

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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POLYPROPYLENE (RCPP) FOR FOOD PACKAGING FILM

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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)

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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 0°C) 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 °C). 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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TABLE OF CONTENTS

i
ii
iii
iv
V
viii
ix
xii
xiii

CHAPTER 1: INTRODUCTION

1.1	Project Background	1
1.2	Problem Statement	3
1.3	Objective	4
1.4	Scope of the Project	5

CHAPTER 2: LITERATURE REVIEW

2.1	Current Packaging Plastics	6
2.2	Polypropylene	7
	2.2.1 Types of polypropylene	8
	2.2.1.1 Homopolymer	9
	2.2.1.2 Block copolymer	10
	2.2.2 Retort cast polypropylene	10
2.3	Polypropylene Film	12
	2.3.1 Polypropylene film in food packaging technology	13
2.4	Film Casting Process	14
2.5	Effect of Process Parameter	15
	2.5.1 Effect of draw ratio	15
	2.5.2 Effect of temperature and stretching ratio	16

	2.5.3	Effect of air gap length on width and temperature profile	18
	2.5.4	Effect of air cooling	19
	2.5.5	Effect of chill roll temperature	20
2.6	Physic	cal and Mechanical Testing	22
	2.6.1	Haze testing	22
	2.6.2	Tensile testing	23
	2.6.3	Impact testing	24
	2.6.4	Thickness testing	25
	2.6.5	Heat sealing testing	26
2.7	Mater	ial Characterization	28
	2.7.1	Fourier transform infrared spectroscopy	28
	2.7.2	X-ray diffraction	30
	2.7.3	Scanning electron microscopy	31
	2.7.4	Differential scanning calorimeter and crystallization	33
2.8	Role o	of Block Copolymer in Cast PP Films	35
2.9	Summ	nary on Previous Researches	36

CHAPTER 3: METHODOLOGY

39 40
40
41
41
42
42
43
44
46
47
47
48
48
49

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1	Haze Testing	51
4.2	Drop Testing	52
4.3	Surface Roughness and COF Testing	54
4.4	Heat Sealing Testing	57
4.5	Tensile Testing	59
4.6	Scanning Electron Microscopy (SEM)	62
4.7	X-Ray Diffraction (XRD)	67
4.8	Differential Scanning Calorimetry (DSC)	69
4.9	Fourier Transform Infrared Spectroscopy (FTIR)	71

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusion	74
5.2	Recommendations	76
5.3	Limitations	77
5.3	Sustainability of RCPP Films	77

78

REFERENCES

APPENDICES

A	Gantt Chart FYP I	84
В	Gantt Chart FYP II	85

LIST OF TABLES

2.1	Mechanical Properties of Common Food Plastics	7
2.2	Barrier Properties of Common Food Plastics	7
2.3	The PP film properties in homopolymer and block copolymer	9
2.4	The advantages of retort pouch packaging	11
2.5	Typical properties of PP, BOPP and PVC films	13
2.6	Crystalline orientation function obtained from different draw ratio	15
2.7	Chill roll temperature and the resulted melting peak obtained from DSC in	20
	N-AFR conditions	
2.8	Mechanical properties of the PP cast film along MD	21
2.9	Thickness test results	25
3.1	Standard involved in physical and mechanical testing	37
3.2	The nomenclature of the multilayered CPP & RCPP film with different	39
	thicknesses	
4.1	Comparison of CPP and RCPP film on haze values based on average	51
	results obtained	
4.2	Comparison of CPP and RCPP film based on drop testing	53
4.3	Comparison of CPP and RCPP film on surface roughness	54
4.4	Static comparison of CPP and RCPP film on COF testing	55
4.5	Kinetic comparison of CPP and RCPP film on COF testing	55
4.6	Comparison of CPP and RCPP films based on melting and crystallization	70
	temperature	
4.7	FTIR absorption bands of typical polymeric materials	71
4.8	Comparison of FTIR absorption bands of CPP and RCPP film	73
5.1	Summary of CPP and RCPP film testing results	76

LIST OF FIGURES

2.1	The polypropylene resin	8
2.2	The polymerization of polypropylene	8
2.3	The PP homopolymer structure	9
2.4	The PP block copolymer structure	10
2.5	The inner and outer structure of retort pouch	11
2.6	The PP impact copolymer in retort pouch	12
2.7	Film casting process	14
2.8	The crystal orientation function versus draw ratio	16
2.9	Stress against strain curves of PP cast film at different ratios	17
2.10	The X-Ray mean crystallite size against area stretching ratio for the PP	17
	films biaxially stretched at different temperatures	
2.11	The effect of air gap length on width profile	18
2.12	The effect of air gap length on temperature profile	19
2.13	The crystal orientation functions in different AFR conditions	19
2.14	The mechanical properties of the cast PP films along machine direction in	21
	various AFR conditions	
2.15	Haze values for various types of PP films	22
2.16	The yield strength & elastic modulus for PP and multilayered PP samples	23
2.17	Elongation at break for PP and multilayered PP/POE samples	24
2.18	The notched and un-notched impact strength of PP and multilayered PP	24
2.19	The effect of temperature on PP film thickness	26
2.20	Polarizing FTIR image at 170°C heat-sealing, (a) 0° and (b) 90°	27
2.21	The FTIR spectra of various PP films	28
2.22	FTIR spectra of various PP films before and after oxidation	29
2.23	2D intensity patterns against azimuthal angle at 2O of cast PP at various	30
	AFR conditions	
2.24	Pole figures of films used in various air cooling conditions (a) N-AFR, (b)	31
	L-AFR, (c) M-AFR	
2.25	The SEM micrographs of the films at different cooling rate conditions, (a)	32

N-AFR and (b) L-AFR

2.26	The SEM micrographs of impact fractured surfaces of multilayered PP	32
	samples at (a) MC-16 (b) MC-32 and (c) MC-128	
2.27	DSC plot of PP Films at heating rate of 10°C/ min	33
2.28	The effect of crystallinity temperature	34
2.29	DSC scans of cast films from 100°C to 120°C	34
2.30	Structure of block copolymer PP	35
3.1	Flow of experimental works	38
3.2	The three (3) layers, (a) CPP films and (b) RCPP films	39
3.3	The process flowchart in making RCPP films	40
3.4	Cast Film Co-Extrusion Process	40
3.5	Hunterlab XE sensor Hazemeter (ASTM D1003)	41
3.6	Mitutoyo SJ-301 Portable Surface Roughness Tester (JIS-B0601)	42
3.7	COF Tester Machine (ASTM D1894)	43
3.8	Classic 513 Gradient Heat Sealer Tester	44
3.9	Tensile tester (Hounsfield, H5KS)	45
3.10	The cutting dimension of CPP and RCPP films (a) TD direction (b) MD	45
	direction and (c) Width	
3.11	The cutting dimension of CPP and RCPP film	46
3.12	CPP and RCPP films filled with 250 ml of water	46
3.13	The FTIR Spectrometer	47
3.14	The DSC (TA Instruments, USA)	48
3.15	X-Ray Diffractometer (Panalytical X'pert Pro)	49
3.16	Scanning Electron Microscopy (Carl Zeiss SMT, United Kingdom)	50
4.1	Comparison between CPP and RCPP film based on haze values	52
4.2	Comparison between CPP and RCPP film based on surface roughness, Ra	55
4.3	Comparison between CPP and RCPP film based on static and kinetic	56
	forces	
4.4	Schematic representation on molecular packing model of RCPP film	57
4.5	Force exerted at heat sealed temperature between CPP 40 and CPP 70 film	58

4.6	Force exerted at heat sealed temperature between RCPP 70 and RCPP 100	58
	film	
4.7	Comparison between CPP and RCPP film based on tensile strength in MD	59
	and TD	
4.8	Comparison between CPP and RCPP film based on modulus in MD and	60
	TD	
4.9	Comparison between CPP and RCPP film based on elongation in MD and	61
	TD	
4.10	Dimensional analysis of 40 µm CPP film	62
4.11	Dimensional analysis of 70 µm CPP film	62
4.12	Dimensional analysis of 70 µm RCPP film	63
4.13	Dimensional analysis of 100 µm RCPP film	63
4.14	Comparison of required layer thicknesses and SEM layer thicknesses of	64
	CPP and RCPP films	
4.15	Comparison of overall required thickness and overall SEM thickness of	65
	CPP and RCPP films	
4.16	SEM testing results at 1000x magnification with $EHT = 10.00 \text{ kV}$, (a)	65
	CPP 40, (b) CPP 70, (c) RCPP 70 and (d) RCPP 100	
4.17	SEM testing results at 2000x magnification with $EHT = 10.00 \text{ kV}$, (a)	66
	CPP 40, (b) CPP 70, (c) RCPP 70 and (d) RCPP 100	
4.18	Comparison of XRD spectrum for CPP and RCPP films	67
4.19	Comparison of degree of crystallinity of CPP and RCPP films	68
4.20	Comparison of DSC Curve for CPP 40 and CPP 70	69
4.21	Comparison of DSC Curve for RCPP 70 and RCPP 100	69
4.22	Comparison of melting temperature and melting enthalpy of CPP and	70
	RCPP film	
4.23	Comparison of FTIR spectra for CPP and RCPP films	72

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			
Ν	-	Newton			
%	-	Percentage			
S	-	Seconds			
ml	-	Millilitre			
°C	-	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 $^{\circ}$ 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 μ m. 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.

Material	РЕТ	HDPE	PVC	LDPE	PP	PS
Characteristics						
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	48.2 - 72.3	22.0 - 31.1	40.6 - 51.6	8.2 - 31.5	31.1 - 41.3	35.8 - 51.7
(MPa)						
Elongation (%)	31 - 301	11 - 1201	41 - 81	101 - 651	101 - 601	1.3 - 2.6
Fracture Toughness	5	-	2.0 - 4.0	-	3.0 - 4.5	0.7 - 1.1
[MPa sqrt (m)]						
Thermal	118	105 - 197	91 - 181	181 - 401	145 - 179	91 – 151
Expansion($10^{-6}(°C)^{-1}$)						
Heat Conductivity	0.16	0.49	0.16 - 0.22	0.32	0.13	0.14
(W/ mK)						
Specific heat (J/ kgK)	1169	1849	1049 - 1461	2301	1926	1171

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

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