the product forms obtained from starch and are a possible replacement for petroleum-based foams. Such foams have been prepared in the past but their sensitivity to humidity has remained a problem. Extensive research over the last few years has been focused on resolving the collapse of the foam at high humidity, improving the cushioning protection and developing an economical foaming process. However, these issues are still problematic and need to be resolved before such biobased foams can gain widespread entry into the marketplace.

Initially, the effects of starch feed rate, the addition of a nucleating agent, and the extruder screw configuration were studied. It was demonstrated that screw configuration plays an important role in the extrusion process and the nucleating agent talc is an effective component with which to control the cell size. An annular die was used to extrude tubular starch foams which were then sliced to yield foam sheets suitable for cushioning protection and insulation of shipping containers. A Box-Behnken statistical design of experiment (DOE) was used to optimize the properties of the foams extruded with various additives. It was found that the density, cell structure and water sensitivity of these foams were affected by the feed rates (e.g. foam composition) of the water, talc and

polyhydroxy ether (PHE). The use of PHE was found to be extremely effective in minimizing water sensitivity.

Because PHE contains Bisphenol A, a suspected endocrine disrupter, another alternative polymer additive – Polyvinyl buytral (PVB) was studied. It was shown that PVB minimizes the moisture sensitivity of the foam and provided a more hydrophobic character. A statistical design experiment was used again to identify the composition and process parameters affecting the physical properties of the foams and to optimize the feed rates of the various additives. The foam extrusion process to make foam sheet was scaled down to a lab scale extruder in order to provide a more convenient technique for exploring different raw materials and formula variations.

The performance (moisture adsorption, cushion curve, and thermal insulation) of the starch foam sheets under different processing conditions and compositions were evaluated. The results indicate that these foams are classified in the moderate fragile level, implying that these foams are suitable as protective packaging of network hardware equipment, personal computers and medical diagnostic apparatus. The starch sheets have similar thermal resistance, R value, compared with polystyrene foams.

Finally, starch phosphate was synthesized using sodium trimetaphosphate and glycerol phosphoric acid by an extrusion method to examine its use as a possible electrorheological fluid or as a flame retardant additive.

The main accomplishment of this research is a starch foam sheet with a significantly high moisture resistance that can be prepared by extrusion using readily available and affordable resin additive. The process and the composition have been used to scale up the manufacturing of these foam sheets for commercial production.

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LIST OF TABLES	vii
LIST OF FIGURES	ix
Chapter 1 Introduction and background	1
1.1 Introduction	1
1.1.1 Objectives	2
1.1.2 Organization of this Thesis	3
1.2 Background	3
1.2.1 Introduction to starch	3
1.2.2 Introduction to extrusion	5
1.2.3 Starch foam extrusion (physical process)	8
Chapter 2 Materials, Methods and Characterizations	12
2.1 Materials	12
2.1.1 Starch and Talc	12
2.1.2 Polymer modifiers – PVOH, PHAE, PHE, and PVB	13
2.2 Experimental	15
2.2.1 Century ZSK-30 co-rotating twin screw extruder	15
2.2.2 Wenger TX-80 extruder	20
2.3 Characterization methods	21
2.4 Statistics and design of experiments methods	25
Chapter 3 Foam extrusion results and discussion	36
3.1 Screw configuration effect	36
3.2 Starch feed rate effect	38
3.3 Effect of talc content	43
3.4 Different modifiers	46
3.4.1 Aqueous PVOH	46
3.4.2 Box-Behnken DOE with PHE and annular die	48
3.4.3 Box-Behnken DOE with PVB	61
3.4.4 Starch foam homogeneity with PVB	
3.5 Scale down starch foam extrusion from Wenger TX-80 to Century ZSK-3	0.79
Chapter 4 Performance characterizations of starch foam sheets	81
4.1 Moisture adsorption and humidity sensitivity	81
4.2 Thermal insulation	89
4.3 Cushion curves	93
4.4 Dynamic Stress-Strain Curve	100
Chapter 5 Starch foam extrusion mechanism	104
5.1 Extensional viscosity and strain hardening	104
5.2 Starch foaming steps	109
5.3 Die design	109

# **TABLE OF CONTENTS**

5.3.1 Strand die	
5.3.1 Annular die	
Chapter 6 Chemically modified starch	
6.1 Starch extrusion with soy based ester	
6.2 Starch phosphate	
6.2.1 Starch phosphate for ER fluid	
6.2.2 Starch phosphate with glycerol phosphoric acid	
6.3 Dihydroxyl starch	
Chapter 7 Conclusions, accomplishments and recommendations for	future work 141
7.1 Conclusions	
7.2 Main accomplishment	
7.3 Future recommendations	
REFERENCES	

# LIST OF TABLES

Table 1 Commercial foam products' property	9
Table 2 A summary of starch foam research	10
Table 3 Screw configuration of Century ZSK-30 extruder (L/D=42)	17
Table 4 Screw configuration of Century ZSK-30 extruder (L/D=20.4)	18
Table 5 Screw configurations for Wenger TX-80	20
Table 6 Different salt solutions for relative humidity	22
Table 7 Calculation for ANOVA	29
Table 8 Cylindrical foam extrusion conditions and diameter of the foams	39
Table 9 cylindrical foam characterizations	42
Table 10 Box-Behnken DOE with PHE and annular die	49
Table 11 Polynomials used to evaluate the foam density and cell diameter	50
Table 12 Design space using polyvinyl butyral	61
Table 13 Box-Behnken DOE for starch foam with PVB	62
Table 14 Box-Behnken DOE experimental results for starch foam with PVB	63
Table 15 Polynomials used to evaluate the foam diameter, density and wear	64
Table 16 Table for 3D plots (noodle diameter and density as responses)	66
Table 17 Experimental conditions and results for starch foams prepared by the Centur     ZSK-30 and Wenger TX-80 extruders.	ry 79
Table 18 Formulation for lab starch foam tube	80
Table 19 Lab starch foam tube characterization	80
Table 20 $k_1$ and $k_2$ values for starch powder	83
Table 21 $k_1$ and $k_2$ values for PELEG model (85% RH)	83

Table 22 flexibility of the foam sheets under different relative humidities at room     temperature	88
Table 23 Soxhlet extraction with different solvents	. 118
Table 24 Products from ozonolysis	. 119
Table 25 Extrusion conditions for thermal plastic starch with esters	. 120
Table 26 Suspensions for electrorheological fluid	. 124
Table 27 Extrusion formulation using sodium trimetaphosphate and sodium tripolyphosphate	. 133
Table 28 Phosphorylate starch using glycerol phosphate disodium salt	. 133
Table 29 Phosphorylate starch using glycerol phosphoric acid	. 133
Table 30 Phosphorylate starch using glycerol phosphoric acid and glycerol phosphate monohydrogen	e . 134
Table 31 Intrinsic viscosity comparison	. 134
Table 32 weights for reactants during DHS synthesis	. 136

# LIST OF FIGURES

Figure 1 Carbon cycle	2
Figure 2 Chemical structures of starch and cellulose	4
Figure 3 Chemical structure of amylose and amylopectin	5
Figure 4 Extruder system	6
Figure 5 Kneading elements, covey elements and barrels	6
Figure 6 Distribution and dispersive mixing	7
Figure 7 Starch plasticization	8
Figure 8 Foam extrusion process	8
Figure 9 Hydroxypropylate reaction	12
Figure 10 Polyhydroxy aminoether synthesis	13
Figure 11 Chemical structure of polyvinyl alcohol	14
Figure 12 Polyhydroxyl ether synthesis	14
Figure 13 Chemical structure of polyvinyl butyral	15
Figure 14 The barrels arrangement for the screw configuration (L/D=20.4)	15
Figure 15 The barrels arrangement for the screw configuration (L/D=42)	16
Figure 16 Screw configuration of Century ZSK-30 extruder (L/D=20)	19
Figure 17 Annular die	21
Figure 18 Screw configuration for Wenger TX-80	21
Figure 19 Thermal conductivity test	24
Figure 20 Sample size from bulk	26
Figure 21 Operating Characteristic Curve ( $\alpha=\beta=0.05$ )	26
Figure 22 t and F distribution curves	27

Figure 23 A: Function vs. polynomial (square terms); B: Function vs. Function vs. polynomial (cubic terms)
Figure 24 Experimental points for Box-Behnken design
Figure 25 DOE for 4 variables
Figure 26 Specific mechanical energy (SME) comparison for two screw configuration. 36
Figure 27 Regular starch foam sheets (left) vs. sheets with braiding problem (right two)38
Figure 28 Four and six holes strand die
Figure 29 Cells in the starch foam
Figure 30 Cell size distribution for cylindrical foams (A: noodle extruded at 460 lbs/hr, B: noodle extruded at 285 lbs/hr)
Figure 31 Characterization of cylindrical foam prepared from a die with six holes 42
Figure 32 Cell size distributions for starch foam with PVOH, different talc levels: A: 0.5wt%, B: 1.3wt%, C: 2.7wt%
Figure 33 Cell size distributions for starch foam with PHAE, different talc levels: A: 0.5wt%, B: 1.3wt%, C: 2.7wt%
Figure 34 starch foam densities vs. PVOH solution concentration
Figure 35 Starch foam resiliencies vs. PVOH solution concentration
Figure 36 Goodness of fit of the calculated polynomials to the experimental values 51
Figure 37 Effects of resin and talc feed rates on the foam density at low (A) and high (B) water feed rates. 53
Figure 38 Effects of water and resin feed rates on the foam density at low (A) and high (B) talc feed rates. 55
Figure 39 Effects of water and talc feed rates on the average cell diameter at low (A) and high (B) resin feed rates
Figure 40 Effects of talc and resin feed rates on the average cell diameter at low (A) and high (B) water feed rates
Figure 41 Goodness of fit of the calculated polynomials to the experimental values. A: Foam diameter B: Density C: Wear

Figure 42 3D plots, noodle diameter as response
Figure 43 3D plots, density as response
Figure 44 Changes in the wear as a function of PVB and water feed rates with no talc and extruding through a small pinhole die (diameter = 10 mm)
Figure 45 Changes in the wear as a function of PVB and water feed rates with talc coextruded at 0.0155 Kg/hr through a large pinhole die (diameter = 20 mm)
Figure 46 Changes in the wear as a function of PVB and talc feed rates with water coextruded at 0.80 Kg/hr through a small pinhole die (diameter 10 mm)
Figure 47 Changes in the wear as a function of PVB and talc feed rates with water coextruded at 0.50 Kg/hr extruding through a pinhole die with a diameter = 16 mm 76
Figure 48 Changes in the wear as a function of PVB and pinhole diameter with water coextruded at 0.80 Kg/hr and no talc
Figure 49 TGA analysis on starch foam with PVB78
Figure 50 Hydroxypropyl high amylose starch powder moisture content vs. time at 23°C
Figure 51 Starch foam (no polymer modifier) moisture content vs. time at 23°C
Figure 52 Starch foam (PVOH as polymer modifier) moisture content vs. time at 23°C 84
Figure 53 Starch foam (PHAE as polymer modifier) moisture content vs. Time at 23°C 84
Figure 54 Starch foam (PHE as polymer modifier) moisture content vs. time at 23°C 85
Figure 55 Starch foam with PVB as polymer modifier moisture content vs. time at 23°C
Figure 56 Moisture content at equilibrium under different RH (starch foam with PVOH as polymer modifier)
Figure 57 Water penetration time for foam sheets (A) foam with different additives (B) foam with different additive content
Figure 58 Starch foam sheets extruded after 5 hours in contact with water. (A) PVOH (B) PHE

Figure 59 Thermal insulation property comparison (A: different additives B: different tal concentration)	lc )1
Figure 60 Starch foam without polymer modifiers cushion curves	)5
Figure 61 Starch foam with PHAE cushion curves9	)5
Figure 62 Starch foam with PVOH cushion curves	)6
Figure 63 Starch foam with PHE cushion curves	)6
Figure 64 Starch foam with PVB cushion curves	97
Figure 65 Polyethylene foam cushion curves	97
Figure 66 Cushion curves comparison (First drop)9	)8
Figure 67 Cushion curves comparison (Fifth drop)9	)8
Figure 68 Starch foam with PVOH at 75% RH and RT9	)9
Figure 69 Starch foam with PVOH and 1.3% talc9	)9
Figure 70 Starch foam with PVOH and 2.7% talc 10	)0
Figure 71 Stress-strain curve 10	)2
Figure 72 First drop cushion curves for 1 inch and 2 inch starch foam	)3
Figure 73 The sh/t v.s. (a/G+1)s curve 10	)3
Figure 74 Strain hardening 10	)4
Figure 75 Uniaxial pull of polymer block10	)4
Figure 76 strain hardening effects on foam and film process (1: force applied to a block, foaming process, 3: film process; a: original state, b: strain weakening, c: stain hardening	2: g) )8
Figure 77 Strand die11	0
Figure 78 Annular die	3
Figure 79 Die pressure (Pa) vs. die gap (m), curve: calculated from the model, two dots: experimental values	5

Figure 80 Reactions in MTPS	116
Figure 81 Ozonolysis	119
Figure 82 Transesterification reaction	120
Figure 83 GC-FID before and after ozonation using Dean-stark setup (The retention for dimethyl azelate is 20.74 minutes)	time 121
Figure 84 FTIR results for the extrudates after soxhletion with acetone (A) MTPS (B MTPS with two phases esters (C) MTPS with one phase ester	8) 122
Figure 85 Soxhletion results (acetone as solvent) for the extrudate	122
Figure 86 Alignment of suspended particles	124
Figure 87 Starch phosphorylation using sodium trimetaphosphate	126
Figure 88 Feed position for starch phosphorylation	127
Figure 89 Rheology measurement setup	128
Figure 90 Dynamic light scattering for starch nanoparticles	129
Figure 91 starch nanoparticles stabilized with phosphate	129
Figure 92 Viscosity v.s. shear rate for ER fluid	130
Figure 93 Starch phosphorylation reaction	132
Figure 94 Reactions to make dihdyroxyl starch	135
Figure 95 Setup for measuring aldehyde group	137
Figure 96 FTIR for starch, DAS and DHS, A: high amylose, B: waxy, C: regular	138
Figure 97 Viscosity vs. shear rate for DHS	139
Figure 98 Dialdehyde content in DAS and DHS	140
Figure 99 annular die (Pin) structure	142
Figure 100 Corrugation in the foam sheet (left: extruded with 10 holes pin, middle: extruded with 6 holes pin, right: extruded with 10 holes pin and small gap)	143

#### **Chapter 1 Introduction and background**

#### **1.1 Introduction**

Advances in petroleum-based polymers have benefited mankind in numerous ways. Most general plastics are petroleum based and hence are derived from nonrenewable resources.

The critical disadvantage of using petroleum-based resources can be understood based on the carbon cycle. As shown in the Figure 1, there are four elements (#1 fossil resources, #2 polymer products, #3 carbon dioxide, and #4 bio-mass) in the cycle. Crude oil is pumped out of the ground and is then converted into products --- polymers, chemicals and fuels ---through chemical processing. These products become carbon dioxide after usage (end-of-life). The carbon dioxide in the atmosphere is fixed through photosynthesis by biomass and agricultural crops. After biomass plants die, it takes millions of years to become fossils. The problem in this carbon cycle is that there is one limiting step, from biomass to fossil resources, which takes too long. If the cycle continues without modification, in time all the carbon will accumulate in biomass and agricultural crops and no petroleum will remain for the production of the products on which we currently rely.



Figure 1 Carbon cycle

It is critical, therefore, to avoid the #1 fossil resource step in this carbon cycle in order to balance the carbon flow rate. This is where bio-based products come into play, by by-passing the fossil resource elements to use technology to directly convert biomass to polymers, chemicals and fuels. Although bio-based polymers have been studied for many years, those polymers still have limitations, such as process instability and poor product performance compared to petroleum- based polymers. Therefore, there is a need investigate the production process itself in order to improve the processability and performance of biobased and biodegradable products.

#### 1.1.1 Objectives

This study focuses on using starch to make useful products - starch foam, thermoplastic starch, etc - and attempts to improve the process stability and performance of products based on starch foam and explores the potential possibility of chemically modifying the starch for define applications.

2

#### **1.1.2 Organization of this Thesis**

This thesis is divided into seven parts: In chapter 1, the need for biobased products from starch is addressed. The chapter also includes a review of products based on starch.

Chapter 2 gives a detailed raw materials information, experimental setup and experimental procedures/characterization methods. This chapter also includes the basics of statistical design of experiments used in this study.

In Chapter 3, the effects of different composition and processing conditions (screw configuration, starch, talc, polymer modifiers) on the properties of the starch foam are studied.

In Chapter 4, the performance properties of starch foam sheets (moisture adsorption, cushioning protection and thermal insulation) are investigated.

In Chapter 5, the focus is on starch foam extrusion mechanism.

In Chapter 6, chemical modifications of the starch (maleated thermoplastic starch with hydrophobic improvement, starch phosphate, dihydroxyl starch) using extrusion are studied.

In Chapter 7, conclusions are drawn based on finished work and future work is suggested.

#### **1.2 Background**

#### **1.2.1 Introduction to starch**

Starch, an abundant, inexpensive and a naturally occurring polymer, provides a good platform from which to manufacture renewable and biodegradable foams for

3

packaging and insulation applications. Starch and cellulose are two common carbohydrates. Starch contains alpha-glucose as its monomer, whereas cellulose contains beta-glucose (Figure 2).



Figure 2 Chemical structures of starch and cellulose

Starch exists in granule structure form and is bimodal and polydispersed, both at the granular and molecular levels.

Amylose is a linear polymer with molecular weight in the range of  $10^5$  to  $10^6$  g/mol. Amylopectin is a branched polymer with molecular weight in the range of  $10^7$  to  $10^9$  g/mol, with branching points ( $\alpha(1-6)$  linkage) occurring every 25-30 glucose units (Figure 3).

The ratio of these two components depends on the source of the starch and can vary from 100% amylopectin to 100% amylose either reported as occurring in nature or as a result of classical plant breeding.



Figure 3 Chemical structure of amylose and amylopectin

# **1.2.2 Introduction to extrusion**

An extruder system is shown in Figure 4. The main components of a twin screw extruder are screw elements and barrels (Figure 5 [1]), motor, feeder and die.

# Extruders : fully modular systems



Figure 4 Extruder system

For interpretation of the references to color in this and all other figures, the reader is

referred to the electronic version of this dissertation.



Figure 5 Kneading elements, covey elements and barrels

Extrusion is typically used for 1) melt blending 2) filler dispersion 3) chemical modification (branching, functionalization etc) 4) Co-polymerization reaction. The combinations of high temperature, high shear and high pressure provide excellent mixing.

There are two different mixing concepts (distributive mixing and dispersive mixing) which are shown in Figure 6. When the kneading disk is narrow, the extruded mixture can easily by pass the top of the disk resulting in more distributive mixing. When the kneading disk is wide, the extruded mixture is more likely to reach the top of the disk/paddle (Figure 6, [1]), resulting in more dispersive mixing.



Figure 6 Distribution and dispersive mixing

Starch has poor thermal processing properties; it decomposes before it melts due to its strong hydrogen bonding association and crystallization. This makes starch unsuitable for thermoplastic applications. However, using a plasticizer in a twin screw extruder with appropriate screw elements can break up the hydrogen bonding within the starch, disrupts the crystalline region (Figure 7) and makes it flow like a thermoplastic material, since water can form hydrogen bonding with starch and release the starch chain in the granule without significantly reducing the starch molecular weight.



Starch granule

Plasticized starch

Figure 7 Starch plasticization

#### 1.2.3 Starch foam extrusion (physical process)

Starch loose-fill foam producing steps (Figure 8): (1) Feed starch, additives and water into a twin screw extruder. Under high pressure, temperature and shear, the starch granular structure is destroyed. (2) As the mixture exits the die, the sudden drop in pressure causes the water to turn into steam that acts as a blowing agent. Screw configuration is an important factor in this process. Commercial foam properties are summarized in Table 1.



Figure 8 Foam extrusion process

Trade name [foam peanuts]	Resiliency	Density (kg/m <sup>3</sup> )
Pelaspan Pac (EPS based)	79.30%	9.6
Flow-Pak S (EPS based)	82.70%	7.5
Star-Kore	70.20%	20.6
Flo-Pak Bio 8	70.10%	16.8
Envirofil	67.80%	22.1
Renature	67.20%	21
Clean Green	68.80%	21.8

Table 1 Commercial foam products' property

Many biodegradable polymers and common petroleum based polymers as additives were extensively studied in order to improve the physical properties of the starch foams ( Table 2) [2-54]. Starch ester was also studied to improve the humidity resistance

of starch foam. Curiously, few researchers focused on the technical aspects (screw

configuration, die design, etc.) of the foam extrusion, each of which is crucial for a

successful process. Also, most of the researchers used strand dies for making cylindrical

foam. This research focuses on the technical/engineering aspects of the starch foam

extrusion, an understanding of the principals involved, investigation of the relationship

between those operational parameters and characterization of starch foam sheets

produced using an annular die.

Materials added to starch and water	Reference
Polyhydroxy aminoether	2
Maleated poly(butylene adipate-co-terephthalate)	3
Epichlorohydrin, acetic anhydride, supercritical carbon dioxide	4
Wheat flour, wheat bran fibers	5
Cellulose fiber	6
Glycerol	7
Sugarcane bagasse fibers, polyvinyl alcohol	8
Epichlorohydrin, supercritical carbon dioxide	9
Supercritical carbon dioxide	10, 11
Polycaprolactone, supercritical carbon dioxide	12
α-cellulose; polylactic acid; polystyrene; glycerol; NaCl; talc; Na <sub>2</sub> CO <sub>3</sub> ; citric acid	13
Paper powder, polypropylene	14
Polylactic acid, Cloisite 10A organoclay	15
Polylactic acid, Cloisite 30B organoclay	16
Polylactic acid, Cloisite 10A, 25A, 93A, 15A organoclay	17
Polylactic acid, Cloisite 30B, Na+, 20A clay	18
Polystyrene, talc, Azodicarbonamide, citric acid	19
Polystyrene, polycarbonate, talc	20
Polylactic acid	21, 22, 23
Egg shell powder as nucleating agent	24
Thermoplastic starch, polylactic acid, carbon dioxide as blowing agent	25
Thermoplastic starch, polystyrene, 1,1,1,2-Tetrafluoroethane	26
Sorbitol, glycerol, poly(ethylene-co-vinyl alcohol)	27
Starch acetate, ethanol as blowing agent	28
Starch acetate, cellulose	29
Starch acetate, corn cob fiber, ethanol	30
Starch acetate, natural fiber, ethanol	31
Starch acetate, cellulose, ethanol	32
Starch acetate, ethanol, Ethyl acetate	33
Starch acetate, water or ethanol as blowing agent	34, 35
Starch acetate, corn stalk fibers	36
Starch acetate + native corn starch	37
Yellow dent corn	38
polyvinyl alcohol, cellulose acetate, polylactic acid, polyhydroxyester ether,	39
polycaprolactone, polyester amide and poly(hydroxybutyrate-co-valerate)	
Poly(ethylene-co-vinyl alcohol)	40
Mater-Bi®	41
Eastar Bio Copolymer®	42
Poly(ethylene-co-vinyl alcohol), polystyrene	43

Table 2 A summary o	of starch	foam research
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# Table 2 (cont'd)

Polystyrene, magnesium silicate, polycarbonate, azodicarbonamide	44
Polystyrene, polymethyl methacrylate	45
Polyalkylene glycol, silica	46, 47
Poly(ethylene-co-acrylic acid), urea, NaHCO <sub>3</sub>	48
>45%, ~70% amylose	49,50,51
Starch ester, modified with alkylene oxide	52
Poly(ethylene-co-acrylic acid), poly(ethylene-vinyl alcohol), Na <sub>2</sub> CO <sub>3</sub>	53, 54

#### **Chapter 2** Materials, Methods and Characterizations

#### **2.1 Materials**

#### **2.1.1 Starch and Talc**

Hydroxypropylated high-amylose (70%) starch (molecular weight: 250K~1000K g/mol) was purchased from Ingredion Incorporated (Westchester, IL). This starch was chosen due to its reduced branching (less cross linking) compared with regular starch, which has a higher amylopectin content. The high amylose starch gives the foam good resiliency due to its linear chain compared to regular starch (30wt% amylose). The high amylose starch was treated with propylene oxide (5wt%) to disrupt hydrogen bonding and thus improve processability (Figure 9).

starch — OH + 
$$H_2C$$
 — CH – CH<sub>3</sub> — starch — O — CH<sub>2</sub> — CH – CH<sub>3</sub>

~ ~ ~

Figure 9 Hydroxypropylate reaction

In commercial scale extrusions, in order to obtain a satisfactory feed rate, the hydroxypropylated high amylose starch is chilsonated (compact granulated) and in pellet form.

Water was used as both a plasticizer and a blowing agent. Talc (hydrated magnesium silicate) was used as a nucleating agent.

#### 2.1.2 Polymer modifiers – PVOH, PHAE, PHE, and PVB

Several polymer modifiers were used to modify the starch foam properties and improve extrusion process. They are polyhydroxyl aminoether (PHAE), polyvinyl alcohol (PVOH), polyhydroxy ether (PHE) and polyvinyl butyral (PVB).

Polyhydroxy aminoether (PHAE) was supplied by the Dow Chemical Co. (Midland, MI), under the trade name of BLOX 110. It is produced by the reaction of Bisphenol A diglycidyl ether with monoethanol amine using a reactive extrusion process (Figure 10).



Figure 10 Polyhydroxy aminoether synthesis

Polyvinyl alcohol (Mowiol 40-88) (Figure 11) was obtained from Kuraray America, Inc. (Houston, TX). It is synthesized by hydrolysis of polyvinyl acetate. The "40" in the grade title indicates 4% water solution. The viscosity is 40cp and the degree of hydrolysis is 88%.



Figure 11 Chemical structure of polyvinyl alcohol

Polyhydroxyl ether (PHE) was purchased from InChem Corporation (Rock Hill, SC) under the trade name PKHH. The polyhydroxyl ether is synthesized by condensation of bisphenol A and epichlorohydrin (Figure 12).



Figure 12 Polyhydroxyl ether synthesis

Polyvinyl butyral (PVB) was supplied by Kuraray America, Inc. (Houston, TX) PVB 60HH was used in all the experiments. The "60" in the title grade refers to the molecular weight, the number is proportional to the molecular weight; "HH" indicates the residual PVOH content, with PVOH 11-14%, PVAc 1-8% and PVOAcetal 78-88%.



Figure 13 Chemical structure of polyvinyl butyral

# **2.2 Experimental**

## 2.2.1 Century ZSK-30 co-rotating twin screw extruder

The laboratory starch foam extrusion was done with a twin screw extruder (Century

ZSK-30) with an L/D of 42:1 (

Figure 15, Table 3) and 20.4:1 (Figure 14 and Figure 16, Table 4). Two sets of screw configuration were used. The numbers in the Figure 14 and Figure 15 are the barrel orders.



Figure 14 The barrels arrangement for the screw configuration (L/D=20.4)



Figure 15 The barrels arrangement for the screw configuration (L/D=42)

#	I/D = 42.1
# 1	L/D = 42.1 28/14
2	60/60
2	60/60
3	60/60
4	42/42
3	42/42
6	28/28
/	28/28
8	20/20
9	20/20
10	KB 45/5/14
11	KB 45/5/14
12	KB 45/5/14
13	KB 45/5/20
14	KB 45/5/20
15	60/60
16	42/42
17	28/28
18	28/28
19	20/20
20	KB 45/5/42
21	KB 45/5/42
22	60/60
23	42/42
24	28/28
25	28/28
26	20/20
27	KB 45/5/14
28	KB 45/5/14
29	KB 90/5/28
30	KB 90/5/28
31	60/60
31	42/42
32	42/42
33	42/42
34	28/28
<u> </u>	28/28
30	28/14
37	20/20 KD 00/5/20
38	KB 90/5/28
39	20/20
40	20/20
41	20/20

Table 3 Screw configuration of Century ZSK-30 extruder (L/D=42)

#	Usable L/D
	=20.4:1
1	28/14
2	60/60
3	60/60
4	60/60
5	42/42
6	28/28
7	28/28
8	KB 45/5/14
9	KB 45/5/14
10	KB 45/5/20
11	KB 90/5/28
12	42/42
13	28/28
14	28/28
15	KB 45/5/42
16	KB 45/5/42
17	KB 45/5/14
18	42/42
19	28/28
20	28/14
21	60/60
22	60/60
23	60/60
24	42/42
25	42/42
26	28/28
27	20/20
28	20/20
29	KB 45/5/14
30	KR 45/5/14
	KD <b>4</b> 3/3/14
31	20/20
31 32	20/20       20/20
31 32 33	20/20 20/20 KB 45/5/28
31   32   33   34	20/20       20/20       KB 45/5/28       KB 45/5/28
31   32   33   34   35	XB 43/3/14       20/20       20/20       KB 45/5/28       KB 45/5/28       20/20
31   32   33   34   35   36	RB 43/3/14       20/20       20/20       KB 45/5/28       KB 45/5/28       20/20       20/20
31     32     33     34     35     36     37	RB 43/3/14     20/20     20/20     KB 45/5/28     KB 45/5/28     20/20     20/20     KB 90/5/28
31     32     33     34     35     36     37     38	RB 43/3/14       20/20       20/20       KB 45/5/28       20/20       20/20       20/20       20/20       KB 90/5/28       KB 90/5/28
31     32     33     34     35     36     37     38     39	RB 43/3/14     20/20     20/20     KB 45/5/28     KB 45/5/28     20/20     20/20     KB 90/5/28     KB 90/5/28     20/20
31     32     33     34     35     36     37     38     39     40	KB 43/3/14     20/20     20/20     KB 45/5/28     20/20     20/20     20/20     KB 90/5/28     20/20     20/20     20/20     20/20     20/20     20/20     20/20     20/20     20/20     20/20     20/20

Table 4 Screw configuration of Century ZSK-30 extruder (L/D=20.4)



Figure 16 Screw configuration of Century ZSK-30 extruder (L/D=20)

A peristaltic pump was used for injecting water into the extruder and accurate single-screw feeders were used for feeding starch and additives. A screw speed of 200rpm was used for laboratory experiments for foam noodle extrusion. The strand die used was 3.1mm in diameter and 12.4 mm in land length. The slit die was 25.4mm in width, 1.27mm in height, and 12.7mm in land length.

When an annular die (0.38mm gap and 54 mm outside diameter, 3.5mm land length) (Figure 17) was used to produce the foam tube, the screw speed was set at 400rpm.

Initially, during start-up, water was pumped into the water feed port at 20-30% of the starch feed rate, and later its flow rate was reduced to about 5-8% of starch. The raw materials were fed individually or pre-blended with each other in the lab scale extruder.

### 2.2.2 Wenger TX-80 extruder

Commercial scale starch foam extrusion was done in a twin screw extruder (Wenger TX-80) with an L/D of 16:1. All materials were fed separately using precalibrated feeders or pumps. An annular die was used to produce foam sheet and a strand die was used to produce foam peanuts (with a high speed cutter). The strand die employed 4 holes and 6 holes with 2.9 mm and 2.3 mm diameters, with land length/diameter ratio 1.5:1. The annular die used to produce the foam sheet has 6.25 inch D<sub>o</sub>, 6.186 inch D<sub>i</sub>, and 0.31 inch L (land length), see Figure 17. The raw materials were fed individually in the commercial scale extruder. The screw configurations used are shown in Table 5 and Figure 18.

Config. #1	Config. #2	Config. #3
	80/120 (single flight, under	80/120 (Single flight,
40/120 (single flight)	cut)	undercut)
40/120 (single flight)	40/120 (single flight)	40/120 (Single flight)
60/60	60/60	60/60
40/120	60/120	40/120
KB 30/4/40	KB 45/3/40	KB 30/4/40
KB 30/4/40	KB 45/3/40	KB 30/4/40
40/120	60/120	40/120
KB 90/8/106.67	KB 45/3/40	KB 45/11/146.67
KB 90/5/50	KB 90/6/80	KB 90/1/10
40/120	KB 45/3/30	40/120
KB 45/4/53.33 (R)	KB 45/3/40	KB 45/3/40
		KB 90/7/93.33 (fist disk
KB 45/4/53.33 (R)	60/120	is 45° with previous disk)
KB 90/3/40	60/120	KB 45/1/10
40/120	60/120	40/120
60/115 (conical)	60/115 (conical)	60/115 (conical)

	Table 5	Screw	configurations	for	Wenger	TX-80
--	---------	-------	----------------	-----	--------	-------



Figure 17 Annular die



Figure 18 Screw configuration for Wenger TX-80

#### 2.3 Characterization methods

The foam products were characterized by the following methods:

Precondition samples: The foam samples collected were conditioned as per

ASTM D-4332 at 23±1°C and 50±2% relative humidity for 3 days before testing.

Density, Expansion Ratio: The density of the foam was calculated from the mass and volume of specimen according to test method ASTM D-3575 (Section 43, Method A). The dimension of the sample was measured using a Vernier caliper graduated to permit measurements to accuracy of  $\pm 0.01$  mm. The expansion ratio was calculated as the ratio of the cross-sectional area of the foam to the area of the opening of the die.

Compressive Strength and Resiliency: Compressive strength was measured on a United Testing Systems SFM-20 tensile testing machine. The specimens were cut into 1 inch long pieces and then were securely fastened lengthwise and compressed with a steel probe with a hemispherical end cap (0.25 inch diameter). By lowering the probe to the foam surface, an initial load of 0.5 N was applied to the specimen for approximately 5 seconds. The probe was lowered further at a rate of 0.5 mm/s for a distance of 3 mm and then held in that position for 1 minute. Compressive strength was obtained by dividing the maximum load over the cross-sectional area of the probe. Resiliency was calculated from the percentage of the compressive force after the 60 seconds holding period divided by the maximum force required to compress the foam by 3 mm.

Cell size characterization: Environmental scanning electron microscope (ESEM) and pocket microscope were used to take pictures on the cutting surface of the foam.

Moisture adsorption: The moisture adsorption under different relative humidity (RH) at room temperature was studied. Different salt saturated solutions were placed under the plate in closed desiccators to create different RH environment (Table 6).

Salt	RH
Potassium acetate	23%
Magnesium chloride	33%
Potassium carbonate	43%
Magnesium nitrate	52%
Sodium bromide	59%
Potassium iodide	70%
Sodium chloride	75%
Potassium chloride	85%

Table 6 Different salt solutions for relative humidity

Cushioning property: The cushioning property of the starch foam sheet was measured by a cushioning testing machine manufactured by Lansmont Corp. (Monterey, CA) following ASTM D-1596 [55] test procedure. In this test a guided platen assembly of known weight was dropped from a known height (0.75m) onto a motionless cushion sample of known bearing area and thickness (50.8 mm thickness). The dynamic shock cushioning characteristics of the sample were obtained through the deceleration-time data that was recorded by an accelerometer.

Insulation property: The thermal conductivities of foam sheet and foam paper were measured using the ice-melt test and Anter Thermal Conductivity Unit, respectively. The Ice-melt test includes the following steps: Make cubical cavity with 6 walls (10 inch \* 10 inch) using starch foam sheets. Place ice in a sealed plastic bag. When the ice is wet, discard any water. Then place the bag into the test package and weigh the water volume after several days.

Calculation:

$$k \cdot 6 \cdot W^2 \cdot \frac{T_1 - T_2}{L} \cdot t_m = M \cdot h_{sf} \implies k = \frac{M \cdot h_{sf} \cdot L}{6 \cdot W^2 \cdot (T_1 - T_2) \cdot t_m}$$
(2-1)

Where  $h_{sf}$  latent heat of ice (J/kg), M is the weight of ice melt (kg),  $t_m$  is the melting time (s), W it the area of one face of the cubic, T<sub>1</sub> is the room temperature, T<sub>2</sub> is the melting temperature of ice (0°C). Control experiments are done using empty corrugated boxes without foams.

The insulation property is also measured by Anter Thermal Conductivity Unit (Figure 19). The sample used is 1 inch diameter disk.


Figure 19 Thermal conductivity test

$$\frac{q}{A} = -k\frac{dT}{dx} \implies \frac{R_{\rm S} + R_{\rm int}}{R_{\rm R}} = \frac{\Delta T_{\rm S}}{\Delta T_{\rm R}}$$
(2-2)

 $R_{int}$  is interfacial thermal resistance, A is the area of the contact surface, q is the heat transfer rate, k is the conductibility,  $\frac{dT}{dx}$  is temperature gradient, and Rs is thermal resistance of sample material,  $R_R$  is the thermal resistance of reference material.  $\Delta T_S$  is temperature difference cross the sample,  $\Delta T_R$  is temperature difference cross the reference material. Calibration must first be done using known thermal conductivity.

materials (reference), R<sub>s</sub> is proportional to 
$$\frac{\Delta T_s}{\Delta T_R}$$

Water penetration time test (hydrophobic test): The hydrophobic character of the foams was measured by monitoring the time it took a water stream to penetrate the foam

sheets. In these experiments the water flow rate was 60 kg/hr, the tube diameter was 8 mm and the vertical distance between the outlet of the tube and the foam surface was kept constant at 20 cm.

Surface wetting test (hydrophobic test): The foam sheets were dipped into water, removed and left undisturbed for five hours. After five hours, photographs were taken of the foam sheets to determine the degree of disintegration.

Wear (hydrophobic test): The resistance of the foams to moisture was measured by wet wear using a Sheen machine (Sheen Wet Abrasion Scrub Tester, model 903/PG manufactured by Sheen Instruments, Ltd, Arlington Heights, IL). The test consists of four scrubbing heads that rub against the test sample under a load over a predetermined period of time. In this test the foam samples were placed on panels and the scrubbing heads were swept back and forth across them. The load was set to 800 grams and the scrubbing speed was set to 37 strokes per minute for a total of 5 minutes.

#### 2.4 Statistics and design of experiments methods

#### Sample size selection

The reason for choosing appropriate sample size: Figure 20, the length of the sticks, if there are much variation in the bulk, more samples are needed in order to represent the bulk. If the stick is uniform, only one sample is need for characterization.

Sample	Bulk		
11-11	TEREST CONTRACTOR CONT		
I			

Figure 20 Sample size from bulk

In order to make sure that the selected sample represented the bulk properties, O.C. curve (Operating Characteristic Curve) (Figure 21) was used for selecting the correct sample size.



Figure 21 Operating Characteristic Curve ( $\alpha=\beta=0.05$ )

The bulk standard deviation for measuring the diameter is approximately 0.4 mm, and the mean difference which is wanted to detect is preferably 1mm, According to the

curve, the sample number is around 10. In the cylindrical foam diameter measurement, 10 samples from different running times were collected to be taken for measurement.

Variation Analysis

t distribution and F distribution (Figure 22) were used to calculate the confidence interval (CI) and variation analysis 56.



Figure 22 t and F distribution curves

The confidence interval was calculated by the following equations.

$$t_{\alpha/2,n-1} = \operatorname{tinv}(\alpha, n-1) \tag{2-3}$$

$$\mu = \overline{y} \pm CI \tag{2-4}$$

$$CI = t_{\alpha/2, n-1} \quad \frac{\sigma}{\sqrt{n}} \tag{2-5}$$

Where  $t_{\alpha/2,n-1}$  is the t distribution value at n degree of freedom and  $\alpha$  possibility, tinv is the Excel® function. The  $\sigma$  is the standard deviation.

ANOVA table was used to determine whether a treatment is effective.

- i is the factor level  $(1 \le i \le a)$
- j is the replicate  $(1 \le j \le n)$
- N is the total number of experiments (N = a\*n)

Source of	Sum of	Degrees of	Mean				
Variation	Squares	Freedom	Square	F0	Fcritical	P value	Conclusion
				Ratio of	Use	Use	Base on
				mean	Excel's	Excel's	rejection
Treatments	SS <sub>Treatment</sub>	a-1	MS <sub>Treatment</sub>	squares	finv	fdist	criteria
Error	SS <sub>Error</sub>	N-a	MS <sub>Error</sub>				
TOTAL	SS <sub>Total</sub>	N-1					

Table 7 Calculation for ANOVA

$$y_{i\bullet} = \sum_{j=1}^{n} y_{ij}; \quad y_{\bullet\bullet} = \sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij}$$
$$SS_{Treatment} = \frac{1}{n} \left( \sum_{i=1}^{a} y_{i\bullet}^{2} \right) - \frac{y_{\bullet\bullet}^{2}}{N}; \quad MS_{Treatment} = \frac{SS_{Treatment}}{a-1}$$
(2-6)

$$SS_{Total} = \left(\sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij}^{2}\right) - \frac{y_{\bullet\bullet}^{2}}{N}; MS_{Total} = \frac{SS_{Total}}{N-1}$$
(2-7)

$$SS_{Error} = SS_{Total} - SS_{Treatment}; MS_{Error} = \frac{SS_{Error}}{N-a}$$
(2-8)

The criteria for effective treatment is to compare the two sources of variation (a treatment and error) and comparing this value ( $F_0$ ) to the F value, if  $F_0$  is located to the far right side of the F distribution curves, the two variations are significantly different and the treatment is effective.

# Design of Experiments

Every function can be extended by the following Taylor expansion (polynomial) and this polynomial can be used directly for the prediction after the coefficients were obtained / regressed through experimental data.

Taylor expansion (n variables)

$$f(x_1 + \Delta x_1, x_2 + \Delta x_2, \dots, x_n + \Delta x_n) =$$

$$\sum_{i=0}^{\infty} \frac{1}{i!} \left( \Delta x_1 \frac{\partial}{\partial x_1} + \Delta x_2 \frac{\partial}{\partial x_2} + \dots + \Delta x_n \frac{\partial}{\partial x_n} \right)^i f(x_1, x_2, \dots, x_n)$$
(2-9)

For functions with two variables:

$$f(x + \Delta x, y + \Delta y) = \sum_{i=0}^{\infty} \frac{1}{i!} \left( \Delta x \frac{\partial}{\partial x} + \Delta y \frac{\partial}{\partial y} \right)^{i} f(x, y)$$
  
$$= f(x, y) + \Delta x \frac{\partial f(x, y)}{\partial x} + \Delta y \frac{\partial f(x, y)}{\partial y}$$
  
$$+ \frac{1}{2!} \left[ (\Delta x)^{2} \frac{\partial^{2} f(x, y)}{\partial x^{2}} + 2\Delta x \Delta y \frac{\partial^{2} f(x, y)}{\partial x \partial y} + (\Delta y)^{2} \frac{\partial^{2} f(x, y)}{\partial y^{2}} \right]$$
  
$$+ \frac{1}{3!} \left[ (\Delta x)^{3} \frac{\partial^{3} f(x, y)}{\partial x^{3}} + 3(\Delta x)^{2} \Delta y \frac{\partial^{3} f(x, y)}{\partial x^{2} \partial y} + 3\Delta x (\Delta y)^{2} \frac{\partial^{3} f(x, y)}{\partial x \partial y^{2}} \right]$$
  
$$+ (\Delta y)^{3} \frac{\partial^{3} f(x, y)}{\partial y^{3}} + \cdots$$

$$= f(x, y) + \frac{1}{1!} \left( \Delta x \frac{\partial}{\partial x} + \Delta y \frac{\partial}{\partial y} \right) f(x, y) + \frac{1}{2!} \left( \Delta x \frac{\partial}{\partial x} + \Delta y \frac{\partial}{\partial y} \right)^2 f(x, y)$$
$$= \frac{1}{2!} \left( \Delta x \frac{\partial}{\partial x} + \Delta y \frac{\partial}{\partial y} \right)^3 f(x, y) + \frac{1}{2!} \left( \Delta x \frac{\partial}{\partial x} + \Delta y \frac{\partial}{\partial y} \right)^2 f(x, y)$$

$$+\frac{1}{3!}\left(\Delta x\frac{\partial}{\partial x}+\Delta y\frac{\partial}{\partial y}\right)f(x,y)+\cdots$$
(2-10)

For example, function with 3 variables:

$$\frac{1}{T} = \frac{w}{T_1} + \frac{1 - w}{T_2} \implies T = \frac{1}{\frac{w}{T_1} + \frac{1 - w}{T_2}}$$
(2-11)

Where, w,  $T_1$  and  $T_2$  are three varibles.

The above equation can be mathematically expanded around (w,  $T_1$ ,  $T_2$ ) = (0.5, 273.15, 273.15):

$$T = T_2 - T_2 \cdot w + T_1 \cdot w + 0.003661 \cdot T_1 \cdot T_2 - 0.0018305 \cdot T_2^2$$

$$-0.0018305 \cdot T_1^2 - 1.63754 \times 10^{-6} \cdot T_2 \cdot T_1^2 - 1.63754 \times 10^{-6} \cdot T_1 \cdot T_2^2 + 1.63754 \times 10^{-6} \cdot T_2^3 + 1.63754 \times 10^{-6} \cdot T_1^3 + \dots$$

When w=0.5, Figure 23 are the response surfaces.



Figure 23 A: Function vs. polynomial (square terms); B: Function vs. Function vs. polynomial (cubic terms)

When the function is expanded to higher order terms, the results of the polynomial are close to the result from the function. So, there are two steps: regression analysis of experimental data with the polynomial to get the value of those coefficients, and then use the polynomial to predict and optimize the process to obtain optimum product properties.

Many of the properties of the starch foams are a function of feed rates of starch, talc and water during the extrusion process. Since there are significant interactions between these factors, changes in one factor while holding the other two constant, does not yield the same response as repeating the same set of experiments and holding the other two factors at a different level. This is due to the effect of one variable depending on the level of the others involved in the process. Thus, a better approach is to use a Box-Behnken statistical design experiment (Figure 24) [57] where the levels of all the variables are changed simultaneously. This approach is also advantageous since it requires fewer experiments, resulting in lower reagent consumption and considerably less laboratory work. It also yields mathematical models with information related to the statistical significance of each factor as well as information on the interaction between the factors. The mathematical models are obtained by selecting appropriate polynomial equations that describe the experimental data. Various statistical analyses can then be used to determine how well the selected model satisfies the data.



Figure 24 Experimental points for Box-Behnken design

If there were 4 variables instead of 3 variables (Figure 24), two variables should stay in the "0" line and the other two variables should in the "-1" or "+1" line, therefore, the total experimental points except center should be  $6 \times 2 + 4 \times 2 + 2 \times 2 = 24$ , and there are usually 5 points in the design space center, so there are 29 experiments totally. Thus, this experiment amount is much less than 81 (3<sup>4</sup>=81, 4 variables at three different levels).



Figure 25 DOE for 4 variables

#### **Chapter 3 Foam extrusion results and discussion**



# **3.1 Screw configuration effect**

Figure 26 Specific mechanical energy (SME) comparison for two screw configuration

Three different screw configurations (as shown in Table 5) were used in starch foam sheet commercial scale extrusions. The first screw configuration has the greatest shear, the second has the lowest shear and the shear generated by the third screw configuration was at an intermediate level (Table 5). Among the three screw configurations, the 2nd screw configuration design is failure; the tube foam has ripples/bumps on the top and bottom. Also, the foam expanded too much, even when adding talc which normally reduces bubble size.

Table 5 Configuration #1 has more mixing effect than Configuration #3, and thus needs more mechanical energy. Configuration #3 is currently used for the normal production of starch foam sheets (commercially sold as Green Cell Foam<sup>TM</sup>).

Screw configuration plays an important role in starch foam extrusion. Unlike plastic extrusion, polymer pellets can be easily fed into and conveyed to the next section. The starch must be in granulated form instead of powder form in order for the screw flight to pick them up while rotating. To avoid water/moisture adhering to the starch and causing a bridging problem, the water feed port should be separated from the starch feed port and also, the feed zone should be kept cool to avoid vaporization of the water. The feed zone includes the largest single pitch screw elements in order to convey rapidly. The pitch of the screw is then reduced in order to force the materials downstream.

The first kneading zone has thin kneading elements with a small stagger angle in order to rapidly convey the materials to the second kneading zone with light kneading/mixing. The second kneading zone has less kneading effect and less degree of fill than the third kneading zone since there are a few 90 degree of kneading disks.

The screw configuration and die design are the two important factors that affect the process. The screw configuration builds the pressure, and the die should have the ability to hold the pressure (force balance). Improper screw configuration will cause problems such as surging, braiding (Figure 27), bumping, or high torque.

37



Figure 27 Regular starch foam sheets (left) vs. sheets with braiding problem (right two)

# 3.2 Starch feed rate effect

The starch feed rate was varied for cylindrical foam extrusion and characterizations were done on the products. In order to increase the starch feed rate to increase the production efficiency, cylindrical foam extrusions with six holes (Figure 28) were also investigated. Compared with petroleum based foam, the bubble cells have a wider distribution (Figure 29).



Figure 28 Four and six holes strand die



Figure 29 Cells in the starch foam

When the starch feed rate decreased from 460 lbs/hr to 285 lbs/hr, the diameter of

the foam decreased from 20 to 16 mm statistically approved by t test. (Table 8)

	1		
	Exp.	Exp.	Exp.
	1	2	3
Starch (lbs/hr)	460	285	560
Polyvinyl alcohol			
(lbs/hr)	36	36	43
Bentonite with color			
(lbs/hr)	117	80	86
Talc (lbs/hr)	3.6	1.4	0
Water (lbs/hr)	61	46	65
Vegetable oil (lbs/hr)	6	6	6
Screw speed (rpm)	286	270	345
Torque (%)	82%	56%	90%
Cutter speed (rpm)	1667	1140	1375
# of holes in the die			
face	4	4	6

	Exp. #1	Exp. #2
$\mu_0$	20	16
(diameter)	mm	mm
t <sub>0</sub>	-0.9	1.86
$t_{\alpha/2,\nu}$	2.26	2.26
$ t_0  < t_{\alpha/2}$		
v ?	Yes	Yes
	$\mu = \mu_0$	$\mu = \mu_0$

Table 8 Cylindrical foam extrusion conditions and diameter of the foams

As the starch feed rate decreased the diameter of the cylindrical foam and the cell diameter decreased accordingly (Figure 30 and Table 9). The density and compressibility increased while resiliency of the foam remained constant.



Figure 30 Cell size distribution for cylindrical foams (A: noodle extruded at 460 lbs/hr, B:

noodle extruded at 285 lbs/hr)

	Exp. 1 [Q]	CI	Exp. 2 [0.65Q]	CI	P value
Diameter (mm) $\downarrow$	19.89	0.29	16.19	0.23	9.52E-15
Density (kg/m <sup>3</sup> ) $\uparrow$	21.08	0.64	31.69	0.73	2.24E-15
Compressibility(Pa) ↑	1.74E+05	1.26E+04	2.86E+05	1.23E+04	2.25E-11
Resiliency ↓	60.10%	2.30%	57.30%	1.30%	0.03
Cell size ( $\mu$ m) $\uparrow$	605.0	55.5	499.9	45.7	0.006

T 11 0	1. 1.	1.0	1	
Table U	culindri	cal toam	charact	terizatione
1 a 0 10	C y IIIIuI I	cai ioain	Charac	ulizations
	,			

As the number of holes increased from 4 to 6, cylindrical foams with inconsistent lengths were extruded. In addition, the cylindrical foam's diameters were also not consistent, which somewhat depended on the position of the holes (Figure 31, P value = 0.021). This is due to the holes location at different levels and therefore different pressures. The flow rate thus varies with materials flowing more rapidly from the bottom holes than the top. This can be corrected by adjusting the land lengths of the die.



Figure 31 Characterization of cylindrical foam prepared from a die with six holes

# **3.3 Effect of talc content**

The effect of different talc levels on the starch foam with PVOH and PHAE as polymer modifiers was investigated.

The talc acts as a nucleating agent which creates new bubble sites during the foaming process. Increasing the talc content (0.5wt%, 1.3wt%, and 2.7wt%) will decrease the cell size of the foam (Figure 32 and Figure 33).



Figure 32 Cell size distributions for starch foam with PVOH, different talc levels: A: 0.5wt%, B: 1.3wt%, C: 2.7wt%

Figure 32 (cont'd)





Figure 33 Cell size distributions for starch foam with PHAE, different talc levels: A: 0.5wt%, B: 1.3wt%, C: 2.7wt%

Figure 33 (cont'd)



The effect of the talc content with PHE and PVB as polymer modifiers was also investigated using design of experiments methods (section 3.4.2 and 3.4.3).

## **3.4 Different modifiers**

#### 3.4.1 Aqueous PVOH

PVOH solution was studied as a polymer modifier in the starch foam extrusion. The PVOH used for preparing the solution was from Mowiol and the grade was 28-99. This indicates that 4% solution of PVOH in water has 28 cps viscosity. Due to the internal hydroxyl bonding it is not easily dissolved in water. The dissolving technique is to suspend the PVOH into cold water and with constant stirring to avoid agglomeration or settling. Low pressure steam is then introduced to heat up the suspension rapidly. When the solution becomes transparent, the steam is discontinued and the solution cooled with stirring to less than 50°C. It can then be diluted to desired concentrations. The foam extrusion with PVOH solution was done using lab extruder Century ZSK-30. The PVOH water and starch ratio was kept at 0.06:1.



Figure 34 starch foam densities vs. PVOH solution concentration



Figure 35 Starch foam resiliencies vs. PVOH solution concentration Different PVOH solution concentrations have little effect on the density and resiliency of the cylindrical foam (Figure 34 and Figure 35), this is probably due to the low addition of PVOH, which has little effect on the bulk foam properties.

# 3.4.2 Box-Behnken DOE with PHE and annular die

It is apparent that many biodegradable or non-biodegradable additives have been used in attempts to control the structure of the foam and improve the stability toward humidity. Only limited success has been achieved in these studies to date.

Table 10 is the operational conditions and product characterization for starch foam with PHE. The design space picked was: 18.1 kg/hr < PHE < 54.4 kg/hr; 0.23 kg/hr < Talc < 2.27 kg/hr; 20.4 kg/hr < Water < 29.5 kg/hr [58].

PHE (kg/hr)	Talc (kg/hr)	Water (kg/hr)	Density [kg/m <sup>3</sup> ]	Thickness [mm]	Cell diameter	Width [mm]	Water penetration time [s]
36.3	1.25	24.9	20.2	27.0	1.14	575	77.4
54.4	1.25	29.5	17.7	28.4	1.19	580	-
36.3	1.25	24.9	19.5	26.7	1.30	580	73.4
54.4	1.25	20.4	25.7	19.4	0.70	520	187.8
36.3	0.23	29.5	11.2	31.9	3.55	730	63.0
18.1	0.23	24.9	16.3	30.8	3.44	-	14.4
18.1	2.27	24.9	18.9	25.5	1.15	600	11.6
36.3	1.25	24.9	18.1	24.2	1.18	640	49.8
36.3	2.27	20.4	21.9	22.4	0.81	600	59.8
18.1	1.25	20.4	20.0	24.3	1.24	620	10.2
18.1	1.25	29.5	18.6	25.3	1.46	650	13.2
36.3	2.27	29.5	21.7	21.0	0.88	620	59.4
36.3	0.23	20.4	17.5	23.2	1.41	730	66.8
54.4	2.27	24.9	17.0	26.2	1.37	710	195.0
54.4	0.23	24.9	21.8	20.0	0.62	590	187.8

Table 10 Box-Behnken DOE with PHE and annular die

A plot of the experimental values as a function of the calculated values (Figure 36) should yield a perfect fit when the data are arranged on a diagonal line with an intercept at the origin. Any deviation from this ideal line as well as any outliers can be determined from the scatter of the data points around the diagonal line. It was found empirically that quadratic polynomials with a few higher terms provided adequate fit to the data:

$$Y = A_0 + A_1 R + A_2 T + A_3 W + A_4 R^2 + A_5 T^2 + A_6 W^2 + A_7 R^* T + A_8 R^* W + A_9 T^* W + A_{10} T^* W^2$$
(3-1)

where R, T and W denote the feed rates of PHE resin, talc and water (in Kg/hr),

respectively and the value of the polynomials coefficients are listed in Table 11.

Constant	Density [Kg/m <sup>3</sup> ]	Cell diameter [mm]
A <sub>0</sub>	-128.5	-0.16343
A <sub>1</sub>	0.5000	-0.08672
A <sub>2</sub>	125.4	-0.4314
A <sub>3</sub>	11.57	0.2407
A <sub>4</sub>	0.00252	-0.00016
A5	-1.533	0.4578
A <sub>6</sub>	-0.2344	-0.00129
A <sub>7</sub>	-0.09994	0.04106
A <sub>8</sub>	0.02005	0.00082
A9	-9.832	-0.1118
A <sub>10</sub>	0.2037	

Table 11 Polynomials used to evaluate the foam density and cell diameter



Figure 36 Goodness of fit of the calculated polynomials to the experimental values.

A: Foam Density, B: Average Foam Cell Size.

The foam density depends on the combination of the feed as shown in Figure 37. The lowest foam density is obtained at the lowest resin feed rate and lowest talc feed rate whether low water concentrations (Figure 37A) or high water concentrations are used (Figure 37B). It is apparent that the density remains almost constant as the resin feed rate is increased while keeping low talc concentrations in the feed. However, maximum density is obtained at the lowest resin feed rate and maximum talc feed rate. This density maximum is more pronounced when the water concentration in the feed is high (Figure 37B). The data further indicate that at low water feed rates only relatively small changes in the density are observed compared to the foams prepared with high water content where either increasing the resin feed rate or decreasing the talc feed rate lead to higher density foams. It is also observed that the changes in the talc concentrations have a more significant effect on the density than either the resin or the water feed rates.



Figure 37 Effects of resin and talc feed rates on the foam density at low (A) and high (B)

water feed rates.

The effect of water concentration in the feed rate is more complex as shown in Figure 38. It is apparent that at the low talc feed rate (Figure 38A) the foam density is inversely proportional to the concentration of the resin and this effect is more pronounced at high water feed rates. In fact, the resin content in the feed has almost no effect when the water feed rate exceeds about 22 Kg/hr. The situation is somewhat different when the talc content is increased. Under these conditions, the foam density appears to decrease through a shallow minimum and then increases again as the water content in the feed is increased (Figure 38B). Under these conditions the resin feed rate has only a minor effect on the foam density leading to slightly denser foams when the resin content in the feed is increased.



Figure 38 Effects of water and resin feed rates on the foam density at low (A) and high (B)

talc feed rates.

The effect of water on the density is easy to understand since the water acts as a blowing agent. It is intimately mixed with the extrudate under high pressure and temperature and then released as steam immediately beyond the die upon exit to atmospheric pressure. Thus, low water concentrations inherently lead to low expansion and high foam density. Similarly, the high density of talc (2.7-2.8 g/cm<sup>3</sup>) greatly impacts the overall density of the foam which is directly proportional to its concentration in the feed. It is important to note that the situation is more complex since it is not sufficient to have only high expansion at the die exit in order to obtain a low density foam. Low density foams can be obtained only if the expanded foams are stable and do not shrink beyond the die. As a result of this shrinkage, a high foam density is obtained at high concentrations of water in the feed. At low water feed rates, insufficient water is available to expand the foam resulting in high density foams. However, at intermediate concentrations sufficient water as a blowing agent is available and no shrinkage occurs resulting in a shallow minimum and low density foams (Figure 38B).



Figure 39 Effects of water and talc feed rates on the average cell diameter at low (A) and

The dimensional stability and the overall structure of the foams as a function of the feed are shown in Figure 39 and Figure 40. The average cell diameter of the foam at low resin and high talc feed rates is very small (about 1 mm) and essentially independent of the talc content in the feed (Figure 39A). However, decreasing the talc content in the feed drastically increases the average cell diameter up to about 5 mm. This increase in the average cell size is more pronounced at high water concentration in the feed compared to a similar feed having low water content where the average cell diameter increases to only 3 mm. It is also observed that at these low resin feed rates the talc has a more pronounced effect on the foam cell diameter than the water content in the feed. Increasing the resin content in the feed leads to a similar response plot (Figure 39B) but the effect of the talc and the water are less obvious and the overall surface is flatter with the majority of the cells being closed cells.



Figure 40 Effects of talc and resin feed rates on the average cell diameter at low (A) and high (B) water feed rates.
The changes in the foam structure as a function of the talc and resin contents in the feed are best observed in Figure 40. At low water content (Figure 40A) the largest average cell diameter is observed at low resin and low talc concentrations. Increasing either of these variables leads to finer morphology and foams with smaller cell sizes. Moreover, the same phenomenon is observed at high water content (Figure 40B) but the effect of these variables on the structure of the foams is more noticeable. Under these conditions the average cell diameter decreases from about 5 mm to about 0.2 mm by increasing the talc content in the feed to 2.5 Kg/hr or to about 2 mm by increasing the resin content in the feed to 55 Kg/hr. The finest cell structure is obtained when the water, resin and talc feed rates are at their maximums.

The structure of the foam as a function of these variables is related to expansion of the extrudate as it exits the die. At this point water vapors can either diffuse into an existing cell (bubble) to further expand it leading to a larger cell diameter or create a new cell (bubble) by overcoming the surface tension barrier. Here the talc acts as a nucleating agent, hence increasing its concentration will decrease the surface tension barrier which will then lead to the formation of new small bubbles. In the absence of talc or at low talc concentrations, water vapor tends to diffuse into an existing cell resulting in the expansion of an existing bubble and produce foam with a larger average cell size. Furthermore, strain hardening is a necessary requirement for the foaming process. In the early stages of the foaming process, the elongation viscosity of the mixture must be low in order to expand the bubbles. However, in the later stages of the foaming process, high elongation viscosity is preferred in order to stabilize the bubbles. The actual composition of the feed has a strain hardening effect on the foam processing since during the foaming water evaporates and the water vapors gradually diffuse into the bubble. Consequently, less water is used as a plasticizer resulting in a higher resin viscosity.

#### **3.4.3 Box-Behnken DOE with PVB**

In the absence of PVB, the foam is very hydrophilic and dissolves rapidly in water. At high PVB feed rates miscibility becomes an issue and results in "chunky" extrudates. Higher talc loadings produce foam with too high a density. Low water feed rates causes high torque on the extruder with possible blockage. High water feed rates result in a large bubble size in the foam or a low drop in die pressure resulting in no blowing at all. Smaller pin-hole will result in lower density foam and larger pin hole diameter in dense or no foam. In consideration of these restrictions, the following design parameters were selected.

	Lowest value	Highest value
PVB feed rate	0.75 Kg/hr	2.5 Kg/hr
Talc feed rate	0	0.031Kg/hr
Water feed rate	0.5 Kg/hr	0.8 Kg/hr
Pin hole diameter	10 mm	20 mm
<b>T</b> 11 10 D	• •	

 Table 12 Design space using polyvinyl butyral

A Box-Behnken statistical design experiment (DOE) was used and the detailed experimental conditions based on the design parameters are listed in Table 13.

				Pin hole
Sample	PVB	Talc	Water	diameter
label #	(Kg/hr)	(Kg/hr)	(Kg/hr)	(mm)
1	1.63	0	0.5	15
2	0.75	0	0.65	15
3	1.63	0.0155	0.65	15
4	2.5	0	0.65	15
5	1.63	0	0.8	15
6	1.63	0.0155	0.65	15
7	0.75	0.0155	0.5	15
8	2.5	0.0155	0.5	15
9	1.63	0.0155	0.65	15
10	0.75	0.0155	0.8	15
11	2.5	0.0155	0.8	15
12	1.63	0.0155	0.65	15
13	1.63	0.031	0.5	15
14	0.75	0.031	0.65	15
15	1.63	0.0155	0.65	15
16	2.5	0.031	0.65	15
17	1.63	0.031	0.8	15
18	1.63	0.0155	0.5	20
19	1.63	0	0.65	20
20	0.75	0.0155	0.65	20
21	2.5	0.0155	0.65	20
22	1.63	0.031	0.65	20
23	1.63	0.0155	0.8	20
24	1.63	0.0155	0.5	10
25	1.63	0	0.65	10
26	0.75	0.0155	0.65	10
27	2.5	0.0155	0.65	10
28	1.63	0.031	0.65	10
29	1.63	0.0155	0.8	10

Table 13 Box-Behnken DOE for starch foam with PVB

There are four independent variables (PVB [Kg/hr], Talc [Kg/hr], Water [Kg/hr] and Pin hole diameter [mm]). The center of the design space was tested for 5 times, so the total experiments were 2\*(6+4+2)+5 = 29.

	Noodle		
Sample	diameter	Density	Wear
label #	(mm)	(Kg/m <sup>3</sup> )	(mm)
1	43	65.9	4.35
2	49.2	40.1	25.63
3	40.9	71.9	3.68
4	45.4	54.7	5.53
5	46.2	44.4	17.86
6	41.9	65.8	6.09
7	36.5	82.2	25.05
8	36.4	108.3	2.07
9	41.5	68.9	4.94
10	45.6	48.4	23.98
11	39.7	65.5	3.95
12	41	65.9	5.12
13	33.6	103.4	2.84
14	37.8	70.4	20.40
15	38.4	72.2	13.82
16	36.2	91.4	3.13
17	38	68.7	4.88
18	35.9	150.6	4.01
19	39.8	129.2	1.59
20	40.6	85.6	14.04
21	39.9	116	4.21
22	38.8	111.7	2.80
23	40.6	113.1	9.10
24	31.8	105.8	3.01
25	55.7	29.2	14.33
26	41	43.5	25.88
27	34.5	75.3	6.74
28	28.8	108.7	3.17
29	36.9	54.1	18.21

 Z9
 36.9
 54.1
 18.21

 Table 14 Box-Behnken DOE experimental results for starch foam with PVB

Box-Behnken DOE results are listed in Table 14. The mathematical models to regress the Box-Behnken DOE responses are obtained by selecting appropriate polynomials. The criteria are to pick polynomials with less higher order terms whose calculated values are close to the experimental value. Thus, a plot of the experimental values vs. calculated values should be in a diagonal line with origin intercept if the regressions yield a perfect fit. The scatter plots will show the goodness of fit. It was found that quadratic polynomials provided adequate fit to the data empirically:

$$Y = \beta_{0} + \beta_{1}X_{1} + \beta_{2}X_{2} + \beta_{3}X_{3} + \beta_{4}X_{4} + \beta_{12}X_{1}X_{2} + \beta_{13}X_{1}X_{3}$$
$$+ + \beta_{23}X_{2}X_{3} + \beta_{24}X_{2}X_{4} + \beta_{34}X_{3}X_{4} + \beta_{11}X_{1}^{2}\beta_{14}X_{1}X_{4}$$
$$+ \beta_{22}X_{2}^{2} + \beta_{33}X_{3}^{2} + \beta_{44}X_{4}^{2}$$
(3-2)

where  $X_1$ ,  $X_2$  and  $X_3$  and  $X_4$  denote the feed rates of PVB resin, talc and water (in Kg/hr), respectively and the value of the polynomials coefficients are listed in Table 15

	Noodle diameter	Density $(K \alpha/m^3)$	Weer (mm)
β0	0.3966	359.8	49.51
β1	-1.446	50.00	-50.01
β2	-1958	6658	-9.706
β3	150.4	-717.1	7.472
β4	0.7670	-22.03	0.4260
β <sub>12</sub>	39.57	118.0	51.84
β <sub>13</sub>	-11.13	-17.20	5.734
β <sub>14</sub>	0.3333	-0.07566	0.5331
β <sub>23</sub>	140.1	-1414	-1235
β <sub>24</sub>	83.34	-312.8	39.90
β <sub>34</sub>	-0.1488	4.733	-3.373
β <sub>11</sub>	0.3962	-8.024	8.331
β <sub>22</sub>	6328	-6897	-1389
β33	-88.98	440.6	56.38
β44	-0.07954	0.9584	-0.01043

Table 15 Polynomials used to evaluate the foam diameter, density and wear





Figure 41 Goodness of fit of the calculated polynomials to the experimental values. A:

Foam diameter B: Density C: Wear

The eight 3D plots are based on the Table 16. There are four variables in the polynomials; the 3D plots are drawn with setting two variables constant (low and high

levels) and the other two	variables as X-axle and	Y-axle respectively.
---------------------------	-------------------------	----------------------

Response		Pin hole		
	Talc (Kg/hr)	diameter (mm)	Water (Kg/hr)	PVB (Kg/hr)
Noodle diameter	Low/High	Small/Big	X-axle	Y-axle
(mm)				
[4 figures]				
Density (Kg/m <sup>3</sup> )	X-axle	Small/Big	Low/High	Y-axle
[4 figures]		_		

Table 16 Table for 3D plots (noodle diameter and density as responses)

Figure 42 is the noodle diameter response dependent on the feed rates. When using small pin holes, increasing talc feed rate greatly decreases the noodle diameter (Figure 42A vs. Figure 42B). The effect of talc feed rate is much less pronounced when a large pin hole is used; the noodle diameter is maintained relatively constant when the talc feed rate is varied (Figure 42C vs. Figure 42D). At low talc feed rate, increasing pin hole diameter decreases noodle diameter (Figure 42A vs. Figure 42C), This may be due to a drop in expansion ratio. However, at high talc feed rate, increasing pin hole diameter increases noodle diameter (Figure 42B vs. Figure 42D). Figure 42A shows that increasing water feed rate increases noodle diameter at low PVB feed rate, however, water feed rate does not affect the noodle diameter when PVB feed rate is high; the effect of PVB feed rate is pronounced when water feed rate is high.



(B) High talc content and small pin hole diameterFigure 42 3D plots, noodle diameter as response



(D) High talc content and big hole diameter

The foam density as a function of the feed rate and pin hole diameter is shown in Figure 43. Generally, increasing the water feed rate decreases the foam density (Figure 43A vs. Figure 43B and Figure 43C vs. Figure 43D). At low talc content, increasing the pin hole diameter significantly increases the foam density (Figure 43B vs. Figure 43D), this is caused by the pressure drop's significant decreased with increasing in pin hole diameter. However, at high talc content, the foam density is not significantly changed by the pin hole diameter (Figure 43A vs. Figure 43C). When using small pin holes, increasing the talc feed rate greatly increases the foam density (Figure 43A and Figure 43B). However, when using a large pin hole, the talc effect is much less pronounced (Figure 43C vs. Figure 43A and Figure 43D vs. Figure 43B). It is observed that a consistently lower density is obtained at lowest talc and PVB feed rates, smallest pin hole, and highest water feed rate.









(D) High water content and big hole diameter

The changes in the hydrophobicity (wear in mm) as a function of the PVB feed rate and the water feed rate of the foam is shown in Figure 44. These data were obtained for the foams that were extruded with no talc using the smallest pinhole die. It is apparent from the data that highest wear (e.g. maximum hydrophilic characteristics) occurs when the starch foam is extruded at the lowest PVB feed rate and highest water feed rate (wear = 41 mm). Increasing the feed rate of the PVB or decreasing the feed rate of water significantly increases the hydrophobicity of the foams. However, changing the PVB feed rate appears to be more significant than changes in the water feed rate. Lowest wear (e.g. high hydrophobicity) under these conditions is obtained at the highest PVB feed rate and at the lowest water feed rate.



Figure 44 Changes in the wear as a function of PVB and water feed rates with no talc and extruding through a small pinhole die (diameter = 10 mm)

The effects of PVB and water feed rates on the wear when talc is coextruded (at 0.0155 Kg/hr) using a larger diameter die (20 mm) is shown in Figure 45. Under these conditions the most hydrophobic foam is still obtained at the highest PVB feed rate and lowest water feed rate. However, the changes in the wear are less pronounced than before when no talc was used and the foam was extruded through a small diameter die. Apparently, adding talc contributes to the hydrophobicity of the foam simply because talc is inherently hydrophobic. It is also important to note that under these conditions the water feed rate has very little effect on the wear and the major changes are directly related to the extrusion rate of the PVB resin.



Figure 45 Changes in the wear as a function of PVB and water feed rates with talc coextruded at 0.0155 Kg/hr through a large pinhole die (diameter = 20 mm)

The effect of the talc on the wear is shown in more detail in Figure 46. Foams with best hydrophobic characters (lowest wear) are obtained when the starch is coextruded with highest levels of PVB and talc as both of these additives are inherently hydrophobic and contribute to the wear as long as they are well dispersed in the foam. Conversely, the most hydrophilic foam is obtained when no talc and the lowest PVB feed rate are used (maximum wear in Figure 46). It is further apparent that the PVB has a greater effect on the wear than the talc. Thus, the wear decreases from 42 mm to 23 mm when the talc feed rate increases to 0.03 Kg/hr at the lowest PVB feed rate but it decreased from 42 mm to 16 mm when the PVB feed rate increases from 0.75 Kg/hr to 2.5 Kg/hr.



Figure 46 Changes in the wear as a function of PVB and talc feed rates with water coextruded at 0.80 Kg/hr through a small pinhole die (diameter 10 mm)

The difference in the impact of talc and PVB feed rates on the wear is best observed under slightly different extrusion conditions. When the water feed rate is reduced to 0.5 Kg/hr and the die diameter is increased to 16 mm, the talc has negligible effect on the hydrophobicity and only the PVB impacts the wear (Figure 47). Thus, under these conditions it is possible to obtain hydrophobic starch foams even when no talc is used.



Figure 47 Changes in the wear as a function of PVB and talc feed rates with water coextruded at 0.50 Kg/hr extruding through a pinhole die with a diameter = 16 mm.

Unlike changing the composition of the foam, it is conceivable that the pinhole diameter should have no effect on the wear. However, this is not the case as evident from Figure 48 where the wear is inversely proportional to the die diameter. Furthermore, this trend is observed at all PVB concentrations but the lowest wear (maximum hydrophobicity) is observed at the highest PVB feed rate and largest die diameter. The die diameter affects the density and the extent of expansion of the foam which, in turn are related to the moisture sensitivity.



Figure 48 Changes in the wear as a function of PVB and pinhole diameter with water coextruded at 0.80 Kg/hr and no talc

### 3.4.4 Starch foam homogeneity with PVB

PVB is commercially produced by reacting polyvinyl alcohol with n-butyl aldehyde. The hydrophobicity of the polymer can be adjusted by controlling the amount of n-butyl aldehyde used to react with the alcohols. Thus, a high degree of reaction leads to few hydroxyl groups in the polymer and a hydrophobic resin. In preliminary experiments it was noted that the compatibility of PVB with the starch foam depends on the grade of the PVB. Specifically, increasing the molecular weight of the PVB and decreasing the concentration of the hydroxyl groups decreased the miscibility of the polymer in the starch. Based on these preliminary experiments it was decided to use grade Mowital B 60HH, as it should provide good miscibility and a high degree of hydrophobicity. However, in order to ensure compatibility of this grade with minimum gross phase separation that could lead to heterogeneous foam morphology, the homogeneity of foams was evaluated. This was done by taking small samples from 9 different locations of the foam and determining the amount of PVB by TGA. Since the decomposition temperature of the unmodified starch foam occurs below 300 °C and PVB decomposes above 350 °C it is possible to establish the relative concentration of PVB in the starch foam. No apparent difference in the concentration of PVB throughout the sample was observed thus indicating that PVB was evenly distributed within the starch foam with no apparent gross phase separation (Figure 49).



Figure 49 TGA analysis on starch foam with PVB

#### 3.5 Scale down starch foam extrusion from Wenger TX-80 to Century ZSK-30

The Wenger TX-80 extruder has a large throughput ~1000 lbs/hr, and is not suitable for R&D. In order to mimic the process, the feed zone of the lab scale Century ZSK-30 extruder was moved to the middle zone to reduce the L/D ratio ( Figure 15) and a modified screw configuration (Figure 16) was chosen in order to mimic Wenger TX-80 screw configuration more closely. The following equation was used to correlate the feed rates between the different extruders.

$\frac{Q_L}{Q_L} = (\frac{D_L}{D_L})^3$	
$Q_s  D_s'$	(3-3)

	Century ZSK-30	Wenger TX-80
Feed rates		
Starch (Kg/hr)	21.5	408
PVB	3.1	59
Talc	0.18	3.4
Water	0.85	41.3
Processing parameters		
Extruder RPM	400	400
Extruder Torque	60%	90%
Temperature profile (°C)	30, 90, 130, 140	55, 75, 110, 140
Specific Mechanical Energy (J/kg)	$7.7 \times 10^{5}$	$5.1 \times 10^{5}$
Foam sheet properties		
Foam width (mm)	203	610
Foam thickness (mm)	8.0	14.8
Foam density $(kg/m^3)$	33.0	27.7

Table 17 Experimental conditions and results for starch foams prepared by the Century

ZSK-30 and Wenger TX-80 extruders

It has been tested that with starch powder and starch pellets a 50:50 ratio is the highest amount of powder that can be fed to the extruder without feed problems due to

bridging in the feed hopper.

The possibility of using oxidized starch to replace the hydroxypropylated high

amylose starch was evaluated using the small scale extruder.

Experimental conditions:

Premixed starches, PVB and talc, total feed rate was kept at 23.2 kg/hr Water feed rate was kept at 1.3 kg/hr (5.6wt% based on starch).

Sample #	chilsonated starch from KTM	Oxidized starch	PVB Based on starch	Talc Based on starch
0	100%	0%	15wt%	1wt%
1	80%	20%	15wt%	1wt%
2	60%	40%	15wt%	1wt%

Table 18 Formulation for lab starch foam tube

Screw speed: 400 rpm. Die used: annular die

Temperature profile: 30, 90, 120, 140 °C

Torque: 48%, die pressure: 450 psi, slight decrease in torque and die pressure was

observed when oxidized starch was added.

Characterization:

Sample #	Thickness	Density
	(mm), eight different locations	$(Kg/m^3)$
0	$7.4 \pm 0.7$	32.8
1	$7.6 \pm 0.5$	32.6
2	$7.6 \pm 0.6$	32.1
- 1		

Table 19 Lab starch foam tube characterization

When the foam tube was extruded, the relative humidity in the room was 17%, and all the foam tubes were observed to be brittle and the foam tube with oxidized starch disintegrated. Preconditioning of the foam tubes at 52% RH, sample #0 and sample #1 were flexible, sample #2 was brittle but not cracked into pieces. The conclusion from these experiments is starch foam made from oxidized starch has decreased flexibility.

# **Chapter 4 Performance characterizations of starch foam sheets**

# 4.1 Moisture adsorption and humidity sensitivity

Due to the hydroxyl group in the starch structure, moisture can be absorbed from the atmosphere due to hydrogen bonding. Figure 50 shows the moisture adsorption vs. time on the hydroxypropyl high amylose starch powder. It is apparent from the shape of the curves that the water absorption was initially fast but the rate of absorption gradually decreased with time and equilibrium was established after about 70 hours.





It is apparent from the absorption data that the absorbed water was directly proportional to the RH as described by the PELEG model:

$$m(t) = m_0 + \frac{t}{k_1 + k_2 t}$$
(4-1)

Where  $m_0$  is weight of the initial adsorbed moisture (at t=0), t is time, m(t) is the weight of adsorbed moisture at t.  $k_1$  and  $k_2$  are two constants. In this model,  $k_1$  and  $k_2$  indicate the absorption rate and the absorption capacity, respectively. Thus, high  $k_1$  values indicate low absorption rate and high  $k_2$  values indicate low saturated moisture contents.

Raw starch has a very high  $k_1$  value and a low  $k_2$  value whereas the starch foam sheet extruded with no polymer modifiers has significantly lower  $k_1$  and  $k_2$  values (Table 20). This significant increase in the adsorption rate and the saturated moisture content of the starch foam are a direct consequence of the degradation of the hierarchal structure of native starch granules under high temperature, high pressure and the presence of water during the extrusion. The data in Table 21 further indicate that adding PVOH does not improve the resistance of the foams to moisture. However, noticeable improvements are observed when PHAE and PHE are used as additives in the process (Table 21). Moisture adsorption of the starch foam products demonstrates a type II adsorption isotherm (this type of adsorption isotherm shows an indefinite multi-layer formation after completion of the monolayer).

The starch foam retains moisture sensitivity (Figure 51). However the foam absorbed moisture faster than the starch powder. Using PHAE, PHE and PVB as polymer modifiers will have lower moisture content under high RH than using PVOH as polymer modifiers (Figure 53-Figure 55). Moisture adsorption on the starch foam products

82

belongs to a type II adsorption isotherm, Surface area (accessible to moisture) got

according to BET equation is  $130m^2/g$ .

RH	23%	33%	43%	52%	59%	70%	75%	85%
k <sub>1</sub>	65.82	52.48	49.32	39.91	36.95	32.95	29.13	28.54
k <sub>2</sub>	11.83	9.47	7.62	6.39	5.93	5.06	4.58	3.75

	<b>k</b> 1	<b>k</b> <sub>2</sub>
Raw starch	28.5	3.7
Starch foam without additive	9.8	3.9
Starch foam with PVOH	9.1	4.0
Starch foam with PHAE	10.3	4.3
Starch foam with PHE	12.8	4.5
	$\gamma$ 1	1 (0 70/

Table 20  $k_1$  and  $k_2$  values for starch powder

Table 21 k<sub>1</sub> and k<sub>2</sub> values for PELEG model (85% RH)



Figure 51 Starch foam (no polymer modifier) moisture content vs. time at 23°C



Figure 52 Starch foam (PVOH as polymer modifier) moisture content vs. time at 23°C



Figure 53 Starch foam (PHAE as polymer modifier) moisture content vs. Time at 23°C



Figure 54 Starch foam (PHE as polymer modifier) moisture content vs. time at 23°C



Figure 55 Starch foam with PVB as polymer modifier moisture content vs. time at 23°C



Figure 56 Moisture content at equilibrium under different RH (starch foam with PVOH as polymer modifier)

The use of PHAE, PHE and PVB as additives to minimize the water sensitivity was found to be extremely effective. These hydrophobic ethers significantly decreased the water penetration time from 4 seconds to 85 seconds when it was added during extrusion (Figure 57). For comparison, PVOH did not improve the hydrophobic nature of the starch foam sheets and the water penetration time did not change significantly compared to the control sheet foams that were extruded with no additives. Although all the additives that were used contain hydroxyl groups to provide compatibility with the starch, the hydrophobic backbone of the hydroxyl ethers was much more effective as it provided better protection against water and improved the humidity resistance of the foam sheets. This protection against high humidity is clearly observed in Figure 58 where wet foams that were extruded with PVOH disintegrated after five hours while similar foams that were extruded with PHE remained intact.





foam with different additive content



Figure 58 Starch foam sheets extruded after 5 hours in contact with water. (A) PVOH (B)

PHE.

Additive	23%	33%	43%	52%	59%	70%	75%	85%
type	RH							
NONE	-	-	-	+	+	+	+	shrink
PVOH	-	-	+	+	+	+	+	shrink
PHAE	-	-	+	+	+	+	+	shrink
PHE	-	-	+	+	+	+	+	+
								slightly
PVB	-	+	+	+	+	+	+	shrink

Table 22 flexibility of the foam sheets under different relative humidities at room

# temperature

The moisture absorption curves of a typical starch foam sheet that was prepared

with PHE are shown in Figure 54 at room temperature (RT) under different relative

humidity conditions. It is apparent from the shape of the curves that the water absorption

was initially fast but the rate of absorption gradually decreased with time.

In this set of experiments the foam sheets retained their shape and flexibility when the RH was between 52% and 75%. Below this lower limit of the RH the foam sheets became brittle but regained their flexibility when the RH was increased back above 50%. It appears that these changes are reversible with no visible loss or degradation in the mechanical properties. However, when the RH was set at or above 85% noticeable shrinkage occurred with visual collapse of the foam cells. Although the foam sheets remained flexible at this high RH, the changes in the cell structures were irreversible and once the foam cell was destroyed, it did not recover even when the foam was placed back at lower RH. Some improvements were noted when additives were incorporated during the extrusion and the foams remained flexible down to 43% RH (Table 22). Only the addition of PHE suppressed the cell collapse up to 85% RH.

### 4.2 Thermal insulation

The basic heat transfer mechanisms of foam insulation materials are conduction and convection. Heat transfer by conduction occurs when energy is transferred through the foam material itself and is related to the composition of the foam itself. Convective heat transfer occurs as a result of energy transfer by the gas molecules in (or through) the foam and is dependent on the type of gas, the density of the foam and the pore structure (e.g. open or closed cells). In general, heat flow through a typical air space is primarily by convection; thus, closed cell foams with large number of small cells and thin walls are most desirable.

The thermal conductivity of foams is a combination of the foam material conduction and convection of air trapped in and is expressed as 1/R-value (thermal resistance). We found that the cell structure of the foam is greatly affected by the amount

89

of resin, talc and water in the feed composition during the extrusion process (as described previously). However, the presence of additives in the feed had only a minor effect on the cell structure and the overall morphology of the foams. Although the thermal resistance of starch foam sheets containing PVOH and PHAE were similar to each other and to the thermal resistance of expanded polystyrene foam (R= $3.6^{\circ}F*ft^{2}*hr/(Btu*in)$ ), the thermal resistance of the starch foam sheet containing PHE was 10% better than the other foams (Figure 59A).

The thermal resistance of the starch foams prepared with PVB is better than that of similar starch foams prepared with polyhydroxy aminoether (PHAE) as well as expanded polystyrene foams. As the nucleating agent content increased in the starch foam sheet, the thermal resistance of starch foam decreased since the density of the foam increased (Figure 59).



Figure 59 Thermal insulation property comparison (A: different additives B: different talc concentration)

Figure 59 (cont'd)



#### 4.3 Cushion curves

Cushioning properties are generally determined based on the ability to provide the necessary protection under shock (impact) and vibration. Shock refers to brief but intense forces, such as dropping, while vibration refers to the less intense but longer duration forces that occur during transportation. Foams intended for packaging are usually classified by determining their ability to absorb shock by dynamic cushioning testing (also commonly known as a cushion drop testing) which indicates how the foam can absorb impacts efficiently and recover its physical shape quickly.

Typical examples of the cushion curves of the control starch foam sheets and foam sheets extruded with different polymer modifiers are shown in Figure 60-Figure 64. It is apparent that the cushion curves shift upward upon multiple drops. The contact surface/bearing area required between the foam sheets and the product can be calculated from the force over the maximum static load and was found to be 0.2 psi. The fragility index, defined as the maximum G force that an item to be packaged can withstand without sustaining damage, can therefore be determined from these tests. Thus, starch foam sheets, 50.8 mm thick, extruded with different polymer modifiers provide sufficient multiple cushion protection<del>s</del> for moderately delicate fragile level (65-80Gs) packaging products. Products in this category include floppy disc drives, networking hardware, personal computers, medical diagnostic apparatus, etc. These data indicate that the starch foam sheets can absorb impacts efficiently and recover their physical shape quickly, making the product ideal for packaging fragile items within a wide range of weights and sizes.

93

Unlike polyethylene foam (Figure 65), the peak acceleration of starch foam at high static loading increases with repeated drop times, this significant increase is mainly due to the corrugation. Therefore, the fifth drop (Figure 67) instead of first drop (Figure 66) cushion curves should be considered to calculate the contact surface for multiple cushion protection. The highest static loading for 2 inch thickness green cell foam and 30 inch drop is 0.4 psi (from fifth drop cushion curve) instead of 1 psi (from first drop cushion curve) assuming the target fragile level is 80G.

It is known that, when the environmental relative humidity reaches 85%RH, the foam sheet shrinks. Figure 68 shows at 75%RH, the cushion performance does not dramatically change.

When the talc level increased (Figure 69, Figure 70), at first drop the peak deceleration decreases and then increases, the lowest peak deceleration shifts from 0.2 psi to 0.6 psi.



Figure 60 Starch foam without polymer modifiers cushion curves



Figure 61 Starch foam with PHAE cushion curves


Figure 62 Starch foam with PVOH cushion curves



Figure 63 Starch foam with PHE cushion curves



Figure 64 Starch foam with PVB cushion curves



Figure 65 Polyethylene foam cushion curves



Figure 66 Cushion curves comparison (First drop)



Figure 67 Cushion curves comparison (Fifth drop)



Figure 68 Starch foam with PVOH at 75% RH and RT



Figure 69 Starch foam with PVOH and 1.3% talc



Figure 70 Starch foam with PVOH and 2.7% talc

## 4.4 Dynamic Stress-Strain Curve

Young's equation:

$$\sigma = E\varepsilon \tag{4-2}$$

Energy absorbed by cushion:

$$U = \int_0^\varepsilon E\varepsilon A \cdot t d\varepsilon = EAt \frac{\varepsilon^2}{2} = \frac{\sigma^2 At}{2E}$$
(4-3)

t= cushion thickness

Potential energy  $U = W_f h$ 

Peak force:

$$F = \sigma A = \sqrt{\frac{2EW_f hA}{t}}$$
(4-4)

$$\sqrt{\frac{2EW_fhA}{t}} - W_f = W * a$$

$$a = \sqrt{\frac{2EGhA}{tW}} - G = G(\sqrt{\frac{2EhA}{tW_f}} - 1) = G(\sqrt{\frac{2Eh}{tW_f}} - 1) = G(\sqrt{\frac{2Eh}{ts}} - 1)$$

$$(4-5)$$

E value is not constant in reality; it will change with the strain.

Energy balance

$$W_{f}h = \int_{0}^{\varepsilon} \sigma \cdot d\varepsilon \cdot t \cdot A$$

$$\frac{sh}{t} = \int_{0}^{\varepsilon_{m}} \sigma \cdot d\varepsilon \qquad (4-6)$$

Force balance at  $\varepsilon_m$ :

$$\sigma_m A - W_f = W \cdot a \implies \sigma_m A - sA = W \cdot a$$
$$\implies \sigma_m = \frac{W_f a}{AG} + s = (\frac{a}{G} + 1)s \tag{4-7}$$

In the stress-strain curve (Figure 71), the area under the curves shows sh/t, and the maxium stress value is (a/G+1)s. Theoretically, from this sh/t vs. (a/G+1)s curve, the peak deceleration for different drop height and foam thickness can be calculated.

sh/t vs. (a/G+1)s curve method can predict polystyrene foam and polyethylene foam cushion performance well. However, with starch foam with different thicknesses, sh/t vs. (a/G+1)s curves derived from cushion curves (Figure 72) are different for different thickness. This is due to the corrugation of the foam plank. sh/t vs. (a/G+1)s curve of 2 inch thickness is higher than that of 1 inch thickness (Figure 73), because the stress strain curves are different, which leads to a different area under the curve. Therefore, this method cannot predict the cushion performance on different thickness foam.



Figure 71 Stress-strain curve



Figure 72 First drop cushion curves for 1 inch and 2 inch starch foam



Figure 73 The sh/t v.s. (a/G+1)s curve

#### **Chapter 5 Starch foam extrusion mechanism**

This chapter describes qualitatively the starch foam extrusion process.

#### 5.1 Extensional viscosity and strain hardening

Strain hardening plays an important role in the foam extrusion process, which can be described as extensional viscosity increase when strain increases at a certain shear rate (Figure 74).



Figure 74 Strain hardening

The relationship between the extensional viscosity and shear viscosity can be derived as follows:



Figure 75 Uniaxial pull of polymer block

Uniaxial pull ( $x_1$  direction), (Figure 75)

The definition of True Strain:

$$d\varepsilon = \frac{dl}{l} \tag{5-1}$$

Taylor expansion:

$$\varepsilon = \int_{l_0}^{l} \frac{dl}{l} = \ln \frac{l}{l_0} = \frac{1}{l_0} (l - l_0) + \frac{1}{2!} (-\frac{1}{l_0^2}) (l - l_0)^2 + \dots$$
(5-2)

If higher order terms are omitted, then it is engineering strain

$$\varepsilon = \frac{l - l_0}{l_0} \tag{5-3}$$

The strain rate is defined by

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{1}{dt} \cdot \frac{dl}{l} = \frac{dl}{dt} \cdot \frac{1}{l} = \frac{v}{l}$$
(5-4)

The derivation of relationship between the extensional viscosity and shear viscosity under one dimensional pull:

Mass conservation over the boundary (Figure 75):

$$\dot{i}n - out + gen = accum$$

$$v_3 \cdot 2 \cdot (x_1 \cdot 2x_2) + v_2 \cdot 2 \cdot (x_1 \cdot 2x_3) + v_1 \cdot 4x_2x_3 = 0$$

$$\Rightarrow \dot{\varepsilon}_{33}x_3 \cdot x_1x_2 + \dot{\varepsilon}_{22}x_2 \cdot x_1x_3 + \dot{\varepsilon}_{11}x_1 \cdot x_2x_3 = 0$$
Set  $\dot{\varepsilon}_{11} = \dot{\varepsilon}$ 

$$\Rightarrow \dot{\varepsilon}_{33} = \dot{\varepsilon}_{22} = -\frac{\dot{\varepsilon}}{2}$$
(5-5)

Internal stress has two components, the fluid pressure p and the stress due to viscous:

$$\tau_{ij} = \eta (\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i})$$

Force balance on  $X_1$  direction

$$\sigma = \sigma_{11} = (p - p_{atm}) + 2\eta \dot{\varepsilon}$$
(5-6)

Force balance on  $X_2$  and  $X_3$  direction

$$0 = \sigma_{22} = \sigma_{33} = (p - p_{atm}) - 2\eta \frac{\varepsilon}{2}$$
(5-7)

 $\sigma$  is the external stress applied.

Solve the above two equation,  $\Rightarrow \sigma = 3\eta \dot{\varepsilon}$  (uniaxial pull) (5-8)

One dimensional pulling, the true strain rate needs to be constant, such as  $\dot{\varepsilon} = 0.1 \text{ s}^{-1}$ , so the length changing rate is not constant

$$\varepsilon(t) = \int_0^t \dot{\varepsilon} dt = \dot{\varepsilon} \cdot t \quad \text{and} \quad \varepsilon(t) = \int_{l_0}^t \frac{dl}{l} = \ln \frac{l(t)}{l_0}$$
  
So:  $l(t) = l_0 \exp(\dot{\varepsilon} \cdot t)$  (5-9)

The cross section area will also change:

Conservation of mass (volume):  $A(t) \cdot l(t) = A_0 \cdot l_0$ 

$$A(t) = A_0 \exp(-\dot{\varepsilon} \cdot t) \tag{5-10}$$

The stress will be:  $\sigma(t) = \frac{F(t)}{A(t)}$ 

So, the transient extensional viscosity at time t:

$$\eta_{E}^{+}(t) = \frac{\sigma(t)}{\varepsilon(t)} = \frac{F(t)}{\dot{\varepsilon} \cdot t \cdot A_{0} \exp(-\dot{\varepsilon} \cdot t)} \text{ at the transient length}$$
$$l(t) = l_{0} \exp(\dot{\varepsilon} \cdot t)$$

If biaxial pull ( $x_1$  and  $x_2$  directions):

$$\dot{\varepsilon}_{11} = \dot{\varepsilon}_{22} = \dot{\varepsilon}$$

From mass conservation:  $\dot{\varepsilon}_{33} = -2\dot{\varepsilon}$ 

$$\sigma_{11} = \sigma_{22} = (p - p_{atm}) + 2\eta \dot{\varepsilon}, \ \sigma \text{ is the external stress applied}$$

$$0 = \sigma_{33} = (p - p_{atm}) - 2\eta \cdot 2\dot{\varepsilon}$$

$$\Rightarrow \sigma_{11} = 6\eta \dot{\varepsilon} \qquad (5-11)$$
So,  $\eta_E^+ = 6\eta$  (biaxial pull)

To non-Newtonian fluid,  $\eta_E^+ = 3\chi\eta$  (uniaxial pull) (5-12)

When a force is applied to melt a block/sheet, strain weakening will selfaccelerate the deformation, since higher strain will cause lower viscosity, which cause the polymer melt deform even faster. Strain hardening will self-regulate to slow down the deformation, and as the strain increases the viscosity also increases correspondingly. Therefore, the strain will be slowed down when a fixed force is applied (Figure 76 (1)). Strain hardening has a self-healing mechanism.

During the foaming process, if the polymer melt is strain weakening, the gas in the polymer will expand to form a large bubble - Since the viscosity is low due to the high strain this size difference will be pronounced. If the polymer melt exhibits strain hardening the gas in the polymer will expand the small bubble and since the viscosity around the large bubble is high due to the high strain, the bubble size difference will be compensated to make the bubble sizes more uniform (Figure 76 (2)).

During blowing film, strain hardening will help stabilize the film as any uneven deformation rate will be offset by increased viscosity (Figure 76 (3)).



Figure 76 strain hardening effects on foam and film process (1: force applied to a block, 2: foaming process, 3: film process; a: original state, b: strain weakening, c: stain hardening)

The shear viscosity of the starch and water extrudate can be described as follows:

$$\eta = K \dot{\gamma}^{n-1} \tag{5-13}$$

$$K = k_0 \cdot \exp(\frac{k_1}{T}) \cdot \exp(-k_2 \cdot Mc)$$
(5-14)

$$n = \exp(\frac{-k_3}{T}) \cdot \exp(-k_4 \cdot Mc)$$
(5-15)

Mc- moisture content, K, n - parameters in power law model, T – temperature,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  - constants

As moisture content decreases, the viscosity exponentially decreases.

Although the starch and water mixture are known not to exhibit strain hardening behavior with a fixed plasticizer (water) content as the extrudate exits the die, it loses plasticizer (water) during the foaming process, thus the mixture has built-in strain hardening behavior.

#### 5.2 Starch foaming steps

The starch foam extrusion process can be understood as follows:

1) Extruder is treated as a mixing machine; the rheology of the final extrudate before the die can be described using the power law model.

2) When the extrudate passes through the die, it experiences significant pressure drop, which can be calculated using die geometry and extrudate viscosity. The high rate of pressure drop causes the nucleation sites.

3) After the extrudate exits the die, the water continues to vaporize and diffuse into and expand the existing bubble.

#### 5.3 Die design

The extruder die geometry is important to the foam extrusion process, as it controls the pressure build at the die and thus the pressure drop rate which causes nucleation under the same operating conditions.

## 5.3.1 Strand die

When strand die is used for the extrusion, the shear stress and shear rate can be calculated using equations:

$$\tau = \frac{R_h \Delta P}{\Delta L} \tag{5-16}$$

$$\dot{\gamma} = \frac{2Q(a+bn)}{R_h An} \tag{5-17}$$

$$\tau = K \dot{\gamma}^n \tag{5-18}$$

Rh: hydraulic radius, flow area / perimeter

Q: volumetric flow rate

a, b: a=0.25; b=0.75 for strand die

The above equations could be derived in easier and more understandable

following way:



Figure 77 Strand die





When the extrusion reach steady state, which means no acceleration

Force balance:

$$\Delta P \cdot \pi r^2 = 2\pi r L \cdot \tau$$

$$\Rightarrow \tau = \frac{\Delta P \cdot r}{2L} \text{ and } \tau_w = \frac{\Delta P \cdot R}{2L}$$
(5-19)

Flow rate:

$$Q = \int_{0}^{R} 2\pi r u dr = \pi \int_{0}^{R} u dr^{2} = \pi \cdot \left[ u(r) \cdot r^{2} \right]_{0}^{R} - \int_{u(r=0)}^{0} r^{2} du ]$$
  
=  $\pi \cdot -\int_{0}^{R} r^{2} \frac{du}{dr} dr = \pi \cdot \int_{0}^{R} r^{2} \dot{\gamma} dr$  (5-20)

Boundary condition:  $u(R) = 0; \tau(R) = \tau_w$ 

$$\frac{\tau}{\tau_w} = \frac{r}{R} \Longrightarrow r = \frac{R}{\tau_w} \cdot \tau \text{ and } dr = \frac{R}{\tau_w} \cdot d\tau$$

$$Q = \pi \cdot \int_0^{\tau_w} \left(\frac{R}{\tau_w}\tau\right)^2 \cdot \gamma \cdot \frac{R}{\tau_w} \cdot d\tau = \frac{\pi R^3}{\tau_w^3} \int_0^{\tau_w} \tau^2 \gamma \cdot d\tau$$
(5-21)

Power law model  $\tau = K \gamma^n$ 

$$Q = \frac{\pi R^{3}}{\tau_{w}^{3}} \int_{0}^{\tau_{w}} \tau^{2} \left(\frac{\tau}{K}\right)^{\frac{1}{n}} d\tau = \frac{\pi R^{3}}{\tau_{w}^{3}} \cdot \left(\frac{1}{K}\right)^{\frac{1}{n}} \cdot \frac{1}{3 + \frac{1}{n}} \cdot \tau^{\frac{3+\frac{1}{n}}{n}} \bigg|_{0}^{\tau_{w}}$$
(5-22)

And plug in  $\tau_w = \frac{\Delta P \cdot R}{2L}$ 

$$\Rightarrow Q = \pi \cdot \left(\frac{\Delta P}{2LK}\right)^{\frac{1}{n}} \cdot \frac{n}{3n+1} \cdot R^{\frac{3n+1}{n}}$$
(5-23)

$$-\frac{dP}{dt} = 2 \cdot K \cdot \left(\frac{Q}{\pi R^3}\right)^{n+1} \cdot \left(\frac{3n+1}{n}\right)^n$$
(5-24)

As shown in the above equation, when the diameter of the strand die is small and throughput is large, it helps to increase the die pressure and thus pressure drop rate. If the viscosity of the polymer mixture prior to exiting the die increases (K increases) e.g. by reducing water content, the die pressure increases.

From the relationship between Q, L, K, n, R and  $\Delta P$  it is useful to predict the die pressure before extrusion trials to avoid pressure overloading.

When running foam peanuts using a strand die, L should be as short as possible. As can be seen from the above equation, the pressure drop rate is independent of land length. If the land length is too long in order to avoid die pressure overloading, the water content is increased so the pressure drop rate is low and bad foaming. This explanation fits experimental observation. As the land length increases foaming is poor since further reduction in the water content is not possible since the die pressure and machine torque are already high. Reducing the total throughput is an effective way to reduce the pressure drop rate. As seen in previous chapter this will reduce foaming. When the starch feed rate was reduced from 460 lbs/hr to 285 lbs/hr, the diameter of the foam decreased from 20mm to 16mm.

#### 5.3.1 Annular die

When the gap of the annular die is very small, (Ro-Ri)/L < 10, it can be treated as two parallel plates.



Figure 78 Annular die

Force balance:

$$\tau = \frac{\Delta P \cdot y}{L} \tag{5-25}$$

On the wall,  $y = \frac{h}{2}$ 

 $\Delta P \cdot w \cdot y = \tau \cdot w \cdot L$ 

$$\tau_w = \frac{\Delta P \cdot h}{2L} \tag{5-26}$$

$$\Rightarrow \frac{\tau}{\tau_w} = \frac{2y}{h} \text{ and } d\tau = \frac{2\tau_w}{h} dy$$

Flow rate calculation (include the power law model):

$$Q = 2 \int_{0}^{h/2} w \cdot dy \cdot u = 2w \int_{0}^{h/2} u \cdot dy = 2w (uy) \Big|_{0}^{h/2} - \int_{0}^{h/2} y \cdot \frac{du}{dy} \cdot dy)$$
  

$$= 2w \int_{0}^{h/2} y \left(\frac{\tau}{K}\right)^{1/n} dy$$
  

$$\Rightarrow Q = 2w \int_{0}^{\tau_{w}} \left(\frac{h}{2\tau_{w}}\right) \cdot \tau \cdot \left(\frac{\tau}{K}\right)^{1/n} \cdot \left(\frac{h}{2\tau_{w}}\right) \cdot d\tau$$
  

$$= 2w \left(\frac{h}{2\tau_{w}}\right)^{2} \cdot \left(\frac{1}{K}\right)^{\frac{1}{n}} \cdot \frac{1}{2 + \frac{1}{n}} \cdot \tau_{w}^{2 + \frac{1}{n}}$$
  

$$\Rightarrow Q = \frac{1}{2} w \cdot h^{\frac{2n+1}{n}} \cdot \frac{n}{2n+1} \cdot \left(\frac{\Delta P}{2LK}\right)^{\frac{1}{n}}$$
(5-28)

$$-\frac{dP}{dt} = K \cdot \left(\frac{2Q}{wh^2}\right)^{n+1} \cdot \left(\frac{2n+1}{n}\right)^n$$
(5-29)

From the above relationship between die geometry, polymer viscosity and die pressure it is also possible to predict die pressure before experiments in order to avoid pressure overloading. For reasons similar to using a strand die the land length of the die should be kept as short as possible to obtain good foaming.

When the gap of the annular die is decreased, the die pressure goes up. This trend fits experimental observation. In lab extrusions with an annular die under the same extrusion conditions decreasing the gap from 1mm to 0.38mm, increased the die pressure from 100psi to 450 psi. In order to maintain the high pressure drop rate, the pressure needed to be reduced at the very front tip for this reason a large die space (space between die PIN and die sleeve) is preferred for an annular die.

Figure 79 is the model fitting using experimental data, where in the annular die design model,  $Q=1.98E-06 \text{ m}^3/\text{s}$  (the density of the melt is  $1.2 \text{ kg/m}^3$ ).



Figure 79 Die pressure (Pa) vs. die gap (m), curve: calculated from the model, two dots:

experimental values

#### **Chapter 6 Chemically modified starch**

#### 6.1 Starch extrusion with soy based ester

Maleated thermoplastic starch (MTPS) (Figure 80) has significant advantage over traditional thermoplastic starch due to low melt viscosity, and ease of blending and processing with other polymers. However, it is moisture sensitive because of the hydrogen bonding with water vapor. In these experiments, maleated thermoplastic starch was extruded with soy based ester and the extrusion process was studied. The reaction mechanism is shown in Figure 80.



Figure 80 Reactions in MTPS







To prove glycerol is chemically or strongly physically bonded into the starch backbone, soxhlet extraction was done with different solvents (Table 23). The results showed that the soxhlet extraction result was dependent on the solvent used. It shows that the glycerol extracted varies when different solvents are used. This is due to the solvent glycerol interaction: Acetone < Ethanol < Methanol. When the solvent-glycerol interaction is stronger, more glycerol will be extracted, the acetyl reaction is an equilibrium reaction, and the reaction will favor the production of glycerol if glycerol is continuously removed from the system. Starch with low molecular weight was also extracted by methanol since it has a lower recovery yield. Acetone was selected for the soxhlet extraction for extruded MTPS with ester.

#	1	2	3
Sample	MTPS	MTPS	MTPS
Solvent	Acetone	Ethanol	Methanol
Weight before (g)	10.058	10.063	10.092
Weight after (g)	9.502	8.078	7.349
Recovery yield (unextracted percentage)	94.5%	80.3%	72.8%
If theoretically only glycerol extracted, the			
recovery yield	80.4%	80.4%	80.4%

Table 23 Soxhlet extraction with different solvents

The unsaturated biodiesel was ozonated in the presence of methanol. The ozonolysis reaction is shown in Figure 81. Basically, the ozone cleaves the carbon-carbon double bond to form the carbonyl group. After reaction and purification by vacuum distillation, the ester mixture (the components are shown in Table 24) has two forms, if water was distillated completely; the ester mixture is one phase. If water was not totally removed, the ester mixture is two phase, the top is oil phase and the bottom is aqueous phase. The two forms of oil mixture were extruded with starch and glycerol with maleic anhydride. The transesterification reaction is shown in Figure 82.



Figure 81 Ozonolysis



Table 24 Products from ozonolysis

Sample	Starch (dried) (g)	Ester (g)	Glycerol (g)	Maleic
				anhydride
				(g)
MTPS	800	0	200	20
MTPS + two phases	700	100	200	20
ester mixture				
MTPS + one phase	700	100	200	20
ester mixture				

The extrusion running conditions are shown in Table 25.

Table 25 Extrusion conditions for thermal plastic starch with esters

The two phase ester mixture is very effective for starch and ester blending extrusion. Both of the residue percentage and FT-IR results show transesterification occurred (Figure 84 and Figure 85). The extrudate with low percent of residue (one phase ester mixture) is unsuitable for use due to phase separation.



Figure 82 Transesterification reaction



Figure 83 GC-FID before and after ozonation using Dean-stark setup (The retention time for dimethyl azelate is 20.74 minutes)



Figure 84 FTIR results for the extrudates after soxhletion with acetone (A) MTPS (B)



MTPS with two phases esters (C) MTPS with one phase ester

Figure 85 Soxhletion results (acetone as solvent) for the extrudate

The FTIR result shows that the ester has grafted onto the backbone of starch with carbonyl group 1720cm<sup>-1</sup> after sample Soxhlet extraction using acetone (Figure 84 B).

The extrudate (MTPS with two phase esters) has a high residual percentage after acetone Soxhlet extraction which also demonstrated ester grafting (Figure 85).

#### 6.2 Starch phosphate

The object of this work is to synthesize starch phosphate using sodium trimetaphosphate and glycerol phosphoric acid by an extrusion method and examine its use as a possible electrorheological fluid or as a flame retardant additive.

#### 6.2.1 Starch phosphate for ER fluid

#### Introduction

Electrorheological fluids (also known as smart fluids) are suspensions of fine, non-conducting particles in an electrically insulating oil that undergos a dramatic and reversible change in their apparent viscosity (in the order of 100,000 times) in response to an external electric field.

The mechanism of the ER fluid is simple: when the electric field is applied, the suspended particles will line up and block the flow of liquid. The principle is shown schematically in Figure 86.



Figure 86 Alignment of suspended particles

Dispersant	Oil	Additive	Ref.
Cellulose	chlorinated oil, liquid paraffin, hydraulic oil, Chlorotoluene, silicone oil	water various electrolytes	[59],[60]
Gelatin	transformer oil, olive oil, mineral oil	none	[61]
Na carboxymethyl- cellulose	paraffin oil, silicone oil, chlorinated solvents	water or water and sorbitan	[62], [63], [64]
Starch (flour)	mineral oil, olive oil, petroleum spirit, Vaseline oil	Water and/or sorbitan oleate or laureate	[65],[66]
Cellulose phosphate	silicone oil	none	[67]
kaolinite carboxy- methyl starch,	silicone oil	none	[68]

A large number of suspensions were studied as show below:

Table 26 Suspensions for electrorheological fluid

A major problem with ER fluids is caused by suspension instability. Over time there is a tendency to settle due to different density of the solid and liquid. In this research starch phosphate nanoparticles were synthesized in an attempt to overcome this obstacle.

### Experimental

Starch phosphorylation was done using extruder (Figure 88). The reaction (Figure 87) was under base condition.



When PH>8:

Figure 87 Starch phosphorylation using sodium trimetaphosphate



Figure 88 Feed position for starch phosphorylation

Experimental procedure:

1: Starch 5 kg/h, Maleic Acid 0.12kg/h, water 1kg/h fed at the beginning of the extruder.

2: Sodium trimetaphosphate (SMTP) 0.22kg/h, water 0.78kg/h, sodium carbonate

0.15kg/h fed at the middle of the extruder.

The extruder temperature is set at 90°C.

Screw speed: 200rpm

Water acts as plasticizer. SMTP is cross-link agent.

After extrusion, the sample was cut into pellets, washed 3 times and dispersed into water at 55°C for 8 hours.

After 4 hours, the upper suspension was collected and particle size was analyzed using

Dynamic Light Scattering:

Phosphorus characterization method:

This method is based on ISO 3946-1982 [69]. Briefly, there are four steps:

1) Concentrated sulfuric acid and nitric acid to digest sample

2) Ammonium molybdate as reaction agent. The following reaction occurs

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_2[P(Mo_2O_7)_6] + 10H_2O_7$$

(Yellow color)

3) Add reducing agent Ascorbic acid to partially reduce  $Mo^{+6}$  to  $Mo^{+5}$  (the solution is blue)

4) Measure the light absorption percentage at wavelength 825 nm with visual spectra photometer

Rheology measurement under high voltage:

The viscosity versus shear rate was measured using a plate-plate rheometer (Figure 89). The shear stress and shear rate can be obtained from the torque applied M and rotating speed  $\omega$  respectively. The 1100v and 1500v voltage were applied for 2200v/mm and 3000v/mm electric field.



Figure 89 Rheology measurement setup

Particle size measurement:

90Plus Particle Size Analyzer (Brookhaven Instruments Corporation, Holtsville,

NY) was used to characterize the particle size.

Ionic exchange for sodium glycerophosphate:

Glycerol phosphate disodium hydrate was ion-exchanged (ion-exchange resin:

Dowex® HCR-W2 hydrogen form, acidic sulphonated polystyrene cation exchange resin)

to designed monohydrogen and dihydrogen form.

Results:

The number average diameter of starch nano particles is 26.6nm. The particle size distribution is given in Figure 90:



Figure 90 Dynamic light scattering for starch nanoparticles



Figure 91 starch nanoparticles stabilized with phosphate

In the starch nano particles suspension, inside particle, starch molecules form hydrogen bonding with themselves. They can not be approached by water molecules, therefore they form a relative "hydrophobic core". On the particle / water interface, there is interaction (hydrogen bonding) between the starch (unbounded –OH group) and water which acts like a surfactant, to keep particles apart. However, the interaction between starch and water will be finally replaced by interaction between the starch molecules. This will cause agglomeration and precipitation.

To avoid these effects the hydroxyl groups on the starch particles were phosphorylated to better stabilize the particle. This should strengthen the interaction between the solute and water and thus avoid retro gradation (Figure 91).



Figure 92 Viscosity v.s. shear rate for ER fluid

It is apparent that the effect of an electric field on the fluid (Figure 92) was not significant, possibly due to a combination of too small particle size, insufficient degree of phosphorylation, and a suspension having too low solid content.

# 6.2.2 Starch phosphate with glycerol phosphoric acid

The starch phosphate reaction is shown in Figure 93, basically, the reducing end (Hemiacetal) of the starch reacts with the hydroxyl group in the glycerol phosphoric acid to form an acetal linkage.


Figure 93 Starch phosphorylation reaction

Extrusion formula	P wt% after purification	
Starch + 30 wt% water + 10wt% sodium trimetaphosphate + 1	0.72 wt%	
wt% sodium carbonate		
Starch + Maleic Anhydride 2.5 wt% + glycerol 20 wt%, after	0.28 wt%	
extrusion, extrude it with sodium trimetaphosphate (10wt%		
based on starch)		
800 g starch + 20 g Maleic anhydride + glycerol 200g + 80 g	0.06 wt%	
sodium trimetaphosphate		
Starch + 20 wt% water + 20 wt% sodium tripolyphosphate	0.03 wt%	

Table 27 Extrusion formulation using sodium trimetaphosphate and sodium tripolyphosphate

Modifying starch with sodium trimetaphospahte under basic condition give the

highest phosphorus percentage grafted when water is the plasticizer (Table 27).

Formula	P wt% after purification
800 g starch + 175 g glycerol + 25 g glycerol phosphate salt	0.13 wt%
+20 g maleic anhydride	

Table 28 Phosphorylate starch using glycerol phosphate disodium salt

When a higher amount of glycerol phosphate salt was used, the process was

unstable, resulted in a high torque and the products were dark in color due to the high

percentage of salt. With low glycerol phosphate disodium salt addition levels, the

phosphorus content was reduced to 0.13% (Table 28). Phosphorus contents of different

formulation (different combination of glycerol phosphate monoester monohydrogen and

dihydrogen form) are shown in Table 29.

Formula				P wt% after
				purification
Dry	Maleic	Glycerol	Glycerol	
Starch (g)	Anhydride	(g)	phosphoric	
	(g)		acid (g)	
800	20	175	25	0.26 wt%
800	20	150	50	0.33 wt%
800	20	125	75	0.56 wt%
800	0	150	50	0.56 wt%
	Formula Dry Starch (g) 800 800 800 800	Formula Maleic   Dry Maleic   Starch (g) Anhydride   (g) (g)   800 20   800 20   800 20   800 0	Formula   Maleic   Glycerol     Dry   Maleic   (g)     Starch (g)   Anhydride   (g)     800   20   175     800   20   150     800   20   125     800   0   150	Formula   Glycerol   Glycerol     Dry   Maleic   Glycerol   glycerol     Starch (g)   Anhydride   (g)   phosphoric     (g)   175   25     800   20   150   50     800   20   125   75     800   0   150   50

Table 29 Phosphorylate starch using glycerol phosphoric acid

#	Regular	Glycerol	Glycerol phosphate		Residue percentage after soxhelt
	Starch	(g)	monoester (g)		using acetone
	(g)		Dihydrogen form		
			Monohydrogen form		
1	800	100	30	70	98.5%
2	800	100	20	80	NA, Very dark extrudate
3	800	100	10	90	NA, Very dark extrudate

Table 30 Phosphorylate starch using glycerol phosphoric acid and glycerol phosphate monohydrogen

Intrinsic viscosity [η]	
(dL/g)	
1.26	
0.099	
0.091	

Table 31 Intrinsic viscosity comparison

The above results show that the phosphate has been grafted into the starch

backbone (Table 30). The decrease in intrinsic viscosity shows that the starch was

hydrolyzed and potentially easily processable (Table 31). Future efforts will be to

increase the phosphorus content while not dramatically decreasing the starch molecular weight.

### 6.3 Dihydroxyl starch

The dihydroxyl starch (DHS) synthesis consists of two steps: (1) Add sodium periodate to oxidize the starch to produce dialdehyde starch (DAS) and (2) Add sodium borohydride to reduce the DAS to produce the corresponding hydroxyls (Figure 94).



Figure 94 Reactions to make dihdyroxyl starch

### 6.3.1 Experimental and characterizations

DHS synthesis steps:

(1) Starch and sodium periodate is put into a flask according to the amount shown in

Table 32. Cover the flask with black plastic bags to avoid light.

(2) Add 500ml distilled water, stir it and let it react at room temperature for 6 hours.

(3) After 6 hours, filter and put it into a flask. Add 500ml distilled water. Add sodium

borohydride, agitate and allow reacting at room temperature for 2 hours.

(4) After reaction, dialysis the solution against distilled water, till the conductivity of the solution inside of the dialysis tube is less than 10.

(5) Freeze dry at low temperature and low pressure to vaporize water.

	40H	100H	40W	100W
High amylose starch	10 g	10 g		
Waxy starch			10 g	10 g
NaIO <sub>4</sub>	4.65 g	13.94 g	4.65 g	13.94 g
NaBH4	1.23 g	3.08 g	1.23 g	3.08 g

Table 32 weights for reactants during DHS synthesis

Characterizations

Determination of aldehyde groups by titration:

The aldehyde groups present in the DAS and DHS were determined by quantitative reduction using sodium borohydride. This method [70] was found to be effective and rapid for determination of aldehyde groups in starch. Briefly, the sodium borohydride reacts with water to evolve hydrogen gas under acid conditions. From the difference of the hydrogen evolved between control sample without aldehyde group and sample with aldehyde group, the amount of sodium borohydride reacted with aldehyde can be determined. The amount of hydrogen was measured by volumetric glass tube [ Figure 95].



Figure 95 Setup for measuring aldehyde group

# FTIR:

The samples were characterized by Perkins Elmer FTIR. The samples were compressed with KBr and ran for 64 scans to achieve a high resolution. The wavelength range:  $4000 \text{ cm}^{-1}$  to  $450 \text{ cm}^{-1}$ .

# 6.3.2 Results and discussions

Three different grades of starch (High Amylose, Waxy, and Regular) were used for the reactions. The FTIR results are shown in Figure 96, the peak around 1720cm<sup>-1</sup> is the carboxyl C=O peak; DAS samples have stronger carbonyl peak than DHS.





Figure 96 FTIR for starch, DAS and DHS, A: high amylose, B: waxy, C: regular.

Figure 96 (cont'd)



Figure 97 Viscosity vs. shear rate for DHS



Figure 98 Dialdehyde content in DAS and DHS

The results show that dihydroxyl starch was successfully synthesized. The solution exhibit shears thinning behavior Figure 97. The Figure 98 shows that amylose is more difficult to oxidize and is easier to reduce once it has been oxidized.

#### **Chapter 7 Conclusions, accomplishments and recommendations for future work**

### 7.1 Conclusions

It has been shown that using polyhydroxyl ether (PHE) and polyvinyl butyral (PVB) are effective polymer modifiers which improve the hydrophobicity (humidity resistance) of starch foam sheets without sacrificing performance properties (cushion protection and thermal insulation). With both a lab scale extruder (Century ZSK-30) and a commercial scale extruder (Wenger TX-80), the foam extrusion processing parameters (functional aid, talc, water, die geometry) were investigated using black box strategy (Design of Experiments). These starch foam sheets can provide the design flexibility required to create a cost effective protective packaging. They are bio-based and completely biodegradable, provide excellent insulation, and are naturally anti-static.

Chemically modified starch was synthesized by extrusion. The extrusion method effectively breaks down the hydrogen bonding within starch to provide plastic like flow in a more efficient technique than conventional solution methods thus reducing manufacturing costs.

Starch phosphate was synthesized using sodium trimetaphosphate and glycerol phosphoric acid as phosphorylation reagent, 1.1 wt% phosphorus was obtained through the phosphorylation. Starch was also extruded with ester monomer (ozonation product from unsaturated oil) to improve the hydrophobicity of the maleated thermoplastic starch.

### 7.2 Main accomplishment

The moisture sensitivity of the starch foam sheet poses a limitation for shipping coolers applications since the moisture will condense onto the sheet surface and gradually

141

dissolve the foam. The main accomplishment of this research is to significantly increase the moisture resistance of starch foam sheet by using a commercially available, economically acceptable resin as additive during the extrusion process. This process is in commercial production.

# 7.3 Future recommendations

1) The foam sheets are corrugated. While this does not affect thermal insulation properties, it does cause the foam to exhibit low static loading for multiple cushion protection (weakness support in the curved location). It will also require more contact surface thus increasing the cost for heavy product shipment packaging. Investigation of the need for corrugation and its potential elimination would significantly increase effectiveness and reduce cost.

Experiments show that when the annular gap is relatively large, the number of holes (Figure 99 and Figure 17) in the annular die is equal to the number of corrugations (Figure 100 left and middle picture). However, when the gap of the annular die narrowed, the corrugation increased (Figure 100 right picture).



Figure 99 annular die (Pin) structure



Figure 100 Corrugation in the foam sheet (left: extruded with 10 holes pin, middle: extruded with 6 holes pin, right: extruded with 10 holes pin and small gap) The die shape (circle outlet shape from the extruder smooth transition to rectangle shape) should be investigated. After the extrusion the foam should be in plank shape (smooth surface) which can be glued together to make larger planks with no corrugations. The slit instead of pinholes in the PIN part also could be tried in foam extrusion to avoid the corrugation.

2) The humidity resistance of thermoplastic starch could be improved by reacting it with butyraldehyde.

3) Polyvinyl alcohol could be reacted with aldehyde derived from ozonation of unsaturated vegetable oil to increase the biobased content.

4) Testing biodegradability of starch foam with PVB (>10wt %)

5) Soy protein concentrate or high gluten content corn flour could be investigated to replace the hydroxypropylated high amylose starch using the modified lab scale extruder.

6) At high polyvinyl alcohol and starch ratio, the strand foam shrinks when coming out of the die, adding stabilizer to offset the permeability difference between water vapor and air may correct the problem.

7) Explore different application for starch foam sheet/paper, such as absorbent pad of meat tray.

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