

**INJECTION MOLDED FOAMED RICE STRAW/LDPE WITH
SODIUM BICARBONATE AND CITRIC ACID FOAMING AGENT:
EFFECT OF FOAMING AGENT COMPOSITION**

NOOR FARHANA BT OMAR

UNIVERSITI TEKNOLOGI MALYSIA

**INJECTION MOLDED FOAMED RICE STRAW / LDPE WITH
SODIUM BICARBONATE AND CITRIC ACID FOAMING AGENT:
EFFECT OF FOAMING AGENT COMPOSITION**

NOOR FARHANA BT OMAR

**A project report submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science (Polymer Technology)**

**Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia**

JULY 2009

*Thanks to Mr. Omar and Mrs. Fatimah
that always gives me support
to complete this research
and special thanks to my siblings
which always cheers me up.*

ACKNOWLEDGEMENTS

In the name of Allah The Almighty, I am grateful for the blessings and love, He let me completing my master project successfully without any big problem.

First and foremost, I would like to extend my highest and up most gratitude to my supervisor, Asscoc. Prof. Dr. Wan Aizan Wan Abdul Rahman for her useful advice as well as guidance in the preparation of this study and help me to understand better about the project.

I also take this opportunity to thank to all the laboratory assistant which are Mr. Su Hee Tan, Mr. Shukor, Mr. Nizam, Mr. Azri, Mr. Nordin and Ms. Zainab for assisting me to use the equipment and the chemical in the Polymer Laboratory lab and also thank you to all the academic staff of the Faculty of Chemical Engineering and Natural Resource which had made this project accomplished.

Last but not least, a special thank to my family and my friends that give me moral support and always behind me when I'm in problem. Thank you, may Allah bless you all.

ABSTRACT

Rice straw-LDPE foamed had been produced by incorporating foaming agent, which was the mixture of sodium bicarbonate and citric acid. The foam structure is produced when temperature is applied and the foaming agent decomposes. The effect of foaming agent composition on the morphology structure, density, water absorption behavior and hardness were studied. The compounding material which were rice straw, LDPE, starch, maleic anhydride and glycerol were mixed in the twin screw extruder. Then, the foaming agent was mixed with the compounded material and injected using the injection molding machine to produce foam product. Samples with foaming agent show the present of the foam structure that increases in size with foaming agent composition. The type of cell form is open cell. For the physical properties, as the amount of foaming agent increases, the density is decreased, the percentage of water absorbed increased and the hardness value is decreased.

ABSTRAK

Busa jerami padi-LDPE telah dihasilkan dengan memasukkan agen pembusaan iaitu campuran natrium bikarbonat dan asid sitrik. Struktur busa terhasil apabila suhu dikenakan dan agen pembusaan terurai. Kesan kandungan agen pembusaan terhadap struktur morfologi, ketumpatan, sifat penyerapan air, dan kekerasan telah dikaji. Bahan-bahan adunan iaitu jerami, LDPE, kanji, malik anhidrid dan gliserol telah dicampurkan ke dalam penyemperitan skru bekembar. Kemudian, agen pembusaan telah dicampurkan dengan bahan-bahan adunan dan disuntik dengan menggunakan mesin acuan suntikan untuk menghasilkan produk busa. Sampel dengan agen pembusaan menunjukkan kehadiran saiz struktur busa semakin meningkat dengan peningkatan kandungan agen pembusaan. Jenis sel yang terbentuk adalah sel terbuka. Untuk ciri-ciri fizikal, apabila kuantiti agen pembusaan meningkat, ketumpatan menurun, kuantiti air yang diserap meningkat dan nilai kekerasan menurun.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE PAGE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYMBOLS AND ABBREVIATIONS	xii
1	INTRODUCTION	1
	1.1 Research background	2
	1.2 Problem statements	4
	1.3 Objectives	5
	1.4 Scope of study	6
2	LITERITURE REVIEW	7
	2.1 Introduction	7
	2.2 Biodegradable composite	8
	2.2.1 Biodegradable food packaging	10
	2.2.2 Biodegradable foam	12
	2.2.3 Nanocomposite	14
	2.3 Rice straw	15

2.4	Low density polyethylene (LDPE)	17
2.5	Additives	18
2.5.1	Introduction	18
2.5.2	Foaming agent	18
2.5.2.1	Sodium bicarbonate	23
2.5.2.2	Citric acid	23
2.5.3	Starch	24
2.5.4	Compatibilizer	24
2.5.4.1	Maleic anhydride	24
2.5.5	Plasticizer	26
2.5.5.1	Glycerol	27
2.6	Foaming method	28
3	METHODOLOGY	33
3.1	Raw materials	33
3.2	Compounding formulation	34
3.3	Sample preparation	34
3.3.1	Rice straw	34
3.3.2	Sodium bicarbonate and citric acid	35
3.3.3	Starch and glycerol	35
3.4	Compounding process	35
3.4.1	Twin screw extruder	35
3.4.2	Pelletizer	35
3.4.3	Injection molding	36
3.5	Testing	36
3.5.1	Morphology structure	36
3.5.2	Density measurement	36
3.5.3	Water absorption	37
3.5.4	Rockwell hardness	37

4	RESULTS AND DISCUSSIONS	38
4.1	Introduction	38
4.2	Morphological structure	38
4.3	Density measurement	41
4.4	Water absorption	43
4.5	Rockwell hardness	46
5	CONCLUSIONS AND RECOMMENDATIONS	49
5.1	Conclusions	49
5.2	Recommendations	50
	REFERENCES	51

LIST OF TABLES

TABLES NO.	TITLE	PAGE
3.1	The blend formulation for foamed rice straw-LDPE with different concentration of sodium bicarbonate and citric acid	34
4.1	Density of the samples	42
4.2	Percent of water absorbed	45
4.3	Rockwell Hardness	47

LIST OF FIGURES

FIGURES NO.	TITLE	PAGE
2.1	Rice straw	15
2.2	Chemical structure of polyethylene (PE)	17
2.3	Chemical structure of sodium bicarbonate	23
2.4	Chemical structure of citric acid	23
2.5	Chemical structure of glycerol	27
4.1	The inverted microscope of the morphology structure of the sample	40
4.2	The density of the samples	42
4.3	Plot of days vs percent of water absorbed	46
4.4	Rockwell hardness	48

LIST OF SYMBOLS AND ABBREVIATIONS

LDPE	-	Linear density polyethylene
°C	-	degree celcius
phr	-	part per hundred
%	-	percent
ρ	-	density
g/cm^3	-	gram per centimeter cube
μm	-	micrometer

CHAPTER 1

INTRODUCTION

Polymer foam is found in numerous applications such as in building and construction industries, automotive industries and packaging industries. This foam was used specifically as weight reduction, thermal insulating or cushioning in various applications. Biodegradable foams are naturally water soluble and sensitive to humidity, while traditional petroleum-based foam is more inert to water [1]. The general purpose of foaming is to save material while maintaining structural integrity and a small amount of insulating ability. The foaming process can be divided into 6 stages which are raw material, conditioning, mixing, growth, cell opening and cure [2].

Depending on the composition, cell morphology and physical properties, polymer foam is divided into two different types which are rigid foam and flexible foam. There are 4 types of foams can be derived according to the size of the foam cells which are macrocellular ($>100\mu\text{m}$), microcellular ($1-100\mu\text{m}$), ultramicrocellular ($0.1-1\mu\text{m}$), and nanocellular ($0.1-100\text{nm}$). Polymer foam can also be defined as either closed cell or open cell foam. In closed cell foam, the foam is isolated from each other and the cavities are surrounded by complete cell walls. In open cell foams, cell walls are broken and the structure consists of mainly ribs and struts [3].

Foamed composite can be produced by incorporating the foaming agent into the formulation. There are two reasons of using chemical foaming agent in injection molding process. First is to reduce significantly the overall product density, creating a truly cellular form which is foam structure. The second reason is to use the foaming

as an anti-sink aid. Minimal reduction in density is achieved by the foaming reduces sink marks as the product cools inside the mould. This is particularly important in thick cross-sections where cooling may take some time [4].

1.1 Research Background

A large portion of food packaging materials, especially foamed product, are made from expanded polystyrene (EPS). EPS possess excellent physical and mechanical properties and relatively inexpensive. The EPS foams are manufactured mainly from petroleum feedstock, used once and discarded into the environment, finally ending up as non-degradable waste [5].

One of effective way to overcome the existed problem is to use natural polymer, such as starch. Furthermore, consumers are demanding food-packaging materials that are more natural, disposal and have potential to be biodegraded, as well as, recyclable. For this reasons, there is an urgent need to study and to develop renewable source based biopolymer that are able to degrade via natural composting process [6]. Starch is inexpensive and readily available and often used as filler for the replacement of petroleum-derived synthetic polymer to reduce environment pollution [5]. Other than that, starch is one of possible alternative material for making foam products. Starch-based foam can be made by using various techniques including compression moulding and explosion process [7].

Benchamaporn Pimpa *et al.* (2007) have produced foamed of sago starch with PVA or PVP acting as cross-linker. This foam is completely biodegradable and cheap compared to other biodegradable polymer. Sago starch/PVA blend is more suitable for foam production because it produced flexible and glossy foam compared to sago starch/PVP blend which produced rigid foam.

Rice straw fiber can also be considered as important potential reinforcing filler for thermoplastic composite because of its lignocelluloses characteristics [8]. Chemically, lignocellulosic rice straw fiber has similar compositions as other natural fibers used in thermoplastic. Various fiber components have different chemical constituents, especially cellulose and residual ash contents, which may contribute differently to the properties of rice straw fiber-reinforced thermoplastic composites. However, these different contributions have not yet been established.

In recent years, the processing solvent or foaming agent such as supercritical CO₂ (scCO₂) has been used to create polymer foams. This is due to the properties of CO₂ that make it ideally suitable to replace the organic solvents that affect on environment such as chlorofluorocarbons (CFC) [9]. David L. Tomasko *et al.* (2009) had done development of CO₂ to produce foam product. But, there are lacking of complete understanding of nucleation of foaming process.

The use of foaming or blowing agents can reduce materials cost and provide significant benefits in the production process [10]. The terms cellular polymer, foamed plastic, expanded plastic and plastic foam are used to denote all two-phase gas-solid systems in which the solid is continuous and composed of a synthetic polymer or rubber. Several methods can be used to prepare foamed plastics, such as sintering small particles or leaching out solid or liquid materials dispersed in the plastic matrix [11]. Another method is chemical foams which use chemical foaming agents (CFAs). It can be either in powder or master batch form. The CFAs will be added into barrel, to be process with resin. In the extruder barrel, CFAs thermally decompose into CO₂ or Nitrogen. Under the process pressure, the CO₂ and Nitrogen is in liquid form, will mix the molten polymer. But, when pressure drop occur at die or mold, the CO₂ and Nitrogen expands into gas bubbles within the polymer matrix. The foamed plastic produced when the polymer cools and the bubble 'freeze' [12].

1.2 Problem Statement

Food-grade foam products especially made from styrene has a particular challenge. There is currently no market for them in terms of recycling and no way to reuse them. The presence of these types of packaging materials in landfills can be problematic on many fronts. Another factor to consider is the rising cost of petroleum. This material also affects the humans and the environment, such as carcinogen after being exposed to styrene [13]. This occurs because of styrene that ingested through food as a result from food packaging or contact materials. Styrene exposure may affect human's nerve system such as depression, muscle weakness, nausea and nose, eye and throat irritation. Foam products that use foaming agents such as hydrofluorocarbons (HFCs), has powerful greenhouse gases, which is several thousand times more potent than CO₂ [13].

Rice straw is a secondary waste material from rice production which is inexpensive. Unfortunately, this benefit was not taken correctly. In Thailand, rice straw which is the inedible remains of the rice crop is not used as efficiently as it should be burn or land filling is a common practice which is not environmentally friendly as it causes significant pollution and waste thus natural resource [14]. Several sosio-ecological issues have increased the focus on off-field utilization of agricultural wastes. Same thing happen in California, where open-burn reduction legislation has put pressure on rice industry to find alternatives for straw waste nearly 1.5 million tons per year. Off-field utilization of the straw provides a potentially attractive alternative of straw disposal but its use remains limited [15].

With many processing issues to be considered, the correct choice of foaming agent can only be made after a technical understanding of its requirements. Even if the foaming agent used is correct for the application, but if it is incorporated in the wrong formulation or incorrect processing parameters, then the foaming will be poor. If the foaming agent decomposes too quickly, the polymer cannot be processed in perfect condition as to maintain the gas within the matrix. Time, temperature and the condition of the polymer matrix must be considered before the material selection [4].

Odinei *et al.*, (2008) had revealed that the foaming agent concentration is also one of the factors that affect the particle size. Low concentration of the foaming agent will produce small particle size of expanded PMMA. This happened due to the fact that the foaming agent tends to diffuse out of the particles after the impregnation step, i.e., during sample manipulation, characterization and storage. Although the loss of foaming agent can be minimized by storage at low temperature, smaller particles have higher surface area/volume ratio than larger particles and are prone to lose more foaming agent.

1.3 Objectives

The main objective to be accomplished in this research is:

To develop foamed polymer composite based on rice straw with low density polyethylene (LDPE) by using sodium bicarbonate and citric acid.

This objective is subdivided into:

- 1) To investigate the morphology of the foamed composite with the different amount of foaming agent used via Fluorescent Microscope
- 2) To determine the density and hardness of the both foamed polymer composite and non-foamed polymer composite
- 3) To identify the water absorption behavior over period of time with respect to composition of foaming agent for foamed polymer composite

1.4 Scope of Study

Biodegradable foam composite was produced in this research by incorporating rice straw into LDPE. Starch was added to make the extrusion process easy by making the rice straw heavy. The compatibilizer, which is maleic anhydride was used to make the LDPE and rice straw compatible to each other. Glycerol which act as the processing aid, also added into this formulation. To produce foamed product, the foaming agent; mixture of sodium bicarbonate and citric acid was used during processing. The amount of the foaming agent had been varied.

The rice straw was first grinded by using grinder, then sieved and dried in the oven. After that, all the materials were put into the twin screw-extruder for compounding purpose. The extrudate was pelletized to produce pellet to be used on injection molding machine. Injection molding machine was used in this research to produce testing sample, which was used for various tests.

Fluorescent microscope was used to investigate the morphology of composite with different concentration of sodium bicarbonate and citric acid. The water absorption behavior over period of time of the foamed composite was studied. The density and hardness of the product were also measured based on specific standard method. Other than that, the hardness characteristics of the samples were measured.

REFERENCES

1. Katrine Sivertsen. *Polymer Foams*. Polymer Physics. 453-456. 2007.
2. S. James. *Proceedings of the Polyurethane Foam Associations Technical Program*. Polyurethane Foam Associations, Inc. 1999.
3. L. James Lee, Changchun Zeng, Xia Cao, Xiangming Han, Jiong Shen and Guojun X. *Polymer Nanocomposite Foams*. Composites Science and Technology. 65. 2344-2363. 2005.
4. Fiona H. *Chemical Blowing Agents: Providing Production, Economic and Physical Improvements to a Wide Range of Polymers*. Plastics Additives and Compounding. 16-21. 2001.
5. Siew Yoong Lee, Kent M. Eskridge, Woon Yuen Koh and Milford A. Hanna. *Evaluation of ingredient effects on extruded starch-based foams using a supersaturated split-plot design*. Industrial Crops and Products. 29. 427-436. 2009.
6. M.A. Del Nobile, A. Conte, G.G. Buonocore, A.L. Incoronato, A. Massaro and O. Panza. *Active packaging by extrusion processing of recyclable and biodegradable polymers*. Journal of Food Engineering. 93. 1-6. 2009.
7. G.M. Glenn and W.J. Orts. *Properties of starch-based foam formed by compression:explosion processing*. Industrial Crops and Products. 13. 135-143. 2000.

8. Fei Yao, Qinglin Wu, Yong Lei and Yanjun Xu. *Rice straw fiber-reinforced high-density polyethylene composite: Effect of fiber type and loading*. Industrial Crops and Products. 28. 63-72. 2008.
9. David L. Tomasko, Adam Burley, Lu Feng, Shu-Kai Yeh, Koki Miyazono, Sharath Nirmal-Kumar, Isamu Kusaka and Kurt Koelling. *Development of CO₂ for polymer foam applications*. The Journal of Supercritical Fluids. 47. 493-499. 2009.
10. Jiang Zhou, Jim Song and Roger Parker. *Microwave-assisted moulding using expandable extruded pellets from wheat flours and starch*. Carbohydrate Polymers. 69. 445-454. 2007.
11. Odinei Hess Gonçalves, Thiago Staudt, Pedro Henrique Hermes de Araújo, Ricardo Antonio Francisco Machado. *Foaming of poly(methyl methacrylate) particles*. Materials Science and Engineering. 29. 479-484. 2009.
12. Jennifer Markarian. *Cost saving opportunities push foaming agents forward*. Plastics Additives and Compounding. 8. 22-25. 2006.
13. M. Lee. *Foam Packaging*. Eco-Cycle Corp. 2005.
14. Y. Thiam Boon. *Properties of bamboo-rice straw-eucalyptus composite panels*. Goliath Industry and Business News. 2005.
15. Matthew D. Summers. *Fundamental Properties of Rice Straw in comparison with Softwoods*. ESPM 286: Physical Properties of Wood. 1-8. 2000.
16. Jennifer Markarian. *Biopolymers present new market opportunities for additives in packaging*. Plastics Additives and Compounding. 10. 22-25. 2008.
17. Valentina Siracusa, Pietro Rocculi, Santina Romani and Marco Dalla Rosa. *Biodegradable polymers for food packaging: a review*. Trends in Food Science and Technology. 19. 634-643. 2008.

18. R.L. Shogren, J.W. Lawton, K.F. Tiefenbacher. *Baked starch foams: starch modifications and additives improve process parameters, structure and properties*. Industrial Crops and Products. 16. 69-79. 2002.
19. Yong Lei, Qinglin Wu, Fei Yao and Yanjun Xu. *Preparation and properties of recycled HDPE/natural fiber composites*. Composites Part A: Applied Science and Manufacturing. 38. 1664-1674. 2007.
20. Guifang Hu, Jingyuan Chen and Jianping Gao. *Preparation and characteristics of oxidized potato starch films*. Carbohydrate Polymers. 76. 291-298. 2009.
21. Xiaofei Ma, Peter R. Chang, Jiugao Yu and Mark Stumborg. *Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites*. Carbohydrate Polymers. 75. 1-8. 2009.
22. Rui Shi, Jingliang Bi, Zizheng Zhang, Aichen Zhu, Dafu Chen, Xinhua Zhou, Liqun Zhang and Wei Tian. *The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature*. Carbohydrate Polymers. 74. 763-770. 2008.
23. M. Pérez-Mateos, P. Montero and M.C. Gómez-Guillén. *Formulation and stability of biodegradable films made from cod gelatin and sunflower oil blends*. Food Hydrocolloids. 23. 53-61. 2009.
24. D. Lutters and R. ten Klooster. *Functional requirement specification in the packaging development chain*. CIRP Annals – Manufacturing Technology. 57. 145-148. 2008.
25. Philippe Viot. *Hydrostatic compression on polypropylene foam*. International Journal of Impact Engineering. 36. 975-989. 2009.

26. Rémy Bouix, Philippe Viot and Jean-Luc Lataillade. *Polypropylene foam behaviour under dynamic loadings: Strain rate, density and microstructure effects*. International Journal of Impact Engineering 36. 329-342. 2009.
27. Perrine Bordes, Eric Pollet and Luc Avérous. *Nano-biocomposites: Biodegradable polyester/nanoclay systems*. Progress in Polymer Science. 34. 125-155. 2009.
28. F.A. Abdel-Mohdy, E.S. Abdel-Halim, Y.M. Abu-Ayana and S.M. El-Sawy. *Rice straw as a new resource for some beneficial uses*. Carbohydrate Polymers. 75. 44-51. 2009.
29. Chuan Ai Chee. *Polystyrene foam blowing agent technology*. Elsevier Science Ltd. 7-8. 1995.
30. J.R. Robledo-Ortiz. *Role of foamed polystyrene in food packaging*. Polymer Testing. 730 – 735. 2008.
31. Sims G.L.A. *Honeywell fully commercializes eco-friendly blowing agent*. Additives for Polymers. 3. 2008.
32. Catherine Nettles Cutter. *Opportunities for bio-based packaging technologies to improve the quality and safety of fresh and further processed muscle foods*. Meat Science. 74. 131-142. 2006.
33. Melissa A.L. Russo, Cathryn O’Sullivan, Beth Rounsefell, Peter J. Halley, Rowan Truss and William P. Clarke. *The anaerobic degradability of thermoplastic starch: Polyvinyl alcohol blends: Potential biodegradable food packaging materials*. Bioresource Technology. 100. 1705-1710. 2009.
34. Vicki Flaris and Shriram Bagrodia. *Advanced Materials from Novel Bio-based Hybrid Resins*. 1-5. 2008.

35. R. Zullo and S. Iannace. *The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure*. Carbohydrate Polymers. 367-385. 2008.
36. Kelly M.. *Uses for Methyl Esters, Glycerol*. National Biodiesel Board. 1999.
37. Silvia Flores, Lucía Famá, Ana M. Rojas, Silvia Goyanes and Lía Gerschenson. *Physical properties of tapioca-starch edible films: Influence of filmmaking and potassium sorbate*. Food Research International. 40. 257-265. 2007.
38. Pablo R. Salgado, Vivian C. Schmidt, Sara E. Molina Ortiz, Adriana N. Mauri and João B. Laurindo. *Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process*. Journal of Food Engineering. 85. 435-443. 2008.
39. Wang Jin, Cheng Xingguo, Yuan Mingjun and He Jiasong. *An investigation on the microcellular structure of polystyrene/LCP blends prepared by using supercritical carbon dioxide*. Polymer. 42. 8265-8275. 2001.
40. Vishu Shah. *Handbook of Plastics Testing Technology*. A Wiley-Interscience Publication. 283-289. 1984.
41. Wason K.. *Endothermic blowing agents compositions and applications*. Patent Genius. 1991.
42. Michael E. Reedy. *Chemical foaming agents improve performance and productivity*. Reedy International Cooperation. 2000.
43. Jiann-Wen Huang. *Unusual thermal degradation of maleic anhydride grafted polyethylene*. Polymer Engineering and Science. 2008.

44. Rhomie L. Heck. *A Review of Commercially Used Chemical Foaming Agents for Thermoplastic Foams*. Journal of Vinyl & Additives Technology. Vol. 4, No. 2. 1998.
45. Arthur H. Landrock. *Handbook of Plastic Foams*. Noyes Publications. p387. 1995.
46. Kelvin T. Okamoto. *Microcellular Processing*. Hanser Publishers, Munich. p9. 2003.
47. Rong GuanBanglong Xiang, Zhaoxin Xiao, Yinglin Li, Deping Lu and Gongwu Song. *The processing–structure relationships in thin microcellular PET sheet prepared by compression molding*. European Polymer Journal. 1022 – 1032. 2003.