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Physico-chemical Properties of Bioplastics and its Application for Fresh-cut Fruits Packaging

（バイオプラスチックの理化学特性とカットフルーツ包装への応用）

Hokkaido University
Graduate School of Agriculture

Division of Environmental Resources
Doctor Course

Huijuan ZHOU

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Abstract

1. Introduction

Climate change and energy shortage are currently key global issues. Plastics account for approximately 5% of worldwide oil consumption. Growing demand for more environmental preservation and resource conservation, greater sustainability is taken into consideration. Plastics, mainly derived from crude oil, comprised 37% of food packaging material, which is more than metal, glass and paper as packaging materials. Therefore, the whole doctoral research aimed to study whether bioplastics, such as polylactic acid (PLA) and bio-based polyethylene (PE), could be an appropriate alternative to conventional petroleum-based plastic for food packaging.

2. Physico-chemical properties of bioplastics as a food packaging

Food packaging is expected to deliver high-quality product during distribution. The selection of packaging form and materials should be primarily based on considerations of food safety, followed by quality, cost, etc. Important properties of common packaging materials are generally mechanical, optical and barrier properties. Mechanical properties include tensile elasticity, tensile stress and breaking elongation, optical properties refer to transparency, haze, etc., and barrier properties involve water vapor transmission rate and gas transmission rate. These characteristics are mainly based on the physical properties such as crystallinity, molecular weight, etc. of bioplastics.

Tensile elasticity of petroleum-based low-density PE (LDPE, thickness: 30 μm), bio-based LDPE (30 μm) and PLA (25 μm) were 223.5, 248.4 and 2555.6 MPa, respectively. This means that PLA possessed highest stiffness among the plastics determined. Tensile elasticity of bioplastics decreased as thickness decreased and as temperature increased, which meant flexibility of bioplastics increased when temperature increased. As temperature decreased, the effect on mechanical properties of plastics increased. Moreover, machine and transverse direction of a plastic sample also affected its mechanical properties. Bio-based LDPE indicated similar mechanical properties to petroleum-based LDPE.

As thickness of petroleum-based PE increased, transparency decreased. For the same thicknesses of LDPE samples, petroleum-based LDPE with lower crystallinity showed higher transmittance of visible light than that of bio-based LDPE representing in higher transparency. The transmittance of visible light of PLA was the highest among the plastics analyzed in this study.

At 23°C and 50% relative humidity, water vapor transmission rate of PLA (25 μm) was 54.4 $g/m^2 \cdot d$, in contrast, the water vapor transmission rates of petroleum-based and bio-based LDPE (30 μm) were 7.3 and 3.7 $g/m^2 \cdot d$. The plastic film provided a resistance to water vapor

transfer across it, thus the molecular structure of plastics could be a factor, which affects water vapor transferring through plastic material. Compared with PE, hydrophilic molecular structure in PLA material indicated higher water vapor transmission.

Due to these physico-chemical properties, bio-based LDPE could be applied as an alternative to petroleum-based LDPE, while PLA, which was bio-based and biodegradable, was brittle and transparent so that it can be applied as food packaging containers.

3. Application of bioplastics for fresh-cut fruits packaging

The market of the chilled fresh-cut produce has witnessed dramatic growth in recent years, stimulated largely by consumer demand for fresh, healthy, convenient and additive-free foods, which are safe and nutritious. Minimally processed fresh-cut fruits are very perishable and usually have a shelf life of 5-7 days at 1-7°C. In this study, packaging containers made from PLA and polyethylene terephthalate (PET) were examined for their ability to preserve the quality of fresh-cut melon and pineapple under low temperature conditions (<10°C). Changes in quality of fresh-cut melon and pineapple packed in PLA and PET containers, including weight loss, juice leakage, surface color, firmness, soluble solids content (SSC), pH, titratable acidity (TA), vitamin C and sensory quality, were evaluated during the storage. Overall quality of fresh-cut melon and pineapple declined regardless of the packaging material. Melon and pineapple cubes in both packages increased in weight loss, juice leakage and TA and also decreased in surface color (L*, a*, b*), firmness, SSC, pH, vitamin C and sensory evaluation. No significant differences in juice leakage, color, firmness, SSC, pH, TA, vitamin C and sensory evaluation of fresh-cut melon and pineapple were observed in either of the packages stored at 4°C.

Melon and pineapple cubes that were stored at 10°C deteriorated on the 10th and 7th sampling day, respectively. Also a large amount of fungi in both fruit cubes was clearly observed in the PET containers. Significant differences in color (L*, a*, b*, ΔE) between the melon cubes in the two packages were recognized after 7-day storage at 10°C. Significant differences in juice leakage and color (L*, ΔE) between the pineapple cubes in the two packages were recognized after 5 days of storage at 10°C. Due to higher water vapor transmission rate and oxygen permeability, the PLA containers used in this study maintained overall quality of fresh-cut melon and pineapple better than did the PET containers at 10°C during 10 days of storage.

4. General conclusions and recommendations

In this study, bio-based PE showed comparable properties to those of petroleum-based PE. The PLA containers, bio-based and biodegradable, used in this study maintained overall quality of fresh-cut fruits better than did the PET containers during storage. In conclusion, bioplastics would be an appropriate alternative for food packaging material from the viewpoint of the environmental preservation and sustainability.

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Chapter 1 Introduction and literature review

1.1 Introduction and background

The term “plastic” is derived from the Greek word “plastikos” meaning fit for moulding, and “plastos” meaning moulded. It refers to the material’s malleability, or plasticity during manufacture, that allows it to be cast, pressed, or extruded into a variety of shapes, such as films, fibres, plates, tubes, bottles, boxes, and much more. Plastic is the general common term for a wide range of synthetic or semi-synthetic materials used in a huge, and growing, range of applications.

Everywhere you look you will find plastics. We use plastic products to help make our lives cleaner, easier, safer and more enjoyable. You will find plastics in the clothes we wear, the houses we live in, and the cars we travel in. The toys we play with, the televisions we watch, the computers we use and the CDs we listen to contain plastics. Even the toothbrush you use every day contains plastics.

Plastics are organic, the same as wood, paper or wool. The raw materials for plastics production are natural products such as cellulose, coal, natural gas, salt and, of course, crude oil. Plastics are today’s and tomorrow’s materials of choice because they make it possible to balance modern day needs with environmental concerns.

Plastics are derived from organic products. The materials used in the production of plastics are natural products such as cellulose, coal, natural gas, salt and, of course, crude oil.

Crude oil is a complex mixture of thousands of compounds. To become useful, it must be processed. The production of plastic begins with a distillation process in an oil refinery. The distillation process involves the separation of heavy crude oil into lighter groups called fractions. Each fraction is a mixture of hydrocarbon chains (chemical compounds made up of

carbon and hydrogen), which differ in terms of the size and structure of their molecules. One of these fractions, naphtha, is the crucial element for the production of plastics.

The two major processes used to produce plastics are called polymerisation and polycondensation, and they both require specific catalysts. In a polymerisation reactor, monomers like ethylene and propylene are linked together to form long polymers chains. Each polymer has its own properties, structure and size depending on the various types of basic monomers used.

There are many different types of plastics, and they can be grouped into two main polymer families: thermoplastics (which soften on heating and then harden again on cooling) and thermosets (which never soften when they have been moulded).

Even at the end-of-life phase, plastics remain a too valuable resource to be simply thrown away. If Europe was exploiting the full potential of plastics for recycling and recovery and applying today's best practices and technologies in an eco-efficient* manner, this would lead to a saving in natural resources equivalent to 25% of France's annual oil consumption and reduction of 9 million tonnes/year of CO2 emissions, which represents a significant contribution to climate protection.

Such improvements will require appropriate actions to ban land filling of plastics and the establishment of recovery-oriented collection schemes. These will need to be aligned with modern sorting infrastructure and improved recycling and recovery in order exploit the fullest potential of this precious resource. Furthermore with a focus on high quality and market standards this will stimulate markets for the more resource efficient use of end-of-life plastics throughout Europe.

Although plastics have been around for about 100 years they are considered to be modern when compared to traditional materials like wood, stone, metal, glass and paper. In

recent decades plastics have enabled numerous technological advancements, new design solutions, eco-performance enhancements and further cost-savings.

Nowadays, thanks to plastics, the only limitation for designers is their imagination. Diminishing natural and non-renewable resources, climate change and an ageing and growing population are some of the main challenges for society to rise up to. If plastics did not exist, we would probably need to invent to tackle thse issues.

1.2 Plastics

1.2.1 Worldwide use of plastics

Plastics are a 21st century material driving the development of pioneering innovations to meet society's biggest challenges. They help improve resource efficiency with smarter, more efficient and sustainable use of natural resources.

Global plastics production increased by 10 million tons (3.7%) to around 280 million tons in 2011, and continued the growth pattern that the industry has enjoyed since 1950 approximately by 9% per annum. Today, climate change and energy shortage are key global challenges. Plastics account for approximately 5% of worldwide oil consumption. The industry still continues to look for new ways to lower the amount of oil used to produce plastics, which means finding alternative raw materials to meet environmental challenges.

Changing lifestyles have dictated the need for foods that offer convenience to the consumer in a myriad of ways, such as minimizing preparation time, easy opening of the container and single service, while also offering high quality throughout an extended shelf life. Plastic packaging has responded to these demands, and creativity with plastics has been limited only by the imagination of the designer.

Polypropylene was discovered in 1954 by Giulio Natta, and commercial production of the resin began in 1957. It is the single most widely used thermoplastic globally. It is a very useful cost-effective polymer and can be injection, moulded, blow-moulded, thermoformed, blown film extruded or extruded into a variety of products. Examples of these include flexible barrier film pouches (including the biaxially oriented packaging film used for crisps and nuts); stackable crates for transport and storage, caps and closures for containers, blow-moulded bottles, thin-walled containers (e.g. margarine tubs, yoghurt cups, food trays) used in the food industry; and tree shelters, soil sieves, fork handles, mulch films, and glass

replacement, window/door frames, water or sewage pipes and geomembranes used in building applications. Polypropylenes are also used in household goods such as bowls, kettles, cat litter trays; personal goods such as combs, hair dryers, film wrap for clothing; and in other packaged goods.

Polyethylene terephthalate (PET)'s discovery is credited to employees of the Calico Printers' Association in the UK in 1941; it was licensed to DuPont for the USA and ICI otherwise, and as one of the few plastics appropriate as a replacement for glass in many circumstances, resulting in widespread use for bottles in Europe.

In 1839, Goodyear invented vulcanized rubber, and Eduard Simon, a German apothecary, discovered polystyrene (PS). Developmental work continued through the nineteenth century on natural/synthetic polymers producing such notables as celluloid for billiard balls, polyvinyl chloride (PVC), which is used in myriad applications, and viscose (rayon) for clothing. Development of modern plastics really expanded in the first 50 years of the twentieth century, with at least 15 new classes of polymers being synthesized . The success of plastics as a material has been substantial; they have proved versatile for use in a range of types and forms, including natural polymers, modified natural polymers, thermosetting plastics, thermoplastics and, more recently, biodegradable plastics. Plastics have a range of unique properties: they can be used at a very wide range of temperatures, are chemical and light-resistant and they are very strong and tough, but can be easily worked as a hot melt. It is this range of properties together with their low cost that has driven the annual worldwide demand for plastics to reach 245 million tonnes (PlasticsEurope 2008) today. Even at a somewhat conservative annual growth rate of 5 percent, a continuation of this trend suggests that at least 308 million tonnes of plastics will be consumed annually worldwide by 2010 (PlasticsEurope 2008). This projected growth is mainly attributed to increasing public demand for plastics. Here we summarize the main types of plastic in use today.

The production of plastic begins with a distillation process in an oil refinery. The distillation process involves the separation of heavy crude oil into lighter groups called fractions. Each fraction is a mixture of hydrocarbon chains (chemical compounds made up of carbon and hydrogen), which differ in terms of the size and structure of their molecules. One of these fractions, naphtha, is the crucial element for the production of plastics.

The two major processes used to produce plastics are called polymerisation and polycondensation, and they both require specific catalysts. In a polymerisation reactor, monomers like ethylene and propylene are linked together to form long polymers chains. Each polymer has its own properties, structure and size depending on the various types of basic monomers used.

Due to their relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in an enormous and expanding range of products

Although literally hundreds of plastic materials are commercially available, only a handful of these qualify as commodity thermoplastics in terms of their high volume and relatively low price. These plastics and their fractional consumption on a global basis are shown below. Low density polyethylene (LDPE), high density PE (HDPE), polypropylene (PP), PVC, PS and polyethylene terephthalate (PET) account for approximately 90 percent of the total demand.

The plastics industry aims to be a responsible partner to policy-makers and other stakeholders in finding solutions to the crucial issues of climate change, energy and resource efficiency, consumer protection and waste management. Plastics have a great potential to help deal with these issues and this is the reason why Plastics Europe is working closely with the value chain to develop a common plastics industry vision and approach.

Plastic plays a major role in delivering and sustaining the quality, comfort and safety of

modern life-styles. Its impressive ratio of cost to performance also means that people of all income groups can enjoy these benefits. But meeting the needs of society is not just about "today". Future generations also have the right to material and other benefits. Meeting the needs of tomorrow is the foundation of the concept of ‘Sustainable Development’. Plastic products are already helping every day to improve people’s lives, whilst conserving natural resources and helping to protect the environment for tomorrow, in a world that is growing in population, with ever-increasing demands for water, food, shelter, sanitation, energy, health services and economic security.

1.2.2 Bioplastics

Bioplastics are not a single kind of polymer but rather a family of materials that can vary considerably from one another. There are three groups in the bioplastics family, each with its own individual characteristics: Bio-based or partially bio-based non-biodegradable plastics such as bio-based PE, PP, or PET and bio-based technical performance polymers such as PTT; Plastics that are both bio-based and biodegradable, such as PLA and PHA or PBS and plastics that are based on fossil resources and are biodegradable, such as PBAT.

Bio-based plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, cornstarch, pea starch or microbiota. Common plastics, such as fossil-fuel plastics, are derived from petroleum; these plastics rely more on fossil fuels and produce more greenhouse gas.

1.2.2.1 Development of bioplastics

The first known bio-based plastic, polyhydroxybutyrate (PHB), was discovered in 1926 by a French researcher, Maurice Lemoigne, from his work with the bacterium Bacillus megaterium. The significance of Lemoigne’s discovery was overlooked for many decades, in large part because, at the time, petroleum was inexpensive and abundant.

The petroleum crisis of the mid-1970s brought renewed interest in finding alternatives to petroleum-based products.

The rise of molecular genetics and recombinant DNA technology after that time further spurred research, so that by the beginning of the 21st century the structures, methods of production, and applications for numerous types of bio-based plastics had become established.

Bio-based plastics that were either in use or under study included PHB and polyhydroxyalkanoate (PHA), both of which are synthesized within specialized microbes, as well as polylactic acid (PLA), which is polymerized from lactic acid monomers produced by microbial fermentation of plant-derived sugars and starches.

Bio-based plastics currently make up an insignificant portion of total world production of plastics. Commercial manufacturing processes are expensive. However, improvements in metabolic and genetic engineering have produced strains of microbes and plants that may significantly improve yields and production capabilities while reducing overall costs. These factors, when added to increasing oil prices and growing environmental awareness, may expand the market for bio-based plastics in the future.

Biodegradable plastics are plastics that are capable of being decomposed by bacteria or other living organisms.

ASTM International defines methods to test for biodegradable plastic, both anaerobically and aerobically, as well as in marine environments. The specific subcommittee responsibility for overseeing these standards falls on the Committee D20.96 on Environmentally Degradable Plastics and Bio based Products. The current ASTM standards are defined as standard specifications and standard test methods. Standard specifications create a pass or fail scenario whereas standard test methods identify the specific testing parameters for facilitating specific time frames and toxicity of biodegradable tests on plastics.

There are two testing methods for anaerobic environments they are the ASTM D5511-12 or ASTM D5526-12 Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions. Both of these tests are used for the ISO DIS 15985 on determining anaerobic biodegradation of plastic materials.

The production and use of bioplastics is sometimes regarded as a more sustainable activity when compared with plastic production from petroleum (petroleum-based plastic), because it relies less on fossil fuel as a carbon source and also introduces fewer, net-new greenhouse emissions if it biodegrades. They significantly reduce hazardous waste caused by oil-derived plastics, which remain solid for hundreds of years, and open a new era in packing technology and industry.

Bio-based plastics have experienced fast growth in the past decade thanks to the public concerns over the environment, climate change and the depletion of fossil fuels. Bio-based plastics account for around 1% of global plastics production. They have experienced a rapid growth over the last decade. In 2011, bio-based polyethylene beverage bottles, yogurt pots and hair care packaging became widely available. This perspective provides an overview of the current global market of bio-based plastics, their material properties, technical substitution potential and future market (for 2020).

Global capacity of bio-based plastics is expected to reach 3.45 million metric tonnes (An SI unit of mass, equivalent to a thousand kilograms. It is often pronounced 'tunny' to distinguish it from the ton). In 2020, Starch plastics, PLA, bio-based polyethylene, polyhydroxyalkanoates (PHA) and bio-based epoxy resin are expected to be the major types of bio-based plastics in the future.

The increased use of renewable resources is an important step towards a solution. Life cycle analysis shows that bio-based plastics enable a significant CO2 saving-up to carbon

neutrality compared to conventional plastics, depending on the feedstock, the product and the application.

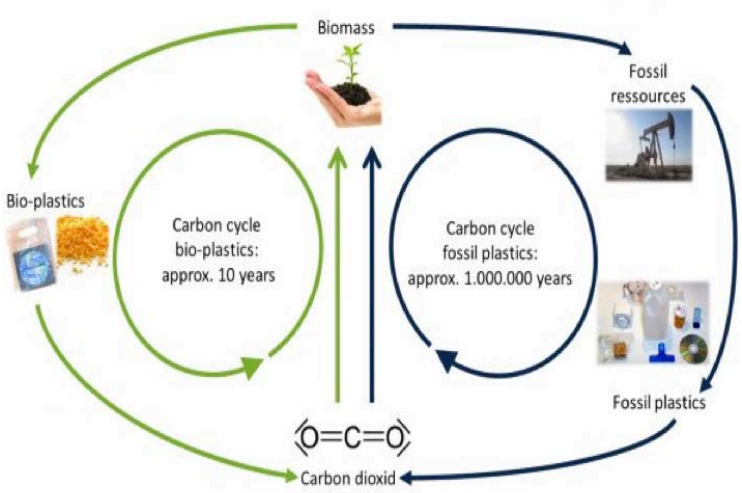

Fig. 1-1 Eco-friendly bioplastics (from European bioplastics)

Many conventional polymers can, in principle, be synthesised from renewable feedstock. For example, corn starch can be hydrolysed and used as the fermentation feedstock for bio-conversion into lactic acid from which poly(lactic acid), PLA, can be produced through chemical processing. Although it's orgin is renewable the polymer cannot be consider 'natural' as it is synthesised within a chemical plant.

1.2.2.2 Bioplastics

1.2.2.2.1 Polylactic acid

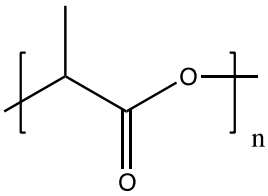

Fig. 1-2 Chemical structural formula of Polylactic acid

Poly(lactic acid) or polylactide (PLA) is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world). Fig. 1-2 shows Chemical structural formula of Polylactic acid. In 2010, PLA had the second highest consumption volume of any bioplastic of the world.

As of June 2010, Nature Works was the primary producer of PLA (bioplastic) in the United States. Other companies involved in PLA manufacturing are PURAC Biomaterials (The Netherlands) and several Chinese manufacturers. Polylactic acid Polylactic acid (PLA) is a linear, aliphatic polyester synthesized from lactic acid monomers. The ester linkages in the polymer are sensitive to both enzymic and chemical hydrolysis. Lactic acid can be produced cheaply by the fermentation of glucose obtained from the starch in biomass such as corn or wheat, or from lactose in whey, or sucrose in molasses. The properties of PLA are similar to LDPE (Low Density Polyethylene) but its rigidity is much higher due to a higher Tg (58 °C compared to −25 °C for LDPE). PLA biodegrades at temperatures above the Tg and therefore can only be composted in industrial composters where high temperatures are generated. Degradation of PLA is primarily due to hydrolysis of the ester linkages, which occurs more or less randomly along the backbone of the polymer. Two major challenges to the stabilization of PLA with regard to hydrolysis are that it is quite permeable to water and the hydrolysis reaction

is autocatalytic. Poly(hydroxyalkanoates)

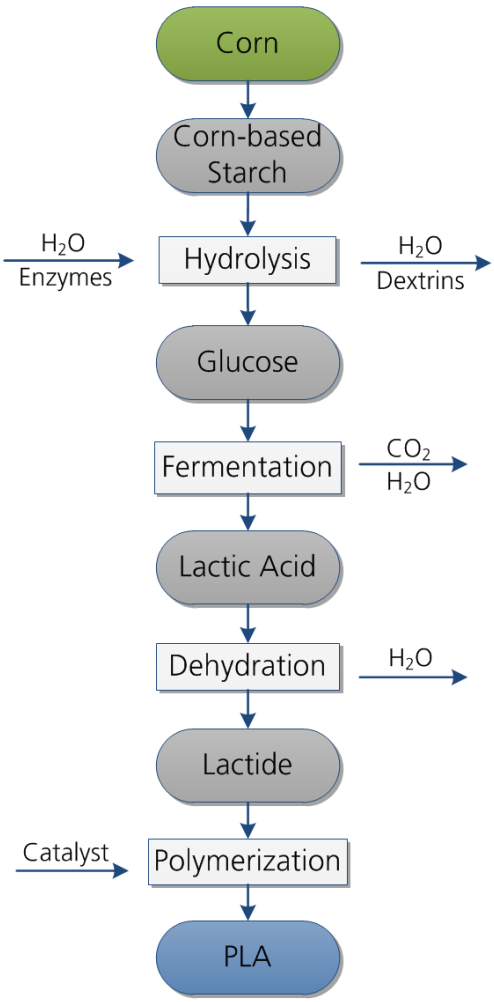

Fig. 1-3 Produce processing of PLA (from Institute for Bioplastics and Biocomposites)

Currently, the ASTM (the American Society of the International Association for Testing and Materials) International resin identification code 7 ("others") is applicable for PLA. In Belgium, Galactic started the first pilot unit to chemically recycle PLA. Unlike mechanical recycling, waste material can hold various contaminants. Polylactic acid can be recycled to monomer by thermal depolymerization or hydrolysis. When purified, the monomer can be used for the manufacture of virgin PLA with no loss of original properties (cradle-to-cradle recycling).

Fig. 1-4 PLA has SPI resin ID code 7 (from wikipedia)

Polylactic acid (PLA) is one of the biomass based materials that has received much attention in the research of alternative biodegradable polymer. Polylactic acid, a resin derived from renewable resources such as plants, has been approved for food packaging applications by the Japanese Hygienic Olefin and Styrene Plastics Association (JHOSPA). As a result, polylactic acid is now usable in the same way as other general-purpose resins in food packaging applications. Polylactic acid has good mechanical, thermal and biodegradable properties, which make it suitable for various end-use applications. However, due to various other limitations and the high cost of polylactic acid, commercialization is difficult.

1.2.2.2.2 Bio-based polyethylene

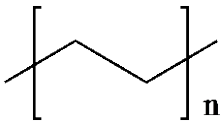

Fig. 1-5 Chemical structure of polyethylene

Bio-based polyethylene (also known as renewable polyethylene) is polyethylene made out of ethanol, which becomes ethylene after a dehydration process. It can be made from various feedstocks including sugar cane, sugar beet, and wheat grain.

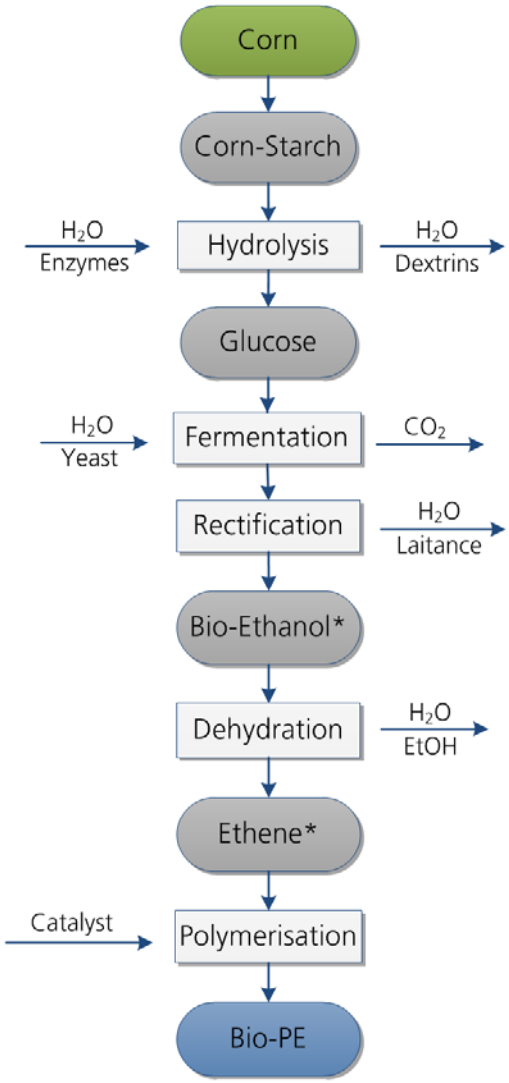

Fig. 1-6 Produce processing of bio-based Polyethylene

(from Institute for Bioplastics and Biocomposites)

One of the main environmental benefits of this project will be the sequestration of roughly 2 kg of CO_2 per kg of polyethylene produced, which comes from the CO_2 absorbed by the sugar cane while growing, minus the CO_2 emitted through the production process. Over 1.5 billion pounds of CO_2 will be annually removed from the atmosphere, which is equivalent to the fossil emission of 1,400,000 Brazilian citizens (according to the Carbon

Dioxide Information Analysis Center in 2004) or 5% of all São Paulo City CO_2 equivalent emissions (according to the São Paulo municipal green house gas emissions inventory in 2005). Renewable polyethylene is non-biodegradable and can be recycled in the same waste streams as traditional polyethylenes (HDPE, LDPE, LLDPE) as it is chemically identical.

Furthermore, the pole is said to be projected to generate its own energy from the burning of the sugar cane bagasse, which will not only power the whole pole, but also will be able to sell enough energy to light up a half million people city, and will be available during the dry season, which is exactly the time when it is most needed, and the hydroelectric plants are short of water reserves.

Braskem and Toyota Tsusho Corporation started joint marketing activities for producing green polyethylene from sugar cane. Braskem will build a new facility at their existing industrial unit in Triunfo, RS and Brazil with an annual production capacity of 200,000 short tons (180,000,000 kg), and will produce high-density polyethylene (HDPE) and low-density polyethylene (LDPE) from bioethanol derived from sugarcane.

HDPE is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching and thus low intermolecular forces and tensile strength.

HDPE is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers and water pipes. One third of all toys are manufactured from HDPE. In 2007 the global HDPE consumption reached a volume of more than 30 million tons.

1.2.3 Plastic packaging

Plastics are high molecular weight polymers that can be molded into desired shapes such as films, trays, containers, bottles, and jars using heat and pressure.

Food packaging lies at the very heart of the modern food industry and very few foods are sold unpackaged. Good packaging prevents waste and ensures that the food retains its desired quality throughout its shelf life.

Packaging has been defined as a bundle of something packed, wrapped or boxed for distribution. The functions of packaging are the services that packaging is expected to deliver, be that during shipment or during the useable life of the product. There are seven major functions or considerations of food packaging: containment, protection, communication, functionality, production efficiency, environmental impact, and consumer safety/regulation.

The selection of packages and packaging materials should be based primarily on considerations of food safety, followed by quality, cost, legal and international issues.

Important properties of common packaging materials generally are mechanical, optical, and barrier properties.

Requirements of Packaging Materials Four primary, interconnected functions of packaging have been identified: containment, protection, convenience, and communication (Robertson, 2013). Foods must be contained before they can be moved from one place to another, and the package must contain the product to function successfully. Without containment, product loss and pollution would be widespread. Protection is often regarded as the primary function of the package: to protect its contents from outside environmental influences such as water, water vapor, gases, odors, micro-organisms, dust, shocks, vibrations, and compressive forces. For the majority of foods, the protection afforded by the package is an essential part of the preservation process(Robertson, 2014).

1.2.3.1 Chemico-physical properties of plastics for food packaging

Plastics are organic polymers with the unique characteristic that each molecule is either a long chain or a network of repeating units. The properties of plastics are determined by the chemical and physical nature of the polymers used in their manufacture, the properties of polymers being determined by their molecular structure, molecular weight (MW), degree of crystallinity, and chemical composition (Ebnesajjad, 2013). These factors in turn affect the density of the polymers and the temperatures at which they undergo physical transitions. Polymer chains can and do align themselves in ordered structures, and the thermodynamics of this ordered state determine such properties as melting point Tm, glass transition temperature (Tg), and mechanical and electrical properties. However, it is the chemical nature of the polymer that determines its stability to temperature, light, water, and solvents, and hence the degree of protection it will provide to food when used as a packaging material.

Common package properties are:

1. Bursting strength—the resistance of a packaging material to a sudden rupture especially due to internal pressure.

2. Coefficient of friction—a measure of the force opposing an applied force parallel to a surface; it is dependent upon the perpendicular force between the material and another material surface.

3. Density—the mass of a material per unit volume.

4. Elongation—the change in length of a material resulting from tensile stress.

5. Gauge—a unit length, 1×10^{-4}in.

6. Gloss—the ratio of light flux specularly reflected from a surface to the total reflected flux.

7. Haze—material opacity due to internal and surface reflections of incident light.

8. Light transmission—the light flux through a material over an interval of time.

9. Modulus of elasticity—a general ratio of a specific form of stress to a specific form of strain; specific examples are Young's modulus, bulk modulus, and shear modulus.

10. Opacity—the ratio of the amount of incident light reflected from a material to the amount of incident light transmitted through the material.

11. Oxygen transmission rate (OTR)—the amount of oxygen passing through a material under specified conditions of time, temperature, pressure, and relative humidity.

12. Tear strength—the force required to tear a material; tearing initiation and tearing propagation are commonly measured.

13. Tensile strength—the maximum force that a material specimen can resist under tension.

14. Tensile stress—a stretching force along an axis.

15. Water vapor transmission rate (WVTR)—the amount of water vapor that passes through a specimen in a set time period under controlled condition of time, temperature, and relative humidity.

Table 1-1 Selected package properties and their relationship to packaging functions

Tensile strength	Protection and containment; package, seal, or seam integrity; prevents external contamination
Water vapor transmission rate	Protection against food degradation by water
Oxygen transmission rate	Protection against food oxidation; prevents growth of micro-organisms
Burst strength	Protection and containment; seal and package integrity; prevents external contamination
Tear strength	Protection and containment; package integrity; packaging operations, distribution

Modern industrialized societies have brought about tremendous changes in life styles and created a demand for greater convenience in household products; the packaging industry has had to respond to those changes. Products designed to increase convenience include foods that are prepared and can be cooked or reheated in a microwave oven, preferably without removing them from their package, and special kinds of packages with dispensing caps, sprays, and other convenience features make products easier to use. Two other aspects of convenience are important in package design. One of these can best be described as the apportionment function of packaging. The relative cheapness of food is largely because of its production on an enormous scale, leading to the need for effective methods of apportioning the product into consumer-sized dimensions. For a product that is not entirely consumed when the package is first opened, the package should be resealable and retain the quality of the product until completely used.

An associated aspect is the shape (relative proportions) of the primary package with regard to consumer convenience (e.g., easy to hold, open, and pour as appropriate) and

efficiency in building into secondary and tertiary packages. The modern methods of consumer marketing would fail were it not for the messages communicated by the package. By allowing brands to be created and standardized, it makes advertising meaningful and large-scale distribution possible. Other communication functions of the package include a universal product code (UPC) that can be read accurately and rapidly, serving instructions, and nutritional information on the outside of the package (Robertson, 2014).

1.2.3.2 Plastic packaging for fruits and vegetables

Packaging process is one of the most important among all of the food manufacturing processes, as it maintains the quality of food products for storage, transportation, and end use (Kelsey, 1985). Packaging prevents deterioration in the quality of foods and beverages due to environmental influences (Restuccia et al., 2010) and contributes to efficient distribution, sales, and consumption. Food packaging is designed to contain and protect foods, to provide required information about the food, and to make food handling convenient from distribution to consumer's table. The primary functions of food packaging are to achieve preservation and the safe delivery of food products until consumption. During distribution, the quality of the food product can deteriorate biologically and chemically as well as physically. Food packaging extends shelf life and maintains the quality and safety of the food products. An important secondary function of packaging is marketing, in addition to providing traceability, indications of tampering, and portion control (Marsh and Bugusu, 2007).

For the consumers, the most important attributes of fresh fruits are flavor and appearance, as well as their safety and nutritional value. Value addition by processing into a ready-to-eat product is an attractive alternative since consumers will spend less time on food preparation. Therefore, their demand of high quality minimally processed food with natural flavor and fresh appearance is greatly increasing. In particular, fresh-cut fruits are tremendously growing segments in retail establishments.

Petroleum-based materials such as polyethylene terephthalate (PET) are commonly used in containers for fresh fruit. Polylactic acid (PLA) containers have properties for being used as substitute for commercial clamshell containers. PLA is biodegradable, recyclable, compostable, made 100% from renewable resources, approved by the Food and Drug Administration for contact with food, and have similar physical and mechanical properties to

PET (Almenar et al., 2008).

The effectiveness of PLA in maintaining the quality of fresh produce such as blueberries and blackberries has been investigated in only a few studies (Joo et al., 2011; Almenar et al., 2010). In all those, biodegradable containers have been shown to be as effective as the petroleum-based ones.

Nowadays, limited tools are available to maintain the quality of fresh-cut products during storage. They are mainly based on the use of modified atmosphere packaging and edible coatings.

The relatively low density of most plastic materials means the end products are lightweight. They also have excellent thermal and electrical insulation properties. However, some can even be made as conductors of electricity when required. They are corrosion resistant to many substances, which attack other materials, and some are transparent, making optical devices possible. They are also easy to mould into complex shapes and forms, allowing integration of different materials and functions. And in the event that the physical properties of a given plastic do not quite meet the specified requirements, the property balance can be modified with the addition of reinforcing fillers, colors, foaming agents, flame retardants, plasticisers etc., to meet the demands of the specific application.

The commercial success of plastics as a packaging product is due to a combination of flexibility (from film to rigid applications), strength, lightness, stability, impermeability and ease of sterilisation. These features make plastics an ideal packaging material for all sorts of commercial and industrial users.

Plastics food packaging, for instance, does not affect the taste and quality of the foodstuff. In fact, the barrier properties of plastics ensure that food keeps its natural taste while protecting it from external contamination. Moreover, the material's unparalleled

versatility is demonstrated in a multitude of applications such as packaging films for fresh meats, bottles for beverages, edible oils and sauces, fruit yoghurt cups or margarine tubs.

The following are just some of the benefits offered by plastics packaging:

The lightest packaging material: While over 50% of all European goods are packaged in plastics, these plastics account only for 17% of all packaging weight. Furthermore, this weight has been reduced by 28% over the past 10 years. Lightweight packaging means lighter loads or fewer lorries needed to ship the same amount of products, helping to reduce transportation energy, decrease emissions and lower shipping costs. It also helps reduce the amount of waste generated.

Food conservation and preservation: Plastics packaging protects and preserves perishable food for longer. It helps reducing waste and the use of preservatives while maintaining the taste and nutritional value of food.

Convenient and innovative: nowadays people want packaging with clear identification and labelling which is easy to open and use. Plastics packaging evolves to provide exactly that. In the near future, for instance, it will integrate printable RFID (Radio-frequency identification) chips based on conductive polymers, providing precious information on the quality and status of products.

Safe and hygienic: Plastic packaging protects against contamination of foods and medicine and helps prevent the spreading of germs during manufacture, distribution and display. Tamper-proof closures provide additional protection and security, while transparent packaging allows people to look at food without having to touch it, cutting down on bruising and other damage.

1.3 Research objectives

Climate change and energy shortage are currently key global issues. Plastics account for approximately 5% of worldwide oil consumption. Growing demand for more environmental preservation and resource conservation, greater sustainability is taken into consideration. Plastics, mainly derived from crude oil, comprised 37% of food packaging material, which is more than metal, glass and paper as packaging materials. Bio-based plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, cornstarch, etc.

From the correlated study in Laboratory of Agricultural and Food Process Enginnering, Hokkaido University, especially from the study of Ms. ROSELIZA BINTI KADIR BASHA and Mr. Tatusya NOBUHARA, the objectives of the dissertation were as follows:

In this study, several typical bioplastics and petroleum-based plastics were tested for their physico-chemical properties. Packaging containers made from PLA and PET were also tested for their ability to preserve the quality of fresh-cut melon under low temperature conditions (<10°C). Therefore, the whole doctoral research aimed: (1) to study whether physico-chemical properties of bioplastics would be comparable to that of petroleum-based plastics as suitable food packaging materials, (2) to compare the effects of a petroleum-based packaging material versus a bio-based packaging material with comparable properties on the changes in quality of fresh-cut fruit and (3) to determine the performance of a bio-based material as a packaging material for fresh-cut fruit under a low temperature condition.

Chapter 2 Physico-chemical properties of bioplastics for food packaging

2.1 Introduction

Plastic is a material consisting of any of a wide range of synthetic or semi-synthetic organics that are malleable and can be molded into solid objects of diverse shapes. Plastics are typically organic polymers of high molecular mass, but they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals, but many are partially natural. Plasticity is the general property of all materials that are able to irreversibly deform without breaking, but this occurs to such a degree with this class of moldable polymers that their name is an emphasis on this ability.

Due to their relatively low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in an enormous and expanding range of products, from paper clips to spaceships. They have already displaced many traditional materials, such as wood, stone, horn and bone, leather, paper, metal, glass, and ceramic, in most of their former uses. In developed countries, about a third of plastic is used in packaging and another third in buildings such as piping used in plumbing or vinyl siding. Other uses include automobiles (up to 20% plastic), furniture, and toys. In the developing world, the ratios may be different - for example, reportedly 42% of India's consumption is used in packaging. Plastics have many uses in the medical field as well, to include polymer implants, however the field of plastic surgery is not named for use of plastic material, but rather the more generic meaning of the word plasticity in regards to the reshaping of flesh.

The world's first fully synthetic plastic was bakelite, invented in New York in 1907 by Leo Baekeland who coined the term 'plastics'. Many chemists contributed to the materials science of plastics, including Nobel laureate Hermann Staudinger who has been called "the father of polymer chemistry" and Herman Mark, known as "the father of polymer physics". The success and dominance of plastics starting in the early 20th century led to environmental concerns regarding its slow decomposition rate after being discarded as trash due to its composition of very large molecules. Toward the end of the century, one approach to this problem was met with wide efforts toward recycling.

The commercial success of plastics as a packaging product is due to a combination of flexibility (from film to rigid applications), strength, lightness, stability, impermeability and ease of sterilisation. These features make plastics an ideal packaging material for all sorts of commercial and industrial users.

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Safe and hygienic: Plastic packaging protects against contamination of foods and medicine and helps prevent the spreading of germs during manufacture, distribution and display. Tamper-proof closures provide additional protection and security, while transparent packaging allows people to look at food without having to touch it, cutting down on bruising and other damage.

Food packaging is expected to deliver high-quality product during distribution. The selection of packaging form and materials should be primarily based on considerations of food safety, followed by quality, cost, etc. Important properties of common packaging materials are generally mechanical, optical and barrier properties. Mechanical properties include tensile elasticity, tensile stress and breaking elongation, optical properties refer to transparency, haze, etc., and barrier properties involve water vapor transmission rate and gas transmission rate. These characteristics are mainly based on the physical properties such as crystallinity, molecular weight, etc. of bioplastics.

Therefore, the objectives of chapter 2 aimed: (1) to study whether physico-chemical properties of bioplastics would be comparable to that of petroleum-based plastics as suitable food packaging materials, (2) to find the possible design of each bioplastics studied as food packaging.

2.2 Materials

Common methods for determining degrees of crystallinity in polymer systems are X-ray diffraction, thermal analysis, vibrational spectroscopy, volumetric methods.

In this study, degrees of crystallinity of plastics were determined by means of X-ray diffraction, thermal analysis.

Samples：petroleum-based polyethylene (petrol-PE), bio-based polyethylene (bio-PE), polylactic acid (PLA), polybutylene succinate adipate (PBSA), petroleum-based polypropylene (petrol-PP), polystyrene (PS) with different thickness from different manufactures, here, PLA and PBSA are bioplastics while PS is petroleum-based plastics.

2.3 Physical properties of bioplastics

Fruits and vegetables are living organisms, which continue to respire and transpire after harvesting. If they want to respire and transpire, oxygen are used and carbon dioxide and other products are produced which can make fruits gets bad. So we use packing materials, which make fruits and vegetables keep longer.

And also the packing should give sufficient protection against mechanical damage caused by transportation or holding, proper packing may minimize physical damage, thereby delaying microbial and enzymatic spoilage.

Important properties of common packaging materials are generally mechanical, optical and barrier properties. Mechanical, optical and barrier properties of plastics are mainly based on the physical properties (crystallinity).

Crystallinity state is the state, which diffracts X ray and exhibits the first-order transition known as melting. A first-order transition normally has a discontinuity in the volume-temperature dependence, as well as a heat of transition, ΔHf, also called the enthalpy of fusion or melting. Percent crystallinity has a big influence on hardness, density, transparency and diffusion. Changes in the crystallinity of thermoplastics result in significant changes in the mechanical behavior of composites containing them. For this reason, the ability to characterize precisely the polymer crystallinity in thermoplastic composites becomes an important requirement.

2.3.1 Experimental equipment for crystallinity

Crystallization of polymers is a process associated with partial alignment of their molecular chains. These chains fold together and form ordered regions called lamellae, which compose larger spheroidal structures named spherulites. Polymers can crystallize upon cooling from the melt, mechanical stretching or solvent evaporation. Crystallization affects optical, mechanical, thermal and chemical properties of the polymer. The degree of crystallinity is estimated by different analytical methods and it typically ranges between 10 and 80%, thus crystallized polymers are often called "semicrystalline". The properties of semicrystalline polymers are determined not only by the degree of crystallinity, but also by the size and orientation of the molecular chains.

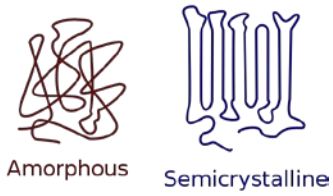

Fig. 2-1 The arrangement of molecular chains in amorphous and semicrystalline polymers

Crystallinity refers to the degree of structural order in a solid. In a crystal, the atoms or molecules are arranged in a regular, periodic manner. The degree of crystallinity has a big influence on hardness, density, transparency and diffusion. In a gas, the relative positions of the atoms or molecules are completely random. Amorphous materials, such as liquids and glasses, represent an intermediate case, having order over short distances (a few atomic or molecular spacings) but not over longer distances.

Many materials, such as glass-ceramics and some polymers, can be prepared in

such a way as to produce a mixture of crystalline and amorphous regions. In such cases, crystallinity is usually specified as a percentage of the volume of the material that is crystalline. Even within materials that are completely crystalline, however, the degree of structural perfection can vary. For instance, most metallic alloys are crystalline, but they usually comprise many independent crystalline regions (grains or crystallites) in various orientations separated by grain boundaries; furthermore, they contain other crystal defects (notably dislocations) that reduce the degree of structural perfection. The most highly perfect crystals are silicon boules produced for semiconductor electronics; these are large single crystals (so they have no grain boundaries), are nearly free of dislocations, and have precisely controlled concentrations of defect atoms.

Crystallinity can be measured using x-ray diffraction, but calorimetric techniques are also commonly used.

Crystallization of plastics is the state, which diffracts X ray and exhibits the first-order transition known as melting. A first-order transition normally has a discontinuity in the volume-temperature dependence, as well as a heat of transition, ΔH_f, also called the enthalpy of fusion or melting. Percent crystallinity has a big influence on hardness, density, transparency and diffusion. Changes in the crystallinity of plastics result in significant changes in the mechanical behavior of composites containing them. For this reason, the ability to characterize precisely the polymer crystallinity in thermoplastic composites becomes an important requirement.

2.3.1.1 Differential Scanning Calorimetry (DSC)

Model DSC-6200 Seiko Instruments Co.Ltd was used to determine crystallinity of plastics. Determination of percent crystallinity by DSC is an indirect method, with the actual parameter measured being the heat of fusion.

Fig. 2-2 Differential Scanning Calorimetry

There are two ways of determining the crystallinity by DSC, the cooling mode and the heating mode. Heating mode used here is that A sample is heated up from ambient temperature in the DSC micro-furnace at a preset rate until it reaches its melting point. The crystallinity of the sample is then calculated by comparing the heat of fusion obtained for the tested sample with that of a reference sample with 100% crystallinity.

Film samples were cut into small pieces, which were 3-5mg. The temperature of

DSC was set to start from 40°C, with a rate of 10°C /min to 240°C.

The heat of fusion per mole of crystalline material can be estimated independently by melting point depression experiment by DSC.

$$X_c\ (\%) = \frac{\Delta H_m\ + \Delta H_c}{\Delta H_f} \times 100, \qquad (2-1)$$

where Xc (%) is percent crystallinity; ΔHm is the heat of fusion (endothermic), ΔHc is the heat of cold-crystallization (exothermic), ΔHf is the heat of fusion for a 100% crystalline material.

Here ΔH_m can be easily measured by calculating the area of endothermic peak by DSC, while the values of ΔHf are published by relative polymer handbooks.

Determination of percent crystallinity by DSC is an indirect method, with the actual parameter measured being the heat of fusion.

The heat of fusion per mole of crystalline material can be estimated independently by melting point depression experiment by DSC.

Here ΔHm can be easily measured by calculating the area of endothermic peak by DSC. The values of ΔHf of PLA, PE, PP are 93, 281, 209 J/g, respectively.

2.3.1.2 Wide-angle X-ray Scattering (WAXS)

Nano-scale X-ray analyzer system (Rigaku Corporation) was used to determine degrees of crystallinity. An hour of continuous scanning angle range used in this study was from 10° to 45° at 40 kV and 30 mA.

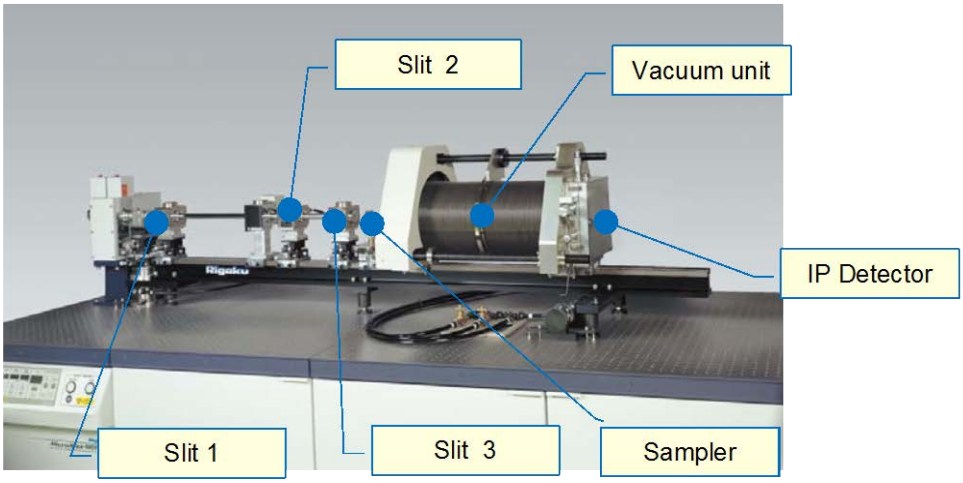

Fig. 2-3 Wide-angle X-ray Scattering (WAXS)

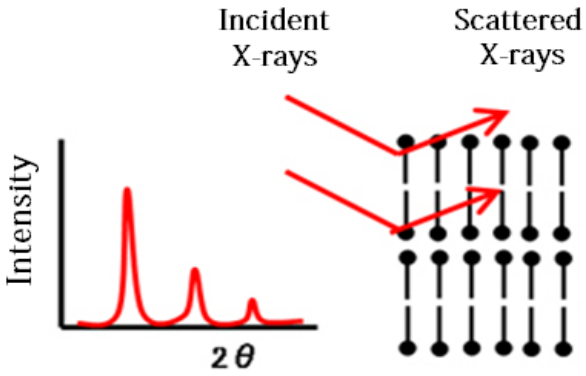

Fig. 2-4 Diffusion patterns of polymers by using a WAXS

2.3.2 Results and discussion

2.3.2.1 Comparison of crystallinity of bioplastics determined by DSC and WAXS

The advantages of DSC to determine percent of crystallinity are sample saving and easy to operation, however viscous flow of amorphous state is endothermal during heating, and recrystallization of polymers also occurs after fusing, which result in complexity of the fusing process of polymers.

Table 2-1 Percent crystallinity of plastics (DSC)

Plastics	Thickness(μm)	Xc[1] (%)	Tf[2] (°C)
LDPE	30	37.6	128.6
	70	36.3	128.4
Bio-HDPE	17	64.1	136.2
	23	63.4	134.6
	30	62.4	129.9
Bio-LDPE	30	22.0	130.7
	70	21.0	130.2
PLA	15	42.9	171.8
	25	41.3	171.4
	35	38.9	171.6
PP	25	32.3	155.2
	40	31.3	154.0
PS	140	0	ND[3]

1 Xc: degree of crystallinity

2 Tf: fusion temperature

3 ND: Not detected

Wide-angle X-ray scattering patterns were simply resolved into contributions from crystalline and amorphous reflections. The absolute degree of crystallinity was then calculated as Ic/(Ic+Ia), where Ic is the diffracted intensity from all resolved crystalline reflections, Ia the diffraction intensity under the amorphous halo, and (Ic+Ia) the total intensity.

Igor pro, version 6.10 (WaveMetrics, Inc, USA) is an interactive software environment for experimentation with scientific and engineering data and for the production of publication-quality graphs and page layouts. This professional software was used to calculate the areas of gaussian intensity curves to determine the relative degree of crystalline of each plastic sample.

From the results, percent of crystallinity decreased as thickness grew as well.

WAXS is regarded to determine the absolute percent of crystallinity, and the

usage of Igor pro has improved the separating capacity of diffraction patterns of polymers, In spite of this the big deviations should be paid attention to.

Table 2-2 Percent crystallinity of plastics (WAXS)

Plastics	Thickness(μm)	Xc(%)
LDPE	20	3.67
	30	2.16
	70	1.50
PLA	15	3.72
	25	3.32
	35	3.36
PBSA	30	4.30
PS	140	0

2.3.2.2 Factors affecting crystallinity of bioplastics

From the results, percent of crystallinity decreased as thickness grew. This was because that during fabrication, as thickness decreased, the stretch increased, shown in fig. 2-6.

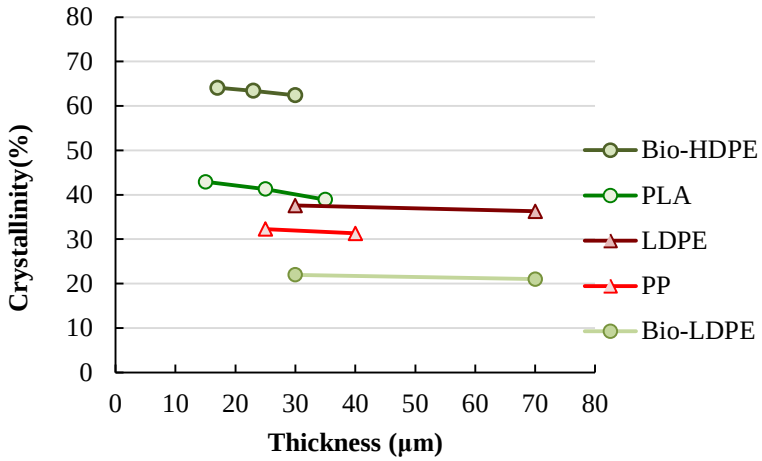

Fig. 2-5 Crystallinity of plastics

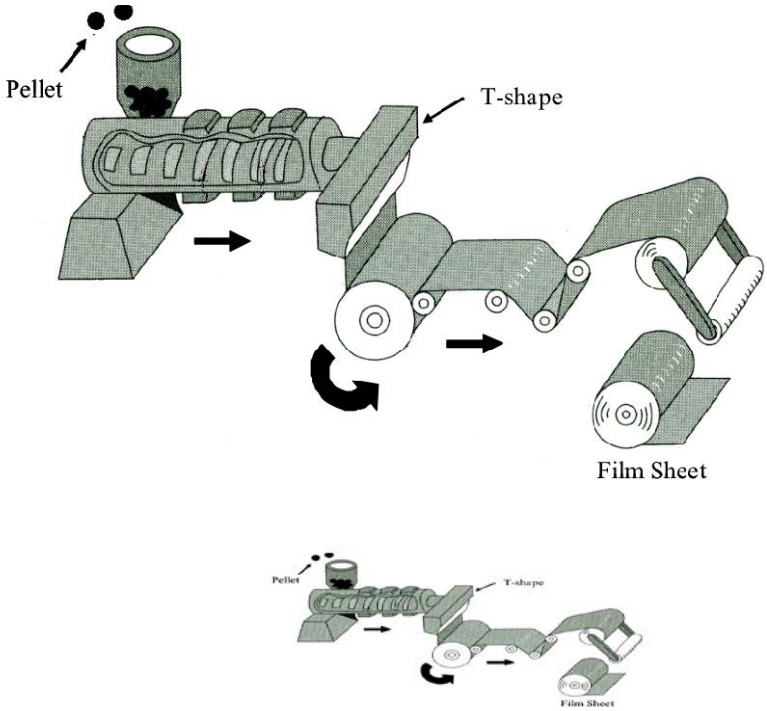

Fig. 2-6 T-die method to fabricate plastic films

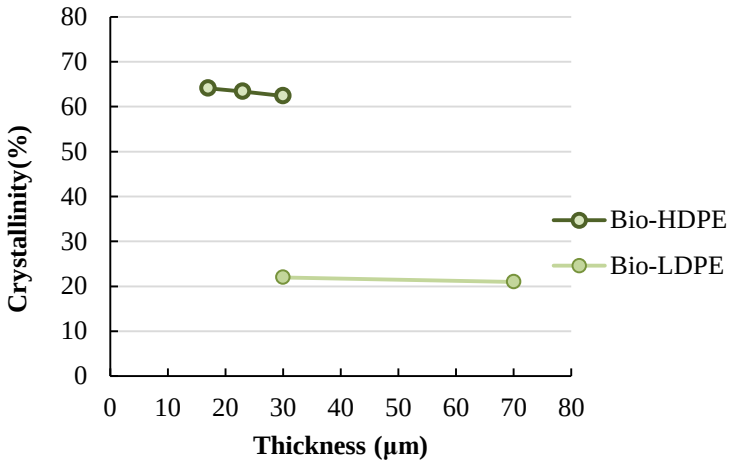

Fig. 2-7 Crystallinity of bio-based PE

Also percent of crystallinity of HDPE were much higher than LDPE (Fig. 2-7). It is because there were more branches in the molecular chain in LDPE than in HDPE (Fig. 2-8), what's more, higher density of HDPE result in better orientation and

arrangement of molecule chain to maintain stable.

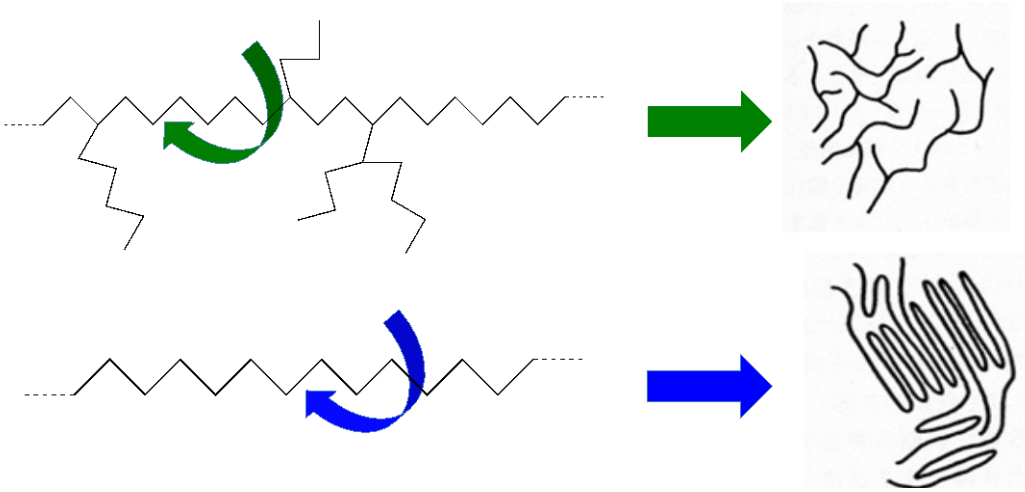

Fig. 2-8 Model of molecular chains of LDPE (upper) and HDPE (lower)

A carbon–oxygen bond, which is a covalent bond between carbon and oxygen, is strongly polarized towards oxygen. A carbon–carbon bond is a covalent bond between two carbon atoms. The most common form is the single bond. Bond lengths for paraffinic C–O bonds are in the range of 143 picometer-less than those of C–C bonds. The C–O bond strength is also larger than C–C. C-O bonds are abundant in molecular chains of PLA, while only C-C bonds exist in molecular chains of PE. Due to this, molecular chains in PE can rotate and fold easier than those in PLA, and which lead to better arrangement of molecular chains.

PE:

PLA:

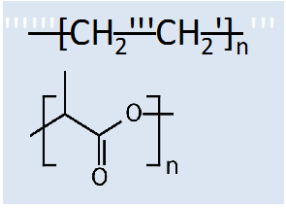

Fig. 2-9 Chemical structures of PE and PLA

What's more, Crystallinity refers to the degree of structural order in a solid. In a crystal, the atoms or molecules are arranged in a regular, periodic manner. Therefore, PE used in this study showed higher crystallinity than PLA.

However, as introduced in introduction that HDPE has a low degree of branching while LDPE has a high degree of short and long chain branching, shown as Fig. 2-8, which means the chains in LDPE do not pack into the crystal structure. As a result of it, percent of crystallinity of HDPE were much higher than LDPE.

2.4 Mechanical properties of bioplastics

2.4.1 Experimental Equipment

These mechanical properties provide an indication of the mechanical performance of the materials. They are tensile properties are most frequently considered, evaluated, and used throughout the industry. Tensile testing provides tensile strength, modulus of elasticity and elongation at break. All film used for the mechanical tests were preconditioned for 24 h at 23°C and 50% RH. The films tested consisted of machine direction (MD) and transverse direction (TD).

The thickness of the film was measured before measuring the tensile properties. The thickness of the film was measured by digital micrometer (Ono Sokki, Japan). The mean value of five measurements had been carried out and it was used as the specimen thickness for water vapor permeability calculation.

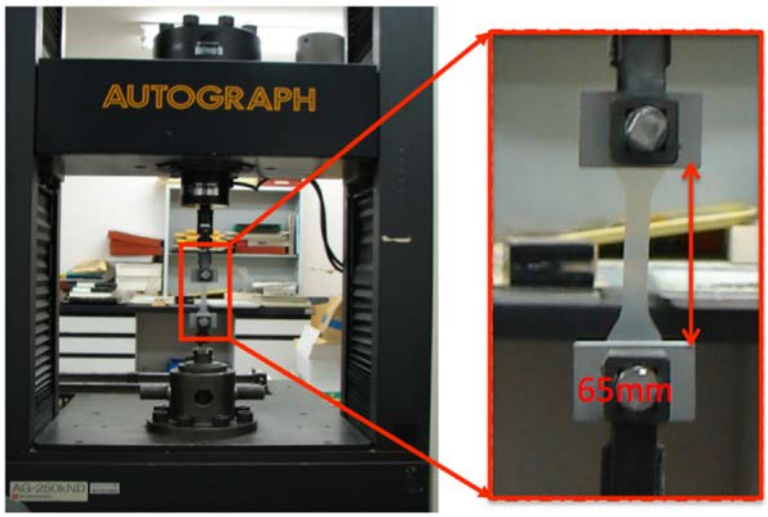

Fig. 2-10 Universal testing machine system (model AG-250kND, Shimadzu, Japan) for measuring mechanical properties

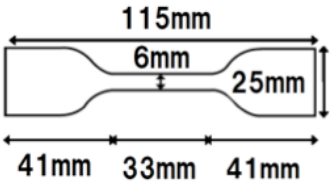

Fig. 2-11 A sketch of dumbbell shaped film sample having dimensions according to JIS K7113 No. 2, JIS K7127 type 5 for measuring mechanical properties

Tensile measurements for tensile strength, elongation at break and modulus of elasticity were performed with the universal testing machine system (model AG-250kND, Shimadzu, Japan) as shown in Fig. 2-10. Film strips were placed in the pneumatic grips of the testing machine, which were set at an initial separation of 65 mm. The crosshead speed was set at 200 mm/min shown in Fig. 2-11. Property values reported here represent an average of the results for tests run on five specimens for each sample. Specimen dimensions were according to JIS K7113 No. 2, JIS K7127 type 5.

Tensile test was performed on test specimen by using tensile testing machine (AG-250kND Shimadu).

In this study, the values of tensile properties (tensile strength, percentage elongation at break and modulus of elasticity) were calculated. As the film elongates, the resistance to the tension increased, and it was detected by a load cell. The tensile strength was calculated by dividing the maximum load in newton by the original minimum cross sectional area of the specimen in square millimeters, and the result was explained in the term of megapascal (MPa).

$$Stress = \frac{Force\ (N)}{Thickness\ (mm) \times Width\ (mm)} \qquad (2-2)$$

$$Strain = \frac{Final\ legth\ (mm) \times Initial\ length\ (mm)}{Initial\ length\ (mm)} \qquad (2-3)$$

Tensile modulus (modulus of elasticity) can be determined by the slope of stress-strain curve and the result was expressed in the unit of mega pascal (MPa).

Tensile speed was 200 mm/min, and initial tense distance was 65mm. Stress-strain curves were obtained By means of this test. Stress on the upper yield point, tensile stress, tensile elasticity and breaking elongation were known from this curve. Each sample was repeated 5 times.

2.4.2 Results and discussion

2.4.2.1 Results of mechanical properties of bioplastics

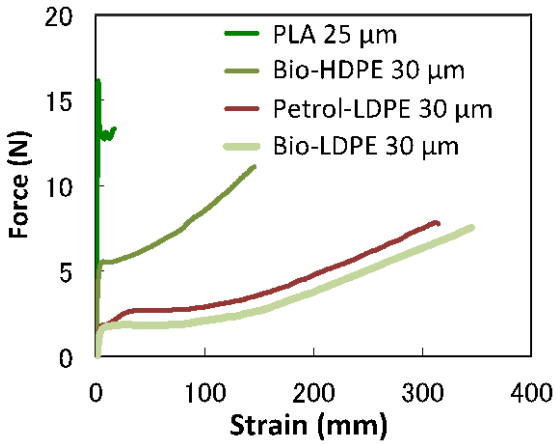

Fig. 2-12 Force-strain curves of plastic samples

From Fig. 2-12, force-strain curves of petroleum-based and bio-based LDPE film samples were close, it was considered that bio-based PE could be used as an alternative to petroleum-based PE because the mutations of both petroleum-based and bio-based PE were almost same. From Fig 12, it's also known that PLA were so brittle that it's better to apply PLA as packaging containers.

Table 2-3 Values of tensile properties of various film materials

Film sample	Tensile strength (MPa)		Elongation (%)		Modulus of elasticity (MPa)	
	MD	TD	MD	TD	MD	TD
Bio-LDPE 30 μm	40.8	33.8	248.4	198.6	491.6	787.6
Bio-LDPE 70 μm	37.5	36.0	227.6	293.4	671.3	814.4
Bio-HDPE 17 μm	75.2	57.7	117.7	1227.2	153.6	559.6
Bio-HDPE 30 μm	69.2	45.2	1002.3	1360.6	177.4	532.9
Petrol-LDPE 30 μm	32.0	29.6	223.5	327.5	447.6	727.6
Petrol-LDPE 70 μm	32.7	32.6	255.8	252.3	705.2	538.4

MD: machine direction

TD: Transverse direction

Tensile strength, percent elongation at break and modulus of elasticity are important parameters that relate mechanical properties of films to their chemical structure (McHugh and Krochta, 1994). Mechanical properties describe in how materials reacting to force cause a material to deform. From the result obtained, a stress-strain curve was developed (Fig. 2-12) to get the tensile strength, percent elongation at break and modulus of elasticity.

2.4.2.2 Factors affecting mechanical properties of bioplastic

The result of tensile tests showed that PLA film broke rapidly after yielding. From previous study in our lab, polybutylene succinate adipate film broke after necking and stress increased with strain above the yield stress. The elongation at break of PBSA film is superior to that of PLA film. However, polylactic acid films had high value of modulus of elasticity showed that they were stiff materials.

This study demonstrated that the film thickness (30 and 70 μm) of PE significantly influenced the tensile properties.

In blown film process, the elongation at break value in machine direction (MD) is usually lower than that in transverse direction (TD) due to the higher orientation occur in machine direction as shown in Table 2-3.

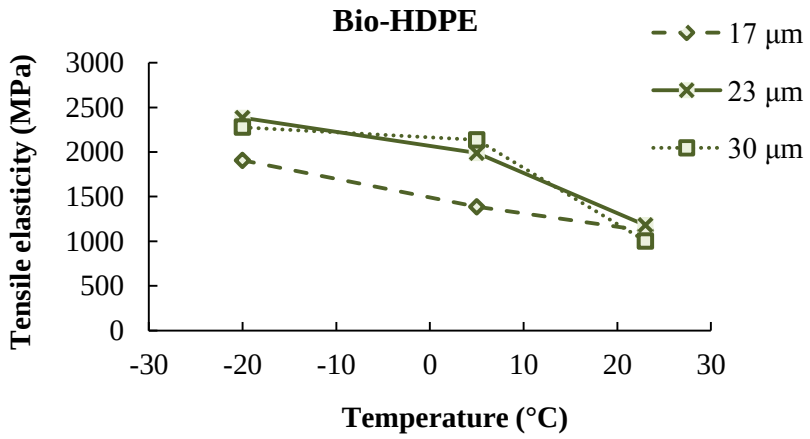

Fig. 2-13 Temperature affected tensile elasticity

As shown in Fig. 2-13, as temperature increased, tensile elasticity decreased. Thus, bio-based HDPE could be applied as food packaging for frozen food.

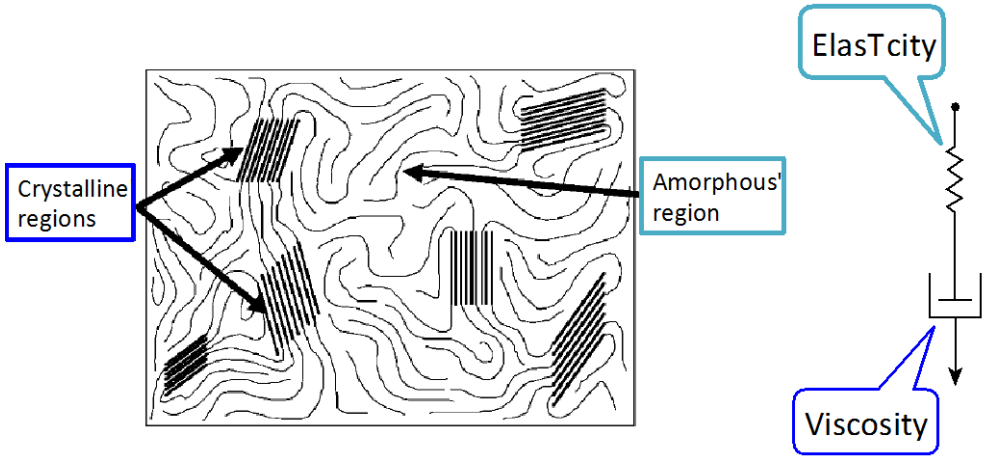

Fig 2-14 Semicrystalline plastics and model of Maxwell element from google image

According to Voigt or Kelvin element and Maxwell element, the mechanical properties of polymers are not single-valued functions of the chemical nature of the macromolecules. This dependence is a consequence of the viscoelastic nature of polymers, which is caused by crystallinity (Xc). What's more, compared with HDPE (high-density polyethylene), LDPE has more branching (on about 2% of the carbon atoms). As a result of this, chains in LDPE do not pack into the crystal structure well. Hence, percent of crystallinity of HDPE were much higher than LDPE. For PE (polyethylene), instantaneous-dipole induced-dipole attraction is small, which leads to small intermolecular forces. Therefore, as crystallinity of PE film grows, the flexibility reduces.

2.5 Barrier properties of bioplastics

Water vapor transmission rate (WVTR) is a factor, which is often very important in determining the suitability of a plastic film for the packaging of many products. Some products need protection from outside air moisture, other require that the moisture contained should not be allowed to evaporate through the package.

This section explains in detail about the equipment, materials and experimental procedure used for determination of water vapor transmission rate. There is a large variety of test methods which can be used for measuring the water vapor transmission rate and usually different market segments require different test methods (Stroek, 2001). Water vapor transmission through polymeric films could be determined on sophisticated and expensive equipment accurately but the availability of equipment can be a problem. This results in a lack of permeability information to select polymeric films for packaging of different fruits and vegetables. To overcome this problem, a simple low cost permeability cell is setting up from modification of ASTM E 96. In Japan water vapour transmission rate is determined by Japanese Industrial Standard for Water Vapor Transmission Rate of Materials (JIS-Z0208). Both techniques have same principle known as cup method. This method is probably the most commonly used technique to determine the transport rate of water vapor through polymeric material.

Most of the studies conducted the water vapor permeability at 25°C instead of 5°C (the temperature at which the quality decay test were conducted) as with the apparatus used it was not possible to reach a temperature as low as 5°C (Muratore et al., 2005; Del Nobile et al., 2006; Conte et al., 2009; Del Nobile et al., 2009). Cup method can be used to determine the water vapor permeability at low to high temperature and various relative humidity (McHugh, 1996; Cuq et al., 1997; Roy et al., 2000b; Hale et al., 2001; Mahajan et al., 2008).

According to ASTM E 96, WVTR can be determined by two ways based on the same testing principle; desiccant method (dry cup method) in which the cup containing desiccant, and water method (wet cup method) in which the cup containing distilled water (ASTM, 2005). Whereas JIS-Z0208, WVTR can be determined based on dry cup method. Wet cup method provided more stable condition, and it was carried out in this study to determine the WVTR particularly to investigate the effect of temperature and relative humidity on WVTR.

In this study, evaluation from the results discusses about the reliability of this method for measuring the WVTR by verifying the results with previous literature review. Various films from biomass-based materials were measured and the WVTR was then compared with conventional plastic films. In addition, the effect of film thickness of polylactic acid will be emphasized.

Wet cup method involves the cup being partially filled with distilled water in order to obtain a specified relative humidity (RH) of moist air (100% RH) inside the cup. The tested film sample/specimen, which covers the cup from the top, has sealed edges in order to ensure the dimensional moisture transfer. The cup with the film sample is placed in the closed chamber with controlled relative humidity and control constant temperature. The mass of the cup with tested sample is recorded in the constant time instants. The water vapor transmission rate is calculated using the equation (2-4). Water vapor transmission rate is the steady water vapor flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and relative humidity at each surface (ASTM, 2005).

$$WVTR = \frac{W/t}{A}, \qquad (2-4)$$

where *WVTR* is water vapor transmission rate (g/m^2·d), *W* is weight change (g), *t* is the time during which *W* occurred, and *A* is the test area (m^2).

$$WVPC = \frac{WVTR \times e}{(p_1 - p_2)}, \quad (2-5)$$

where *WVPC* is water vapor permeability coefficient (g·m/m^2·d·Pa), *e* is film thickness (m) and p_1 and p_2 are water vapor partial pressure (Pa) inside and outside the cup, respectively.

$$p = p_s \times \frac{RH}{100}, \quad (2-6)$$

where *p* is water vapor partial pressure, p_s is saturated water vapor pressure for pure water at a specific temperature and *RH* is relative humidity (%).

2.5.1 Experimental equipment and conditions

2.5.1.1 Wet cup method

In this study, a slightly modified form of the commonly used cup test, ASTM E 96 (Standard Test Methods for Water Vapor Transmission Rate of Materials) was used to measure the permeance of film samples. In the standard test, the material to be evaluated is sealed as a lid onto a dish or cup, containing either desiccant (Dry Cup Test) or liquid water (Wet Cup Test). Next, the whole test assembly is placed into a controlled atmosphere chamber at 50% relative humidity. Periodically weighing the cup and film sample assembly determines the rate of mass gain or loss, and in turn the permeance of the material, but there are only two relative humidity differences and each spanning a 50% relative humidity range.

Fig. 2-15 Cup equipment based on Japanese Industrial Standard

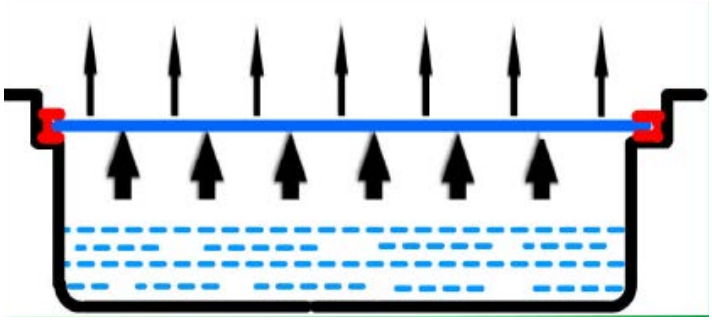

Fig. 2-16 Wet cup method

Fig. 2-17 Wet cup maintained in incubator

Diameter of specimen, vapor transmission area, and diameter of cup inside are 6.5 cm, 28.27 cm^2 and 6.0 cm respectively. PLA with different thickness of 15μm, 25μm, 35μm were used in this study.

Table 2-4 Relative humidity differences in saturated salt solution at 5, 15, 23°C

Saturated salt solution	Relative humidity differences (%)		
	5°C	15°C	23°C
Sodium chloride	24.4	24.6	24.7
Magnesium nitrate	40.8	43.7	46.0
Magnesium chloride	66.4	66.8	67.1

2.5.1.2 Temperature and humidity conditions

The modification to the ASTM cup method was applied in this study at different temperatures (5, 15, 23°C) and various relative humidities (20 - 70%). Saturated salt solutions, used to control relative humidity, allowed the film sample to be tested through

various relative humidity differences. It is a property of most salts that when in the form of saturated solution within a given temperature range creates an environment of constant relative humidity. In the cup method, at least three assemblies are needed; cup (sample dish), testing environment and weighing appliance.

2.5.2 Results and discussion

2.5.2.1 Results of water vapor transmission rate of bioplastics

Table 2-5 Water vapor transmission rate of Polylactic acid determined at 5°C

Film	Thickness	WVTR($g/m^2 \cdot d$), 5°C		
		24.4%ΔRH	40.8%ΔRH	66.4%ΔRH
Polylactic acid	15	18.08	30.46	46.98
	25	12.35	20.16	30.34
	35	10.05	17.05	25.11

Table 2-6 Water vapor transmission rate of Polylactic acid determined at 15°C

Film	Thickness	WVTR($g/m^2 \cdot d$), 15°C		
		24.6%ΔRH	43.7%ΔRH	66.8%ΔRH
Polylactic acid	15	29.11	50.01	81.08
	25	19.38	32.61	53.98
	35	15.49	27.94	43.23

Table 2-7 Water vapor transmission rate of Polylactic acid determined at 23°C

Film	Thickness	WVTR($g/m^2 \cdot d$)		
		24.7%ΔRH	46.0%ΔRH	67.1%ΔRH
Polylactic acid	15	43.65	80.05	129.68
	25	31.94	54.37	83.94
	35	24.90	44.00	69.33

Temperature and relative humidity differences are the most important factors which affect water vapor transmission rate. From table 2-5, 2-6, 2-7, we may easily see that WVTR increases as PLA film samples get thinner, relative humidity differences (ΔRH) grow, and temperature rise. As temperature increased, water vapor transmission rate (WVTR) of plastic samples increased. When relative humidity differences increased, WVTR of plastics increased. Meanwhile, the thicker a film is, the less water vapor can transmit through it.

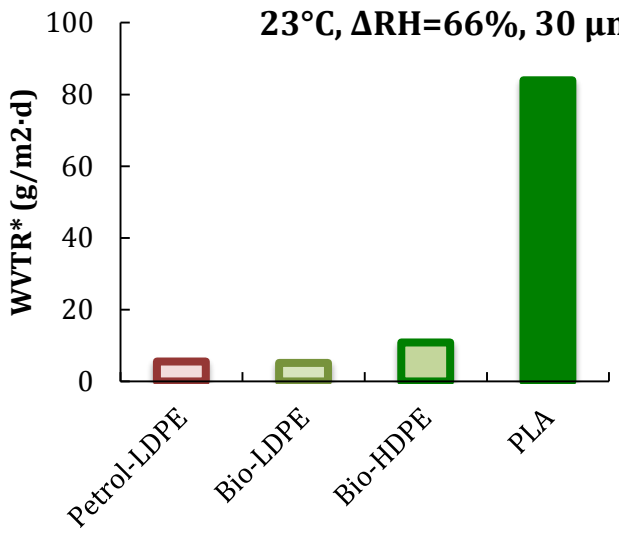

Fig. 2-18 Water vapor transmission rates of several typical plastics and bioplastics

2.5.2.2 Factors affecting water vapor transmission rate of bioplastics

Water vapor transmission rate was measured at 23°C and 85% relative humidity difference PLA (35 μm) and PBSA (30 μm) films have higher water vapor transmission rates which with the values of 103.0 g/m^2·d and 313.2 g/m^2·d, respectively. For comparison, water vapor transmission rates of petrol-based polyethylene films were 7.3, 7.2 and 7.3 g/m^2·d for LLDPE 25 μm, LDPE 25 μm and LDPE 30 μm respectively. PLA film with greater thickness demonstrated lower WVTR. McHugh et al. (1993) reported that, as film thickness increased, the film provided an increased resistance to mass transfer across it and the equilibrium water

partial pressure at inner film surface increased.

Fresh-cut fruits, mushrooms and other vegetables and fruits with high respiration and transpiration rate require high water vapor transmission rate to keep fresh. So in this study, PLA, which is rigid and with high water vapor transmission rate, could be applied as fresh-cut fruit packaging.

2.6 Optical properties of bioplastics

Transparent plastics are used primarily when clarity of vision through the material is a concern. Transparent colored materials transmit the portion of the visible spectrum that allows the eye to see the desired color. Most plastic materials are not transparent. Transparency is required most for food packaging for judgments of consumers whether buy the product or not.

Choosing the best transparent plastics for packing product will depend greatly on its functional performance requirement in the field. In order to assist in selecting the appropriate material for application of food packaging, transparency was investigated in this section.

Because CIE Tri-Stimulus Color Measurement and Ultra-Violet and Visable (UV/VIS) light absorption and transmission are two of the fundamental optical properties testing for plastics, transparency was evaluated by transmittance (T, in %), WI (whiteness index) in this study.

2.6.1 Experimental and conditions

2.6.1.1 Transmittance

Color is an important property of biomass based film materials because it could affect the consumer acceptance. Some materials allow much of the light that falls on them to be transmitted through the material without being reflected. Materials that allow the transmission of light waves through them are called optically transparent.

Some materials allow much of the light that falls on them to be transmitted through the material without being reflected. Materials that allow the transmission of light waves through them are called optically transparent. Because Ultra-Violet and Visable (UV/VIS) light absorption and transmission are two of the fundamental optical properties testing for plastics,

transparency was evaluated by transmittance (T, in %) in this study. Optical properties were examined according to ISO 13468-1:1996 by using a UV-VIS spectrophotometer at the wavelength of 400~800 nm in every 5 nm.

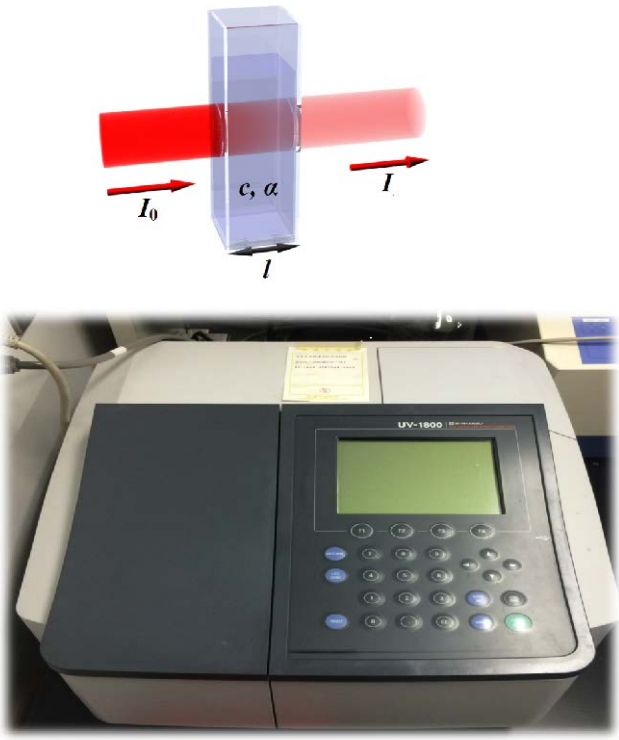

Fig. 2-19 UV-Vis spectrophotometry and its principal

2.6.1.2 Whiteness Index (WI)

Whiteness index (WI) were calculated from spectral distribution of plastic samples.

According to JIS-K-7105, color values of the films were measured with Minolta CR-400 chroma meter (Konica Minolta Sensing, Inc. Japan), using the CIE scale L* a* b*. CIE L*(lightness), a*(red-green) and b* (yellow-blue) values are measured using reflectance measurements.

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \qquad (2-7)$$

WI of plastic samples was determined by placing samples on black reference. Plastic samples were covered over black reference ((L_0: 25.96, a_0: 0.69, b_0: -0.10)), L, a, b values of samples were determined by using chroma meter.

2.6.2 Results and discussion

Optical properties of importance with thermoplastic polymers include clarity, haze, color, transmittance, reflectance, gloss, and refractive index. The clarity of a film indicates the degree of distortion of an object when viewed through the film, with 'see-through' clarity referring to the ability of the film to resolve fine details of fairly distant images viewed through the film (Robertson, 2014).

2.6.2.1 Results of optical properties of bioplastics

Table 2-8 Optical values and crystallinity of plastic samples

Plastics	Thickness (μm)	White Index	Transmittance at wavelength of 400-800 nm (%)	Crystallinity (%)
Bio-based	17	37.6	46.8-59.1	72.3
HDPE	30	42.1	43.1-57.3	69.9
Bio-based	30	40.4	55.2-74.3	37.6
LDPE	70	39.8	56.4-75.4	36.3
Petrol-based	30	38.7	82.8-89.4	22.0
LDPE	70	39.5	73.3-85.7	21.0
PP	25	36.1	88.5-92.1	32.3
	40	35.9	86.3-91.0	31.3
PLA	15	34.7	89.4-92.2	42.9
	25	34.7	90.0-91.2	41.3
	35	34.8	89.3-91.3	38.9
PBSA	30	41.5	54.4-83.2	-[1]
PLA sheet	270	34.0	77.7-86.4	25.9
PS sheet	130	36.3	80.7-85.3	ND[2]

1 Degree of crystallinity of PBSA samples couldn't be determined without knowing heat of fusion value.

2 ND, not detected, PS detected in this study was atactic polystyrene, which was amorphous.

2.6.2.2 Factors affecting optical properties of bioplastics

As thickness of petrol-based PE grew, transparency decreased, which can also be inferred from Beer Lambert Law. As it is known to us all that as wavelength of light increases, refractive index of material increases, which improves transparency of plastics.

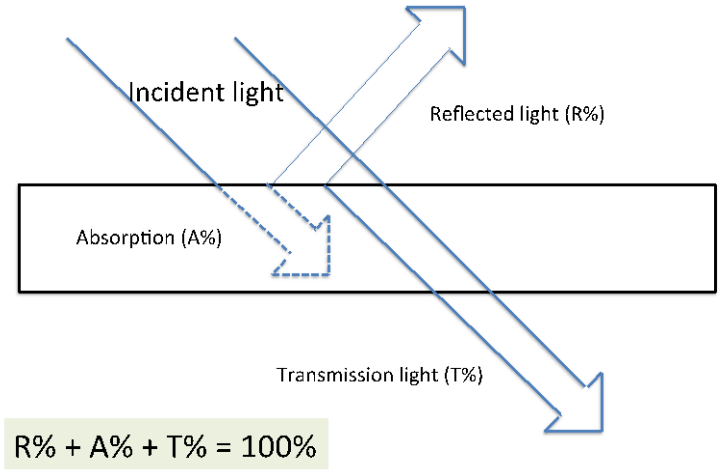

Fig. 2-20 Simple model of incident light passing through a plastic sample

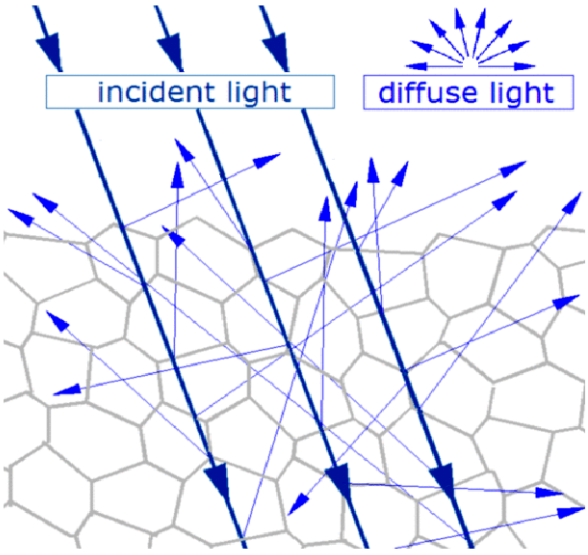

Fig. 2-21 Scattering occuring when incident light passing through semicrystalline plastics (from google image)

For the same thicknesses of LDPE samples, petrol-based LDPE with lower crystallinity

showed higher transmittance than bio-based LDPE, which results in higher transparency. Some thermoplastics do not fully crystallize below the glass transition temperature (Tg), retaining some or all of their amorphous characteristics.

For a specified plastic sample, the absorption caused by this sample is fixed, so the more the difference between amorphous and crystalline states is, the more scattering occurs. Amorphous and semi-amorphous plastics are used when high optical clarity is necessary, as light is scattered strongly by crystallites larger than its wavelength. Furthermore, during the processing of bio-based plastics, more plastic additives have been used, which reinforce scattering. According to those reasons, WI and transmittance of plastic samples were reduced when light pass through higher crystalline plastics.

Optical properties of plastics are related to both the degree of crystallinity and the actual polymer structure. The loss of transparency of plastics results from refraction, absorption and scattering of light. Refractive index, reflection coefficient and dissipation coefficient affect transmittance most. Therefore, degree of crystallinity, size of crystalline, molecular weight and molecular structure play big roles in optical properties of plastics.

2.7 Conclusions

Temperature, process direction, thickness, chemical structure, producing process, etc. affect mechanical, optical and barrier properties.

As thickness increased, crystallinity, transparency and water vapor transmission rate decreased, while tensile elasticity increased. These due to film fabrication during the processing.

As temperature increased, tensile elasticity decreased, while water vapor transmission rates increased.

Relative humidity also affected water vapor transmission rate. As relative humidity differences increased, water vapor transmission rate increased.

Special functional group, such as ester functional group with shorter band length, or higher intermolecular and intramolecular force, affected mechanical properties.

Bio-LDPE, flexible, modestly transparent and with low WVTR, could be applied as shopping bags. Bio-HDPE, tough, translucent and with low WVTR, could be applied as caps for paper milk box. PLA, Rigid, with good transparency and high WVTR, could be applied as food packaging containers.

Meanwhile, by controlling produce processing, using additives, combining with some plastics, bioplastics could be made their best use, such as shopping bags, plastic wraps, packaging containers and soft drink bottles.

Chapter 3 Application of bioplastics for fresh-cut fruits packaging

3.1 Introduction of fresh-cut fruits

Fresh-cut fruit and vegetables represent an important food segment of interest to growers, processors, retailers and consumers. Fresh-cut products are more perishable than whole produce because they are physically altered from their original state during processing operations. Although they remain in a fresh state, fresh-cut products are living tissues characterized by an accelerated metabolism. Quality in fresh-cut product preparation and distribution is crucial in terms of food safety, quality and environmental impact. Cultivation is still a fundamental part of the supply chain, but the complex market dynamics require detailed knowledge of all stages in the supply chain. In the last 20 years, the fruit and vegetable market has developed a rich array of new products. At the same time, consumers have become more concerned about health and a proper diet and have increased the demand for healthy fruit and vegetables and guaranteed products. Globalization has shown that production systems need a new approach that should focus on safety and quality rather than quantity and has shown that a fully integrated and complex supply chain must be able to fulfill the consumers' needs. This chapter has considered critical points concerning the safety and quality of produce, which should be controlled by growers, who represent the first stage in the fresh-cut supply chain, and the technologies used by processors to maintain quality and guarantee safety. An optimal cultivation management on the farm, an efficient and rapid harvesting, proper postharvest handling and storage are key factors that favor the quality of the raw material. Quality raw material enhances processing and final product quality, leading to increased competitiveness in the market for the fresh-cut producer. This, in turn, leads to increased bargaining power of,

in particular, processors and retailers.

Sales of fresh-cut fruit in the U.S. have been increasing at rates of 7% to 54% growth. Sales of fresh-cut melon have also been increasing at the fastest rate, and expected to continue over the next few years (Martín-Belloso and Soliva-Fortuny, 2011). Fresh-cut produce has become popular because of consumers' demand for more convenient foods. However, fresh-cut fruits are very perishable and usually have a shelf life of 5-7 days at 1-7°C (Rico et al., 2007). Fresh-cut processing alters the integrity of fruits and vegetables, leading to negative effects on product quality such as browning, off-flavor development, texture breakdown, and growth of microorganisms. Thus, shelf-life of fresh-cut fruit commodities are inevitably shortened (Lee et al., 2003; Martín-Belloso, 2006; Oms-Oliu, 2007; Raybaudi-Massilia et al., 2007).

Minimally processed fresh-cut melon with relatively higher pH (>5.2) than that of other fruits (Zhang et al., 2013) is considered to be highly perishable (Soliva-Fortuny and Martín-Belloso, 2003). Previous studies on quality preservation of fresh-cut melon have focused on edible coatings, modified atmosphere packaging (MAP), an absorbent pad, mild heat and calcium treatment, and UV radiation (Raybaudi-Massilia et al., 2008; Fernández et al., 2010; Lamikanra and Watson, 2007; Manzocco, et al., 2011). However, there have been few studies on bio-based packaging for quality conservation of fresh-cut melon.

Various materials are currently used for packing fresh produce. The market is dominated by polyethylene terephthalate (PET) and polystyrene (PS) for rigid containers and polyolefins for bags, and all of the materials are made from petroleum-based polymers. One alternative is the use of bio-based packaging

materials. According to European Bioplastics (2015), total amount of bioplastic production was 1.7 million tonnes. Non-biodegradable bioplastic production was 60.9% and biodegradable bioplastic was 39.1% of the total production. Non-biodegradable bio-based PET had the highest production at 35.4%, followed by biodegradable and compostable polylactic acid (PLA) at 16.1% of the total bioplastics production. It was reported that the bioplastics market would continue to grow and would have a 5% share of the entire plastic packaging market within 20 years (Byun and Kim, 2014).

Polylactic acid (PLA), biodegradable, made from natural resources such as corn or sugar cane (Garlotta, 2001; Kale et al., 2007; Zhang and Sun, 2005), is one of the most widely available bio-based plastic materials. PLA possesses mechanical properties comparable to those of PET and PS (Auras et al., 2005). It is transparent and it is food contact approved by the US Food and Drug Administration (FDA) (John et al., 2007; Almenar et al., 2008) and can be degraded in a composting system (Kijchavengkul and Auras, 2008). Thus, PLA would be a good alternative for food packaging material from the viewpoint of the environmental conservation and sustainability. Most PLA packaging application are limited to rigid packaging. PLA has been tested as a packaging material for some types of fresh produce and it has been shown to be useful for quality conservation of fruits. Almenar et al. (2008) reported that blueberries packaged in PLA containers remained fresher during storage at 10 or 23°C than did fruits packaged in common commercial packages, vented clamshell containers.

In this study, packaging containers made from PLA and PET were tested for their ability to preserve the quality of fresh-cut melon under low temperature conditions (<10°C). The choice of packaging material was made with the following objectives:

(1) to compare the effects of a petroleum-based packaging material versus a bio-based packaging material with comparable properties on the changes in quality of fresh-cut melon and (2) to determine the performance of a bio-based material as a packaging material for fresh-cut melon under a low temperature condition.

3.2 Materials and methods

3.2.1 Fresh-cut operations

Fresh and sound melons (‘Rupia red’ cultivar), harvested at Biratori, Hokkaido, Japan, with the same sizes and ripening degrees were purchased from a local supermarket in Sapporo, Japan. Prior to the experiment, the melons were stored at 4°C for 24 hours. Before cutting, the outer surfaces of the melons were washed thoroughly with cool tap water to remove surface dirt and melons were scrubbed with a clean produce brush, as specified by the U.S. FDA 2005 Model Food Code Section 3-302.15. The melons were hand-cut with a sharp knife into eight slices; sharp sterile knives were used to reduce the stress produced during processing. Melon slices were parallel to the longitudinal axis, and blossom stem-ends, seeds, placenta and peel were discarded. The pulp was hand cut in trapezoidal shaped sections (Silveira et al., 2010). Each cube was about 20 g.

3.2.2 Packaging materials and packaging

Water vapor transmission rate (WVTR) and water vapor permeability coefficient (WVPC) of both packaging materials (PLA and PET) were measured by a modified technique of the wet cup method according to the American Society for Testing and Materials (ASTM) E 96 (ASTM, 2005). Plastic sheets of PLA and PET containers were sealed on cups that contained 15 mL of distilled water. Test cups were placed in desiccators at a relative humidity of 54% maintained by a saturated magnesium nitrate solution and were stored in a incubator at 23°C, with the relative humidity difference inside and outside the cup being 46%. The sealant used for attaching the specimen to the sample dish was a combination of 20% bee wax and 80% paraffin. WVTR and WVPC were calculated using the following formulas:

$$WVTR = \frac{W/t}{A}, \quad (3-1)$$

where WVTR is water vapor transmission rate (g/m^2·d), W is weight change (g), t is the time during which W occurred, and A is the test area (m^2).

$$WVPC = \frac{WVTR \times e}{(p_1 - p_2)}, \quad (3-2)$$

where WVPC is water vapor permeability coefficient (g·m/m^2·d·Pa), e is film thickness (m) and p_1 and p_2 are water vapor partial pressure (Pa) inside and outside the cup, respectively.

$$p = p_s \times \frac{RH}{100}, \quad (3-3)$$

where p is water vapor partial pressure, p_s is saturated water vapor pressure for pure water at a specific temperature and RH is relative humidity (%).

As shown in Fig. 3-1, 210 g of fresh-cut melon cubes was placed inside each of the PLA containers with a volume of 850 mL (Risupack Co. Ltd., Japan), which were snap-fit, and 280 g of fresh-cut fruit was placed inside each of the commercial PET containers with a volume of 1120 mL (FP Corp., Japan). After filling, the containers

Fig. 3-1 Fresh-cut melon cubes in polylactic acid (PLA) and polyethylene terephthalate (PET) containers (right: PLA, left: PET)

were divided into two groups and stored in darkness at 4 and 10°C for 10 days. Physical and physicochemical analyses of melon cubes stored in each type of container and at each storage temperature (3 replications for each packaging condition) were carried out on each sampling day (0, 1st, 3rd, 5th, 7th and 10th days) during storage.

3.2.3 Quality items for evaluation of fresh-cut melon

3.2.3.1 Weight loss

The weight of each package of fresh-cut melon was determined on day 0 and on each sampling day using a digital precision balance (±0.01 g) (CPA 62025, Sartorius Japan K.K.). Values of weight loss are shown as the percentage loss of the initial total weight.

3.2.3.2 Juice leakage

Melon cubes were packed in snap-fit containers and stored at 4 and 10°C for 10 days. Juice leakage of the samples recovered with a syringe was evaluated by weighing the amount of juice loss from the fruit at increasing storage periods. Results are shown as liquid quantity (g) recovered per 100 g of fresh-cut melon in the package (Manzocco et al., 2011).

3.2.3.3 Surface color measurement

Fresh-cut melon color was measured directly with a Minolta CR-400 chroma meter (Konica Minolta Sensing, Inc., Japan) using the CIE scale L* a* b*. The equipment was calibrated using a standard white tile. The maturation pattern of melon starts from the fruitlets at the base of the fruit and moves up to the crown, resulting in different stages of maturity of the fruitlets throughout the whole fruit. Because of such

a complex fruit anatomy and maturity pattern, fresh-cut melon cubes are non-uniform in color and texture. Therefore, each value represents the mean of a duplicate determination of 15 different samples of each storage condition. CIE L*(lightness), a*(red-green) and b* (yellow-blue) values are determined by reflectance measurements. The parameter ΔE (Rizzo and Muratore, 2009) is defined as the visible difference of color. This value was calculated as follows:

$$\Delta E = \sqrt{(L^* - L_0)^2 + (a^* - a_0)^2 + (b^* - b_0)^2}, \quad (3-4)$$

where the parameters of melon cubes on the initial day were L0=61.15, a0=15.45 and b0=39.57.

3.2.3.4 Firmness

Tissue softening is one of the major problems that limit the shelf life of fresh-cut fruit, and firmness is an important factor that influences the consumer acceptability of these products. The firmness of the fresh-cut melon cube center was measured as the force applied by a flathead probe of 10 mm in diameter with the crosshead speed set at 0.5 mm/s. The fruit cubes were compressed by 50% using a Rheo Meter (NRM-2002J, Rheotech Corp., Japan). Fifteen fruit cubes of each packaging condition on each sampling day were measured, and the values were averaged. The results are shown as force in Newtons (N).

3.2.3.5 Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C

Flavor is composed of sugar, organic acids and aromatic compounds. Differences in sensory quality have been based on the level and proportion of these flavor components (Almenar et al., 2010). Melon pieces, by the fact of being alive, continue the respiration process, consuming sugars and varying SSC levels, which reflect sugar contents (Lamikanra et al., 2000).

Flavor was positively correlated with pH and SSC, confirming consumers' preference for fruits with a high pH and high sugar content. Twelve fruit cubes from each packaging condition were wrapped in paper towels and squeezed by hand. The expressed juice was used for determination of SSC, pH, TA and vitamin C. SSC was measured at 20°C by using a pocket refractometer (PAL-1, Atago Co. Ltd., Japan), and results are shown in Brix (°). The value of pH was measured with a pH meter (JF 18, Horiba Ltd., Japan). TA was determined by diluting each 1-mL aliquot of melon juice in 50 mL of distilled water and titrating to pH 8.1 using 0.1 mol/L sodium hydroxide (NaOH). Total acid contents were determined as citric acid equivalents (Montero-Calderón et al., 2008). The quantity of vitamin C was determined by using ascorbic acid reflectoquant test strips in combination with an RQflex® plus 10 reflectometer (Merck Millipore Corp., Germany) (Merck KGaA, 2012)

3.2.3.6 Sensory analysis

Sensory evaluation of fresh-cut melon was carried out. Samples were given to panelists in a completely randomized order. The sensory quality of the fresh-cut melon under each packaging condition was evaluated by using a panel of 10 untrained judges, researchers and students of the Laboratory of Food Processing and Engineering of Hokkaido University in Japan. Odor, color and overall acceptance were selected as quality attributes. A structured scale was used for odor, color and overall acceptability of melon cubes: 3, very good; 2, good; 1, fairly good; 0, fair; -1, slightly poor; -2, poor; -3 very poor. During the test sessions, the sample presentation order was randomized and sensory evaluation was carried out on the 0, 5^{th} and 10^{th} sampling days.

3.2.3.7 Statistical analysis

Data were subjected to one-way and factorial analysis of variance (ANOVA) using Statistical Product and Service Solutions version 22 (SPSS Inc., Chicago, IL, USA). Significant differences between means of all measurement items among storage conditions and each sampling day during the 10 days of storage were determined by Tukey's post hoc comparison test ($p < 0.05$).

3.3 Results and discussion

As shown in Fig. 3-2, melon cubes that had been stored at 10°C were greatly deteriorated on the 10th sampling day. A large amount of fungi was clearly observed in the PET containers. Much worse spoilages and smells of alcohol in PET containers at 10°C were also noted by panelists during sensory evaluation. Quality changes of fresh-cut melon were determined for 7 days for melons stored at 10°C and for 10 days for melons stored at 4°C.

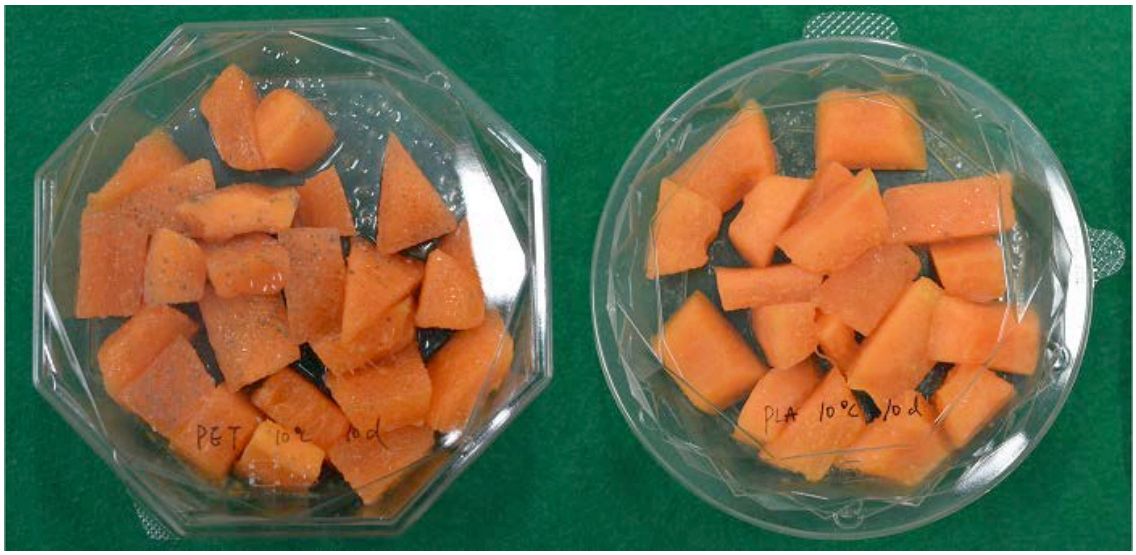

Fig. 3-2 Spoilage of fresh-cut melon cubes in polylactic acid (PLA) and polyethylene terephthalate (PET) containers at 10°C on the 10th sampling day (right: PLA, left: PET)

3.3.1 Quality changes of fresh-cut melon during storage

3.3.1.1 Weight loss

Confirmation of leakproofness was carried out. The amounts of air leakages through gaps between the lids and bottoms of the PLA and PET containers were so small that both types of containers could be regarded as being airproof (data not shown).

Loss of moisture is the major reason for fruit weight loss and it is the result of respiration and transpiration processes occurring during postharvest. In closed packaging systems, moisture loss of fresh produce is determined mainly by the permeability to water vapor of the packaging material (Joo et al., 2011).

As can be seen in Fig. 3-3, ‘Rupia red’ fresh-cut melon in PLA and PET containers showed a progressive loss of weight during storage. Throughout the storage period, there were significant differences between weight losses in the PLA and PET containers at 4 or 10°C. In closed packaging systems, moisture loss of the fresh produce is determined mainly by the permeability to water vapor of the material.

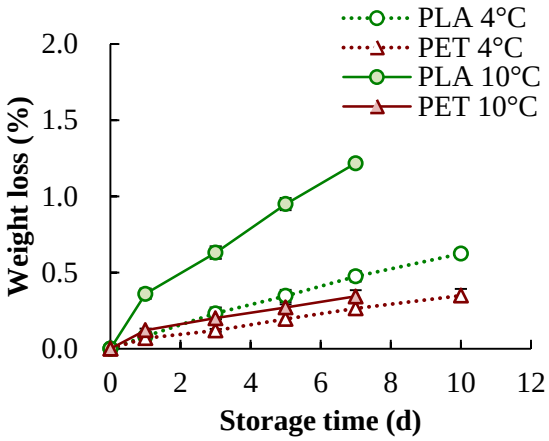

Fig. 3-3 Weight loss of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=3)

Fig. 3-3 shows the differences in fresh-cut melon weight loss caused by the packaging material.

Greater weight loss were observed for the PLA-packaged melon than for the PET-packaged melon: 0.62% vs. 0.35% at 4°C on the 10th sampling day and 1.22% vs. 0.34% at 10°C on the 7th sampling day. The greater weight loss of melon cubes in the PLA containers was due to the higher water vapor transmission rate (WVTR) of PLA. Values of 18.18 and 2.09 g/m2·d were measured for PLA and PET used in this study at standard room temperature of 23°C and 46% relative humidity differences (Table 3-1). Similar results for WVTR and WVPC were obtained in other studies (Auras et al., 2003; Auras et al., 2005). Greater differences in fresh-cut melon weight

loss at a higher temperature are shown in Fig. 3-3. Shriveling and loss of plumpness are dependent on temperature. The higher the temperature is, the greater the effect of the plastic container can be. A weight loss of more than 5% is a cause of reduction in

Table 3-1 Water vapor transmission rate (WVTR) and water vapor permeability coefficient (WVPC) of PLA and PET containers at 23°C and 46% relative humidity differences

Material	Thickness (μm)	WVTR (g/m^2·d)	WVPC ($g·m/m^2·d·Pa$)
PLA	270	18.18	3.80E-06
PET	240	2.09	0.39E-06

retail value of vegetables and fruits (Almenar et al., 2008). Weight loss of 5-10% or more has been shown to be associated with a significant reduction in the firmness of fresh products (Almenar et al., 2010). Weight losses of fresh-cut melon stored at 4°C and 10°C in the PLA and PET containers were less than 1.5%, indicating that PLA containers were as suitable as PET containers for moisture conservation of fresh-cut

melon during storage at 4°C and 10°C.

3.3.1.2 Juice leakage

Results for juice leakage from fresh-cut melon pieces inside the containers during the 10-d at 4 and 10°C are shown in Fig. 3-4. No significant differences in juice leakage were found between the different packaging and temperature conditions.

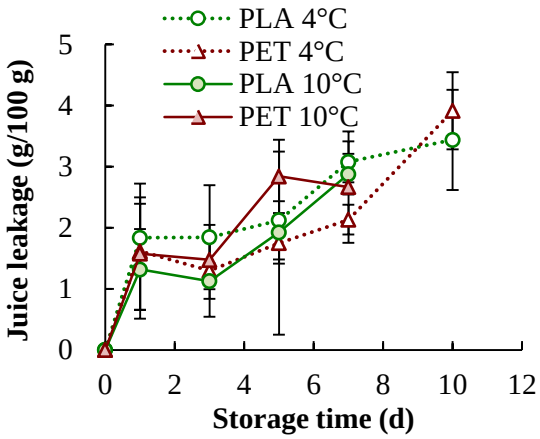

Fig. 3-4 Juice leakage of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=3)

3.3.1.3 Surface color measurement

Color is the most evident parameter by which consumers' judge fresh-cut melon quality. Change in color parameters L*, a* and b* of fresh-cut melon were studied throughout the 10-day storage at 4 and 10°C. More initial statistical differences of melon cubes in PET containers in ΔE, calculated by color spaces L*, a* and b* among packaging conditions, were observed (Fig. 3-5). These meant melon cubes lost redness and yellowness gradually during the storage in both containers.

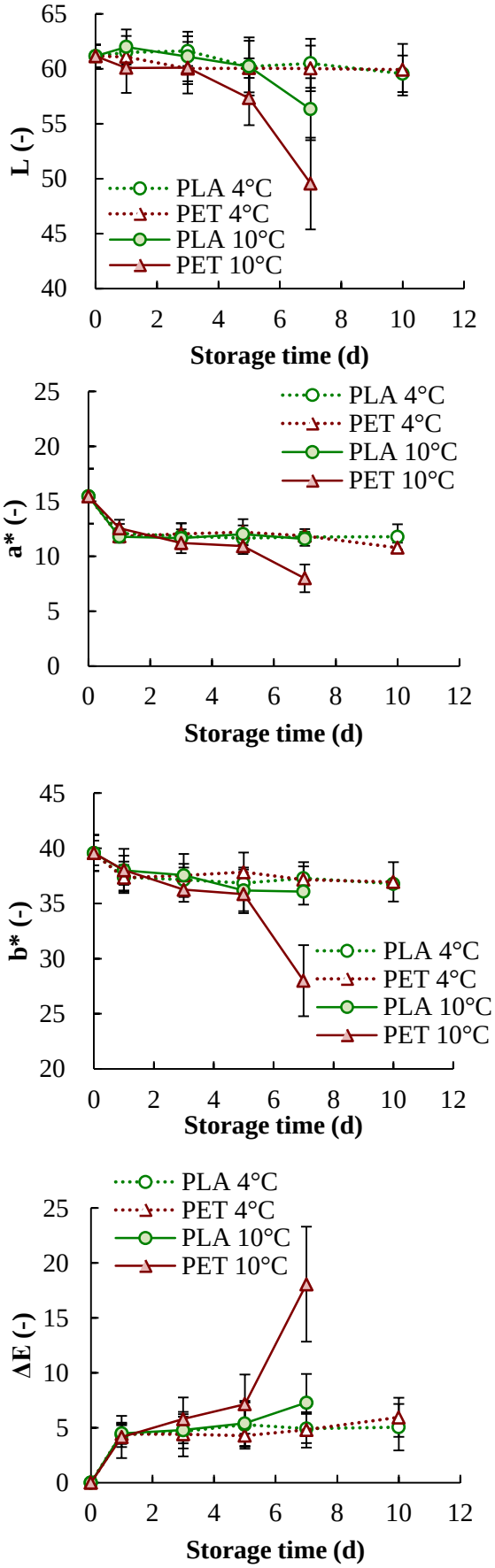

Fig. 3-5 Color parameters (L^*, a^*, b^*, ΔE) of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

Color changes in L*, a* and b* values of sample cubes in PET containers were larger than those of sample cubes in PLA containers during the storage period. Compared with the L* and b* values on the initial day, the values of sample cubes stored at 10°C in PET containers on 7th sampling day decreased by about 27% and 42%, respectively. Physiologically, this could be attributed to wounding of living tissue in the fresh-cut process, which starts a cascade of metabolic reactions that can result in discoloration and other undesirable phenomena that can render the product unmarketable. Temperature also showed an influence on color parameters. All of the color changes resulted from browning of sample cubes.

3.3.1.4 Firmness

Texture of fresh-cut fruit is a very important quality parameter. Firmness of fresh-cut melon cubes in PLA and PET containers decreased from 7.4 N to 4.4-4.7 N throughout the storage period at 4 and 10°C (Fig. 3-6). Firmness values of samples stored in PLA containers at 4°C were the highest throughout the storage period. The storage temperature of 10°C, compared to storage at 4°C, increased the respiration of

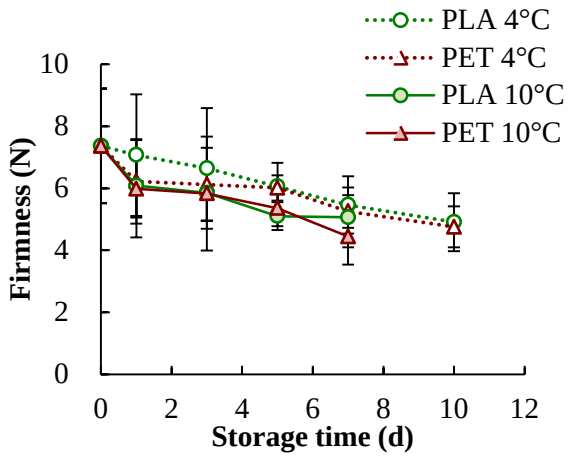

Fig. 3-6 Firmness of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

the fruit and gave rise to some enzymatic processes that caused softening of the fresh-cut melon cubes. No significant difference was found in texture firmness values of fresh-cut melon in PLA and PET containers during storage.

3.3.1.5 Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C

As shown in Fig. 3-7, in general, SSC, pH and vitamin C of fresh-cut melon in PLA and PET containers declined during storage at 4 or 10°C. TA values showed only slight increases. The containers and temperatures showed no effect on SSC during storage. No significant difference in pH or TA between the packaging materials was found before 5 days of storage at 10°C. On the 7th sampling day, the values ranged from 6.2 to 6.7 for pH and 1.8% to 2.3% for TA. There were no significant differences in SSC, pH, TA and vitamin C of fresh-cut melon cubes in PLA containers at 4°C during storage.

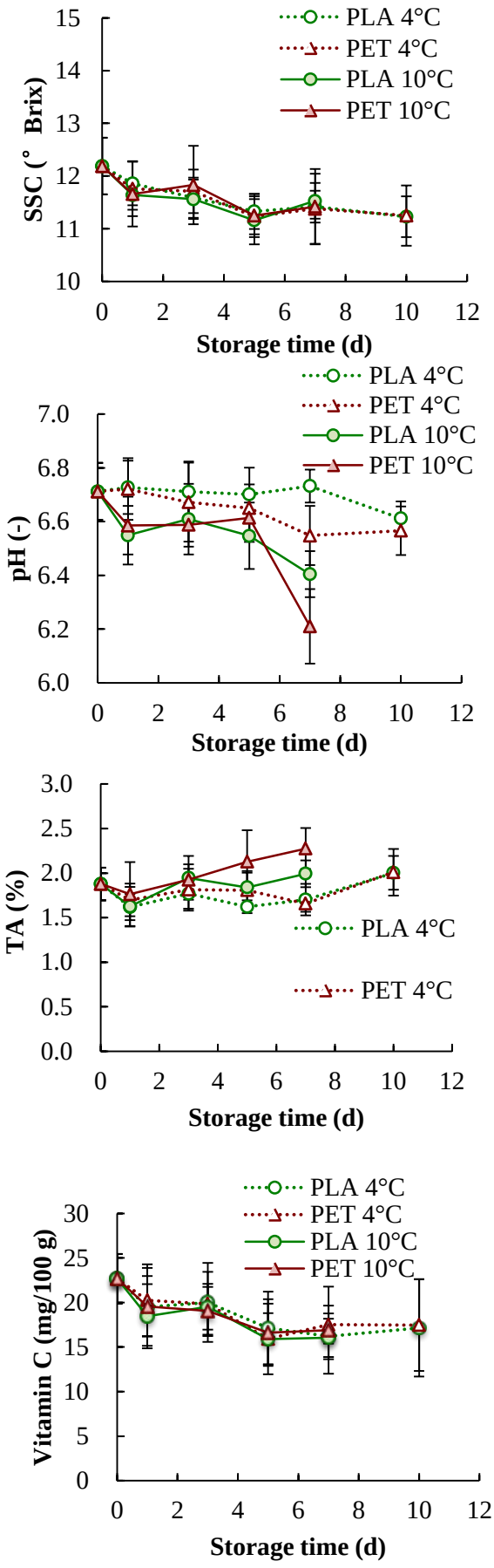

Fig. 3-7 Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

3.3.1.6 Sensory analysis

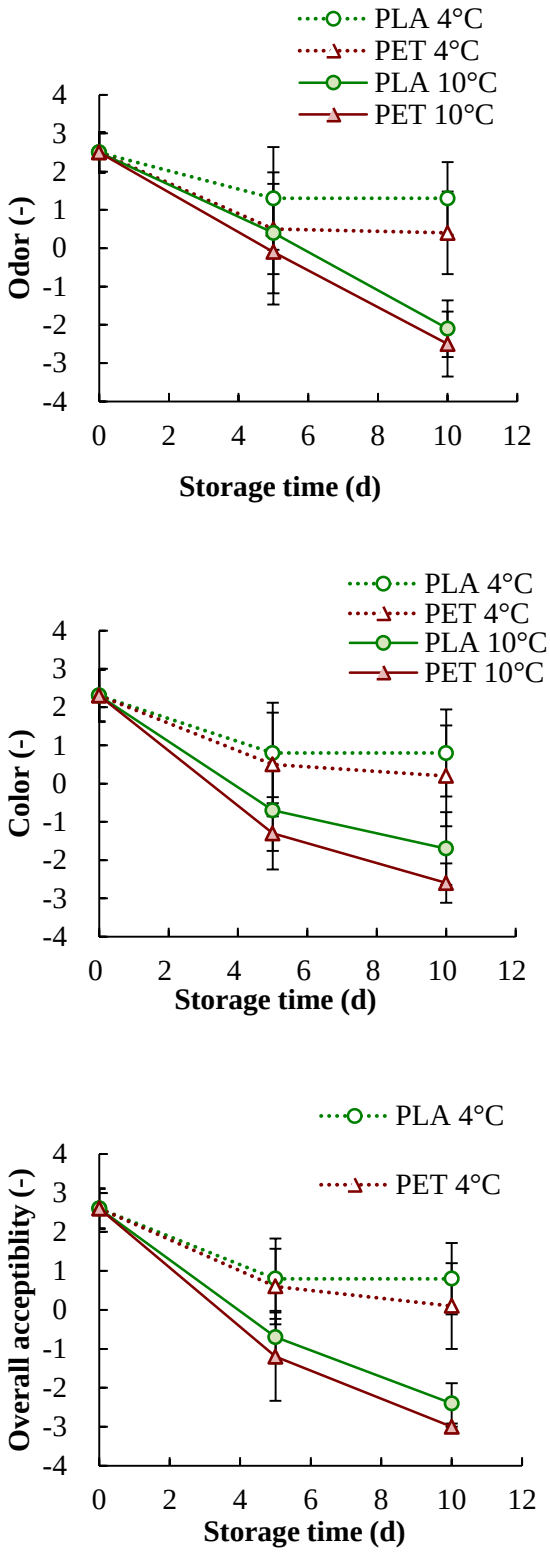

Fig. 3-8 Sensory analysis (odor, color and overall acceptability) of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage

Appearance is one of the most critical factors in the initial purchase of fresh and fresh-cut products. Appearance therefore needs to be maintained in order to attract consumer preference and choice. Odor and color play the most important factors for help consumers make decisions. Fig. 3-8 shows that the scores of odor, color and overall acceptability of sample cubes in all storage conditions declined throughout the storage. The panelists indicated that differences between melon cubes packaged in different containers at different temperatures were mainly based on color, odor and overall acceptability. Spoilage of melons cubes was observed at 10°C, especially in PET containers on the 10th sampling day. Although there were no significant differences between PLA and PET at the same temperature, melon cubes in PLA containers showed higher scores during sensory evaluation.

3.3.2 Overall evaluation of the fresh-cut melon

When fresh fruits are cut and handled in production, the internal tissues of the fruits are directly exposed to the environment and the fruits tissue corresponds to the damage by increasing its respiration rate to survive and repair the damage (Garrett, 1999). Due to increase in respiration of fresh-cut fruits, water/water vapor in the environment around the fruits will be increased. Higher moisture content in fruits and headspace atmosphere in packaging increase non-enzymatic browning, enzyme activity, mold and bacteria growth (Krochta, 2006). In addition, the higher humidity environment would promote spoilage of fresh-cut fruits in a packaging. As shown in Table 3-1, PLA indicated significantly higher water vapor transmission rate than that of PET, and Mochizuki (2005) also reported that water vapor permeability of PLA was about 10 times higher than that of PET. PLA packaging increased more weight loss in fresh-cut melon cubes during the storage in this study (Fig. 3-3). However, in turn, this weight loss would result in less color change and also inhibition of mold growth in fresh-cut melon stored in the PLA containers than those in the PET containers.

In addition, melon respires by taking oxygen and giving off carbon dioxide, the packaging material must be permeable to these gases (Garrett, 1999). Fresh-cut process increased respiration of melon cubes, so that oxygen inside the packaging containers was consumed very quickly. Mochizuki (2005) reported that oxygen permeability of PLA was over 10 times as high as that of PET. Due to much lower oxygen permeability of PET material, the fresh-cut melon might start anaerobic respiration, which might be reasonable for the production of alcohol and an increase of spoilage even further in fresh-cut melon cubes during storage in this study. Consequently, the PLA containers maintained appearance and quality of fresh-cut

melon better than those of PET containers during storage.

3.4 Discussions

The results showed that overall quality of fresh-cut melon declined during storage. Melon cubes in both packages showed increases in weight loss, juice leakage, surface color (ΔE), and TA and decreases in surface color (*L**, *a**, *b**), firmness, SSC, pH, vitamin C and sensory evaluation. No significant difference in color, firmness, pH, TA or sensory evaluation was found between the different packages at 4°C. However, due to larger water vapor and oxygen permeability of PLA than that of PET, significant differences in color of melon cubes between in the PLA and in PET containers were found on the 7th sampling day of storage at 10°C. The PLA containers used in this study maintained quality of fresh-cut melon better than did the PET containers in overall quality conservation of fresh-cut melon at 10°C during 10 days of storage.

Therefore, with consideration of sustainability and quality conservation performance, bio-based PLA is a suitable alternative to petroleum-based PET for storage of fresh-cut melon in retail markets.

Chapter 4 General conclusions and recommendations

Food packaging is expected to deliver high-quality product during distribution. The selection of packaging form and materials should be primarily based on considerations of food safety, followed by quality, cost, etc. Important properties of common packaging materials are generally mechanical, optical and barrier properties. Mechanical properties include tensile elasticity, tensile stress and breaking elongation, optical properties refer to transparency, haze, etc., and barrier properties involve water vapor transmission rate and gas transmission rate. These characteristics are mainly based on the physical properties such as crystallinity, molecular weight, etc. of bioplastics.

Tensile elasticity of petroleum-based low-density PE (LDPE, thickness: 30 μm), bio-based LDPE (30 μm) and PLA (25 μm) were 223.5, 248.4 and 2555.6 MPa, respectively. This meant that PLA possessed highest stiffness among the plastics. Tensile elasticity of bioplastics decreased as thickness decreased and as temperature increased, which meant flexibility of bioplastics increased when temperature increased. As temperature decreased, its effect on mechanical properties of plastics increased. Moreover, machine and transverse direction of a plastic sample also affected its mechanical properties. Bio-based LDPE indicated similar mechanical properties to petroleum-based LDPE.

As thickness of petroleum-based PE increased, transparency decreased. For the same thicknesses of LDPE samples, petroleum-based LDPE with lower crystallinity showed higher transmittance of visible light than that of bio-based LDPE representing in higher transparency. The transmittance of visible light of PLA was the highest among the

plastics analyzed in this study.

At 23°C and 50% relative humidity, water vapor transmission rate of PLA (25 μm) was 54.4 g/m2·d, in contrast, the water vapor transmission rates of petroleum-based and bio-based LDPE (30 μm) were 7.3 and 3.7 g/m2·d. The plastic film provided a resistance to water vapor transfer across it, thus the molecular structure of plastics could be a factor, which affects water vapor transferring through plastic material. Compared with PE, hydrophilic molecular structure in PLA material indicated higher water vapor transmission.

Due to these physico-chemical properties, bio-based LDPE could be applied as an alternative to petroleum-based LDPE, while PLA, which was bio-based and biodegradable, was stiff and transparent so that it can be applied as food packaging containers.

The market of the chilled fresh-cut produce has witnessed dramatic growth in recent years, stimulated largely by consumer demand for fresh, healthy, convenient and additive-free foods, which are safe and nutritious. Minimally processed fresh-cut fruits are very perishable and usually have a shelf life of 5-7 days at 1-7°C. In this study, packaging containers made from PLA and polyethylene terephthalate (PET) were examined for their ability to preserve the quality of fresh-cut melon under low temperature conditions (<10°C). Changes in quality of fresh-cut melon packed in PLA and PET containers, including weight loss, juice leakage, surface color, firmness, soluble solids content (SSC), pH, titratable acidity (TA), vitamin C and sensory quality, were evaluated during the storage. Overall quality of fresh-cut melon declined regardless of the

packaging material. Melon cubes in both packages increased in weight loss, juice leakage and TA and also decreased in surface color (L*, a*, b*), firmness, SSC, pH, vitamin C and sensory evaluation. No significant differences in juice leakage, color, firmness, SSC, pH, TA, vitamin C and sensory evaluation of fresh-cut melon were observed in either of the packages stored at 4°C.

Melon cubes that were stored at 10°C deteriorated on the 10th and 7th sampling day, respectively. Also a large amount of fungi in both fruit cubes was clearly observed in the PET containers. Significant differences in color (L*, a*, b*, ΔE) between the melon cubes in the two packages were recognized after 7-day storage at 10°C. Due to higher water vapor transmission rate and oxygen permeability, the PLA containers used in this study maintained overall quality of fresh-cut melon better than did the PET containers at 10°C during 10 days of storage.

In this study, bio-based PE showed comparable properties to those of petroleum-based PE. The PLA containers, bio-based and biodegradable, used in this study maintained overall quality of fresh-cut fruits better than did the PET containers during storage. In conclusion, bioplastics would be an appropriate alternative for food packaging material from the viewpoint of the environmental preservation and sustainability.

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Physico-chemical Properties of Bioplastics and its Application for Fresh-cut Fruits Packaging

March, 2016

Huijuan ZHOU

Laboratory of Agricultural and Food Process Engineering
Division of Environmental Resources
Graduate School of Agricultural Science, Hokkaido University
Kita-9, Nishi-9, Kita-ku, Sapporo, Hokkaido, Japan
Tel. and Fax.: +81-11-706-2558

Reference thesis

Hokkaido University
Graduate School of Agriculture

Division of Environmental Resources
Doctor Course

Huijuan ZHOU

Research Achievements

Research Paper

1. **Huijuan ZHOU,** Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA. 2016. Comparative Quality Changes of Fresh-cut Melon in Bio-based and Petroleum-based Plastic Containers during Storage. *Environ. Control Biol*., **54** (?), ?-?. (Accepted on Jan 6, 2016, in press)

Conference presentations

1. **Huijuan ZHOU,** Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA. Crystallinity of bioplastics for food packaging, Hokkaido Branch of The Japanese Society of Agricultural Machinery and Food Engineers (Ebetsu), 2015.
2. **Huijuan ZHOU,** Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA. Mechanical and optical properties of bioplastics for food packaging, The Japanese Society of Agricultural Machinery and Food Engineers (Iwate), 2015.
3. **Huijuan ZHOU,** Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA. Physical properties of bio-based plastics applied in food packaging, Hokkaido Branch of the Japanese Society for Food Science and Technology (Hakodate), 2015.
4. **Huijuan ZHOU,** Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA. Comparative quality changes of fresh-cut melon in bio-based and petroleum-based containers during storage, Hokkaido Branch of the Japanese Society of Agricultural Machinery and Food Engineers (Iwamizawa), 2014.

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Comparative Quality Changes of Fresh-cut Melon in Bio-based and Petroleum-based Plastic Containers during Storage

Huijuan ZHOU, Shuso KAWAMURA, Shigenobu KOSEKI, Toshinori KIMURA

School of Agricultural Science, Hokkaido University, Sapporo, 060-8589, Japan

Fresh-cut melon, 'Rupia red' cultivar, was packaged in snap-fit closed packages made from polylactic acid (PLA) and polyethylene terephthalate (PET) and stored at 4 and 10°C for 10 days. Changes in quality of fresh-cut melon, including weight loss, juice leakage, surface color, firmness, soluble solids content (SSC), pH, titratable acidity (TA), vitamin C and sensory quality, were evaluated throughout the storage period. Overall quality of fresh-cut melon declined regardless of the packaging material. Melon cubes in both packages showed increases in weight loss, juice leakage and TA and they showed decreases in surface color (L^*, a^*, b^*), firmness, SSC, pH, vitamin C and sensory evaluation. No significant difference in color, firmness, pH, TA or sensory evaluation was observed either of the packages at 4°C, but significant differences in color (L^*, a^*, b^*, ΔE) between the melon cubes in the two packages were found after 7 days of storage at 10°C. Due to larger water vapor and oxygen permeability, the PLA containers used in this study maintained overall quality of fresh-cut melon better than did the PET containers at 10°C during 10 days of storage. Bio-based PLA is a suitable alternative to petroleum-based PET for storage of fresh-cut melon.

Keywords: fresh-cut melon, polylactic acid, polyethylene terephthalate, quality changes

INTRODUCTION

Sales of fresh-cut fruit in the U.S. have been increasing at rates of 7% to 54% growth. Sales of fresh-cut melon have also been increasing at the fastest rate, and expected to continue over the next few years (Martín-Belloso and Soliva-Fortuny, 2011). Fresh-cut produce has become popular because of consumers' demand for more convenient foods. However, fresh-cut fruits are very perishable and usually have a shelf life of 5-7 days at 1-7°C (Rico et al., 2007). Fresh-cut processing alters the integrity of fruits and vegetables, leading to negative effects on product quality such as browning, off-flavor development, texture breakdown, and growth of microorganisms. Thus, shelf-life of fresh-cut fruit commodities are inevitably shortened (Lee et al., 2003; Martín-Belloso, 2006; Oms-Oliu, 2007; Raybaudi-Massilia et al., 2007).

Minimally processed fresh-cut melon with relatively higher pH (>5.2) than that of other fruits (Zhang et al., 2013) is considered to be highly perishable (Soliva-Fortuny and Martín-Belloso, 2003). Previous studies on quality preservation of fresh-cut melon have focused on edible coatings, modified atmosphere packaging (MAP), an absorbent pad, mild heat and calcium treatment, and UV radiation (Raybaudi-Massilia et al., 2008; Fernández et al., 2010; Lamikanra and Watson, 2007; Manzocco, et al., 2011). However, there have been few studies on bio-based packaging for quality conservation of fresh-cut melon.

Various materials are currently used for

Corresponding author: Shuso KAWAMURA, tel/fax: +81-11-706-2558.
e-mail: shuso@bpe.agr.hokudai.ac.jp

packing fresh produce. The market is dominated by polyethylene terephthalate (PET) and polystyrene (PS) for rigid containers and polyolefins for bags, and all of the materials are made from petroleum-based polymers. One alternative is the use of bio-based packaging materials. According to European Bioplastics (2015), total amount of bioplastic production was 1.7 million tonnes. Non-biodegradable bioplastic production was 60.9% and biodegradable bioplastic was 39.1% of the total production. Non-biodegradable bio-based PET had the highest production at 35.4%, followed by biodegradable and compostable polylactic acid (PLA) at 16.1% of the total bioplastics production. It was reported that the bioplastics market would continue to grow and would have a 5% share of the entire plastic packaging market within 20 years (Byun and Kim, 2014).

Polylactic acid (PLA), biodegradable, made from natural resources such as corn or sugar cane (Garlotta, 2001; Kale et al., 2007; Zhang and Sun, 2005), is one of the most widely available bio-based plastic materials. PLA possesses mechanical properties comparable to those of PET and PS (Auras et al., 2005). It is transparent and it is food contact approved by the US Food and Drug Administration (FDA) (John et al., 2007; Almenar et al., 2008) and can be degraded in a composting system (Kijchavengkul and Auras, 2008). Thus, PLA would be a good alternative for food packaging material from the viewpoint of the environmental conservation and sustainability. Most PLA packaging application are limited to rigid packaging. PLA has been tested as a packaging material for some types of fresh produce and it has been shown to be useful for quality conservation of fruits. Almenar et al. (2008) reported that blueberries packaged in PLA containers remained fresher during storage at 10 or 23°C than did fruits packaged in common commercial packages, vented clamshell containers.

In this study, packaging containers made from PLA and PET were tested for their ability to preserve the quality of fresh-cut melon under low temperature conditions (<10°C). The choice of packaging material was made with the following objectives: (1) to compare the effects of a petroleum-based packaging material versus a bio-based packaging material with comparable properties on the changes in quality of fresh-cut melon and (2) to determine the performance of a bio-based material as a packaging material for fresh-cut melon under a low temperature condition.

MATERIALS AND METHODS

Fresh-cut operations

Fresh and sound melons (‘Rupia red’ cultivar), harvested at Biratori, Hokkaido, Japan, with the same sizes and ripening degrees were purchased from a local supermarket in Sapporo, Japan. Prior to the experiment, the melons were stored at 4°C for 24 hours. Before cutting, the outer surfaces of the melons were washed thoroughly with cool tap water to remove surface dirt and melons were scrubbed with a clean produce brush, as specified by the U.S. FDA 2005 Model Food Code Section 3-302.15. The melons were hand-cut with a sharp knife into eight slices; sharp sterile knives were used to reduce the stress produced during processing. Melon slices were parallel to the longitudinal axis, and blossom stem-ends, seeds, placenta and peel were discarded. The pulp was hand cut in trapezoidal shaped sections (Silveira et al., 2010). Each cube was about 20 g.

Packaging materials and packaging

Water vapor transmission rate (WVTR) and water vapor permeability coefficient (WVPC) of both packaging materials (PLA and PET) were measured by a modified technique of the wet cup method according to the American Society for Testing and Materials (ASTM) E 96 (ASTM,

2005). Plastic sheets of PLA and PET containers were sealed on cups that contained 15 mL of distilled water. Test cups were placed in desiccators at a relative humidity of 54% maintained by a saturated magnesium nitrate solution and were stored in a incubator at 23°C, with the relative humidity difference inside and outside the cup being 46%. The sealant used for attaching the specimen to the sample dish was a combination of 20% bee wax and 80% paraffin. WVTR and WVPC were calculated using the following formulas:

$$WVTR = \frac{W/t}{A}, \quad (1)$$

where *WVTR* is water vapor transmission rate (g/m^2·d), *W* is weight change (g), *t* is the time during which *W* occurred, and *A* is the test area (m^2).

$$WVPC = \frac{WVTR \times e}{(p_1 - p_2)}, \quad (2)$$

where *WVPC* is water vapor permeability coefficient (g·m/m^2·d·Pa), *e* is film thickness (m) and p_1 and p_2 are water vapor partial pressure (Pa) inside and outside the cup, respectively.

$$p = p_s \times \frac{RH}{100}, \quad (3)$$

where *p* is water vapor partial pressure, p_s is saturated water vapor pressure for pure water at a specific temperature and *RH* is relative humidity (%).

As shown in Fig. 1, 210 g of fresh-cut melon cubes was placed inside each of the PLA containers with a volume of 850 mL (Risupack Co. Ltd., Japan), which were snap-fit, and 280 g of fresh-cut fruit was placed inside each of the commercial PET containers with a volume of 1120 mL (FP Corp., Japan). After filling, the containers were divided into two groups and stored in darkness at 4 and 10°C for 10 days. Physical and physicochemical analyses of melon cubes stored in each type of container and at each storage temperature (3 replications for each packaging condition) were carried out on each sampling day (0, 1st, 3rd, 5th, 7th and 10th days) during storage.

Fig. 1 Fresh-cut melon cubes in polylactic acid (PLA) and polyethylene terephthalate (PET) containers (right: PLA, left: PET)

Weight loss

The weight of each package of fresh-cut melon was determined on day 0 and on each sampling day using a digital precision balance (±0.01 g) (CPA 62025, Sartorius Japan K.K.). Values of weight loss are shown as the percentage loss of the initial total weight.

Juice leakage

Melon cubes were packed in snap-fit containers and stored at 4 and 10°C for 10 days. Juice leakage of the samples recovered with a syringe was evaluated by weighing the amount of juice loss from the fruit at increasing storage periods. Results are shown as liquid quantity (g) recovered per 100 g of fresh-cut melon in the package (Manzocco et al., 2011).

Surface color measurement

Fresh-cut melon color was measured directly with a Minolta CR-400 chroma meter (Konica Minolta Sensing, Inc., Japan) using the CIE scale L^* a^* b^*. The equipment was calibrated using a standard white tile. The maturation pattern of melon starts from the fruitlets at the base of the fruit and moves up to the crown, resulting in different stages of maturity of the fruitlets throughout the whole fruit. Because of such a complex fruit anatomy and maturity pattern, fresh-cut melon cubes are non-uniform in color and texture. Therefore, each value represents the mean of a duplicate determination of 15 different samples of each storage condition. CIE L^*(lightness), a^*(red-green) and b^* (yellow-blue) values are

determined by reflectance measurements. The parameter ΔE (Rizzo and Muratore, 2009) is defined as the visible difference of color. This value was calculated as follows:

$$\Delta E = \sqrt{(L^* - L_0)^2 + (a^* - a_0)^2 + (b^* - b_0)^2}, (4)$$

where the parameters of melon cubes on the initial day were L_0=61.15, a_0=15.45 and b_0=39.57.

Firmness

Tissue softening is one of the major problems that limit the shelf life of fresh-cut fruit, and firmness is an important factor that influences the consumer acceptability of these products. The firmness of the fresh-cut melon cube center was measured as the force applied by a flathead probe of 10 mm in diameter with the crosshead speed set at 0.5 mm/s. The fruit cubes were compressed by 50% using a Rheo Meter (NRM-2002J, Rheotech Corp., Japan). Fifteen fruit cubes of each packaging condition on each sampling day were measured, and the values were averaged. The results are shown as force in Newtons (N).

Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C

Flavor is composed of sugar, organic acids and aromatic compounds. Differences in sensory quality have been based on the level and proportion of these flavor components (Almenar et al., 2010). Melon pieces, by the fact of being alive, continue the respiration process, consuming sugars and varying SSC levels, which reflect sugar contents (Lamikanra et al., 2000).

Flavor was positively correlated with pH and SSC, confirming consumers' preference for fruits with a high pH and high sugar content. Twelve fruit cubes from each packaging condition were wrapped in paper towels and squeezed by hand. The expressed juice was used for determination of SSC, pH, TA and vitamin C. SSC was measured at 20°C by using a pocket refractometer (PAL-1, Atago Co. Ltd., Japan), and results are shown in Brix (°). The value of pH was measured with a pH meter (JF 18, Horiba Ltd., Japan). TA was determined by diluting each 1-mL aliquot of melon juice in 50 mL of distilled water and titrating to pH 8.1 using 0.1mol/L sodium hydroxide (NaOH). Total acid contents were determined as citric acid equivalents (Montero-Calderón et al., 2008). The quantity of vitamin C was determined by using ascorbic acid reflectoquant test strips in combination with an RQflex® plus 10 reflectometer (Merck Millipore Corp., Germany) (Merck KGaA, 2012)

Sensory analysis

Sensory evaluation of fresh-cut melon was carried out. Samples were given to panelists in a completely randomized order. The sensory quality of the fresh-cut melon under each packaging condition was evaluated by using a panel of 10 untrained judges, researchers and students of the Laboratory of Food Processing and Engineering of Hokkaido University in Japan. Odor, color and overall acceptance were selected as quality attributes. A structured scale was used for odor, color and overall acceptability of melon cubes: 3, very good; 2, good; 1, fairly good; 0, fair; -1, slightly poor; -2, poor; -3 very poor. During the test sessions, the sample presentation order was randomized and sensory evaluation was carried out on the 0, 5th and 10th sampling days.

Statistical analysis

Data were subjected to one-way and factorial analysis of variance (ANOVA) using Statistical Product and Service Solutions version 22 (SPSS Inc., Chicago, IL, USA). Significant differences between means of all measurement items among storage conditions and each sampling day during the 10 days of storage were determined by Tukey's post hoc comparison test ($p< 0.05$).

RESULTS AND DISCUSSION

As shown in Fig. 2, melon cubes that had been stored at 10°C were greatly deteriorated on the 10th sampling day. A large amount of fungi was clearly observed in the PET containers. Much worse spoilages and smells of alcohol in PET containers at 10°C were also noted by panelists during sensory evaluation. Quality changes of fresh-cut melon were determined for 7 days for melons stored at 10°C and for 10 days for melons stored at 4°C.

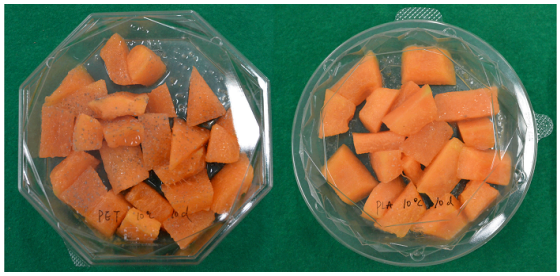

Fig. 2 Spoilage of fresh-cut melon cubes in polylactic acid (PLA) and polyethylene terephthalate (PET) containers at 10°C on the 10th sampling day (right: PLA, left: PET)

Weight loss

Confirmation of leakproofness was carried out. The amounts of air leakages through gaps between the lids and bottoms of the PLA and PET containers were so small that both types of containers could be regarded as being airproof (data not shown).

Loss of moisture is the major reason for fruit weight loss and it is the result of respiration and transpiration processes occurring during postharvest. In closed packaging systems, moisture loss of fresh produce is determined mainly by the permeability to water vapor of the packaging material (Joo et al., 2011).

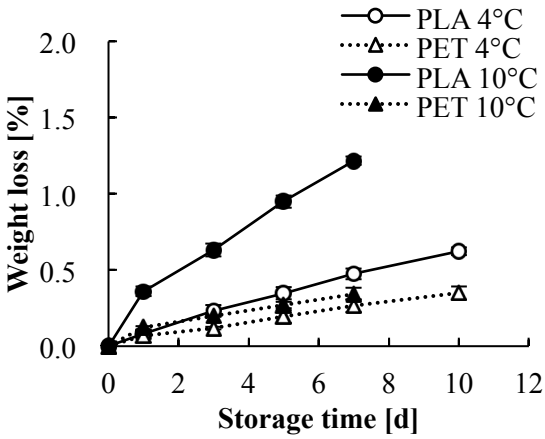

Fig. 3 Weight loss of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=3)

As can be seen in Fig. 3, 'Rupia red' fresh-cut melon in PLA and PET containers showed a progressive loss of weight during storage. Throughout the storage period, there were significant differences between weight losses in the PLA and PET containers at 4 or 10°C. In closed packaging systems, moisture loss of the fresh produce is determined mainly by the permeability to water vapor of the material. Fig. 3 shows the differences in fresh-cut melon weight loss caused by the packaging material. Greater weight loss were observed for the PLA-packaged melon than for the PET-packaged melon: 0.62% vs. 0.35% at 4°C on the 10th sampling day and 1.22% vs. 0.34% at 10°C on the 7th sampling day. The greater weight loss of melon cubes in the PLA containers was due to the higher water vapor transmission rate (WVTR) of PLA. Values of 18.18 and 2.09 g/m^2·d were measured for PLA and PET used in this study at standard room temperature of 23°C and 46% relative humidity differences (Table 1). Similar results for WVTR and WVPC were obtained in other studies (Auras et al., 2003; Auras et al., 2005). Greater differences in fresh-cut melon weight loss at a higher temperature are shown in Fig. 3. Shriveling and loss of plumpness are dependent on temperature. The higher the temperature is, the greater the effect of the plastic container can

Table 1. Water vapor transmission rate (WVTR) and water vapor permeability coefficient (WVPC) of PLA and PET containers at 23°C and 46% relative humidity differences (N=3)

Material	Thickness (μm)	WVTR (g/m^2·d)	WVPC (g·m/m^2·d·Pa)
PLA	270	18.18	3.80E-06
PET	240	2.09	0.39E-06

be. A weight loss of more than 5% is a cause of reduction in retail value of vegetables and fruits (Almenar et al., 2008). Weight loss of 5-10% or more has been shown to be associated with a significant reduction in the firmness of fresh products (Almenar et al., 2010). Weight losses of fresh-cut melon stored at 4°C and 10°C in the PLA and PET containers were less than 1.5%, indicating that PLA containers were as suitable as PET containers for moisture conservation of fresh-cut melon during storage at 4°C and 10°C.

Juice leakage

Results for juice leakage from fresh-cut melon pieces inside the containers during the 10-d at 4 and 10°C are shown in Fig. 4. No significant differences in juice leakage were found between the different packaging and temperature conditions.

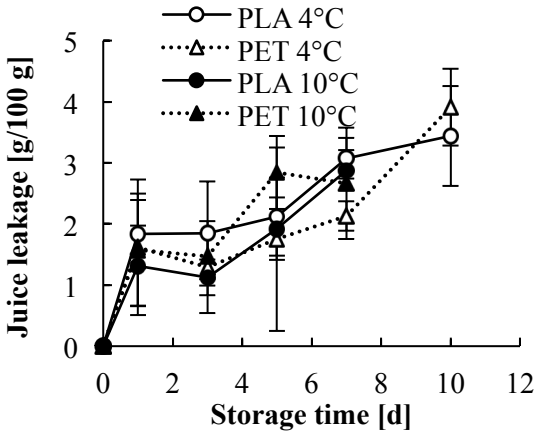

Fig. 4 Juice leakage of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=3)

Surface color measurement

Color is the most evident parameter by which consumers judge fresh-cut melon quality. Change in color parameters L^*, a^* and b^* of fresh-cut melon were studied throughout the 10-day storage at 4 and 10°C. More initial statistical differences of melon cubes in PET containers in ΔE, calculated by color spaces L^*, a^* and b^* among packaging conditions, were observed (Fig. 5). These meant melon cubes lost

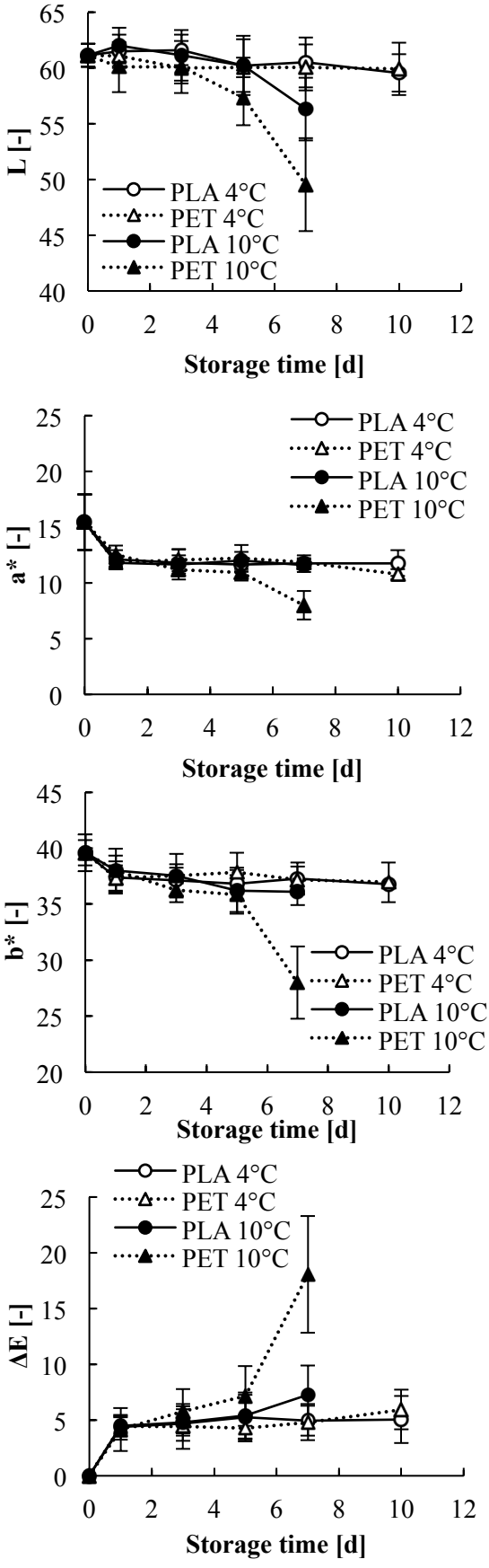

Fig. 5 Color parameters (L^*, a^*, b^*, ΔE) of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

redness and yellowness gradually during the storage in both containers.

Color changes in L^*, a^* and b^* values of sample cubes in PET containers were larger than those of sample cubes in PLA containers during the storage period. Compared with the L^* and b^* values on the initial day, the values of sample cubes stored at 10°C in PET containers on 7th sampling day decreased by about 27% and 42%, respectively. Physiologically, this could be attributed to wounding of living tissue in the fresh-cut process, which starts a cascade of metabolic reactions that can result in discoloration and other undesirable phenomena that can render the product unmarketable. Temperature also showed an influence on color parameters. All of the color changes resulted from browning of sample cubes.

Firmness

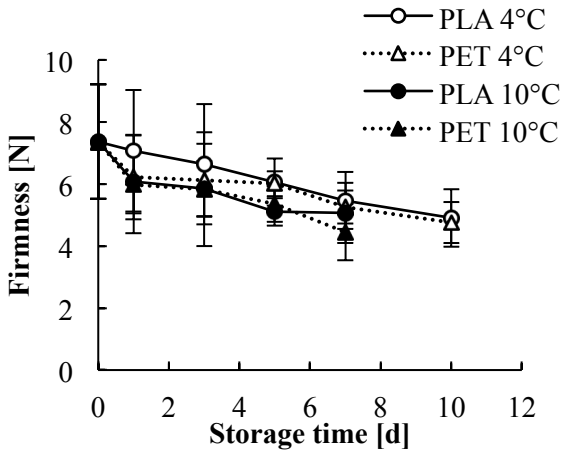

Fig. 6 Firmness of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

Texture of fresh-cut fruit is a very important quality parameter. Firmness of fresh-cut melon cubes in PLA and PET containers decreased from 7.4 N to 4.4-4.7 N throughout the storage period at 4 and 10°C (Fig. 6). Firmness values of samples stored in PLA containers at 4°C were the highest throughout the storage period. The storage temperature of 10°C, compared to storage at 4°C, increased the respiration of the fruit and gave rise to some enzymatic processes that caused softening of the

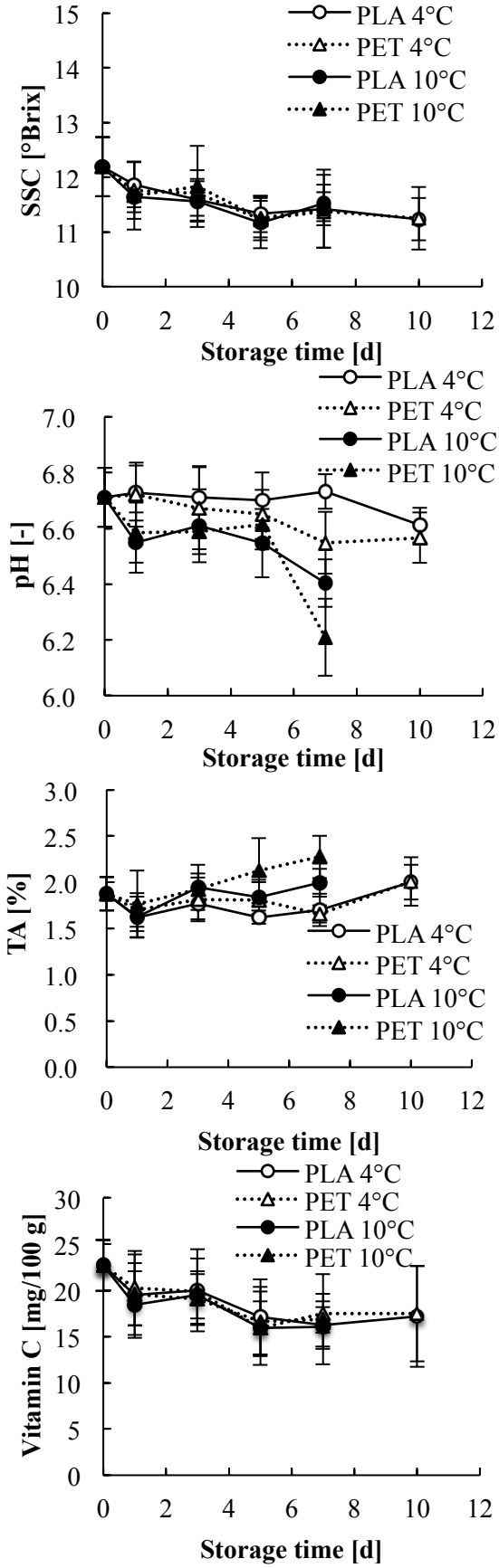

Fig. 7 Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

fresh-cut melon cubes. No significant difference was found in texture firmness values of fresh-cut melon in PLA and PET containers during storage.

Soluble solids content (SSC), pH, titratable acidity (TA) and vitamin C

As shown in Fig. 7, in general, SSC, pH and vitamin C of fresh-cut melon in PLA and PET containers declined during storage at 4 or 10°C. TA values showed only slight increases. The containers and temperatures showed no effect on SSC during storage. No significant difference in pH or TA between the packaging materials was found before 5 days of storage at 10°C. On the 7th sampling day, the values ranged from 6.2 to 6.7 for pH and 1.8% to 2.3% for TA. There were no significant differences in SSC, pH, TA and vitamin C of fresh-cut melon cubes in PLA containers at 4°C during storage.

Sensory analysis

Appearance is one of the most critical factors in the initial purchase of fresh and fresh-cut products. Appearance therefore needs to be maintained in order to attract consumer preference and choice. Odor and color play the most important factors for help consumers make decisions. Fig. 8 shows that the scores of odor, color and overall acceptability of sample cubes in all storage conditions declined throughout the storage. The panelists indicated that differences between melon cubes packaged in different containers at different temperatures were mainly based on color, odor and overall acceptability. Spoilage of melons cubes was observed at 10°C, especially in PET containers on the 10th sampling day. Although there were no significant differences between PLA and PET at the same temperature, melon cubes in PLA containers showed higher scores during sensory evaluation.

Overall evaluation of the fresh-cut melon

When fresh fruits are cut and handled in production, the internal tissues of the fruits are directly exposed to the environment and the fruits tissue corresponds to the damage by increasing its respiration rate to survive and repair the damage (Garrett, 1999). Due to increase in respiration of fresh-cut fruits, water/water vapor in the environment around the

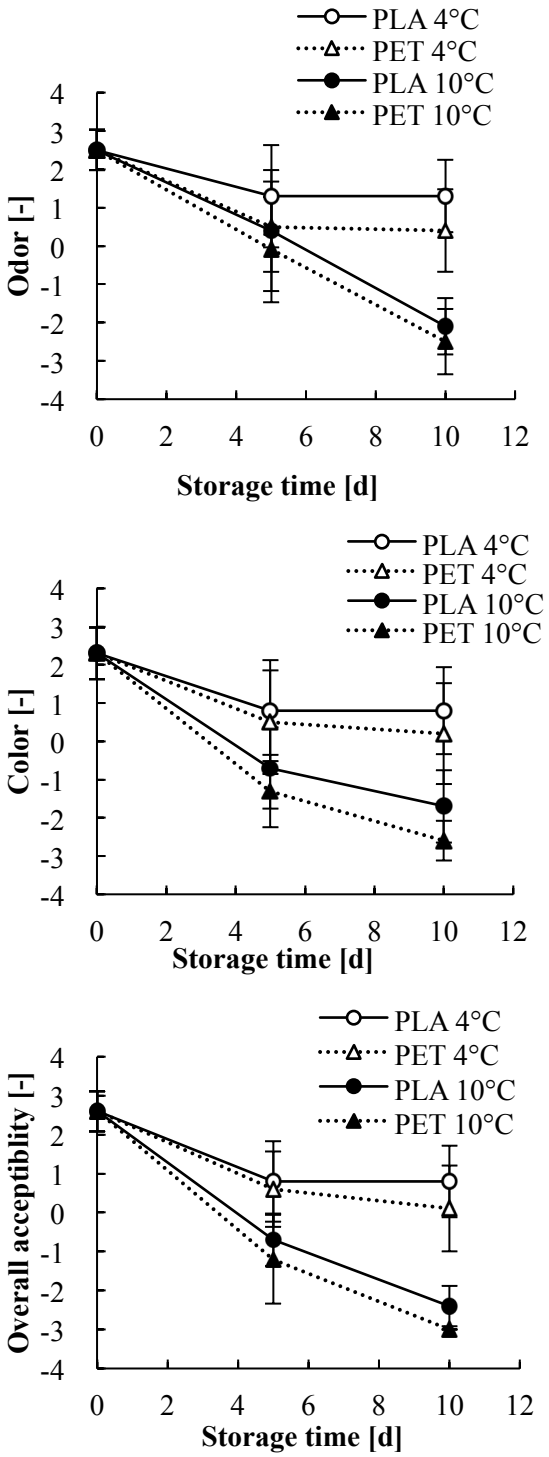

Fig. 8 Sensory analysis (odor, color and overall acceptability) of fresh-cut melon cubes packaged in PLA and PET containers at 4 and 10°C during 10 days of storage (N=10)

fruits will be increased. Higher moisture content in fruits and headspace atmosphere in packaging increase non-enzymatic browning, enzyme activity, mold and bacteria growth (Krochta, 2006). In addition, the higher humidity environment would promote spoilage of fresh-cut fruits in a packaging. As shown in Table 1, PLA indicated significantly higher water vapor transmission rate than that of PET, and Mochizuki (2005) also reported that water vapor permeability of PLA was about 10 times higher than that of PET. PLA packaging increased more weight loss in fresh-cut melon cubes during the storage in this study (Fig. 3). However, in turn, this weight loss would result in less color change and also inhibition of mold growth in fresh-cut melon stored in the PLA containers than those in the PET containers.

In addition, melon respires by taking oxygen and giving off carbon dioxide, the packaging material must be permeable to these gases (Garrett, 1999). Fresh-cut process increased respiration of melon cubes, so that oxygen inside the packaging containers was consumed very quickly. Mochizuki (2005) reported that oxygen permeability of PLA was over 10 times as high as that of PET. Due to much lower oxygen permeability of PET material, the fresh-cut melon might start anaerobic respiration, which might be reasonable for the production of alcohol and an increase of spoilage even further in fresh-cut melon cubes during storage in this study. Consequently, the PLA containers maintained appearance and quality of fresh-cut melon better than those of PET containers during storage.

CONCLUSION

The results showed that overall quality of fresh-cut melon declined during storage. Melon cubes in both packages showed increases in weight loss, juice leakage, surface color (ΔE), and TA and decreases in surface color ($L^* a^* b^*$), firmness, SSC, pH, vitamin C and sensory evaluation. No significant difference in color, firmness, pH, TA or sensory evaluation was found between the different packages at 4°C. However, due to larger water vapor and oxygen permeability of PLA than that of PET, significant differences in color of melon cubes between in the PLA and in PET containers were found on the 7th sampling day of storage at 10°C. The PLA containers used in this study maintained quality of fresh-cut melon better than did the PET containers in overall quality conservation of fresh-cut melon at 10°C during 10 days of storage.

Therefore, with consideration of sustainability and quality conservation performance, bio-based PLA is a suitable alternative to petroleum-based PET for storage of fresh-cut melon in retail markets.

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