INVESTIGATION OF BLOCK COPOLYMER EFFECT ON THE PHYSICAL AND MECHANICAL PROPERTIES OF RETORT CAST POLYPROPYLENE (RCPP) FOR FOOD PACKAGING FILM

This report submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering

by

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Signature : ……………………………………

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Date : 26th June 2018

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee are as follow:

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(PROF. DR. QUMRUL AHSAN)

ABSTRAK

Tujuan kajian ini adalah untuk menganalisis kesan kopolimer blok berbanding dengan kesan homopolimer pada sifat fizikal dan mekanikal serta mengkaji morfologi filem ‘cast polypropylene’(CPP) dan ‘retort cast polypropylene’ (RCPP) untuk filem pembungkusan makanan. Filem CPP dan RCPP juga dikenali sebagai filem berlapis kerana ia terdiri daripada tiga lapisan. Terdapat enam ujian fizikal dan mekanikal (kekaburan, kekuatan impak, kekasaran permukaan, ujian geseran, kestabilan termal dan kekuatan tegangan) dan empat kaedah pencirian (SEM, DSC, XRD dan FTIR) telah dianalisis dalam kajian perbandingan ini. Kajian perbandingan ini dijalankan untuk meningkatkan kekuatan impak filem pembungkusan makanan kerana kerapuhan suhu rendah merupakan masalah utama dengan filem homopolimer CPP. Kerapuhan suhu rendah ini disebabkan oleh sifat penghabluran tinggi dalam struktur homopolimer PP semasa pemprosesan pada suhu yang lebih rendah (di bawah 0ºC) yang menyebabkan kerapuhan filem meningkat dan mengurangkan kekuatannya. Oleh itu, kopolimer blok telah diperkenalkan untuk mengatasi masalah ini kerana filem kopolimer blok digabungkan dengan monomer yang mempunyai sifat-sifat pengedap haba yang baik. Hal ini demikian kerana, filem berlapis CPP terdiri daripada homopolimer (PP) manakala filem berlapis RCPP terdiri daripada kopolimer blok (PP+PE) dalam lapisan teras. Kajian perbandingan berdasarkan ujian fizikal dan mekanikal dan struktur molekul ini menunjukkan dengan ketara bahawa, filem berlapis RCPP mempunyai kekuatan impak yang baik, kekuatan tegangan yang baik, pengedap haba yang tinggi, ciri geseran yang baik, kestabilan termal dan kekristalan yang tinggi berbanding dengan filem CPP disebabkan oleh kesan kopolimer blok.

ABSTRACT

The aim of this research is to analyze the block copolymer versus homopolymer effect on the physical and mechanical properties and to investigate the film morphology of cast polypropylene (CPP) and retort cast polypropylene (RCPP) for food packaging film. The CPP and RCPP films are also known as multilayer films since it's made up of three layers. About six physical and mechanical testing (haze, drop, surface roughness, coefficient of friction, heat seal and tensile) and four characterization method (SEM, DSC, XRD and FTIR) have been used in this comparison study. This comparison study is conducted to improve the impact energy performances of food packaging film since low temperature brittleness is the major problem with the homopolymer CPP films. This low temperature brittleness attributed due to the nature of high crystallinity in a homopolymer PP structure which results in poor impact strength and increases the film brittleness during co-extrusion process at lower temperatures (below 0 ºC). Therefore, development of block copolymer has been introduced to overcome this problem since the block copolymer films incorporated with monomers with good heat sealant properties. It is because, the multilayer CPP film mainly made up of homopolymer (PP) while the multilayer RCPP film is made up of block copolymer (PP+PE) in the core layer. The findings of this comparison study based on physical and mechanical testing and molecular structures significantly shows that, the multilayer RCPP film has better impact strength, tensile strength, heat sealing, good frictional characteristics, thermal stability and degree of crystallinity compared to multilayer CPP film due to block copolymer effect.

DEDICATION

Dedicated to
my beloved father, Shellahmutto Mutusame
my appreciated mother, Ponnamah Vadamalai
my adorable brothers and sisters,
my supportive friends,
for giving me moral support, money, cooperation, encouragement and also understandings.
Thank You So Much & Love You All Forever!

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LIST OF ABBREVIATIONS

PP	-	Polypropylene
CPP	-	Cast Polypropylene
RCPP	-	Retort Cast Polypropylene
PE	-	Polyethylene
HDPE	-	High Density Polyethylene
PET	-	Polyethylene Terephthalate
BOPP	-	Biaxial Oriented Polypropylene
PVC	-	Polyvinyl Chloride
FTIR	-	Fourier Transform Infrared Spectroscopy
XRD	-	X-Ray Diffraction
SEM	-	Scanning Electron Microscopy
DSC	-	Differential Scanning Calorimetry
EPR	-	Enhanced Permeability and Retention
N-AFR	-	No Air Flow Rate
L-AFR	-	Low Air Flow Rate
M-AFR	-	Medium Air Flow Rate
H-AFR	-	High Air Flow Rate
DR	-	Draw Ratio
MD	-	Machine Direction
TD	-	Transverse Direction
MC	-	Multilayer Sample
ASTM	-	American Society for Testing and Materials
ISO	-	The International Organization of Standardization
EHT	-	Accelerating Voltage

LIST OF SYMBOLS

µm	-	Micrometer
cm	-	Centimeter
mm	-	Millimeter
kg	-	Kilogram
g	-	Gram
N	-	Newton
%	-	Percentage
s	-	Seconds
ml	-	Millilitre
ºC	-	Degree Celcius
MPa	-	Mega Pascal
GPa	-	Giga Pascal
ΔH_m	-	Melting Enthalpy
J/ mm	-	Joule per Millimeter
cm^{-1}	-	Reciprocal Centimeter
W/ mk	-	Watts per Meter Kelvin
g/ cm^3	-	Gram per Centimeter Cubic

CHAPTER 1

INTRODUCTION

This chapter is exposed to the beginning of the research project. "Investigation of block copolymer effect on the physical and mechanical properties of retort cast polypropylene (RCPP) for food packaging film" emphasized on the study of competitor films, perhaps only in CPP and RCPP. This chapter also includes the problem statement, objective and scope respectively.

1.1 Research Background

Food packaging plays an important part in preserving food. It has been developed basically from a holder to contain food and to preserve the food quality. The principal roles of food packaging are to protect food products from outside influences and damage and to provide consumers with ingredient and nutritional information (Breil, 2013). Therefore, the processing of food without the food packaging can jeopardize human health as it is influenced by direct contact with physical, chemical, and biological contamination.

Various types of polymers as food packaging film have been widely used in the food industry. The common polymers used in food packaging industry are polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polystyrene (PS). These polymers have exceptional behavior that allows the packaged food to withstand the rigors of consumer handling, transportation, refrigeration, abrasion and irradiation.

However, the polypropylene has replaced the use of polystyrene (PS) in many food packaging applications. It is because the polypropylene has low cost, high toughness, resistance to stress cracking and has good chemical properties. Polypropylene (PP) also one of the most versatile and economic barrier films ever used in packaging applications (Yoon *et al.,* 2015). Therefore, polypropylene (PP) is widely used in packing biscuits, snacks, frozen foods and dried foods.

In addition, the development of food packaging film in food packaging also shows some significant results in preserving the food quality. The polypropylene (PP) film is economical due to its low density and is replacing the other materials in the packaging industry as well. The polypropylene (PP) film also increased the life span of the food and beneficial to consumer in terms of refuge and caliber.

In general, most plastic food packaging is a multilayer film oriented due to their high mechanical strength, good heat sealability, and ease of excellent machine suitability. This food packaging film orientation dramatically improves the properties such as stiffness and tensile strength while reducing the elongation. Besides that, the film is implemented in food packaging to protect the food from decompose because some foods are perishable due to moisture effect.

However, through an extensive research on common plastics, the food-material interactions can cause the leaching of toxic chemicals into food and environmental impact (Tabassi, 2014). Therefore, multilayer cast polypropylene (CPP) is widely being used as food packaging films among the various types of polymers due to its crucial properties. CPP films for flexible food packaging are produced from a combination of various grades of PP homopolymer. The crucial properties of CPP film are it has a clear transparent film with good optical properties, high tensile strength, exhibits good heat sealability, low flexural moduli, high impact strength, low moisture permeability and puncture resistance.

On the other hand, the development of thermally stable polymers is an area of extensive ongoing interest in food packaging film and the thermal conductivity of food packaging depends on temperature, composition, and porosity of the material. Therefore, food packaging also needs appropriate thermal degradation for thermal processing such as retort and sterilizing process in order to preserve the quality of the food. Since, CPP film is more resistant to oxidative pyrolysis as oxygen diffuse into the material which is inhibited by the high density and crystalline of polypropylene (PP), it lowers the thermal stability of the material.

Therefore, multilayer retort cast polypropylene (RCPP) film is introduced since it allows the sterile packaging by aseptic processing with the combination of various grades of PP block copolymer. RCPP film is clear and transparent with high impact strength which produced by a co-extrusion process where the molten polymers are extruded through a flat die to shape a thin film. It is harder and stronger than the low density polyethylene film. Besides, the RCPP film also has good moisture barrier properties, high wear resistance, high heat sealability and resistance at low cost.

1.2 Problem Statement

Polypropylene is a semi-crystalline material produced by polymerization process with catalyst, depending on the desired spectrum of properties. Nowadays, most of the homopolymers CPP film is produced by a co-extrusion process. Co-extrusion process is a process used to combine the different materials with different properties in a sandwich construction.

The processing parameters have a high influence on film properties depends on the raw materials used. The die temperatures and chill roll temperatures are the two most influences of processing on homopolymer CPP films. It is because increasing the die temperature can result in the marginal improvements to the transparency.

Moreover, controlling the chill roll temperature in homopolymer CPP films also one of the major concerns in the co-extrusion process. It is because, the homopolymer CPP films will have lower clarity when the co-extrusion viscosity mismatched. Therefore, the homopolymer CPP film brittleness increased as resulted in poor impact strength performances. It especially occurred at lower temperature (below 0 °C) due to the nature of high crystallinity in PP structure during processing.

In addition, the high extrusion temperature also can lead to discoloration when processing the homopolymer CPP films in plasma treatment where is used to remove the unwanted organic contaminants to increase the wettability. The preferred thickness range for films extruded using the chill role process is within 40 to 100 µm. The brittle and fibrous heat seals due to low melt temperature or low cooling rate also one of the drop back and critical issue in processing the homopolymer CPP films. It is because the brittle and fibrous heat seals can lead to the leaching of chemical compounds into the foods and the safety in terms of consumptions can be jeopardized.

Regardless, the low temperature brittleness is the major problem with the homopolymer CPP films, but it can be overcome by the development of a block copolymer (PP+PE) resin in retort cast polypropylene (RCPP) since the block copolymer films incorporated with monomers with good heat sealant properties. Besides, several additives such as anti-block and slip additive have been used in order to improve the impact energy performances of homopolymer CPP films.

1.3 Objective

The objectives of this research project are:

1. To analyze the block copolymer versus homopolymer effect on the physical and mechanical properties of multilayer retort cast polypropylene (RCPP) film.

2. To investigate the film morphology of multilayer retort cast polypropylene (RCPP) film using characterization tools.

1.4 Scope

The scope of this research is narrow down to the comparison study between the cast polypropylene (CPP) and retort cast polypropylene (RCPP) film. Therefore, the effect of the block copolymers and homopolymers on thickness between these two films was measured by scanning electron microscopy (SEM). In addition, the experimental study of physical and mechanical properties of multilayer retort cast polypropylene (RCPP) film were tested under the haze, surface roughness, coefficient of friction, drop, heat sealing and tensile testing. The qualitative information on molecular components and structures of these films was obtained by using Fourier Transform Infrared Spectroscopy (FTIR). Besides, the differential scanning calorimeter (DSC) method was used to study the thermal transitions of these films upon heating. X-ray diffraction (XRD) method was used for identification of polycrystalline phases in these films.

CHAPTER 2

LITERATURE REVIEW

This chapter emphasized on the theory of current packaging plastics, polypropylene, retort cast polypropylene, processing of polypropylene film, testing and characterization methods involved in the research. The main purpose of this chapter is to provide a detailed explanation in a chronological order from the materials and the processes involved until the testing and characterization. In addition, the role of block copolymer effect and the previous research on the development of cast polypropylene films in food packaging industries is also discussed.

2.1 Current Packaging Plastics

According to Clarke *et al.* (2016), the plastic industry commonly uses the polyethylene terephthalate (PET), polystyrene (PS), high density polyethylene (HDPE), and polypropylene (PP) as the primary components in food packaging plastics. Every food packaging plastic used in a food industry has their precise properties. Although those materials offer safety for the food it stores, they frequently lack in both mechanical and barrier properties and provide minimum guide to prevent harm (Chin, 2010).

The tensile strength is one of the tested properties in food packaging film because it will indicate the resistance to stress and strain respectively. In addition, oxygen and water transfer are the most essential aspects among the barrier properties (Miquelard *et al.,* 2013). It is because the oxygen and water in food packaging can frequently accelerate the decay of food. Table 2.1 and 2.2 depicts the mechanical and barrier properties of all six generally used plastics respectively.

Table 2.1: Mechanical Properties of Common Food Plastics (Chin, 2010)

Material Characteristics	PET	HDPE	PVC	LDPE	PP	PS
Density (g/ cm^3)	1.35	0.959	1.3 – 1.58	0.925	0.905	1.05
Elasticity (GPa)	2.77 – 4.15	1.09	2.42 – 4.12	0.17 – 0.28	1.14 - 1.55	2.28 – 3.28
Yield Properties (MPa)	59.30	26.1 – 33.2	40.8 – 44.7	9.1 – 14.4	31.1 – 37.1	-
Tensile Properties (MPa)	48.2 – 72.3	22.0 – 31.1	40.6 – 51.6	8.2 – 31.5	31.1 – 41.3	35.8 – 51.7
Elongation (%)	31 - 301	11 - 1201	41 - 81	101 - 651	101 - 601	1.3 – 2.6
Fracture Toughness [MPa sqrt (m)]	5	-	2.0 – 4.0	-	3.0 – 4.5	0.7 – 1.1
Thermal Expansion($10^{-6}(°C)^{-1}$)	118	105 - 197	91 - 181	181 - 401	145 – 179	91 – 151
Heat Conductivity (W/ mK)	0.16	0.49	0.16 - 0.22	0.32	0.13	0.14
Specific heat (J/ kgK)	1169	1849	1049 - 1461	2301	1926	1171

Table 2.2: Barrier Properties of Common Food Plastics (Chin, 2010)

Material	Oxygen Gas Transition	Carbon Dioxide Gas Transitions	Water Vapour	Seal Temperature (°F)	Drop Test	Chemical Resistance
PET	14	72	3.5	154	Good	Good
HDPE	186	581	0.4	251	Fair/ Good	Fair/ Good
PVC	17	27	3.0	160	Good	Fair/ Good
LDPE	300	2700	1.3	220	Fair/ Good	Fair/ Good
PP	135	390	0.3	260	Fair	Fair/ Good
PS	330	1160	8.5	220	Fair	Fair/ Good

2.2 Polypropylene

Polypropylene is a synthetic resin or called as addition polymer as shown in Figure 2.1. It is made from the combination of propylene monomers which are widely being used in food packaging films. As shown in Figure 2.2, the PP is made from the Ziegler-Natta polymerization and metallocene catalysis which is derived from the propylene monomer (Elsayed, 2003).

In addition, polypropylene is thermoplastic elastomers that have proper temperature resistant properties. Therefore, it has remarkable mechanical properties which include exact