POPCORN FOR CUSHIONING PURPOSE

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ABSTRACT

Hoi Po Cheng M. Sc. (Bioresource Engineering)

POPCORN FOR CUSHIONING PURPOSE

In the packaging industry, cushioning products are usually made of plastic materials, such as polystyrene. The insulation and lightweight character make it more popular and convenient to use. However, the extensive use of it creates more waste leading to an environmental problem. Usually the cushioning foams are discarded after being used for inbox protection as packaging material; eventually they end up in a landfill. Most plastic foams are not biodegradable, which cannot be composted and will create more and more waste that affects the ecological system. In the mean time, foams made up of bio-degradable materials are considered. In general, biodegradable plastics are starch-based or cellulose-based, and the biodegradable components can be found in corn (e.g. corn starch, and corn cob). Instead of extracting the corn component, here popped corn kernel will be investigated for its suitability in packaging applications.

Using popcorn as a packaging material, its water sensitivity is a concern. Moisture absorption from the surrounding may affect the internal starch matrix. This could affect the ability of popcorn in protection. In order to determine the influence of different moisture contents on popcorn, mechanical tests were carried out in comparison to two commercial loose-fills, expanded polystyrene (EPS) and starch-based foams. The results show that popcorn had a good ability of support under compression, and also show a stable deformation rate when compared to the two commercial loose-fill materials. In addition, popcorn had a better resistance to tumbling motion compared to the starch-based loose-fill. It is suggested that popcorn can be an alternative to the starch-based loose-fill.

As a food-grade starch material, popcorn raises some concerns when compared to synthetic starch-based foams, such as deterioration or degradation. Deterioration is usually due to bacterial growth, which is expected in high moisture food. When popcorns were conditioned into different moisture contents for mechanical test preparation, the outcomes showed that mold growth occurred on popcorn with moisture contents over 30%. Results show that the popcorn within 20% moisture content can perform well for protective function.

Another concern is rancidity caused by lipid degradation. If the surrounding environment is not stable, the oil content of popcorn can be oxidized and lead to a possibility of rancidity. To solve this potential problem, oil removal is suggested here. In order to find out an efficient way to remove oil of popcorn for packaging use, oil removal from intact grain kernels prior to popping and from popped kernels were studied. De-oiled intact grain kernels were then popped to determine their popping ability. Results show that oil removal at grain kernel stage was not efficient; while the treated (de-oiled) kernels retained their popping ability. During the extraction process, oil extracted from popped kernels shows a much higher yield than grain kernels. Therefore, oil removal at popped stage is preferred.

RÉSUMÉ

Hoi Po Cheng M. Sc. (Génie des Bioressources)

MAIS SOUFFLÉ POUR BUT D'AMORTISSEMENT

Dans l'industrie de l'emballage, les produits d'amortissement sont généralement font de matériaux plastiques tel que le polystyrène. Leurs caractères isolants et légers en fait un usage courante et pratique. Par contre, leurs utilisations fréquentes créent un problème environnemental dû aux déchets. Lorsque la mousse coussinée a terminé sa fonction protectrice lors de l'emballage, elle est normalement mise dans les déchets et aboutie dans un dépotoir. La plupart des mousses plastiques ne sont pas biodégradables; elles créent de plus en plus de déchets qui ne peuvent être décomposées et en bout de ligne, affecte le système écologique. Entre temps, les mousses faites de matériaux biodégradables peuvent être considérés. Les plastiques biodégradables communs sont à base d'amidon ou à base de cellulose; ces composantes d'amidon et de cellulose sont retrouvés dans le mais (par exemple, la fécule de mais et l'épi de mais). Les grains maïs souflés sera soumis à des tests d'efficacités dans l'usage d'empaquetage.

En utilisant les grains de maïs souflés dans l'empaquetage de matériel, l'absorption de l'humidité des objets environentes affecterait la matrix interne de l'amidon. Cela deviendrait un désavantage à l'utilisation des grains. Pour déterminer l'efficacité des grains dans différents environnements humides, des tests mécaniques ont été émis pour comparer celui-ci à deux types de rembourags: EPS et des mousses à base d'amidon. Les résultats démontraient que les grains supportaient bien les grandes pressions et avaient un

ratio de déformation plus stable comparé aux deux autres matériaux d'empaquetage. De plus, les grains avaient une plus grande résistance aux culbutages que les mousses à base d'amidon et serait plus avantageux dans l'empaquetage.

Le maïs souflé est un amidon de nature alimentaire et ceci porte quelques soucis en comparaisons aux amidons synthétiques qui ont une tendance de détérioration et de dégradation de moindre importance. La détérioration est souvent due au développement bactérien habituellement retrouvé dans les amilements à haut niveau d'humidité. Quand les grains de maïs souflés ont été testés dans divers environnements humides, les résultats ont démontré que de la bactérie se développait seulement dans des environnements contenant 30% ou plus d'humidité. De plus, les résultats ont démontré que les grains étaient très efficaces dans son rôle protection dans des environnements contenant environ 20% d'humidité.

D'autres soucis conernant la rancidité causé par la dégradation des lipides ont été évoqués. Si l''environnement proche des grains est instable, l'huile qui se trouve dans le maïs souflé pourrait s'oxider et mener à la rancidité. Pour résoudre ce problème, l'extraction de l'huile serait fortement recommandée. Pour trouver la meilleure solution pour extraire l'huile contenue dans les grains de maïs souflé, des extraits d'huile retiré avant et après la cuisson des grains ont été étudiés. Des grains dont leur huile ont été extraites ont été chauffés pour déterminer leur capacité d'éclatement. Les résultats démontrent que l'extraction de l'huile conetnue les grains au stade de pré-cuisson étaient inefficace, tandis que les grains traités gardaient leur capacité d'éclatement. Durant le processus d'extraction, les grains dont l'huile a été extraite avant et après la cuisson démontrent des résultats similaires. Donc, l'extraction de l'huile des grains de maïs souflés éclatés serait préférable dans notre cas.

ACKNOWLEDGEMENTS

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NOMENCLATURE

a_w	Water activity
AW	Amount of water required for conditioning (ml)
E	Energy (J)
EPS	Expanded polystyrene
ERH	Equilibrium Relative Humidity (%)
ε	Strain (mm/ mm)
F(x)	Force measured at displacement x (N)
L	Initial height of the sample (mm)
δL	Sample deformation (mm)
MAE	Microwave Assisted Extraction
M1	Initial mass (g)
M2	Final mass (g)
MC	Moisture Content (%, wet basis)
m_i	Initial mass of sample (g)
MC_i	Initial moisture content of sample (%)
MC_f	Final moisture content of sample (%)
SEM	Scanning Electron Microscope

FORMAT OF THESIS

This specification given in Part C “Manuscript-based thesis” in Section I “Thesis Preparation” of the “Thesis Preparation and Submission Guidelines” is followed for preparation of this thesis. The entire text of the applied format is quoted here:

> “**C. Manuscript-based thesis:**
> As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research. The structure for the manuscript-based thesis must conform to the following:
>
> 1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly-duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis.)
>
> 2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges preceeding and following each manuscript are mandatory.
>
> 3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts.
>
> The thesis must include the following:
>
> 1. a table of contents;
> 2. a brief abstract in both English and French;
> 3. an introduction which clearly states the rational and objectives of the research;

4. a comprehensive review of the literature (in addition to that covered in the introduction to each paper);
5. a final conclusion and summary;
6. a thorough bibliography;
7. Appendix containing an ethics certificate in the case of research involving human or animal subjects, microorganisms, living cells, other biohazards and/or radioactive material.

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defence. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers…"

CONTRIBUTION OF AUTHORS

The research project was conducted in the Department of Bioresource Engineering, Macdonald Campus, McGill University, Montreal. The work is done by Hoi Po Cheng, author of this thesis. Professor Raghavan is the supervisor and Yvan Gariépy and Jianming Dai are the co-authors of the papers in helping experimental setup and reviews.

The authorship for the papers are as follows:

1st paper (Chapter III): H.P. Cheng, Y. Gariépy, and G.S.V. Raghavan

2nd paper (Chapter IV): H.P. Cheng, J. Dai, and G.S.V. Raghavan

I. GENERAL INTRODUCTION

1.1 Introduction

Popcorn as a common snack has a lot of flavours, for example, butter, caramel, cheddar cheese...etc. It has high carbohydrates, protein, and is low in fat and is considered as a kind of healthy food. Without any artificial flavouring (preservatives or butter), other than a healthy snack, popcorn can be considered as a natural packaging material. The internal cell structure of popcorn contains cavities inside the cell, which establishes foamy-like structure. This structure provides protective cushioning properties similar to the function of the commercial plastic loose-fill foams.

Plastic waste has exploded to large amounts in different industrial sectors. It also appears in different forms; plastic wastes commonly include packaging containers (e.g. bottles, box, or plastic bags), packaging cushions (for protective and/ or insulation purposes), and equipment components...etc. Most plastic packaging materials are not biodegradable, and it creates a huge disposal problem. Although some of them are degradable, the material composition remains a contamination potential. For example, if the plastics contain toxic additives, the degradation of plastic may release toxic compounds to the soil and may contaminate the underground water. This cannot be avoided unless the landfill materials are screened for its natural origin and non-toxic nature.

According to many recycling programs, a lot of plastic packaging materials can be recycled or reused. The environmental problem can be minimized if everyone collects the used materials to recycle or reuse. However, when the packaging materials applied in protective use especially loose-fills, collection for reuse or recycling of them is more difficult. These materials are usually being discarded as garbage instead of being collected for reuse or recycling due to the small amount at individual level. Finally the garbage goes to landfills leading to the question of degradability of the material. Therefore, biodegradable materials are being developed and some are competitive with the petroleum-based (plastic) materials in terms of their strength. Biodegradable materials also have some environment related problems: the release of methane, carbon dioxide or other toxic gases. Methane and carbon dioxide are the major source of global warming, as they become greenhouse gases if the gases cannot be collected and used for energy recovery.

Using biodegradable material products does not imply to encourage people to maintain their disposal habit. If no one is going to change the disposal habit, the landfill problem mentioned above also cannot be solved, and may create further problems. It must be clearly emphasized that the use of biodegradable materials is essential since not all the plastics are 100% recycled or reused. Some of them will end up in garbage or in a landfill finally. Those plastics which mostly end up at the landfill site should comply with biodegradable quality as it is a better way to solve the landfill problem. Normally all plastic packaging materials, especially cushioning materials, end up as garbage after their primary purpose (protection). In order to solve the environmental problem due to these non-biodegradable materials, bio-degradable materials are to be used extensively.

Biodegradable foams are preferable in order to replace the plastic foams. There are pure starch-based foams, which are acceptable in terms of degradability, but the protection performance characteristics may not be as good as the plastic ones. Improved biodegradable-plastic foams are therefore needed. They have the characteristics of both plastic and starch foam. They can be cellulose-based or starch-based. Starch or cellulose is blended to the polymer and used in the manufacturing process which is similar to the petroleum based plastic foam. It may take more processing time, greater energy and elevated cost. Popped corn kernel (Popcorn) is suggested as an alternative of which could have reasonable energy and cost related attributes. It is completely natural. Its compatible strength attributes with plastic loose-fills need to be understood. Heat is the major energy used for popping. The manufacturing process (popping) time is much shorter than the starch- or cellulose- based foams. Some companies in Canada use popcorn to protect parcels and show a great savings in switching to popcorn from petroleum based foam (Livesey, 1990). Furthermore, used popcorns can be considered for bird feeding. Its natural biodegradable character can also solve the problems associated with non-biodegradable plastic foams in landfills.

Similar to other biodegradable foams, popcorn is sensitive to moisture. If the popcorn is surrounded by a high humidity environment, its physical and mechanical strength will be affected. The humidity directly affects the moisture content of popcorn as the popcorn can absorb the moisture from the surrounding. As popcorn is a food grade material, deterioration and microbial growth due to unstable environment are also of concern. Therefore, this aspect needs to be investigated as well. Deterioration usually is due to the lipid degradation of the oil components. Removal of oil from popcorn is suggested to avoid the lipid degradation. It is the intent of this thesis to study these aspects.

1.2 Hypothesis

The physical and mechanical properties of popcorn could be affected by the moisture content. It is possible to link the strength attributes to the moisture content. Also oil in the popcorn may create problems such as rancidity. This affects the storability of the popcorn for long-term use.

1.3 Objectives

The objectives of this study are:

1. To establish the moisture content level at which the popcorn will be suitable for packaging use. In addition, the physical and mechanical properties of popcorn at different moisture content levels are to be investigated.

2. To determine the possibility of extracting oil content of the popcorn at the kernel stage and popped stage by using conventional and microwave-assisted extraction. Also, the pop-ability of kernel after extraction process is to be established.

1.4 Scope

Literature review in Chapter II introduces the plastic cushioning foams, biodegradable foams and popcorn. Their cushioning performance assessment will be provided. The experimental part of the study is based on the seeds (cultivar unknown) bought from normal channels of commercial establishment.

II. LITERATURE REVIEW

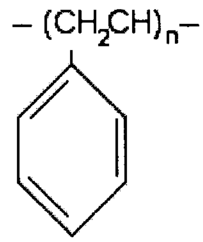
2.1 Review on Plastic Packaging foams

Plastic packaging foams are usually used for cushioning function. They are light weight, good insulation, shock absorbing and good for protection. Packaging foams are usually made of polystyrene. They can be moulded to the shape of the protected product, or supplied in the form of loose-fill. Loose-fill foam can be more flexible in use than moulded shape, and is usually employed for light weight objects while moulded foam is used for heavier objects (Hernandez et al., 2000).

Loose-fill is commonly used for mail order items. It was being sold in 1960 by the plastic companies as expanded polystyrene (PS) resin. The major advantage of PS loose-fills is the low density, which lowers the shipping cost. Also it is cost effective in order to produce the resin as small beads in petrochemical plants. However, loose-fill is not suitable for heavy or large items. It could be crushed under weight, shifted from vibration, or settle under the item during shipping or distribution. Also settling under heavy items could happen. Overfilling can avoid the shift and settling problem (Chiles, 1993).

2.1.1 Polystyrene Plastic Foam

Polystyrene (PS) is the most common packaging foam. Its basic chemical structure is:



Often, it is incorrectly referred to "Styrofoam", which is a Dow Chemical Company trademark for building insulation (Hernandez et al., 2000). The Styrofoam was originally adopted in 1942 for its buoyancy function by the Coast Guard for use in a six-man life raft (Dow Company, 2004). Suh et al. (2000) studied the lightweight cellular plastics and scanning electron microscope (SEM) of the intercellular structure of polystyrene foam as shown in Figure 2.1.

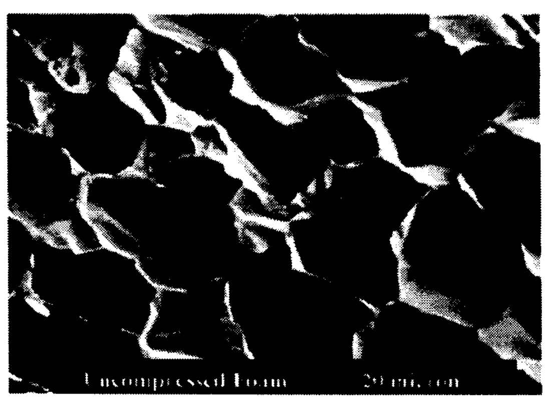


Figure 2.1. SEM of an uncompressed Polystyrene foam

Polystyrene foam is relatively chemically inert, and it is widely used in food packaging. The polystyrene foam coffee cup is an example of such use. The cup is an inexpensive container for hot drinks, which utilizes the light weight and insulation properties of the material. In addition, polystyrene foam possesses a shock-absorbing capability thus making it as a good cushioning material. When PS is used as a cushioning material, it is either moulded into shapes (expended polystyrene) or extruded into forms (Hernandez et al., 2000).

2.1.1.1 Expanded polystyrene

Expanded polystyrene is made of PS beads with impregnated hydrocarbon blowing agent, which produces bubbles in the plastic. Pentane is the common agent. By heating the PS beads, the beads are expanded and pentane is vaporized. Once the expanded beads reach their equilibrium, they are introduced by steam and packed into the mould under high pressure. The beads fuse together forming semi-rigid foam. The foam can be formed into desired shapes according to the mould (Hernandez et al., 2000).

2.1.1.2 Extruded polystyrene

Extruded polystyrene foam is produced by extrusion instead of moulding. The melted PS resin is mixed with a blowing agent and a nucleator inside an extruder, and the whole blend is extruded. The nucleator is used to provide the site with bubble growth in uniformity and to form desired cell size. The commonly used nucleators are talc, citric acid, and citric acid with sodium bicarbonate. The blowing agent is a hydrocarbon or hydrocarbon blend in the form of liquid or pressurized gas. Carbon dioxide has been used recently as a blowing agent. In the past, Chlorofluorocarbons (CFCs) were commonly used, but are no longer allowed to be used due to the environmental impact in ozone depletion. Hydro-chlorofluorocarbons (HCFCs) cause less ozone depletion and are used in some countries as blowing agents. However, they cannot be used in the U.S. (Hernandez et al., 2000).

2.1.2 Environmental Concern

Choosing a cushioning material is based on the cost and the performance. PS foams are widely used because of the low cost and the shock absorption capability. However, due to its wide use, environmental attention has been highlighted. The PS loose-fills are generally treated as disposal waste rather than recycling material. As a result, the handling of loose-fills scatters them as litter on both land and ocean. There is a risk that the loose-fills are being mistakenly consumed as food by animals, especially by marine animals. This may block the animal's digestive tract. Other concerns are from the manufacturing process itself. The process is a source of environmental pollution. Not only does the manufacture of styrene and blowing agents for PS cause pollution; but also the non-qualified materials and the products are likely to be discarded form the factory. Styrene is toxic and volatile. When the PS products containing styrene residual is discarded to the landfill, the styrene is more likely to be released to the environment. Further, it should be noted that PS foams that are used for food application should not contain any toxicity (Chiles, 1993).

2.2 Biodegradability

From the environmental aspect, biodegradable product made from natural material is preferred. Biodegradable is one kind of "degradability" of the material. When a material is defined as "degradable", it means that under certain conditions this material will result in loss of its mechanical integrity and/ or chemical identity. Usually water solubility is one of the mechanisms involved (e.g. the break down of the material bonding due to the composting activity). The influential factors could be sunlight exposure, water solubility, micro-organisms consumption, or any combination of them. The terms "photodegradation", "hydrodegradation" and "biodegradation" are all used depending on the source of degradation. It should be noted that the difference between photodegradation and biodegradation is due to the source of degradation. Photodegradation is generally defined as significant loss in mechanical properties after exposure to sunlight, which results in the reduction of the molecular weight of the polymer. The material's chemical identity remains the same, as in the case of photobiodegraded polyethylene which is still polyethylene but in smaller fragments. In contrast, biodegradable is defined as the capability of material being broken down into carbon dioxide, methane, water and humus-type material by micro-organisms during a certain period of time. The biodegraded material suffers a complete loss of chemical identity in the process (Selke, 1996).

2.3 Biodegradable foams

The most common biodegradable foams are made from starch. Starch-based foams are produced by plasticizing the starch and additives with water in an extruder and then moulded into a variety of desired shapes. They are usually made in the form of loose-fills. Starch-based foams are considered as environmental friendly because of their water soluble property and they can be easily degraded (i.e. biodegradable). However, when these foams subjected to a very high humidity, their strength may be weakened by the high moisture absorption. Other concerns are rodent and insect infestation due to the starch (Hernandez et al., 2000). Also, these starch foams are made of pure starch and thus have a heavier density than PS foams. They lack of resiliency and toughness, and easily produce fragments leading to dust (Chiles, 1993).

2.3.1 Biodegradable plastic foams

In order to maintain the PS foam performance and improve the biodegradability, the use of plastic polymer combined with starch or cellulose in producing biodegradable plastics is preferred. These types of foams provide better performance than 100% starch foam, and make the plastic biodegradable. However, the production process is more complicated, as the starch is sensitive to high temperature during processing. Plasticizers are used to improve the process so that the blends can be produced using standard techniques, such as extrusion (Selke, 1996). The amount of plasticizer also affect the water sensitivity. Lourdin et al. (1997) found that with higher the plasticizer content, the starch-material samples were more sensitive to ambient humidity, due to the increase of hydrogen bonds between plasticizer and water.

Wang et al. (1995) studied the cushioning materials made from wheat and corn starches. These cushioning materials have higher water absorption rate, and more unrecoverable deformation than expandable polystyrene foam. In terms of water absorption, such foams have the advantage with respect to the attributes of degradation.

Bhatnagar and Hanna (1995) compared plastic foam made with corn starch and polystyrene (PS), and corn starch with polymethylmethacrylate (PM) in the commercial PS packaging foams. They found that the performance properties of starch-based loose-fill foams are comparable with the commercial PS loose-fill. These starch-PS/ PM blended foams function better than the 100% starch loose-fill. It shows that some starch-based plastic foam can perform as well as commercial plastic foams.

Other than starch, cellulose and natural fibres are also used in the manufacturing of packaging material. Guan and Hanna (2004) studied the physical and mechanical properties of extruded foam composed of starch acetate and cellulose/corn cob. Figure 2.2 and Figure 2.3 show the electron scans of extruded foam with corncob and cellulose, respectively. The electron scans demonstrate that the corncob cells are not distributed evenly, and have significant cell size differences. In contrast, cellulose foams had uniform cell size and evenly distributed cell structure, and the cells conform to hexagonal/ pentagonal shape. The foams are produced from starch acetate blended with ground corncobs, and are compared to the blending with cellulose, under different ethanol contents. The ethanol penetration strengthens the starch acetate-fibre matrix, while corncob blends produced inferior linkages and cell development compared to cellulose blends. Study shows that higher corncob content results in higher compression strength (Guan and Hanna, 2004).

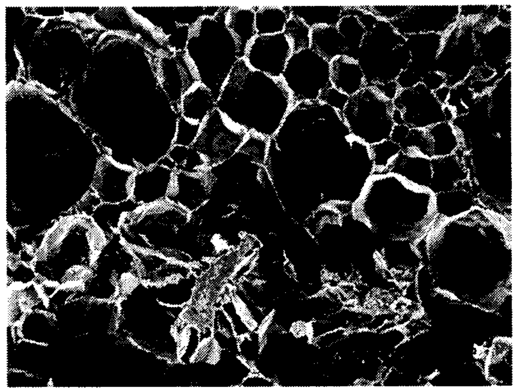


Figure 2.2. Scanning electron micrograph of extruded foam with 16.5% ethanol and12.5% corncob.

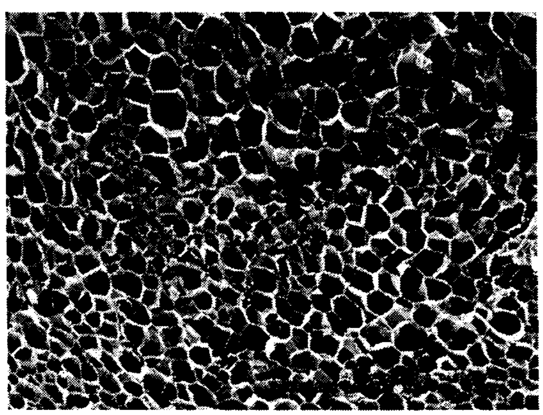


Figure 2.3. Scanning electron micrograph of extruded foam with 16.5% ethanol and12.5% cellulose.

2.4 Energy Use

Chiles (1993) studied the energy use of PS loose-fill and pure starch-based loose-fill. The information on energy used was based on a volume of 40 cubic meters of material. The PS loose-fill consumed a wide range of energy from 7.4 million kJ up to 21.1 million kJ. Loose-fills produced from recycled materials consumed about 7.4 million kJ; while loose-fills made from virgin materials with no subsequent recycling consumed about 21.1 million kJ. An average value of energy use by half recycled material and half virgin material was determined to be 16.3 million kJ. The starch-based loose-fills energy use was determined using fossil-derived energy criteria in terms of oil, natural gas and coal use, including that needed for the farming operation in corn production (source of corn starch), irrigation, transportation, drying and milling. The total energy consumption in that case was about 6.4 million kJ. Approximately 5.5 million kJ were used in the loose-fill manufacture including process of corn production until starch extraction; 0.9 million kJ were used for the expansion process. This value does not account for its reuse. In addition, there were some indirect energy inputs, linked with the use of fertilizer, herbicides and insecticides during corn production.

2.5 Review on Popcorn

The cultivation of popcorn seeds and the "popping" process are the major energy input in arriving at the final product "popcorn". The energy used to produce popcorn for packaging would not be any higher than energy used for starch-based loose-fill products. Popcorn is one of the varieties of corn; it has the same basic plant structure, kernel structure and kernel component compared to the other types of corn.

2.5.1 General introduction of corn

Corn is also called *maize* and *Indian corn.* In some countries, the term "corn" is used to designate other crops. For example, in England, wheat; in Scotland and Ireland, oats; some parts of Africa, sorghum (Benson and Pearce, 1987). Corn belongs to the grass family; it is within the same family as wheat, oats, barley, rye and sorghum. Botanists classify the corn plant as shown in Table 2.1.

Table 2.1. Classification of Corn plant (Wallace and Bressman, 1949)

BOTANICAL DIVISION	NAME	CHARACTERISTICS
Family	Gramineae	Fibrous root system, leaves alternate, two-ranked, parallel veins in leaves, split leaf sheath, ligule, stems cylindrical with solid nodes, flowers in more or less chaffy spikelets.
Tribe	Tripsace (Maydeae)	Male and female flowers in separate spikelets on the same plant.
Genus	*Zea*	Grain borne on a lateral cob, the ripened grains greatly exceed the glumes.

A mature corn plant is illustrated in Figure 2.4. It has a fibrous root system. An erect stalk has a single leaf at each node with leaves in two opposite ranks. Each leaf consists of a sheath. The undeveloped shoot for an ear is surrounded by the leaf sheath. Corn is a cross-pollinated species and it is a monocot. The tassel (male) is located at the top of the stalk and the ears (female flowers) are located at the end of short branches on the same plant. The ears grow and contain 300 to 1000 developed kernels arranged in rows along a cob (Benson and Pearce, 1987).

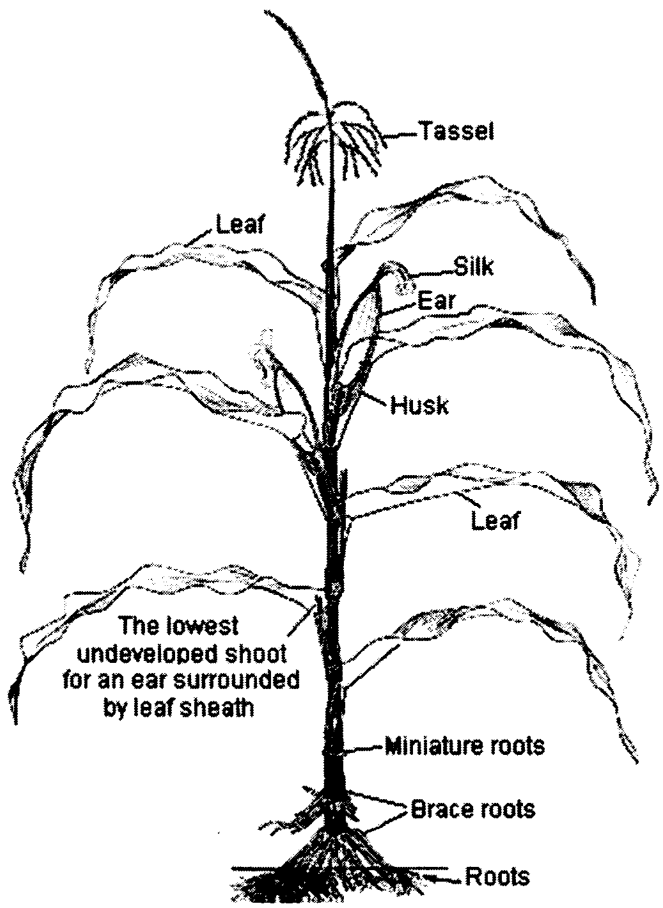


Figure 2.4. Skeleton of a mature corn plant (Wallace and Bressman, 1949).

2.5.2 General Structure of corn kernels

All varieties of corns have the same basic kernel structure (Figure 2.5). In general, a corn kernel contains three major parts: germ, endosperm and pericarp. The germ is composed of embryo and scutellum. The scutellum is a nutritive organ for the embryo and makes up 10-12% of the kernel dry weight. Endosperm constitutes 82-84% of the kernel dry weight. The cells are closely packed with starch granules and embedded in a continuous protein matrix. The endosperm is composed of floury and horny endosperms. Usually the floury endosperm is called the soft starch part, and horny endosperm is called the horny starch. The cells of horny endosperm are more compact (higher density) than floury endosperm. Pericarp is an outermost structure of the kernel. It can be considered as the seed coat. It makes up of 5-6% of kernel dry weight. It adheres tightly to the outer surface, aleurone (Watson, 1987).

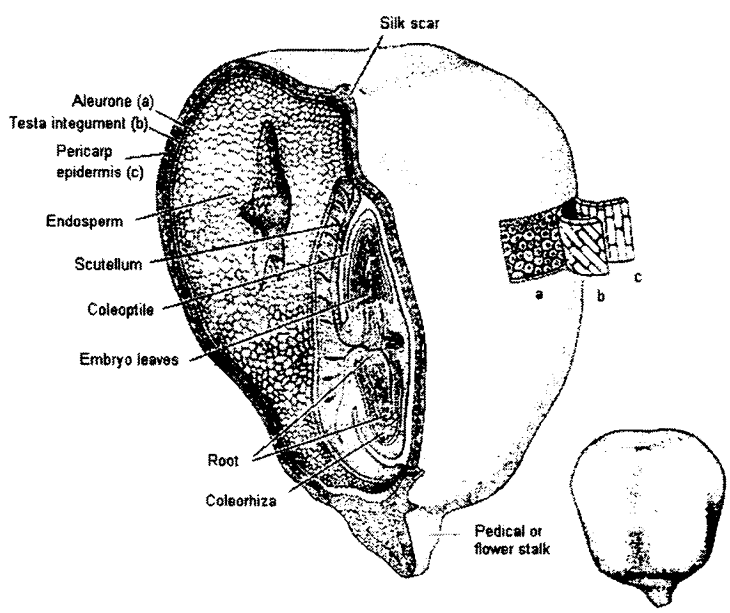


Figure 2.5. Mature corn kernel structure (Paliwal, 2000a).

2.5.3 General composition of corn kernels.

The nutritional composition of the kernel consists mainly of water, protein, fat, carbohydrates, starch, ash, and vitamins. Table 2.1 gives the average composition of various parts of corn kernel on a dry weight basis.

Table 2.2. Composition of the parts of the corn kernel. (Paliwal, 2000c)

Composition (%)	Endosperm	Embryo	Pericarp	Scutellum
Starch	87.6	8.3	7.3	5.3
Fat	0.8	33.2	1.0	3.8
Protein	8.0	18.4	3.7	9.1
Ash	0.3	10.5	0.8	1.6
Sugar	0.6	10.8	0.3	1.6
Balance	2.7	18.8	86.9	78.6
Dry weight of whole kernel (%)	83.0	11.0	5.2	0.8

On the whole kernel basis, the starch content is about 72 -73%. The starch is a major component of the corn, which is mainly present in the endosperm. Other than starch, protein is also another component contained in the endosperm. The endosperm contains 74% of the kernel protein. Other components such as ash and lipids are stored richly in the germ. The ash is the mineral element; the germ contains about 78% of the kernel mineral. The most abundant component is phosphorus. These mineral elements are important for the embryo growth and development (Watson, 1987).

The oil content in a normal corn kernel is about 3.5-5.0% of the corn grain (Sprague, 1955). It is mainly stored in the germ, amounting to 83% of the kernel lipids. The greater part of the germ lipids are triacyglycerides, which is known as the commercial corn oil upon extraction (Watson, 1987).

2.5.4 Oil component

Crude corn oil consists of a mixture of triglycerides (Triacylglycerols), free fatty acids, phospholipids, sterols, tocopherols, waxes and pigments. The fraction of triglycerides has a greater amount than other lipids present in the oil. Approximately 99% of the refined oil is composed of triglycerides. Typically, corn oil is more stable than other vegetable oils because it has relatively low linolenic acid content (Orthoefer and Sinram, 1987).

2.5.4.1 Fatty Acid Composition

Fatty acids are composed of hydrocarbon chains of 16 to 20 carbons. Each chain has up to three double bonds. The structure of fatty acids (Figure 2.6) is in zigzag conformation of hydrocarbon chains. The pathway of biosynthesis of fatty acids is also shown (Weber, 1987).

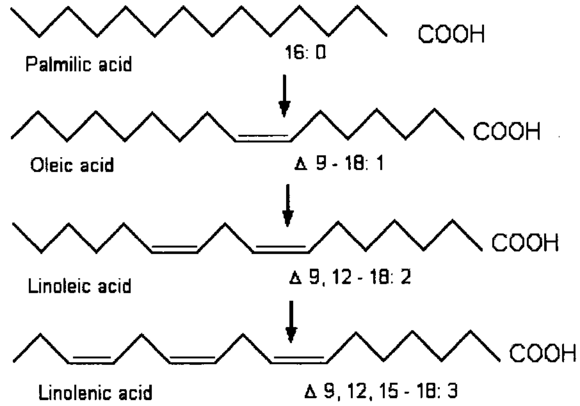


Figure 2.6. Chemical structure and biosynthetic pathways of fatty acids.

Corn oil has a high level of polyunsaturated fatty acid, linoleic acid (18:2). It is considered as a healthy source in the diet because of the nature of polyunsaturated fatty acid. The low level (<1.0%) of linolenic acid (18:3) and the high level of natural antioxidants make the corn oil a stable oil (Weber, 1987). Table 2.2 shows the fatty acid composition of corn oil.

Table 2.3. Fatty acid composition of Corn oil (Weber, 1987).

	Fatty Acid Composition, %				
Oil	16:0[a]	18:0	18:1	18:2	18:3
Corn	11.0	2.0	24.1	61.9	0.7

[a] Fatty acids are identified according to the number of carbon atoms and number of double bonds: palmitic acid, 16:0; stearic acid, 18:0; oleic acid, 18:1; linoleic acid, 18:2; linolenic acid, 18:3.
*Reference: Liebovitz and Ruckenstein (1983)

2.5.4.2 Triacylglycerols (Triglycerides)

Triacyglycerols (TG) are the complex mixture resulting from the possibility of multiple combination of fatty acid. In the TG molecule, three fatty acids are esterified to the hydroxyl groups of glycerol. Stereospecific analysis of TG of corn indicates that fatty acids have a non-random distribution among the three positions which are illustrated in Figure 2.7. Saturated acids: palmitic and stearic, are predominately at the sn-1 and sn-3 position. It was found that over 98% of fatty acids of unsaturated and linoleic acid are dominant at the sn-2 position. The placement of fatty acid at different position of a TG structure directly affects the physical properties, nutritional value, stability of the oil (Weber, 1987).

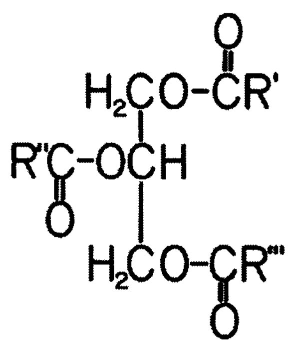


Figure 2.7. Triacylglycerol structure. R′ indicate alkyl chain of fatty acid at *sn*-1 position, R′ at the *sn*-2 position, and R‴ at the *sn*-3 position in stereospecific numbering (*sn*) of carbon atoms of glycerol. (Weber, 1987)

2.5.4.3 Oil at high temperature

Weber (1987) reported that the high temperature can affect the corn oil, and he performed that the high temperature can influence the TG molecule. Yoshida and Kajimoto (1984) also studied the thermal oxidation of corn oil. The oil was heated to 180°C, and the TG molecules of the thermally oxidized oil were isolated by using silver nitrate-silica gel with the thin-layer chromatography (TLC). The results showed that TG with five or six double bonds were oxidized faster than those with one to four. Sahasrabudhe and Farn (1964) studied corn oil after heating it to 200°C for 48hours. They found that the fatty acids in the outer position of TG were slightly more susceptible to heat than in the sn-2 position.

2.5.4.4 Corn oil extraction

Corn oil is usually recovered from the dried germ, by either mechanical method or solvent extraction, or combination of both. In the mechanical method, screw expellers press the oil from the germ under high pressure and moderate heat. The expelling process can remove 90% of oil from the germ, and about 80% of oil can be recovered with a screw expeller (Orthoefer and Sinram, 1987).

In the solvent extraction process, the dried germs are leached by a solvent, such as hexane. After leaching, the extracted meal is pressed to remove as much oil as possible out of the oil-solvent solution. The solvent is then removed by distillation. The extraction process is carried out in a closed system, thus minimizing solvent loss. During extraction, some of the lipids may break down into free fatty acid and glycerine. They are relatively unstable, and need to be removed. A refining process is usually required, especially when the oil is treated for human consumption (Sprague, 1955).

2.5.5 Corn varieties

There are many kinds of corn varieties in the world. The varieties are basically classified in accordance with their different kernel texture or the internal structure. In general, the distinction between corn varieties is based on the endosperm and kernel constitution, kernel colour, shape, the place where it is grown, maturity and the specific use (Paliwal, 2000b). For example, flint, dent, floury, and pop corn; all have distinct shapes externally, and also vary in starch component distribution (Figure 2.8).

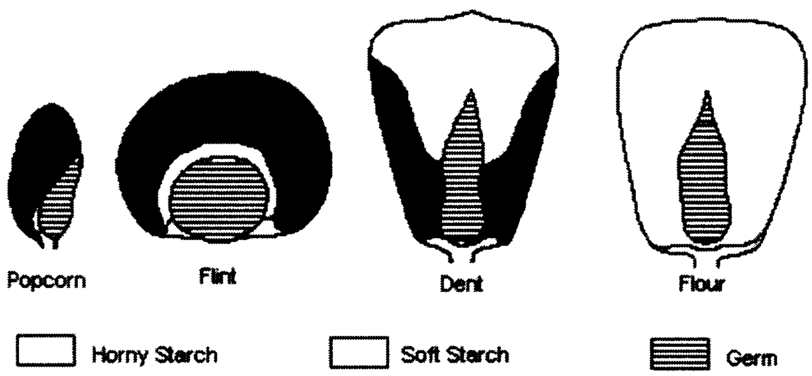


Figure 2.8. Kernel texture, from left to right, popcorn corn, flint corn, dent corn and floury corn (Wallace and Bressman, 1949).

Flint, Dent, Floury, Sweet, Waxy and Popcorn are the common types of corn, and their differentiation is described below.

Flint

Flint corn kernels are round, hard and smooth. It has a thick and hard endosperm which is made up of hard corneous starch; some soft starch is located in the very centre of the grain. It is preferred for human food (Paliwal, 2000b).

Dent

Dent corn is the most common type of corn grown for grain and silage. The endosperm has more soft starch than flint. When the grain starts drying, the soft starch at the top of the kernel contracts, the dented, tooth-like appearance gives it the name "dent" corn. Most of the dent corn is either white or yellow. And white is preferred as human food, while yellow is largely used for animal feed (Paliwal, 2000b).

Floury

The endosperm of floury corn is composed of very soft starch, and it is easily ground. Upon drying, the kernels tend to shrink uniformly and as a consequence, very little or no dent occurs (Zuber and Darrah, 1987).

Sweet

Several mutant genes condition the endosperm to make it sweet. In the United States, sweet corn is an important crop for human food, being consumed directly in fresh form or as canned and frozen products. The mutants used for sweet corn prevent or reduce the rate of sugar conversion to starch (Zuber and Darrah, 1987).

Waxy

Waxy corn has a dull wax-like appearance on its endosperm. The common starch in flint and dent types is made up of approximately 70% amylopectin and 30% amylase. Waxy starch is entirely made up of amylopectin. Waxy corn in specific industrial markets is being used for starch production (Paliwal, 2000b).

Popcorn

This is an extreme form of flint corn with a higher percentage of hard starch. The hard endosperm occupies most of the kernel; and only a small amount of soft starch is in the basal part of the grain. The kernels are small, with a thick pericarp. The kernels vary in shape from round to oblong. When it is heated, the kernel pops and the endosperm bursts out. The kernels, with low moisture content (about 14%), are heated to a temperature above 170°C to make the kernel pop (Paliwal, 2000b).

2.5.6 Structure of Popcorn kernel

Similar to other corn species, popcorn kernel consists of three major structural parts: pericarp, germ and endosperm. Depending on the popcorn variety, the pericarp can be thick or thin. The pericarp is a tough protective layer surrounding the kernel and participates in the popping action. It serves as a pressure vessel enclosing and containing the endosperm. It is also an important factor in popcorn quality. The germ contributes the least to popping phenomenon. Popping does not alter the germ chemically or physically (Hoseney et al., 1983).

The endosperm consists of two parts: translucent (horny) and opaque (floury). Hoseney et al. (1983) studied the internal structure of popcorn kernel; the scanning electron micrographs of the kernel structure are shown in Figure 2.9(a-d). The translucent endosperm contains closely-packed polygonal starch granules ranging from 7 to 18μm in diameter. The opaque endosperm contains large, smooth spherical granules with many inter-granular spaces. Figure 2.9a shows the kernel structure, composed of translucent endosperm (TE), opaque endosperm (OE) and germ (G). Figure 2.9b shows the tightly packed TE with no air space and with polygonal–shaped starch granules. Between the starch granules are a protein matrix and numerous protein bodies. Figure 2.9c shows the opaque endosperm with starch granules in more spherical shape and more air space. There is also a protein network that holds the starch granules together. Figure 2.9d shows the pericarp composed of many tightly packed layers. Inside the pericarp, there is a single layer of thick-walled aleurone cells, which are the outer layer of the endosperm (Hoseney et al., 1983). Compared to other field corn, e.g. dent corn, popcorn contains more translucent endosperm and higher protein-carbohydrate ratio (Wu et al., 1992).

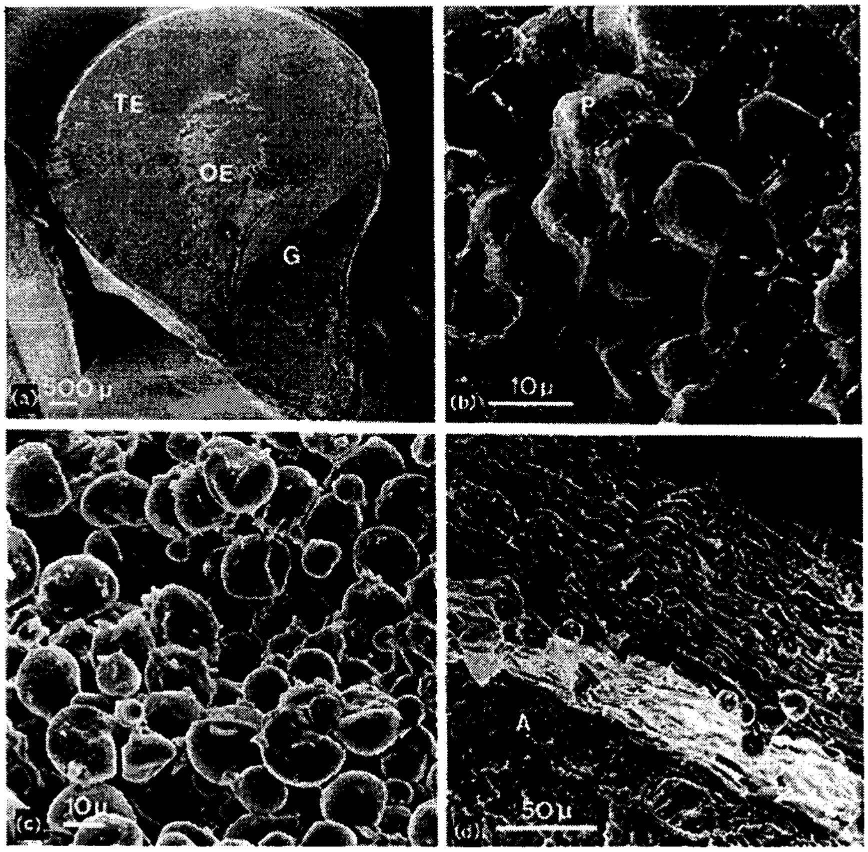


Figure 2.9. Scanning electron micrograph of (a) a longitudinal section of an un-popped popcorn kernel; (b) the translucent endosperm, showing starch and protein bodies (P), (c) opaque endosperm; and (d) the outer edge of the kernel, showing the aleurone (A) and the pericarp.

2.5.7 Popping mechanism

High temperature is important to pop popcorns. The major mechanism for popping is the vaporization of the internal kernel moisture when the kernel is subjected to a high temperature. When temperature rises to the popping temperature (about 177°C), the water inside the kernel is superheated (Hoseney et al., 1983). The water becomes vapour and escape. While the pericarp of the kernel is acting as a protective layer preventing water to escape. Then the pericarp becomes acting like a pressure vessel and the water vapour pressure builds up within individual starch granules. At the same time the starch softens. The internal pressure forces the starch granules in the opaque endosperm, forming a central vapour-filled pore and stretching the pericarp. Softened starch granules in the endosperm lose their structural strength before pericarp ruptures. Then, small bubbles appear in the opaque endosperm and merge into a bubble-like central pore. At that moment, the pressure in the space builds up and forces the starch granules apart; it causes the rupture of pericarp. The rupture of the pericarp destroys the confinement of the translucent endosperm (Wu et al., 1992). The individual starch granules are gelatinized and expanded by heat, dried and left in a three dimensional network. The expended endosperm forms a "bubble-like" structure causing the gelatinized starch granules (Reeve and Walker, 1969). Parkers et al. (1999) illustrates the air bubble (ab) formed in the starch foam of an endosperm cell by light and scanning electron microscope (SEM) (Figure 2.10).

The entire expanding process occurs in a very short time and this is how "popping" occurs. This expansion can cause the popcorn to increase in volume by 14 to 20 times (Wu et al., 1992).

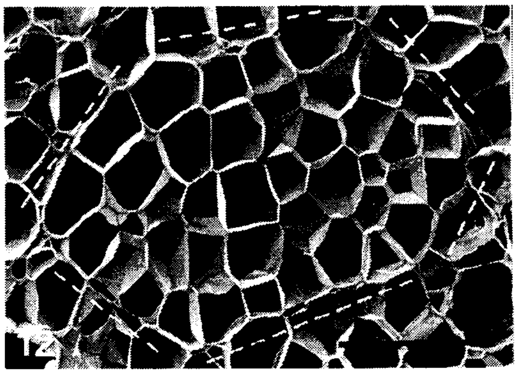


Figure 2.10. Cut surface of popcorn showing the outline of an endosperm cell (indicated by dashes) filled with starch foam, each air bubble (ab) is formed from one expanded starch granule. SEM, bar = 100μm

2.5.8 Structure of a popped kernel

Hoseney et al. (1983) illustrated the photos of an entire popped kernel (Figure 2.11) and the internal structure of a popped kernel (Figure 2.12) under SEM. The popped kernel shows the germ (G) and pericarp (P) and the outside of the aleurone (A). The pericarp (seat cost) was flipped over and the internal structure of starch was exposed through the expansion.

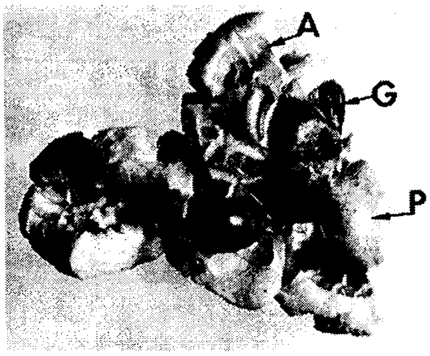


Figure 2.11. A popped kernel, showing the germ (G), pericarp (P), and the outside of the aleurone (A) (Hoseney et al., 1983).

Figure 2.12a shows the pericarp after popping. Figure 2.12b shows the outer aleurone (A) after popping. Figure 2.12c shows the expanded starch and the protein bodies (P) are visible and apparently without changing structure. Figure 2.12d shows the endosperm in partly popped kernel, with starch granules resulting from intact to expanded forms. Large voids appear in the opaque endosperm as a result of popping. Although the pericarp is free to separate from the endosperm, it ends up as being attached to the kernel. In the translucent endosperm, the expansion continues until the granules become as a thin film; while in the opaque endosperm, the bubble-like structure or voids allow water vapour to evaporate and form the starch foam network (Hoseney et al, 1983).

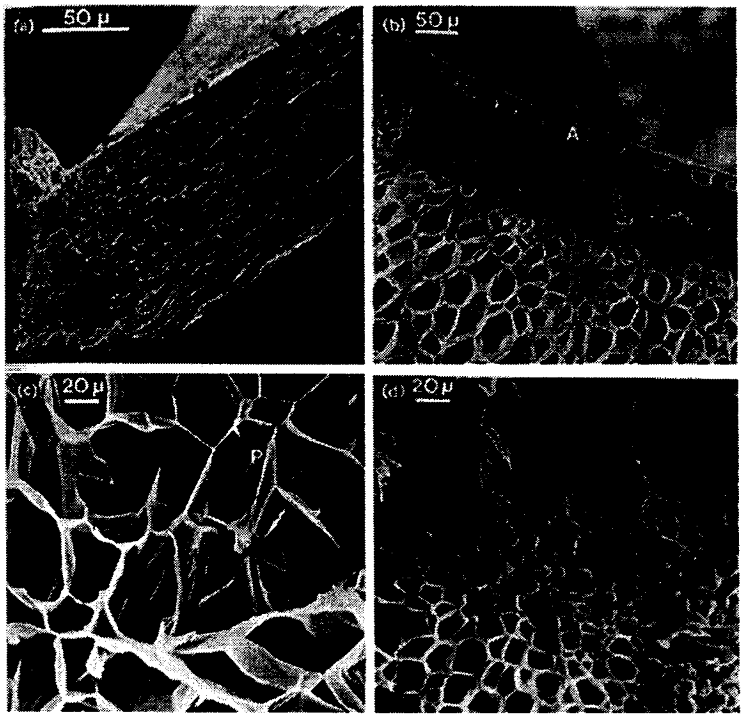


Figure 2.12. (a) pericarp free as a result after popping; (b) the aleurone (A) after popping; (c) the internal structure of endosperm after popping. Protein bodies (P) stay intact; (d) the endosperm in a partly popped kernel, with starch granules resulting from intact to expanded forms.

2.6 Quality concerns on Popcorn

Starch-based loose-fill and popcorn are both biodegradable. These products contain food-grade component which also raise the quality concern as in food quality. However, as a complete natural food material popcorn has higher possibility on deteriorative changes than synthetic starch-based loose-fill. The quality and performance of popcorn as a packaging material would be of interest in this study.

In general, food quality includes nutrition value, safety, stability, sensory experience and consumer acceptance (Cardello, 1998). In terms of packaging material, quality factors should include the deterioration or degradation possibility, and the performance quality in term of physical and mechanical properties.

2.6.1 Deterioration concern

Food deterioration usually is due to microbial growth, enzyme-catalyzed changes, non-enzymatic browning and oxidation. These deteriorative changes are mostly related to the moisture content, water activity, temperature and pH. Usually, high moisture content food has a high water activity value. Water activity indicates the activity of water in food material, and not necessarily corresponds to moisture content. Water activity, a_w, is the ratio of vapour pressure in a food material and vapour pressure of pure water at the same temperature. At steady state, a_w is related to equilibrium relative humidity (ERH) of the surrounding as in Equation 2.1 (Roos, 2001).

$$ERH = a_w \times 100\% \qquad [2.1]$$

2.6.1.1 Microbial growth

Most bacteria, molds and yeasts are likely to grow in high moisture foods with a_w value of 0.9 to 0.999, which usually contain 50% moisture content by weight. The growth of micro-organisms requires a minimum a_w, in addition to optimal pH and temperature. The minimum a_w for microbial growth is 0.62, which allows xerophilic yeast growth. Increasing of a_w would allow molds and other yeast growth and eventually bacterial growth (Roos, 2001).

2.6.1.2 Lipid degradation

Lipid degradation is caused by hydrolytic and /or oxidative reactions. Hydrolysis produces free fatty acids that act as the substrate for subsequent oxidation reactions. Rancidity could be produced by hydrolytic reaction or oxidation reaction (Galliard, 1983). Rancidity causes the development of off-flavours, texture or colour changes, and reduce in storage time. There are many factors affecting lipid oxidation, such as the presence of free fatty acid, oxygen concentration, temperature, and moisture content. A rapid oxidation could occur in dried food with a very low moisture content (a_w <0.1). However, increasing of a_w to a value of about 0.3 could retard the reaction, and the oxidation rate increases again when the value of a_w increases to 0.5 to 0.85 (Nawar, 1998).

2.6.1.3 Carbohydrate degradation

The stability of carbohydrates usually depends on the browning and hydrolytic reactions. Browning reaction contribute to flavour and colour of foods. The flavour development contributes to expect flavour, and also can contribute to off flavours.

Browning can be affected by temperature, moisture content and water activity. Conversion of sucrose to invert sugar and of lactose to glucose and galactose are the hydrolytic reactions. These reactions are acid or enzymatically catalyzed, or both. For example, corn syrup is produced from corn starch through the acid and enzymatic hydrolysis. The process is the degradation of starch polymer, sometimes starch gelatinization step is also required (Gordon and Davis, 1998).

As mentioned in the previous section, the formation of popcorn's foam structure is a rapid cool down of gelatinization of starch granule with the superheated water vapour. Thus, excess water can be a plasticizer that changes the solid state of starch into viscous rubbery states. The occurrence of similar degradative reaction could result in collapse of starch structure (Gordon and Davis, 1998). This could affect the performance of popcorn as a packaging material.

2.6.2 Performance Assessment

In order to understand the performance of cushioning materials, tests are carried out for specific properties which can be mechanical, physical or both. The following properties are usually studied for the performance of loose-fill foams:

1. Moisture content
2. Compressive stress
3. Resiliency
4. Friability
5. Foam Structure
6. Density
7. Colour

2.6.2.1 Moisture Content

Most plastic foams are water resistant; the surrounding humidity may not affect much of their performance. However, the performance of biodegradable foam, which is made of starch or material which is sensitive to water, may change when they are subjected to a high humidity environment. It is important to understand how the performance varies with moisture contents. Tatarka and Cunningham (1996) studied the loose-fill foam properties. They conditioned the test specimens with varying humidity and temperature conditions and then determined the corresponding moisture content and the mechanical properties of the specimen in order to understand how different environment could affect the foams.

2.6.2.2 Compressive stress

Compressibility indicates the rigidity of the foam (Fang and Hanna, 2001). There are many compression test methods for food grade cereal. For example, multi-probe puncture and Kramer Shear Press are the appropriate methods for such applications (Johnson, 2003). Popcorn is a cereal snack, which can be used as packaging material and the results can be compared with other loose-fills foams. The Kramer Shear Press test is preferred for comparing the suitability of these types of materials. Figure 2.13 shows an example of Kramer Shear Press equipment. Compression force is applied to shear through the sample (Figure 2.14), and the applied load corresponding to the compressed displacement will be shown as the output result.

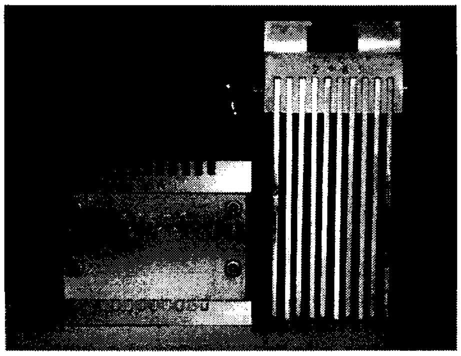


Figure 2.13. Kramer Shear Press

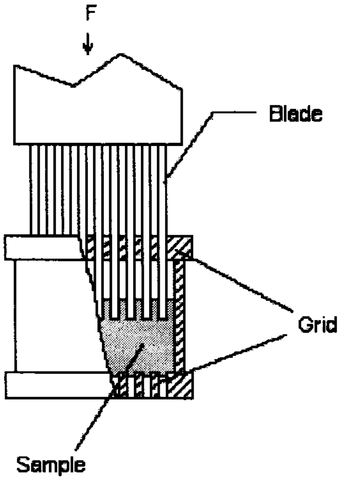


Figure 2.14. Schematic diagram of Kramer Shear Press

A typical load-displacement (Stress-strain) diagram obtained from an Instron machine is illustrated in Figure 2.15. The straight line crossing through the steepest linear region of the curve can determine Young's Modulus, which is the change in specimen stress per unit change in strain where the stress and strain are proportional for tensile and compressive tests. The stress-strain relationship is expressed as the slope of the initial linear portion of the curve where the y-axis is the stress and the x-axis is the strain. Instron Universal Testing machine software can calculate the Young's Modulus and other parameters such as energy to break point and toughness; they can be displayed as the output result (Instron, 1990).

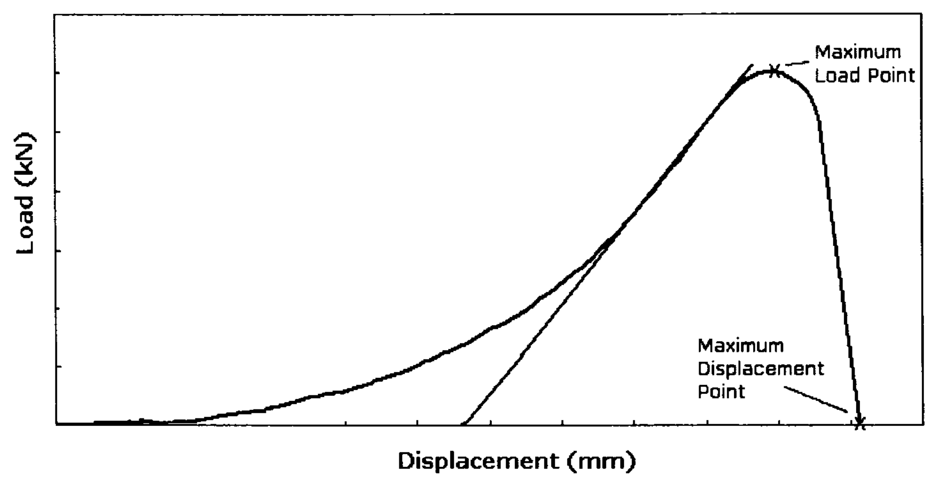


Figure 2.15. Typical stress-strain diagram

2.6.2.3 Resiliency

Resiliency describes the foam's ability to regain its original shape after compression, or the ability of the compressed part to regain its original position. Tatarka and Cunningham (1996) determined resiliency of loose-fill foams in terms of the percentage of elastic recovery after compressive deflection. The test specimen was compressed by 3mm and held for 60 seconds. The resiliency was then determined as the percentage of the compressive force after the 60 seconds hold divided into the maximum force required for the 3mm deflection.

2.6.2.4 Friability

Friability is a parameter that describes the foam fragmentation after tumbling. Tumbling is a mechanism that combines of abrasion and impaction. The ASTM standard test method C421-88 determines the tumbling friability of preformed block-type thermal insulation. Test specimens of cube shape are put into a closed wooden box and rotated for 10 min. at a speed of 60 rpm. The mass loss of the specimens resulting from the tumbling is determined. Figure 2.16 shows the schematic diagram of the Friability test.

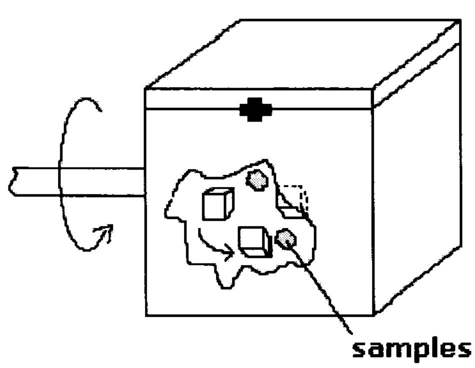


Figure 2.16. The schematic diagram of the Friability test

2.6.2.5 Foam Structure

Foam structural properties include size, shape and the internal cell foam structure (including components). These attributes are related to the foam's physical and mechanical properties. For biodegradable materials, these characteristics may affect their biodegradability. Lui and Peng (2003) found that the change in die shapes of biodegradable extruded foams had a significant effect on the foam expansion, compressibility and biodegradability. The internal foam structure directly affects the compressibility of the foams. Usually an electron micrograph (SEM) is used to scan the internal foam structure, so that cavity and the network structure can be easily seen. More cavities can reduce the density of the foam, but it may affect other functional characters, such as compressibility (Bhatnagar and Hanna, 1995).

2.6.2.6 Density

Density attribute can be divided into unit density and bulk density. Unit density is the weight-to-volume ratio of an individual loose-fill foam specimen. It is calculated by dividing the individual foam mass over its displaced volume. Bulk density is the mass-to-volume ratio of a large quantity of loose-fill foam; it indicates the packing efficiency of the foam. If the unit density is higher than the bulk density, then it will give a low packing efficiency (Tatarka and Cunningham, 1996).

2.6.2.7 Colour

Colour change is one of the physical properties. The colours of the specimens before and after certain conditioning or treatment are usually measured for comparison. Colour is produced by the red, green and blue lights. The measurement of colour is usually recorded in terms of value of "L", "a" and "b". "L" is the coefficient for lightness, which ranges from 0 (black) to 100 (white). While "a" and "b" ranging from positive to negative value and defined as: "a" (red), "-a" (green), "b" (yellow), "-b" (blue). The positive to negative "a" and "b" are on the same plane and perpendicular to each other, while the "L" is a vertical axis that can reflect the lightness or darkness of corresponding colour (Clydesdale, 1998).

CONNECTING STATEMENT

After the introduction of popcorn as a loose-fill alternative in Chapter I and literature review in Chapter II, popcorn was tested for packaging purpose and compared with commercial loose-fills in the following chapter.

III. MECHANICAL PROPERTIES OF POPCRON AT DIFFERENT MOISTURE CONTENTS

3.1 Abstract

Popcorn is a biodegradable material that can be used as a cushioning material for inbox packaging of fragile and delicate items. However, popcorn is hygroscopic and it can absorb water from the surrounding air and can be damaged when placed in direct contact with water. It is anticipated that internal moisture content changes can severely alter its physical/mechanical properties thereby making it less suitable for possible packaging use. In this study, popcorn samples were conditioned to different moisture contents ranging from 0% to 50%. Physical and mechanical properties were then measured and compared to those of commercially available samples of expanded polystyrene and starch based loose fill materials. The results did confirm the superiority of expanded polystyrene as the best material for loose fill. Also, the results have shown that popcorn had good compressive strength with better resistance to abrasion than the starch based material tested. Popcorn samples with over 30% moisture content suffered severe shrinkage and were found unsuitable for packaging.

3.2 Introduction

In the United States, the packaging industry is a $100-billion market and it is considered among the third largest industrial sector in the country. It is presently estimated that the loose-fill produced by manufacturers is approximately 45 million pounds each year according to the Plastic Loose Fill Council (PLFC). However, what is even more astonishing is that the packaging and packaging operations' industry is the largest employer in the United States.

Most packaging materials are multi-functional and they are designed for shock absorption, water resistance, abrasion protection, acoustic/ heat insulation, etc. However, our disposal habits of these non-biodegradable materials create an environmental problem. Recent studies have shown that starch-based materials are the alternative to petroleum-based (plastic) products, if composting infrastructures exist and plastic foam recycling is impractical (Tatarka and Cunningham, 1998). In order to be environmental friendly, through reducing the amount of garbage in landfill sites, biodegradable or natural cushioning materials such as shredded newsprints, cardboard, starch and popcorns, should be considered as a replacement of the plastic packaging material. They provide adequate cushioning protection and stabilization of articles packaged for shipping (Tatarka and Cunningham, 1998).

Starch-based loose-fills are biodegradable and are sensitive to water. Some materials can be dissolved in water and they have a tendency to be more brittle than plastic loose-fills. In that aspect, the popcorn behaviour is very similar to starch-based loose-fills. In addition, as a food grade material, the water can affect the physical stability (Roos, 2001), and the increase of moisture content can cause microbial growth (Walstra, 2003). In this study, the effect of moisture content on the physical and mechanical properties of popcorn were measured and compared to those of commercially available expanded polystyrene (EPS) and starch-based loose-fills.

3.3 Objectives

The objectives of this study were twofold:

- To assess the effect of moisture contents ranging from 0 to 50% on the mechanical properties of popcorn;
- To measure and compare the mechanical properties of popcorn samples to that of commercially available EPS and starch based loose-fill materials.

3.4 Materials and Methods

The properties of popcorn and two types of commercially available loose-fill materials were measured using a compression test and a friability test. In this study, popcorn samples were conditioned to moisture contents (MC) of 0%, 10%, 20%, 30%, 40% and 50%. Commercial loose-fill materials were tested as is, without prior conditioning, in order to understand their "as received" properties.

3.4.1 Popcorn sample preparations

Orville Redenbacher's Original ™ popping corns were purchased from a local store. The corn kernels were packaged in 850g plastic jars. The kernels were popped with a Toastmaster's Hot Air Popcorn Popper model 6202CAN.

3.4.1.1 Moisture content conditioning of Popcorn

Once popped, popcorn samples were brought to the appropriate MC levels in a stainless steel conditioning chamber. The required quantity of water was poured in a small container closed with a perforated lid. The water container was placed at the bottom of the conditioning chamber and the popcorn. The amount of water required for conditioning was determined using Equation 3.1:

$$\text{AW} = \frac{m_i \times (MC_f - MC_i)}{100 - MC_f} \quad [3.1]$$

Where,

AW = amount of water required (ml)

m_i = initial mass of sample (g)

MC_i = initial moisture content of sample (%)

MC_f = final moisture content of sample (%)

The chamber lid was secured and sealed with a plastic seal-tape. Figure 3.1 shows the schematic diagram of the conditioning chamber. The popcorn will absorb water and bring it to equilibrium after the conditioning period. The conditioning period was 10 days at room temperature.

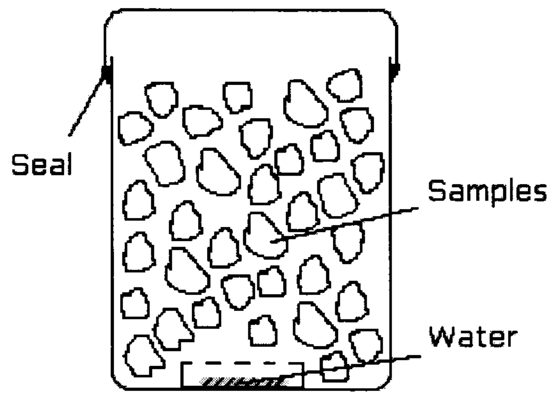


Figure 3.1. Schematic diagram of the conditioning chamber

Bone-dry (MC = 0%) samples of popcorn were obtained by drying the popped samples in an oven set at 103°C for 72 hours. The moisture contents for all conditioned popcorn were measured again at the time of testing to confirm that the desired moisture level is reached. It followed the ASAE standard described in section S352.2 (ASAE, 1995). The dried samples were placed in a sealed container with anhydrous calcium sulphate for 10 days of conditioning.

3.4.1.2 Commercially available loose-fill materials

The two loose-fill materials used in this study were the FLU-PAK S, non-biodegradable polystyrene material (EPS), and the biodegradable starch-based ECO-FOAM. These samples were not conditioned and tested as received.

3.4.2 Testing Procedures

3.4.2.1 Compression Test

A Kramer shear press was used to assess and compare the compressive performance of the samples. The press was mounted on an Instron Universal Testing Machine model 4502 equipped with a 500N load cell. The dimensions of the cavity of the press were 65.7 mm by 66.9 mm by 63.5 mm high. The test consisted of filling the cavity with the material and compressing the sample at a constant speed of 80 mm/min. Strain (ε) and compression energy (E) were then calculated from the recorded force vs. displacement curve. Averages were calculated from the three sets of specimens. The energy, E, required to compress the sample up to a force of 500N was calculated as follows:

$$E = \int_{0}^{500N} F(x)\,dx \qquad [3.2]$$

where,

F(x) = force measured at displacement x (N)

E = the area under the force vs. displacement curve (J)

Strain (ε) was a measure of sample deformation when a force of 500N was applied to it. ε was calculated using Equation 3.3. The initial height of the sample, L, is 63.5mm in the test, which is the height the press cavity.

$$\varepsilon = \frac{\delta L}{L} \qquad [3.3]$$

where,

δL = sample deformation at 500N (mm)

L = initial height of the sample (mm)

3.4.2.2 Friability Test

The tumbling friability test was based on the ASTM standard test method C 421-88 entitled: "Standard Test Method for tumbling friability of Preformed Block-Type Thermal Insulation" (ASTM, 1988).

Figure 3.2. The test box and the wooden blocks for Friability test

Friability corresponding to percentage of specimen fragments after tumbling in a 190 x 197 x 197mm wooden box (Figure 3.2) with 19mm solid wooden cubes. The test consisted of placing 12 pieces of test sample in the box along with 24 wooden cubes. The box was then rotated at a speed of 60 rpm for 10 min. Sample mass was measured before and after tumbling. Sample averages were then performed from five replicates. The following equation is used to determine the mass loss:

$$\text{Mass loss, \%} = [(M1 - M2)/M1] \times 100 \qquad [3.4]$$

where,

M1 = initial mass

M2 = final mass

3.4.3 Data Analysis

The collected data were analyzed by *XL*STAT-Pro ver.7.1. Analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine if sample means were determined at the 0.05 level of significance. Regression models were developed with the assistance of CurveExpert 1.38 software Package (Hixson, TN, USA). The package uses the Levenberg-Marquandt method to solve nonlinear regressions.

3.5 Results and Discussions

In this study, kernels of popcorn were popped in a tabletop hot air unit and samples were conditioned to MC ranging from 0 to 50% over a 10 day period. Samples were then subjected to compressive and friability tests, the results are presented below.

3.5.1 Effect of Moisture Content on the Physical Properties of popped Popcorn samples

3.5.1.1 Physical Appearance

The physical appearance of popped popcorn samples were monitored after popping and after conditioning. After popping, popped kernels were well expanded and uniform in colour and shape, which were the characteristic of the freshly popped popcorn. Number of un-popped kernels was minimal indicating the kernels' MC was adequate for popping. The average MC of freshly popped popcorn was 4%.

The physical appearances of the samples conditioned between 0 to 20% MC were similar to the freshly popped popcorn. As shown in Figure 3.3, samples conditioned to 30% had shrunk noticeably. Unfortunately, samples conditioned to 40 and 50% had lost their characteristic shape, were sticky and parts of them covered with molds. They were no longer suitable for further testing.

At 30% moisture level, the popcorn was in the beginning of glass-transition state, the starch matrix became weakened by the moisture and collapsed; thus shrinkage occurred. At 40% and 50% moisture level, the molecules of popcorns were in the glass-transition state, which is heading to a melting stage according to the increase of moisture content. At the same time, the high level of moisture content enhanced the microbial growth, thus molds appeared. Those popcorns with higher than 30% moisture content were considered not suitable for packaging use.

Figure 3.3. Popcorn; *Left*: original popcorn; *right*: 30% MC popcorn.

The dry popcorn cannot be conditioned satisfactorily in order to obtain a 0% MC. Instead, a mean value of 0.8% MC was achievable and it would represent the dry condition. The conditioned popcorns which were brought to mechanical testing and labelled as follows:

Table 3.1. Summary of conditioned popcorns carried to mechanical tests.

Moisture content (MC)	Label
0.8%	MC-1
4%*	MC-2
10%	MC-3
20%	MC-4
30%	MC-5

Remarks: * MC of fresh popped kernels without conditioning.

3.5.1.2 Compression Strength

The effect of MC on the compressive strength of popped popcorn samples was measured using an Instron Universal Testing Machine equipped with a Kramer shear press. Energy (E) dissipated during compression and sample deformations were recorded and compared. A Load-displacement curve of freshly popped popcorn (MC-2) is presented in Figure 3.4. It is a typical curve for the other conditioned popcorns. As the sample was compressed at a constant speed to the limited load of 500N, the applied force and the displacement (deformation) recorded by the load cell kept on increasing smoothly with no visible yield or break points.

Table 3.2 summarizes the output results of strain and energy corresponding to the different conditioned popcorns. As shown in Table 3.2, strain (ε) ranged from 0.572 to 0.739 and the highest value were associated with samples with the highest MC and the lower value of ε associated with samples with the lower MC. With exception of the mean values of ε recorded under MC-1 and MC-2, all differences were significant at the 0.05 level.

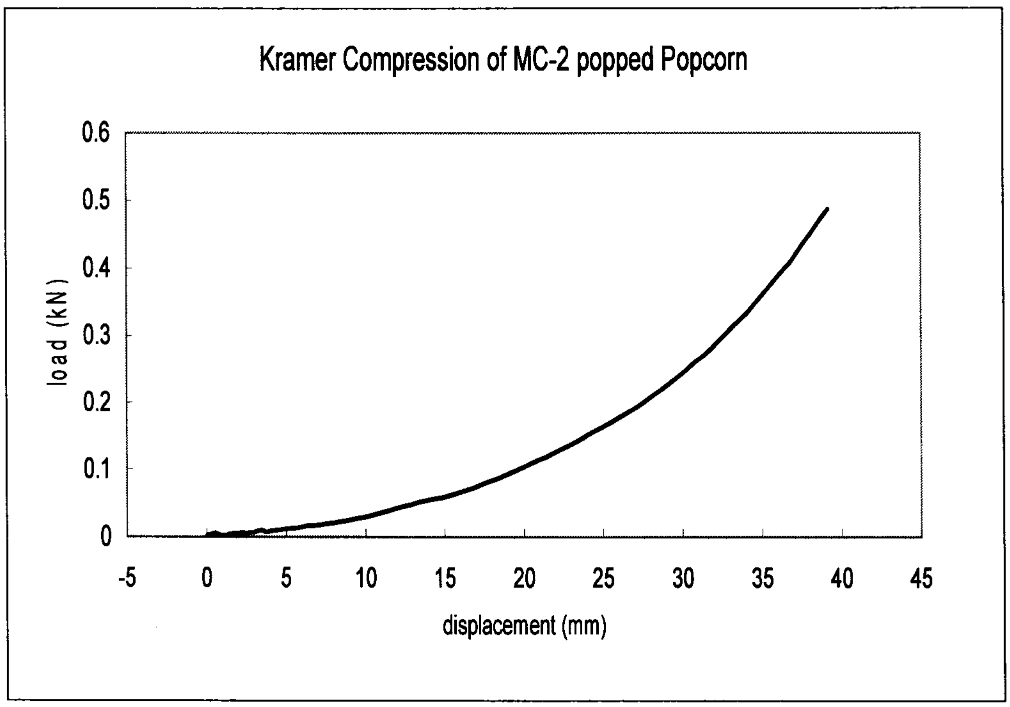


Figure 3.4. Load/ Displacement curve of MC-2 popped popcorns.

Table 3.2. Mean values of strain and energy dissipated of popcorn samples conditioned to different MC.

Treatment	Strain (mm/mm)	Energy (J)	Remarks (MC=)
MC-1	0.578[a]	5.194[a]	0.8%
MC-2	0.572[a]	5.674[b]	4%
MC-3	0.655[b]	5.681[b]	10%
MC-4	0.686[c]	4.527[c]	20%
MC-5	0.739[d]	3.578[d]	30%

* Mean values reported in this table are based on three readings.
**Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

Strain values were plotted against their corresponding MC values (Figure 3.5) and the relationship represented with a first order regression model. The equation is presented below and the coefficient of determination (R^2) value for the model was 0.95:

$$\varepsilon = 0.0058MC + 0.5711 \qquad [3.5]$$

where MC is the percentage of moisture in the samples. This model is very useful to predict the strain as a function of popcorn MC within the range of 0.8 to 30%.

As shown in Table 3.2, the amount of energy dissipated during compression varied from 3.578 to 5.681 J. The lowest E value was recorded in samples with the highest MC; and the highest value was in between the range of MC-2 and MC-3. The mean values of E under MC-2 and MC-3 were not significantly different from each other but significantly higher than the values calculated for the other conditions. The E values were plotted against their corresponding MC values in Figure 3.6. The model best describing the relationship was a rational model which is also known as a weighted inversed polynomial model (Dette et al., 1999). The equation is presented below and the coefficient of determination (R^2) value was excellent at 0.99:

$$E = \frac{(0.50079 + 0.3832MC)}{(1 + 0.024MC + 0.0034MC^2)} \qquad [3.6]$$

This regression model can be used to determine E as a function of popcorn MC in the range between 0.8 and 30%.

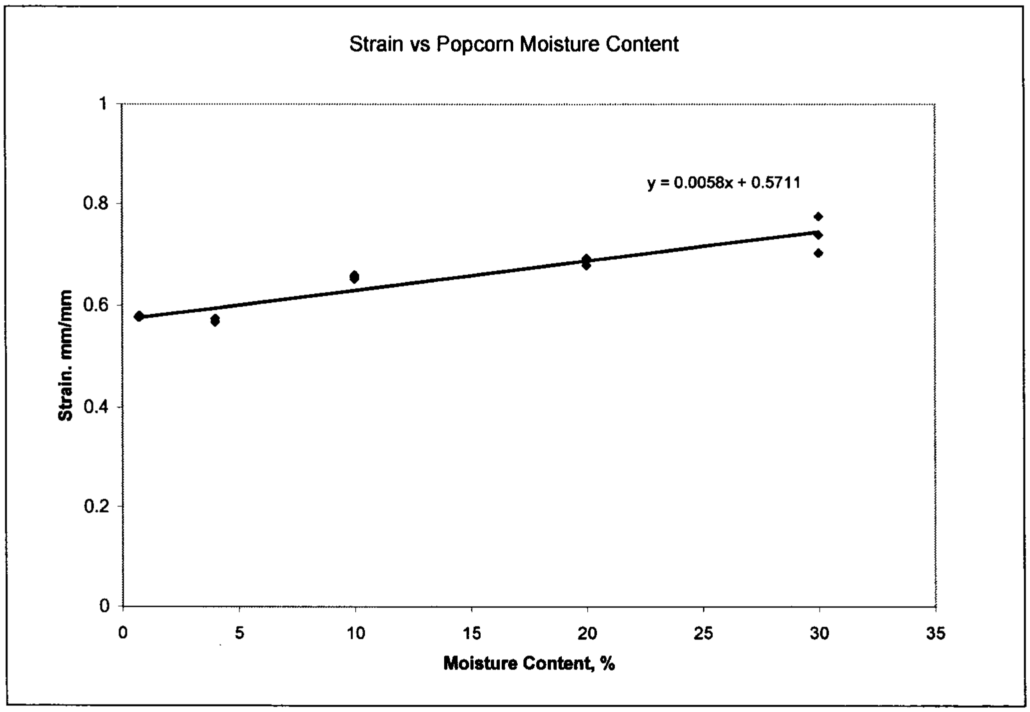


Figure 3.5. Strain (ε) at 500N as a function of popcorn sample moisture content

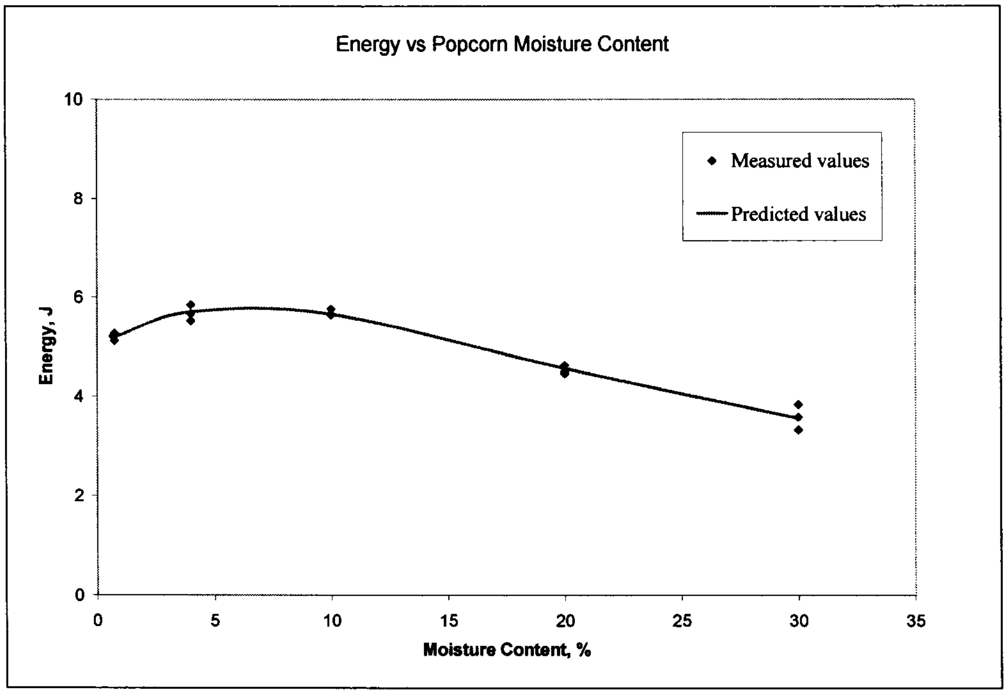


Figure 3.6. Measured and predicted Compression Energy (E) as a function of popcorn sample Moisture content

The important criteria in selecting loose-fill packaging materials are their ability to sustain minimal deformation and to absorb energy when subjected to external stresses. Based on these requirements popcorn samples with MC around 4% (MC-2) was probably the best sample tested.

3.5.1.2 Friability

The effect of MC on the friability of popped popcorn samples was studied using the tumbling apparatus described in the ASTM Standard C421-88. Friability was expressed as the percentage of sample fragments after tumbling samples with solid wooden blocks in a closed box.

Results from the five MC conditions tested are presented in Table 3.3. Highest percentage of fragments was recorded under MC-2 and the lowest under MC-5. The friability appeared to be inversely related to popcorn MC with a slight peak at around MC-2. the difference between the mean friability values for MC-4 and MC-5 was not significant. All other differences were significant at the 0.05 level.

Table 3.3. Mass loss of popcorns in % after Friability test.

Treatment	Mass loss (%)
MC-1	52.013^{a}
MC-2	57.295^{b}
MC-3	44.913^{c}
MC-4	35.480^{d}
MC-5	31.596^{d}

*Mean values presented are based on five readings.
**Duncan groupings: Means with the same letters are not significantly different with a confidence of 95 %

Friability values were plotted against their corresponding MC values in Figure 3.7. The model best describing the relationship was a modified Hoerl model which belongs to the power model family. The regression equation is presented below (Equation 3.7) and the model was in good agreement with the observed value with an R^2 of 0.93.

$$\text{Friability} = \frac{114.7919\,(0.4964)^{1/MC}}{MC^{0.3764}} \qquad [3.7]$$

This regression model can be used to predict sample friability, tested under the same conditions, as a function of popcorn MC in the range of 0.8 to 30%.

The physical appearance of samples after testing is also an important factor for packaging use. Figures 3.8 to 3.11 illustrate some samples of MC-1 to MC-4 after friability test. All the samples led to a wing detachment state after friability test. They all had a very similar shape. During tumbling, the wings were removed and the major part (sphere core) of the popcorn remained without much damage or break down. The reasons for that may be due to the joint parts of the wings having the weakest structural strength. When tumbled, the wings would be easily detached from the sphere core. This action would be similar to polishing the popcorn. Referring to the MC-4 popcorn, small wing edges were not detached completely (Figure 3.11). The results show that it has the least mass compared to the popcorn samples. Samples MC-2 had greater mass loss than other conditioned popcorns. It shows that the change in moisture level may alter the elasticity or flexibility of popcorn, which directly affect the resistance to abrasion and impact.

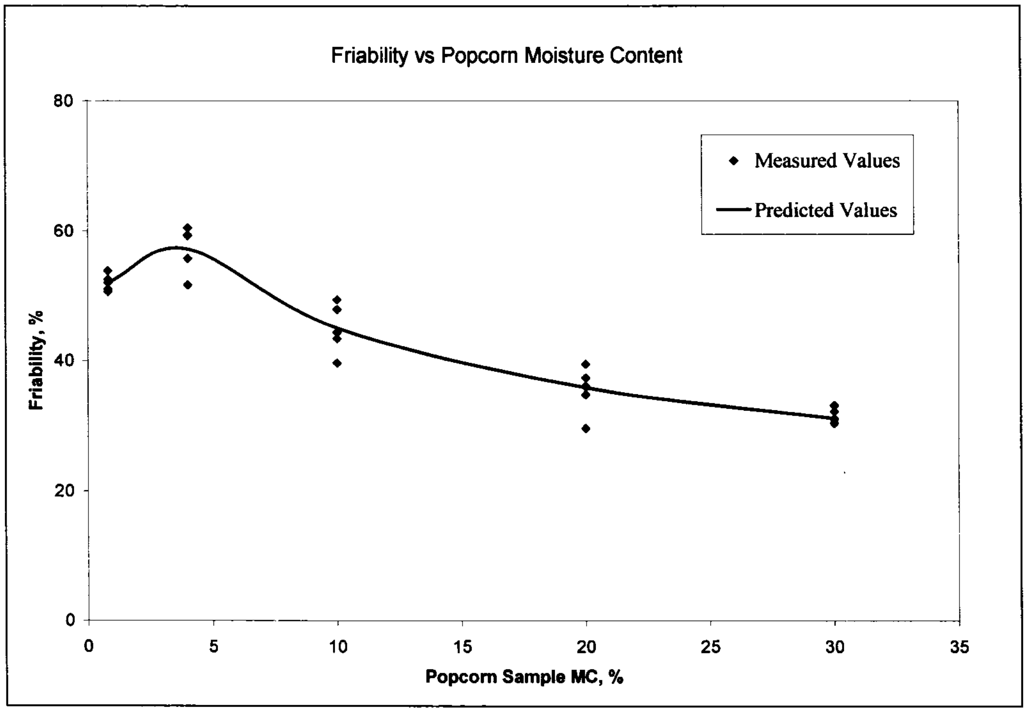


Figure 3.7. Measured and predicted Friability as a function of popcorn sample moisture content.

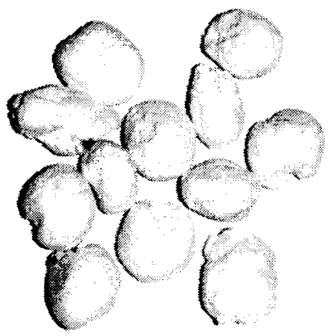


Figure 3. 8. MC-2 samples: after friability.

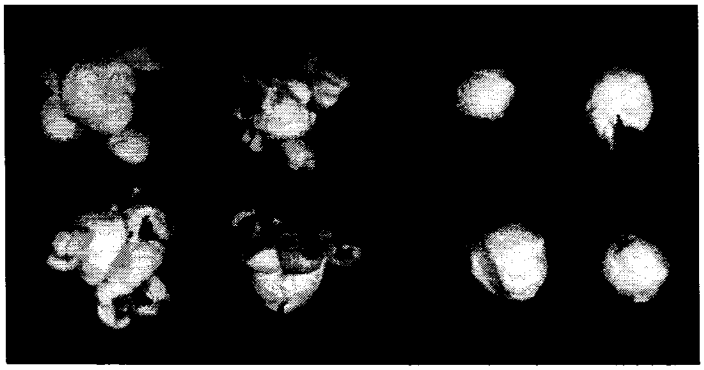


Figure 3.9. MC-1 samples; *Left*: before friability; *Right*: after friability.

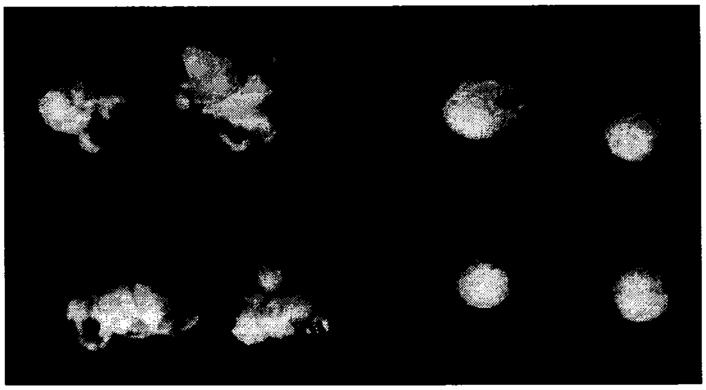


Figure 3.10. MC-3 samples; *Left*: before friability; *Right*: after friability.

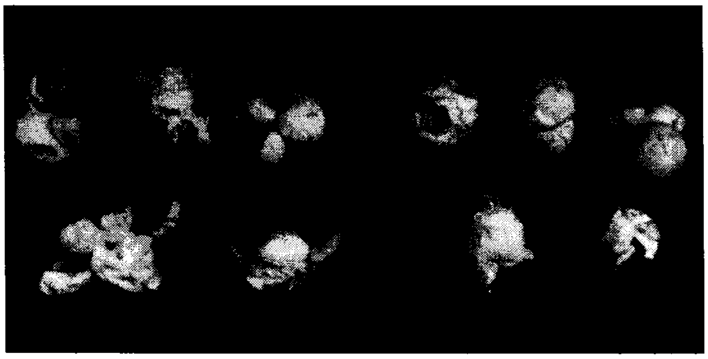


Figure 3.11. MC-4; *Left*: before friability; *Right*: after friability.

3.5.2 Comparative performance of popcorn, EPS and starch-based loose-fill materials

Compressive strength and friability of MC-2 popcorn sample (freshly popped) was compared to two commercially available EPS and starch-based loose-fill materials and the results are presented below.

3.5.2.1 Comparative Compressive Strength

Figure 3.12 shows the load-displacement curve of popcorn and the EPS and starch-based foams under Kramer Compression to 500N load. The two commercial foams show a similar trend of curve. It is noted that the two types of loose-fill foams had a larger displacement at the beginning up to about 0.2kN. Popcorns resulted in a more proportional trend and lesser deformation than the two foams. The popcorns shows a stronger support under compressive stress than the two foams used.

Results obtained from the compressive tests are presented in Table 3.4. At a force of 500N, both EPS and starch based samples had deformed by more that 90% and the difference between the two materials was not significant at the 0.05 level. Under the same load, popcorn sample had deformed by 57% and this value was significantly lower. The mean E values dissipated during the compression force ranged from 4.688 J for EPS to 5.674 J for popcorn. All the differences observed between the three types of samples tested were significant at 0.05 level. From the result, it is clear that compressive strength of popcorn samples appeared superior to either commercially used EPS or starch-based materials. Popcorn sustained less deformation and it was able to dissipate more energy when subjected to a compressive force of 500N.

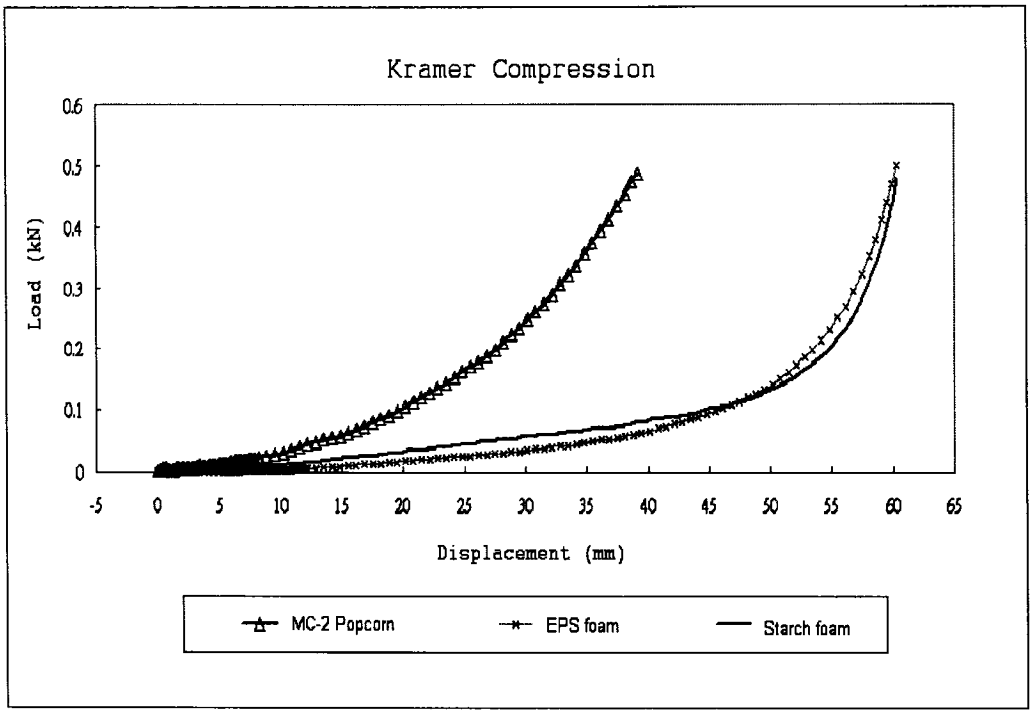


Figure 3.12. Load - displacement curve of MC-2 popcorn, EPS and starch foams.

Table 3.4. Mean values of strain and energy dissipated of Popcorn (MC-2), EPS and Starch-based loose-fill materials

Treatment	Strain (mm/mm)	Energy (J)
MC-2 popcorn	0.572[a]	5.674[a]
Starch foam	0.909[b]	4.993[b]
EPS foam	0.900[b]	4.688[c]

* Mean values reported in this table are based on 3 readings.
**Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

3.5.2.2 Comparative Friability

Results from the friability test indicated that only EPS samples could sustain tumbling impacts by the wooden cubes without breakage (Table 3.5). Both starch-based loose-fills and popcorn samples with friability values of about 57%, sustained considerable damage compared to the EPS. However there was no difference between starch-based foam and popcorn.

Table 3.5. Mean values of friability of MC-2 popcorn, EPS and starch-based foams.

Treatment	Friability (%)
MC-2 popcorn	57.295^{a}
Starch foam	57.376^{a}
EPS foam	0.000^{b}

*Mean values are based on five readings.
**Duncan groupings: Means with the same letters are not significantly different with a confidence of 95 %

It should be noted that the pattern of fragmentation also affects the protection capability. It is important to understand how these materials deform (or fragment) after tumbling. Figures 3.13 to 3.15 illustrate the EPS and starch foams after the friability test. EPS samples resulted in minimal damage or deformation (Figure 3.13). They were compacted slightly after tumbling and without fragmentation. EPS foams had stronger resistance to abrasion and impact. However, Starch foams fragmented after tumbling and broke into fine pieces (Figure 3.14 and 3.15). In Figure 3.15 most parts of the foams are deformed into powder and adhered to the surface of the test box.

Figure 3.13. EPS foam; *Left*: before friability; *Right*: after friability.

Figure 3.14. Starch-based foams, *Left*: before Friability; *Right*: largest pieces collected for mass loss

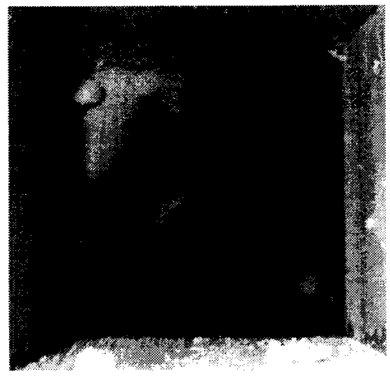


Figure 3.15. Starch-based foam fragments inside the friability test

Comparing the starch-based foams to the popcorns, popcorn resulted in wing loss (Figure 3.5) and the major sphere core remained, which continues to carry out its protective function; however, the fragment pattern of starch foams shows the least resistance to abrasion and impact, which may lead to a poor protective capability when tumbling motion occurs. In this case, popcorn shows a better resistance to movement motion than starch-based foam.

3.6 Conclusion

The results of conditioned popcorn showed that when internal moisture contents at 30% or over, shrinkage occurred and popcorn became sticky and molds grew on the surface. Within 20% MC, popcorns did not have obvious physical change; that moisture level does not affect the basic structure of popcorn molecules. Through mechanical tests, the results showed that the popcorn without conditioning had a better compressive strength than the conditioned popcorns. Thus, the moisture change affects the physical and mechanical properties of popcorn. The relative humidity should be considered as a major factor affecting the strength of popcorn when it is used as a packaging material.

The EPS and starch-based foams show a similar trend of deformation under compression, easily deformed at the beginning under loading. While popcorn deformed more gradually, a proportional curve was obtained within of 500N. The two Loose-fill materials maintain a good supportive strength in compression, while popcorn performed less rapid deformation under constant loading. Under friability test, EPS foam performed the best during testing, but it is not biodegradable. Comparing the two biodegradable materials: starch-based foam and popcorn, they show a similar numerical mass loss. When referring to the cause of mass loss, starch-based foam was fragmented into pieces (and fine dust); it showed that it had a poor resistance to tumbling motion. This results in reducing the protection ability. On the other hand, popcorn had a better resistance. The mass loss was mainly due to detachment of the popcorn wings. The major sphere core remained intact maintaining its protective function. As a packaging material, protection is not just static; the tumbling motion due to transportation also needs to be considered. The dynamic test results show that popcorn has a better resistance to tumbling motion and it can retain its protective function as compared to the starch-based foam.

It is suggested that popcorn can be an alternative to the starch-based foam, as it is natural, environmental friendly and economical. It is stable under compression. In addition, popping is the major process; it has less processing procedure when compared to the loose-fill production from virgin or recycled materials.

3.7 References

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CONNECTING STATEMENT

The previous chapter shows the mechanical performance of popcorn to be compatible with commercial loose-fill. However, lipid degradation is one of popcorn quality concerns when applying popcorn as packaging material. In Chapter IV, removal of popcorn oil is suggested to avoid the rancid potential. The possibility of oil removal at kernel stage of popcorn was also investigated.

IV. DE-OILING POPCORN

4.1 Abstract

For a potential application of popcorn as a packaging material, removal of its oil component to prevent rancidity and degradation is essential. In order to achieve de-oiled product, oil removal at grain kernel and popped kernel stages were studied. The de-oiling process of popcorn was compared at two different stages, before popping (kernel stage) and after popping (popped-kernel stage). Two methods of oil extraction, microwave-assisted and conventional were used and compared. During the experiment, hexane was used as extraction solvent. Microwave-assisted extraction (MAE) was carried out using temperature control not to vaporize the solvent. The extraction temperature was set at 70°C. Due to the limitation in the instrument, the low density of popped popcorn was impossible to be immersed into the solvent inside the MAE extracting tube. Hence, the MAE method is not suitable for oil extraction at the popped kernel stage. The de-oiling process at popped-kernel stage was studied only through conventional method. The results showed that the popping ability of popcorn kernels after extraction by either method was not affected. The study also revealed that oil can be extracted at the popped stage with a more satisfactory result compared to the extraction at kernel stage.

4.2 Introduction

In general, corn kernel contains about 4.5-5% of oil, with 85% of oil contained in the germ (Reiners, 1978). To extract the corn oil, ground kernels are usually applied. The oil content is measured as the amount of lipid extracted from ground grain by non-polar solvents, such as hexane, petroleum ether, or diethyl ether (Weber, 1987). Commercially, hexane is used for oil extraction from corn germs (Mounts and Anderson, 1983). The diffusion rate between solvent and the corn particles is affected by the corn particle size. Finer particles can attain a more efficient extraction at a fixed temperature and solvent concentration (Chein et al., 1990). In this study, the possibility of extracting oil from grain kernel (without grinding) was investigated.

When referring to popcorn to be used as a loose-fill packing material, deterioration possibility is highlighted, for example by lipid degradation. The presence of oil in popcorn may attract pest or have a tendency of becoming rancid during long term storage. Rancidity is a result of lipid degradation, resulting from the oxidation of lipids converting the fatty acid esters into free fatty acids. The degree of rancidity depends on the level of free fatty acid, therefore some oils with high level of fatty acid are easier to become rancid than others. Normally, corn oil has 16 or 18 carbon fatty acid and in low levels, this retards the onset of rancidity (NPAL, 2001). However, rancidity in popcorn still remains an issue if the storage environment is not stable. Remove the oil from popcorn can prevent this potential problem. Besides, popcorn de-oiling may be a necessary procedure to produce low fat healthy snack; and the extracted oil may also be used as food or solvent for drug preparations and manufacture of rubber substitutes (Sprague, 1955).

This study investigated whether de-oiling can be achieved for popcorn, especially at grain stage as grain storage is easier and save more space than the popped popcorn storage. In the study, oil extraction from popcorn was performed at two different stages: grain stage and popped kernel stage. The application here is to produce de-oiled popcorn, thus, popping ability of grain kernels after extraction process were also studied. Conventional heating and microwave-assisted extraction (MAE) methods were applied here.

4.3 Objective

The objective of this study is to reduce or remove the oil from popcorn when popcorn is applied for packaging use. In order to achieve this, the following steps are taken:

1) To extract oil from grain kernels and popped kernels.
2) To study the popping ability of grain kernel after extraction.
3) To compare the oil recovery of ground kernel, grain and popped kernel.

4.4 Materials and Methods

4.4.1 Materials

Orville Redenbacher's Original popping corns were purchased from local stores. The corn kernels come in a plastic bottle of 850g. Figure 4.1 shows the test sample of the kernels. All popping process was carried out using a hot air popcorn popper (Toastmaster, 6202CAN), illustrated in Figure 4.2. For the entire extraction process, hexane was used as the solvent and which was purchased from Fisher Scientific (Nepean, ON, Canada).

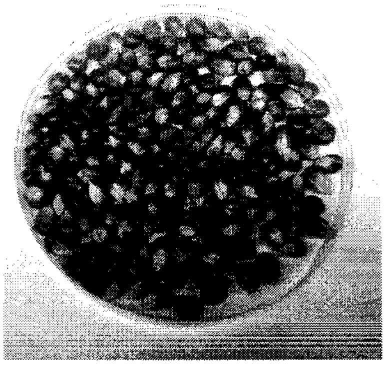


Figure 4.1. Original kernels before testing

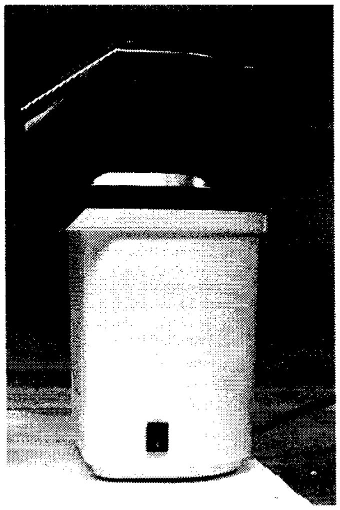


Figure 4.2. Hot-air Popper

Conventional hotplate reflux extraction and microwave-assisted extraction were applied. STAR system 2 (CEM, Matthews, NC, USA) microwave equipment was used for the microwave-assisted extraction processes. The system is equipped with an IR temperature sensor and is part of the software for temperature control. Figure 4.3 shows the schematic diagram of the Microwave system.

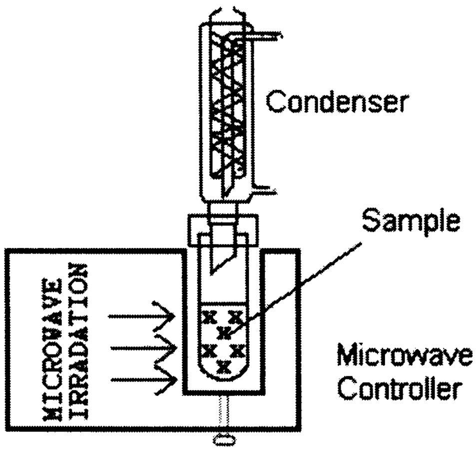


Figure 4.3. Schematic diagram of microwave-assisted extraction system

Microwave-assisted extraction (MAE) is an extraction method that may require less time to prepare the sample and less solvent consumption than conventional extraction methods (Pan et al., 2000). The reduced organic solvent consumption is an important step towards the greening of the analytical laboratory (News, 1995). Microwave-assisted extraction uses microwaves as energy source. The volumetric and selective heating of microwave heating are responsible for the special characteristics of MAE as compared to conventional extraction methods.

4.4.2 Methods

The experiment was mainly divided into 2 stages: grain kernel extraction and popped kernel extraction. After extraction, the de-oiled kernels were popped by a hot air popper to test for the popping ability. The surface colour of the de-oiled popped popcorn was also determined.

For the MAE method, the desired extraction temperature was not achieved due to low density characteristic of popcorn. The popcorn stayed on the top layer of the solvent. Therefore, the MAE method could not be carried out for the popped material. Only the hotplate reflux method was used for the popped stage. Here, the popped material was forced to into the solvent which could not be performed by the MAE equipment.

4.4.2.1 Extraction Procedure

Procedure 1. *Grain kernel stage extraction using hotplate reflux:* Thirty grams of original kernel was placed in a 250mL conical flask, followed by addition of 100mL of hexane. The extraction was carried out at 70-75°C for 30 min. and 60 min. using a hotplate. After extraction, the solvent and the kernel were filtered. The filtrate was evaporated to obtain the oil. The oil amount was determined by measuring the weight of substrate with the container minus the container weight. The oil amount was then divided by the original mass of kernel in order to obtain a percentage (mass/ mass) value.

Procedure 2. *Ground kernel extraction using hotplate reflux:* Thirty grams of ground kernel was heated to 70-75°C with 100mL of hexane for 60 minutes using a hotplate. After extraction, the solvent and the kernel were filtered. The filtrate was evaporated to obtain the oil. This value was considered as the original oil content for comparison.

After extraction, the solvent and the kernel were filtered. The filtrate was evaporated to obtain the oil. This value was considered as the original oil content for comparison.

Procedure 3. *Grain kernel stage extraction using MAE:* Thirty grams of kernel samples were put in a glass vessel of the microwave system and 60mL of hexane added. The temperature was controlled at 70°C during the whole process. The extraction time is 30min.

Procedure 4. *MAE extraction of dehydrated corn:* Dehydrated kernel was prepared using oven for 72 hours at 103°C. After oven drying, it was put in a closed jar immediately with anhydrous calcium sulfate to cool down. Procedure 3 was repeated for the dehydrated kernel.

Procedure 5. *MAE of ground kernel:* The procedure was the same as procedure 3 except that ground kernel was used.

Procedure 6. *Popped stage extraction:* Six grams of whole and crushed popped popcorn were extracted with 150mL hexane at 70-75°C for 60 minutes using hotplate. Oil content obtained here are in term of oil mass (in gram) per popped popcorn mass (in gram). A "Yield factor" is used to convert all the oil content in term of oil mass per kernel mass.

All the procedures were repeated for five replicates. Table 4.1 shows a summary of the experimental design with different conditions. The labels of different conditions will be used in the result section.

Table 4.1. Summary of the experimental design with different conditions.

Method	Kernel state	Extraction time	Label
Conventional	Ground	60 min	KREF
	Whole grain	60 min	60CK
	Whole grain	30 min	30CK
	Popped (ground)	60 min	60PC
	Popped (whole)	60 min	60PP
Microwave	Ground	30 min	30MC
	Whole grain	30 min	30MK
	Whole grain (dehydrated)	30 min	30MD

4.4.2.2 Determination of Popping quality on de-oiled grain kernels

After oil extraction, the grain kernels were placed in an open container inside the fume hood to evaporate the solvent for 24 hours. The grains were conditioned for 10 days in a closed container. It provided a stable environment to equilibrate the moisture content of the grains before popping. For dehydrated grain, conditioning is done by adding water to balance its moisture level back to 13% which is its original level. The moisture content measurement followed the ASAE standard described in section S352.2 (ASAE, 1995). The amount of water needed is determined by the following equation:

$$\text{Moisture added (mL)} = \frac{\mathrm{m_i} \times (MC_f - MC_i)}{100 - MC_f} \qquad [4.1]$$

Where,

m_i = initial mass of sample (g)
MC_i = initial moisture content of sample (%)
MC_f = final moisture content of sample (%)

Approximately 15-18g of corn was placed in a hot air popper cavity. During the popping process, the strong hot air from the popper can occasionally propel some un-popped kernel out of the machine. In order to obtain more accurate popping result, the blown-out kernels were put back into the popper. The number of kernel (before and after popping), the number of popped popcorn produced and their mass were all recorded. The popcorn produced in terms of numbers can also suggest as to how the treatment affects the popping quality.

4.4.2.3 Determination of Yield Factor for Extracted Oil at Popped stage

When oil was extracted from popcorn, the oil content obtained is expressed as percentage of popped kernel. In order to estimate the oil content obtained from popped kernel in terms of grain kernel, a yield factor is needed to express oil content in terms of grain kernel mass. A popping yield factor is determined by dividing the mass of grain kernel by the mass of popped popcorn produced as illustrated in Equation 2. The value of yield factor is in terms of mass per mass. The yield factor is determined by using the original kernels in the following equation:

$$popping\ yeild\ factor = \frac{\text{popped kernel mass (g)}}{\text{grain kernel mass (g)}} \qquad [4.2]$$

This factor was determined experimentally from three different grain masses of 10g, 15g and 20g. The corresponding mass of popped kernel produced was recorded. The experiment for the kernel popping was repeated five times for all the three masses. An average value of popping yield factor was determined by using Equation 4.2. It is to be noted that this particular factor is only applied to this experiment based on the selected hot air popper's efficiency and the selected popcorn kernel samples used. The oil content extracted by popped popcorn in terms of grain can be determined by multiplying this yield factor with the oil content per popcorn mass.

4.4.3 Surface colour of de-oiled popcorn

The surface colour of popcorn was compared after extraction. The round sphere part of the popped popcorn was measured by MINOLTA Chromameter CR300. The values of L, a & b were recorded. L is the lightness coefficient, ranging from 0 (black) to 100 (white) on the vertical axis. Positive "a" value is purple-red and the negative is blue-green on the horizontal axis. Positive "b" represents yellow and the negative value represents blue on the second horizontal axis.

4.4.4 Data Analysis

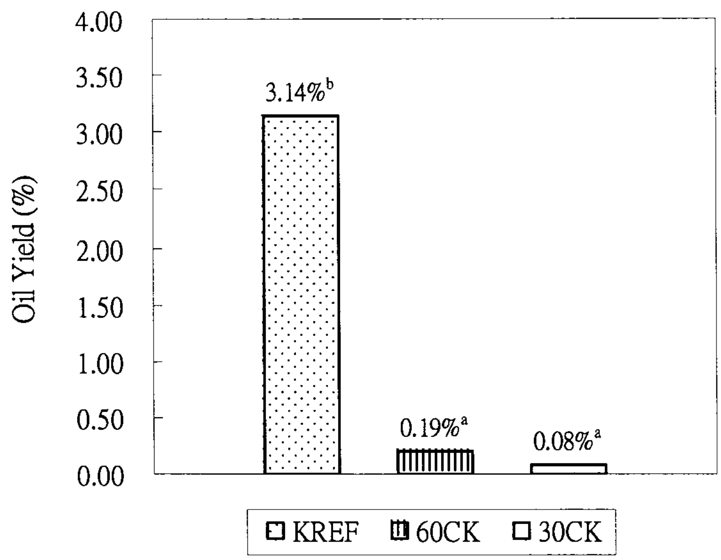
The collected data were analyzed by *XL*STAT-Pro ver.7.1. Analysis of variance (ANOVA) and Duncan's multiple range tests were used for comparison. Significant differences were determined at the 0.05 significance level for all cases.

4.5 Results and Discussion

The extracted oil was determined as a percentage of the grain kernel produced. At popcorn stage, the extracted oil was multiply by a conversion factor (mass yield) which was found to be 1.15 in this study.

4.5.1 Grain stage extraction

Figure 4.4 illustrates the amount of oil extracted (oil yield, %) by conventional method. Ground kernel and grain kernel were processed. With 60 min. extraction (60CK) the amount of oil extracted was almost double as compared to the 30 min. extraction (30CK), but they are not significantly different to each other. However, the amount of oil obtained at 60CK is about 6% of the oil obtained by ground kernel (KREF). The large difference shows that it is not efficient to extract oil at grain stage by conventional method. Also, it is believed that the hard shell (pericarp) of the grain is the main reason for the low amount of oil extraction, which acts as an obstructer.



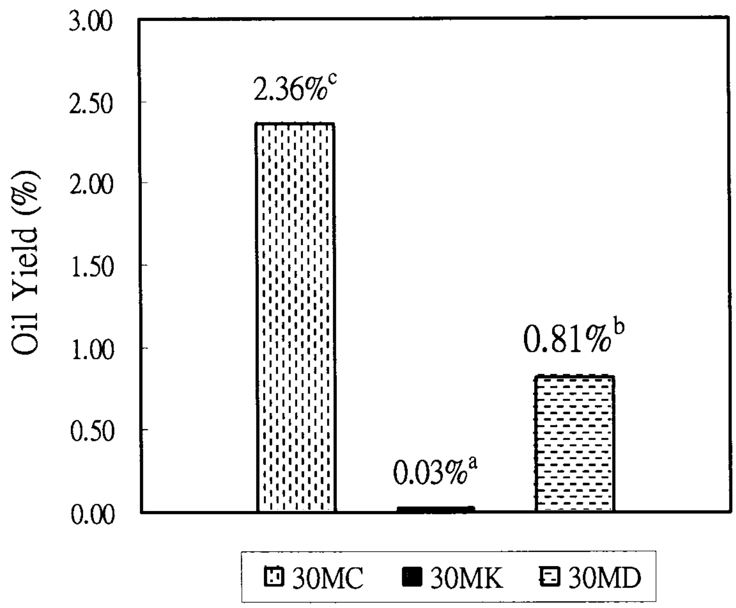
Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

Figure 4.4. The yield of oil extraction by conventional method.

Figure 4.5 illustrates the amount of oil extracted (oil yield, %) by MAE method. Oil content extracted from the ground kernel, grain kernel, and dehydrated grain kernel are presented. The extracted amounts are significantly different from each other. Amount of oil extracted from 30MC has the highest value than the other two kernels extracted by microwave. The amount of oil extracted from dehydrated kernels (30MD) is larger than grain kernels (30MK). MAE is based on the activation of polar component within kernel to motivate the non-polar component (oil) to dissolve into the solvent. However, the result shows that oil obtained from dehydrated kernel (30MD) was about 27 times more than from grain kernel without treatment (30MK). As the kernels were dehydrated thus losing water (the polar component), it helped to obtain a higher amount of oil from the matrix.

The reason for the 30MD in higher oil content is attributable to the drying process. Most of the oil stored in the germ might have been dislodged internally by the oven heat (105°C). Also it might have changed the diffusion characteristics of the seed coat. It is suggested that these changes led to the better oil extraction capability by the MAE method.

The result also shows that 30 minute extraction with grain kernel is not as effective as the ground kernel. Ground kernel shortened the contact distance between solvent and the extract that enhanced the extraction surface area. Thus, ground kernel results in a better yield.



Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

Figure 4.5. The yield of oil extraction by MAE method.

4.5.1.1 Popping ability of de-oiled grain kernels

After extraction, all the de-oiled grain kernels were popped and Table 4.2 summarizes the result of the popped popcorn as a percentage of number of popcorn produced in relation to the number of grains used. Dehydrated kernels (30MD) were re-hydrated to 13% MC before popping. Other de-oiled grain kernels were popped without any addition of moisture.

Table 4.2. Results of the popping quality of kernels

Method	60CK	30CK	30MK	30MD
Popping Ratio	99%^{a}	100%^{a}	100%^{a}	95%^{b}

Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

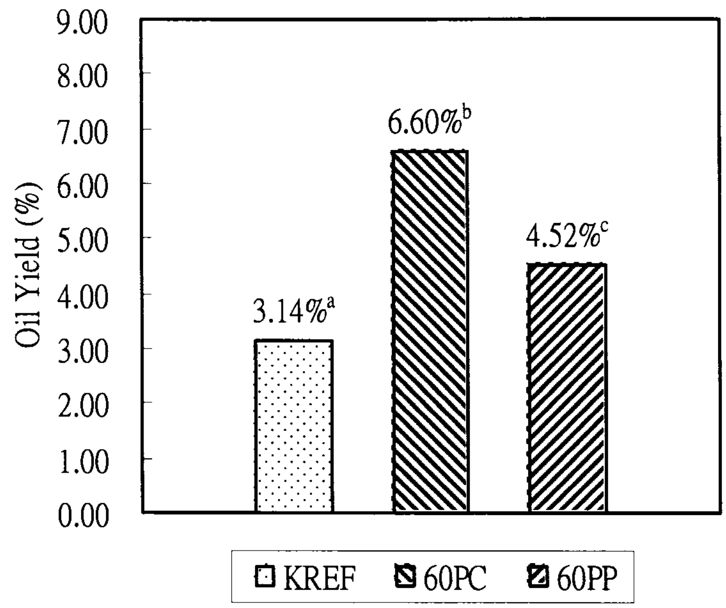
The result shows that the kernels of 60CK, 30CK, 30MK are not significantly different in popping ratio. They were almost 100% pop-able after extraction. The extraction process did not affect much on their popping ability. The popping mechanism was mainly caused by the internal moisture vaporization of the kernel. But, in this case popping may also be due to the vaporization of solvent residue. Although solvent was evaporated before popping, small amount of solvent might have remained in the de-oiled kernel. It is technically difficult to either determine the amount of solvent remained in the de-oiled kernels or to remove the solvent completely from the kernels. When the kernels are subjected to popping, the high temperature environment which is over 180°C would evaporate the remaining solvent from the kernel at the time of popping.

In general, the kernels can be popped after the extraction process in any of the extraction method. The de-oiling does not have much influence on the popping ratio. However, the dehydrated kernels show a slight decrease in the popping ratio, and the dehydration process would be the major cause. It might have affected the kernel component or structure leading to the changes in popping characteristics.

4.5.2 Popped stage extraction

The amount of oil extracted from the popped kernel (60PC, ground and 60PP, whole) is compared with the initial oil content obtained from the ground kernel (KREF). The result is presented in Figure 4.6. The oil yield of the popcorn was about 4.52% and it is close to the value of the ground popcorn whose value is 6.6%. The oil yield in the popcorn stage extraction shows a higher yield than the ground kernel (grain) extraction.

In the popping process, the lipids are released from the germ to the endosperm. The inner and other parts of the kernels are "flipped-over" when popped. As a result, the majority of germ is being exposed and easier for oil release. Extraction surface area is also increased which helps the extraction process. Furthermore, the high temperature at popping might have broken down some of the component into other forms of lipids. Therefore, the lipid component extracted from the popcorn is higher than the ground kernel. From the aspect of using popcorn as a packing material, the main intent is to remove oil from popcorn, and this result shows that the efficient way of removing lipids or obtaining oil is at popcorn stage.



Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

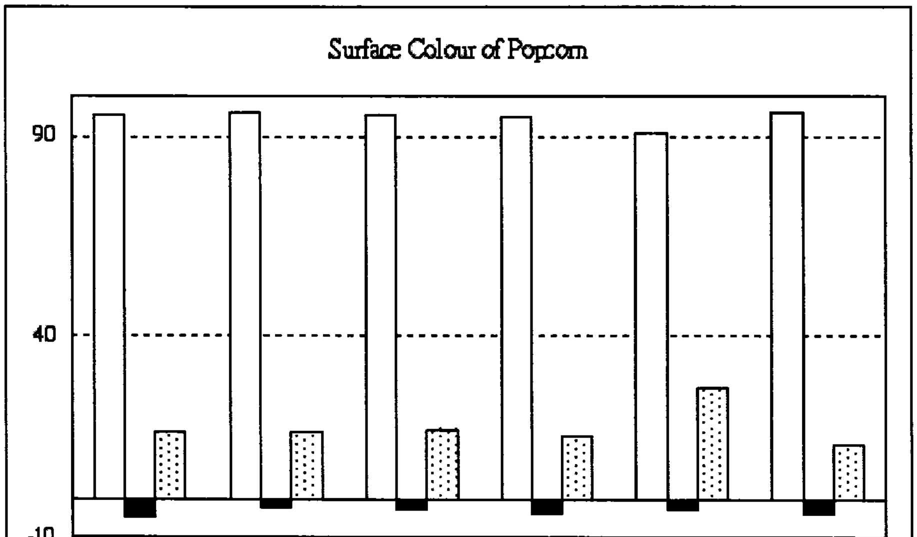
Figure 4.6. The yield of oil extraction at popcorn stage and ground kernel

4.5.3 Surface colour of de-oiled popcorns

The surface colour of popcorn was measured as a comparison for all the methods. The colour of all the samples were measured in L, a and b scale which are presented in Figure 4.7. The result shows that the de-oiled samples are not significantly different from the original value (KREF, as popcorn with no treatment).

The extraction process did not affect much of the colour of popcorn prior to popping. It may be due to the low amount of oil extracted, and / or the low amount of oil present in popcorn which does not affect much of its colour. Extraction at the popcorn stage gives the whitest colour, which could be due to the amount of oil removed and the extraction method used.

The dehydrated kernel (30MD) shows a browner colour than other popcorns. The colour of it is significantly different from others, while the colour of other treatments is not significantly different from one another. Thus, dehydration treatment could be the reason affecting the endosperm of the kernels during popping. The pre-heat treatment might lead to Maillard reaction that causes the browning. When more heat was subjected to the kernels, a brownish colour occurs. It also shows that the method of kernel preparation and method of extraction could directly affect the colour of popcorn.



	KREF	60CK	30CK	30MK	30MD	60PP
L	95.73^{a}	95.84^{a}	95.71^{a}	94.94^{b}	91.17^{c}	95.83^{a}
a	-4.45^{a}	-2.29^{a}	-2.64^{a}	-3.69^{ab}	-2.73^{b}	-3.60^{ab}
b	16.60^{a}	16.55^{a}	17.09^{a}	15.26^{a}	27.08^{b}	13.57^{a}

Duncan groupings: Means with the same letters are not significantly different with a confidence of 95%

Figure 4.7. Surface colour of de-oiled popcorn

4.6 Conclusion

Throughout this study, it is found that the extraction method at grain kernel stage is not efficient by either conventional or MAE methods. With an outer shell (pericarp and endosperm) protection, the oil is difficult to extract from the germ. Moreover, in this study, extraction by MAE methods did not show a better efficiency than the conventional method at grain kernel stage extraction. Extraction for a longer period has minor influence on the popping ratio. Popping characteristics of popcorn is affected by the dehydration and dehydration operation.

Results show that extraction at popcorn stage leads to a higher value of oil extracted. Thus, de-oiling at popped popcorn stage is suggested when popcorn is used as a packaging material. This can minimize the rancidity problem caused by the lipids.

4.7 References

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V. GENERAL CONCLUSIONS AND RECOMMENDATIONS

Selecting popcorn for cushioning purpose as loose-fills in packaging is friendly to the environment. It is completely natural. The production is simpler than synthetic loose-fills as heating is the only requirement for popping. In Chapter III, popcorn shows a good compressive strength and abrasion/impact resistance. These mechanical properties are comparable to the existing plastic foam. Popcorn shows a better performance than starch-based foam in dynamic testing. The results show that within 20% moisture content, the popcorn can maintain a good mechanical strength. If the humidity of the environment allows the popcorn moisture content to be maintained within 20% (this MC value is for the type of popcorn used in this study, other types of popcorn may vary in this value), it is suggested to use popcorn for packaging.

In general, corn oil is considered as a stable oil. If it is subjected to a stable environment, the risk of rancidity occurring in popcorn is minimal. In addition to pest and temperature control, the potential problem of that food grade material can be minimized through de-oiling. In Chapter IV, removal of oil was studied to explore the possibility of oil removal at kernel stage of popcorn. De-oiled grain kernels can improve the storability which can save more space in store than popped kernel. Test results show that it is not advantageous to remove oil at that stage. Nevertheless, the de-oiled kernel after the extraction treatment retains the popcorn properties: pop. The oil extraction at popped stage results in higher yield. To produce de-oiled popcorn, the de-oiling process at popped stage is recommended. The final product (popped) after de-oiling can be used for packaging; the chance on rancidity is minimal. Furthermore, solvent is removed (evaporated) after extraction, but small amount of residue may be retained. The popcorns thus prepared are to be used for non-consumption (non-food) purpose.

In order to have further understanding of popcorn, the packaging test at different temperatures and humidity which can affect the moisture content of popcorn would be recommended. Other physical parameters such as size, shape unit density, and bulk density corresponding to moisture content change are to be studied. As food grade material, storability of popcorn in an unstable environment should also be investigated. Removal of oil from popcorn with different methods needs to be carried out in future investigations. It may help to understand the possibility of de-oiling at the grain kernel stage, which could help in either packaging industry or the food industry to determine whether de-oiled popcorn kernel can be consumed when just popped.

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