

## Investigation of Plastomer Effect on the Properties of Multilayer Cast Polypropylene for Food Packaging Film

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### ABSTRACT

Cast polypropylene (CPP) multilayer films, manufactured by co-extrusion of polypropylene raw material were used in packaging of various products such as food, cloth, cosmetics and pharmaceutical. The nature of low crystallinity in PP structure during processing, the film brittleness results poor impact strength especially at lower temperature (below 0° C). Among CPP films, cast films can be plasticized to improve the impact resistance. This study aims to evaluate the effect of the addition of plastomer on physical and mechanical properties of multilayer CPP films with different thicknesses. Present work also includes characterization of CPP films by Scanning Electron Microscopy, X-ray Diffraction and Fourier Transform Infrared Spectroscopy. The impact strength of the film was determined through free-falling dart method. The tensile strength of CPP films has increased about 11.6 %~31.7 % with the presence of plastomer. In addition, the impact strength was improved by approximately 110 %, 90 % and 37 % for film thickness of 60 µm, 70 µm and 80 µm respectively. Along with a significant increase in the mechanical properties, a considerable improvement in the haze of CPP films with plastomer also been observed. Thus, CPP film that contains plastomer may have potential to replace certain applications of PE film in flexible packaging.

Keywords: Cast polypropylene film, Plastomer, Crystallinity, Sealant, Impact strength.

### 1. Introduction

The principal roles of food packaging are to protect food products from outside influences and damages [1]. Food packaging industries commonly use the high density polyethylene (HDPE), polyethylene terephthalate (PET), polystyrene (PS), and polypropylene (PP) as the primary components in food packaging plastics [2]. Among various types of polymers, polypropylene (PP) is one of the widely used materials for making into multilayer packaging films as it can form a clear glossy film with a high strength and puncture resistance [3]. It is also one of the most versatile and economic barrier films ever used in packaging application [4]. It is also one of the most versatile and economic barrier films ever used in packaging application [4, 5]. Good optical properties, high tensile strength and puncture resistance can be obtained by oriented crystal structure of polypropylene that appeared as a clear glossy film [6,7]. In addition, PP is not easily being affected by the changing in humidity as it has moderate permeability to gases and odors including a higher barrier to water vapors from atmosphere [8].

Thin PP films are normally produced through upward blown and film casting co-extrusion process [9, 10]. Basically, there are two popular types of stretch films which are cast stretch film or cast polypropylene film (CPP) and blown stretch film. Blown film is tough and resilient whereas the cast film is soft and easy to be stretched. Due to differences in the process and rapid quenching at chill roll, cast film can provide better gloss, clarity and soft films over that of blown films. Through film casting co-extrusion process, it will minimize the crystalline growth, size and concentration. Besides that,

cast film is produced at a higher throughput rate than blown film [2,11].

However, low temperature brittleness is the major problem with the homopolymer CPP films. Therefore, incorporating block polymer of PP and PE to CPP film makes retort cast polypropylene (RCPP) film which has improved heat sealing properties with high strength and impact resistance. One of the major drawback as of CPP film is that the failure was mainly contributed from the storage condition at 0° C coupled with high thickness which is above 60 µm [12]. This is attributed to the nature of PP with high glass transition temperature ( $T_g$ ), reported -10 °C compared to PE -100 °C. Below  $T_g$ , CPP begins to act as stiff and glassy solids, impact resistance is largely decreased and low energy brittle fracture becomes the main cause of failure. Raw materials used for thin and thick films are identical but thinner film has to be produced at lower line speed during production. This may indirectly influence the crystallinity and amorphousness of PP formation which is yet to be explored. In addition, the increment of film thickness from 25 µm to 80 µm have resulted in the haziness increment from 2.8 % to 8% respectively. [13]. Plastomer is a type of ethylene alpha olefin copolymer that bridge the gap between elastomers and plastics developed in the last decades. Addition of plastomers in flexible packaging is newly introduced as polymer modifiers to improve processing performance and film properties.

In the present work, a comparative study has been made to analyze plastomer effect on the physical and mechanical properties and morphology of multilayer cast polypropylene films. The core layer of CPP film contained plastomer was prepared by mixing 12 wt.% of

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plastomer of which contains 16 wt.% polyethylene (PE) with 84 wt.% of polypropylene (PP) and was subsequently blended with skin and sealant layers. The experimental study of physical and mechanical properties of CPP films with and without addition of plastomer were determined through haze, drop, impact and tensile testing. In addition, X-ray diffraction (XRD) method was used for identification of polycrystalline phases in these films and the plastomer effect on the variation in thickness was analysed by scanning electron microscopy (SEM). The elastomeric and plastic properties of PE allow improved impact strength and toughness of commercially available CPP films.

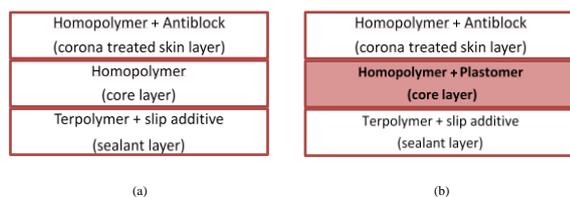
## 2. Material and Methods

### 2.1 Raw Materials

The NP and WP CPP films were prepared from the polypropylene (PP) material through the cast film co-extrusion process. The films were provided by the San Miguel Yamamura Plastic Film Sdn. Bhd, Melaka, Malaysia. The nomenclature of the multilayered NP and WP films with different thicknesses are shown in Table 1. Figure 1 shows the sequence of each layer of CPP films. The anti-block additive was included in the skin layer to allow easier processing and handling while the slip additive in sealant layer to reduce friction.

**Table 1** Sample identification of CPP films produced.

Sample Id	Film Thickness (µm)	CPP (no plastomer)	CPP (with plastomer)
Lamination grade CPP	60	60NP	60WP
	70	70NP	70WP
	80	80NP	80WP

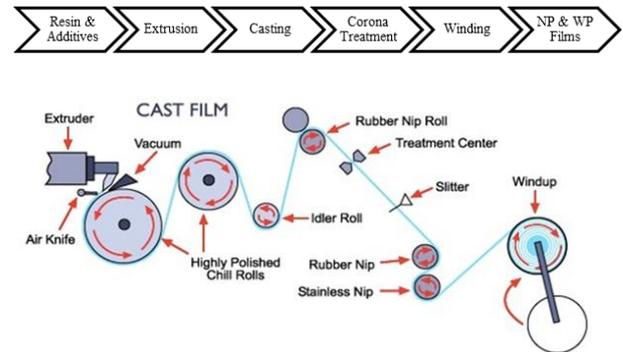


**Fig. 1** Sequence of three (3) layers of (a) NP and (b) WP CPP film.

### 2.2 Production of CPP films

Film processing method using Reifenha Usser CPP machine comprises of six (6) stages as shown in Fig. 2. Six (6) samples in rolled form were prepared by cast film technology. Firstly, a mixture of raw materials for each extruder was prepared by 3 different semi batch automixers. Then the raw materials were heated by extruder heating barrels and the melt temperatures for every extruder were controlled, i.e., EA: 245-250 °C, EB: 250-260 °C and EC: 240-245 °C. Afterwards, the molten PP flew through a die at 230 °C, and nipped to a chill roll where temperature was controlled at 22 °C as to quench the molten PP into a semi crystalline PP film. It was then passed through the second chill roll for further

cooling. The core layer of WP CPP film was prepared by mixing 12 wt.% of plastomer of which contains 16 wt.% of polyethylene (PE) with 84 wt.% of polypropylene (PP). Next, the skin layer surface of the film was passing through corona treatment at 11kW. Subsequently core layer was blended with skin and sealant layers. Finally, the film was wound into roll form.



**Fig. 2** Production of CPP films.

### 2.2 Testing

The haze, tensile, and impact properties of the CPP film samples are evaluated by performing the physical and mechanical testing. Table 2 shows the standard involved in physical and mechanical testing.

**Table 2** Standards involved in physical and mechanical testing.

Testing	Standard
Haze testing	ASTM D1003
Tensile testing	ASTM D638
Impact Strength	ASTM A1709
Drop testing	ASTM D109

#### 2.2.1 Haze testing

The hazemeter was set up to transmit a beam of light through the sample and measured the diffusion of light from its original path. The lower the haze value better the optical properties of the film. The haze testing was carried out by a Hunterlab ColorQuest XE sensor hazemeter (USA) which has an incandescent light source with geometrically arranged photocells. Films were cut into 10 cm x 10 cm and placed between the light source and the photocells.

#### 2.2.2 Tensile testing

The test films are prepared with width of 15 mm along the machine direction (MD) and transverse direction (WD) and length of 200 mm. The tensile testing films were conducted by Hounsfield H5KS universal testing machine at a cross head speed 1 mm/min. The tensile modulus was calculated from the initial part of the slope from stress-strain curves. Five (5) samples from each group were tested and the average value was calculated.

### 2.2.3 Impact Testing

A falling dart impact tester (Lab Think) was used to determine the energy required to puncture plastic film from a free falling dart. A dart with a hemispherical head diameter of  $38.10 \pm 0.13$ -mm dropped from a height of  $0.66 \pm 0.01$  m. This energy required is expressed in terms of the weight (mass) of the dart falling from a specified height which would result in 50 % failure of specimens tested.

### 2.2.4 Drop Testing

An in-house drop test was carried out to simulate the actual handling of laminated CPP end user applications. The film is cut into A4 size and sealed to a rectangular bag. The rectangular bag is loaded with different weights resin ranging from 50g, 100g and 150g and sealed them tightly. The samples were placed in a freezer with temperature of  $-10$  °C for one and two months, the samples were then taken out from freezer and being dropped from 1.5m height to check the impact strength of film samples. The observation of each sample was recorded.

## 2.3 Characterization of CPP films

Both NP and WP CPP films were characterized through differential X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) and the film thicknesses were analysed by scanning electron microscopy (SEM).

### 2.3.1 X-Ray Diffraction (XRD)

In XRD analysis, sharp diffraction peaks occurred indicates crystalline regions while amorphous regions resulted in broad halos. The regular arrangement of atoms and molecules in diffraction pattern of polymers usually contains a combination of both. Degree of crystallinity can be estimated by integrating the relative intensities of the peaks and halos. X-ray diffraction was conducted using an X-ray diffractometer (Model Panalytical X'pert Pro) where the graphite crystal monochromator was used to set the  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.542$  Å) within the range of 40 kV and 40 mA. In addition, the Cu X-ray goniometer scanning from  $10^\circ$  to  $90^\circ$  was used to detect the diffraction profiles with X'pert High score software. The degree of crystallinity was calculated by using the Eq. 1 stated as below:

$$X_c (\%) = (A_c / A_c + A_a) \times 100\% \quad (1)$$

where,  $A_c$  is the area under crystallinity peak and  $A_a$  is the area under amorphous peak.

### 2.3.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was conducted using the JASCO FTIR-6100 spectrometer to collect data of the presence of functional groups of cast PP film. A beam of infrared light was pass through a potassium bromide pallet (KBr) pallet to obtain an infrared spectrum with resolution  $5\text{cm}^{-1}$ , accumulation of 125 scans). The measurement was based on the absorption of infrared light at certain frequencies recorded from the vibration modes of atomic groups within the molecules. In this

project, the functional group of CPP films were analyzed within spectra range from  $4000$  to  $400\text{ cm}^{-1}$ .

### 2.3.3 Scanning Electron Microscopy (SEM)

Initially, film samples were sputter coated with gold of 5-10 nm thick using SC 7620 mini sputter coater (Quorum,) about 120 seconds to make films conductive so that the samples can inhibit charges for topographic examination. Finally, films were examined under scanning electron microscope (EVO-50 Carl Zeiss SMT) with an accelerating voltage of 10 kV to measure the different layers of films. The nominal thickness of film and the average thickness of each layer measured from the 10 photo micrographs obtained from film section thickness by scanning electron microscopy.

## 3 Results and Discussion

### 3.1 Haze Testing

Figure 3 shows the films haziness plots for both NP and WP CPP films, and the lower haze denotes higher film clarity [14]. Both plots revealed that the film haziness increased with the film thickness from  $60\ \mu\text{m}$  to  $80\ \mu\text{m}$ , however the haze of WP films are lower compared to NP films. This is an additional advantage of plastomer to improve the clarity of thicker film, though PE film is known to be hazy.

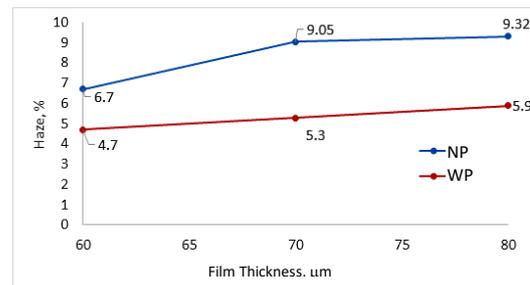


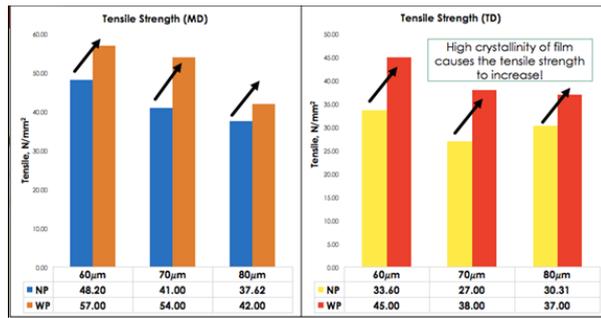
Fig. 3 Haze results for both NP and WP CPP films.

### 3.2 Tensile Properties of Films

Figure 4 (a) and (b) show the tensile strength of NP and WP films in for machine direction (MD) and transverse direction (TD) respectively. The results revealed that tensile strength for MD reduced with the increase of film thickness. This may be due to the crystallinity of PP polymer (c.f. to figure 8) [15]. In overall, the tensile strength of WP improved compared to NP for both MD and TD with the presence of plastomer. Obviously, tensile strengths of the NP and WP films both at MD and TD decrease when the thickness of the film increases because of the confinement from the layer boundaries at lower thickness where molecules are more tightly packed and aligned. The aligned molecules have more intermolecular Van der Waals force, which makes them lock tighter resulted in higher strength [16]. Holistically for any film, strength in TD is always lower than that in MD for weak intermolecular Van der Waals force.

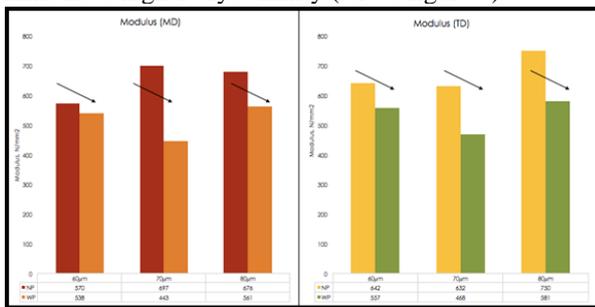
(a)

(b)



**Fig. 4** Tensile strength in (a) MD and (b) TD of NP and WP CPP films.

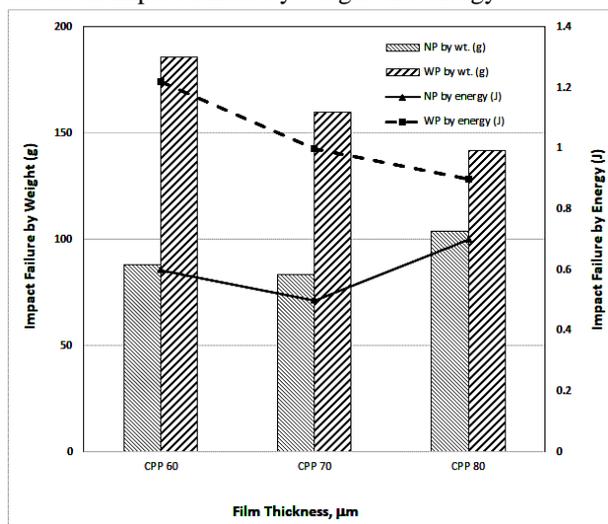
The stiffness of the CPP film is related with the film modulus property. Figure 5(a) and (b) display the modulus properties for both NP and WP CPP films at MD and TD, respectively. It was observed that the film modulus decreased, which implies that the film stiffness reduced with the presence of plastomer. In general, the more ethylene monomer is added in case of WP film, the greater the impact resistance, with correspondingly lower stiffness and tensile strength [5] but the crystallinity effect on tensile modulus is strong as WP films have higher crystallinity (c.f. to figure 8).



**Fig. 5** Tensile modulus in (a) MD and (b) TD of NP and WP CPP films.

### 3.3 Impact Properties of Films

The film impact strengths are displayed in Figure 6 based on impact failure by weight and energy.



**Fig. 6** Impact failure by weight (g) and energy (J) of NP and WP CPP films.

The results indicated that the impact strengths by weight for 60WP, 70WP and 80WP have increased compared to 60NP, 70NP and 80NP from 88g to 186g, 84g to 160g and 104g to 142g respectively and therefore, the impact strength was improved by approximately 110 %, 90 % and 37 % for film thickness of 60 µm, 70 µm and 80 µm respectively with an addition of plastomer. Based on the observation it can be inferred that crystallinity in WP CPP films may added the impact resistance with the reduction of stress concentration effect as observed by other researchers [12] and the WP CPP films have higher impact resistance compared to NP CPP film due to obvious stress whitening and necking process resulted from block copolymer effect influenced by crazing and shear shielding [17]. In addition, for films with plastomer clearly demonstrated the reduction in impact strength with the increase of film thickness which may attribute from the constrained effect due to raise in film thickness.

Table 3 reveals the drop test results for 80NP and 80WP films at -10 °C storage dropping from 1.5m height with the load ranging from 50g to 150g. The results revealed that 80NP films failed for all the test even for the load with 50g. This may be due to the brittleness of PP film at lower temperature which is close to the glass transition temperature ( $T_g$ ). However, 80WP films showed remarkable improvement for the film sample tested after one month and passed for the 100g load after 2 months of incubation in the freezer. The addition of plastomer in core layer may reduce the glass transition temperature ( $T_g$ ) of PP further from -28°C.

**Table 3** In-house drop test for NP and WP CPP 80 films.

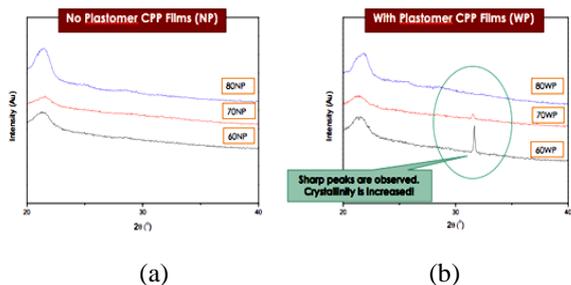
Load (g)	Load drop from a height of 1.5 m			
	Film Conditions			
	Stored at -10 °C for 1 month		Stored at -10 °C for 2 months	
	80NP	80WP	80NP	80WP
50	Failed	Passed	Failed	Passed
100	Failed	Passed	Failed	Passed
150	Failed	Passed	Failed	Failed

### 3.4 Film Crystallinity by X-ray Diffraction (XRD)

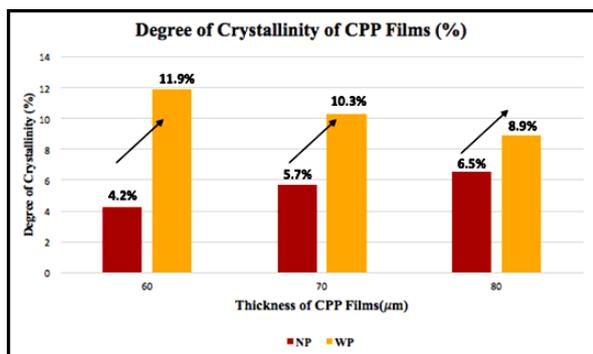
Figure 7 shows the comparison of XRD spectrums for CPP films with and without plastomer. NP films show amorphous state of the films while with plastomer of CPP (WP) shows more crystalline state. This is due to the stretching in the bonding occurred after adding plastomer caused the increase in the crystallinity of the films [15,18,19].

Figure 8 confirms the results of XRD spectrums by indicating the increase in crystallinity (determined from Equation 1) in WP CPP films of different thicknesses with the presence of plastomer. However, the

crystallinity decreases gradually with the raise of the WP CPP film thickness.



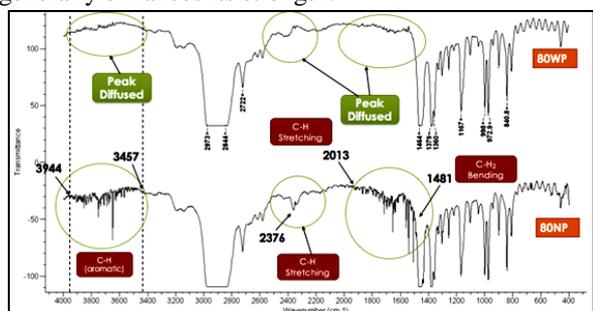
**Fig. 7** Comparison of XRD spectrums of CPP films (a) without plastomer and (b) with plastomer.



**Fig. 8** Degree of crystallinity of NP and WP CPP films.

### 3.4 Chemical Functional Groups of Films by FTIR

The presence of chemical compounds and changes of functional groups between 80NP and 80WP films were evaluated and compared IR spectra (Figure 9). The peaks at the band  $2723\text{cm}^{-1}$  and  $2360\text{cm}^{-1}$  of WP film are diffused. This may be due to the adding of plastomer caused stretching at the C-H bonding. The stretching will affect the crystallinity of the film structure. The degree of crystallinity can have a significant influence on the mechanical properties because it affects the extent of the intermolecular secondary bonding. Therefore, increasing of the crystallinity of CPP film generally enhances its strength.

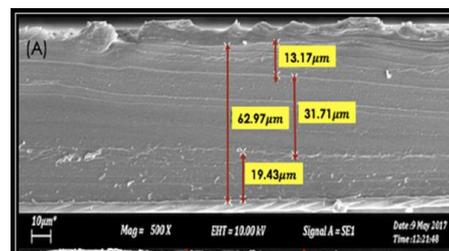


**Fig.9** FTIR spectroscopy of NP and WP CPP 80 films.

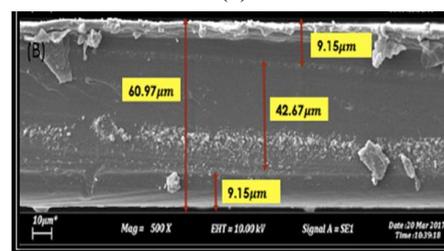
### 3.3 Film Thickness

SEM of 60NP and 60WP show the skin, core and sealant layers of the films [Figure 10 (a) and (b).] It is clearly observed that addition of plastomer caused expanded core layer which compressed the skin and

sealant layer and resulted reduction in their thicknesses. In addition, film layers were deformed critically at some point and increased the propagation of cracking at the middle or edge of the film [12].



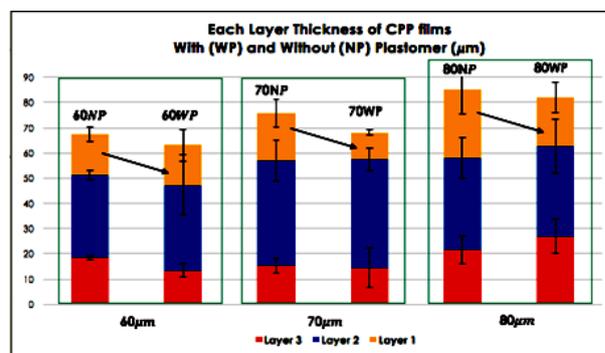
(a)



(b)

**Fig. 10** SEM of section thickness of (a) NP and (b)WP CPP 60 films.

Figure 9 shows the resultant effect of plastomer on the nominal thickness and the average thickness values of each layer measured from the film section by scanning electron microscopy. During processing, the overall thickness of the films due to ease of deforming the films with the aid of plastomer.



**Fig. 11** Layer thickness values of NP and WP CPP films.

## 4. Conclusions

The study of this research was to analyze the plastomer effect on the physical and mechanical properties of cast polypropylene film and to investigate the film morphology of multilayer NP CPP and WP CPP films utilizing characterization tools. Plastomer had contributed in enhancing the physical and mechanical properties in terms of tensile strength and impact strength performances of the CPP films. In addition, WP CPP films exhibit higher impact resistance which has been enhanced by the plastomer effect. The WP CPP films are able to withstand higher impact failure weight and maintain its performances under

extreme environment. The crystallinity of both films were evaluated by XRD spectrum. WP CPP had higher crystallinity due to plastomer effect resulting from the efficient bond stretching towards the film structure. As the crystallinity of film increased, the film mechanical properties improved. The WP CPP films revealed better optical properties with higher clarity because it has better transparency due to crystallinity. Thus, CPP film that contains plastomer has solved not only customer quality issue, but is able to widen the application of CPP film and potentially to replace certain applications of PE film in flexible packaging.

## 5. Acknowledgement

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## 6. References

- [1] Lechevalier, V., Packaging: principles and technology, *Handbook of Food Science and Technology 2*, pp 269-271, John Wiley & Sons, Inc., 2016
- [2] McKeen, L.W., Introduction to use of plastics in food packaging, *Plastic Films in Food Packaging: Materials, Technology, and Applications*, pp 1-15, Elsevier Inc., 2012.
- [3] Calafut, T., Polypropylene Films, *Plastic Films in Food Packaging: Materials, Technology, and Applications*, pp 17-20, Elsevier Inc 2012.
- [4] Yoon, C. S., Hong, S. I., Cho, A. R., Lee, H. S., Park, H. W. and Lee, K. T., Analysis of the causes of deformation of packaging materials used for ready-to-eat foods after microwave heating, *Korean Journal of Food Science and Technology*, Vol.47, No.1 pp 63-69, 2015.
- [5] Riley, A., Basics of polymer chemistry for packaging materials, *Packaging Technology Fundamentals: Materials and Processes*, pp 263-286, 2012.
- [6] Ashizawa, H., Joseph, E., James S. and White, L., An investigation of optical clarity and crystalline orientation in polyethylene tubular film, *Polymer Engineering*, vol. 24, no.13, pp. 1035-1042, 1984.
- [7] Bayazian, H., Yadgari, A., Morshedian, J., Jamshidi, A. and Razavi-Nouri, Evaluation of morphology and crystallinity of biaxially oriented polypropylene films, In AIP Conference Proceedings, paper no. 2065, <https://doi.org/10.1063/1.5088335>, 2019.
- [8] Sadeghi, F., Ajji, A. and Carreau, P. J., Analysis of microporous membranes obtained from polypropylene films by stretching, *Journal of Membrane Science*, vol. 292, no.1, pp 62-71, 2007.
- [9] Emblem, A., Plastics properties for packaging materials, *Packaging Technology Fundamentals: Materials and Processes*, pp 287-309, 2012.
- [10] Hisham A. Maddah, Polypropylene as a promising plastic: a review, *American Journal of Polymer Science*, vol. 6, no. 1, pp 1-11, 2016.
- [11] Emblem, A. and Emblem, H., Packaging technology fundamentals, materials and processes, *Woodhead Publishing Limited*, 2012.
- [12] Li, W. P. and Huang, H. X., Revealing toughening mechanism for alternating multilayered polypropylene/poly (ethylene-co-octene) sheets, *Polymer Testing*, vol. 41, pp 245-251, 2015.
- [13] Morris, A., The science and technology of flexible packaging multilayer films from resin and process to end use, *Plastics Design Library Pdl Handbook Series*, Elsevier Inc., 2017.
- [14] K. Resch, Wallner, G.M., Teichert, C., Maier, G. and Gahleitner, M., Optical properties of highly transparent polypropylene cast films: influence of material structure, additives and processing conditions, *Polym. Eng. Sci.*, vol.46, no.4, pp 520-531, 2006.
- [15] Gahleitner, M., Milev, D., Gloger, D., Androsch, R. and Tranchida, D., Polymer structure effects on crystallization and properties in polypropylene film casting, In AIP Conference Proceedings, paper no.1914, , <https://doi.org/10.1063/1.5016762> 1914, 130001, 2017.
- [16] Abdel-Mohti, A., Garbash, A. N., Almagahwi, S. and Shen, H., Effect of layer and film thickness and temperature on the mechanical property of micro-and nano-layered PC/PMMA films subjected to thermal aging, *Materials*, vol.8, no.5, pp 2062-2075, 2015.
- [17] Burt, T. M., Jordan, A. M. and Korley, L. T., Toward anisotropic materials via forced assembly coextrusion, *ACS Applied Materials and Interfaces*, vol.4, no.10, pp 5155-5161, 2012.
- [18] Laihonon, S., Gedde, U. W., Werner, P.-E. and Martinez-Salazar, J., Crystallization kinetics and morphology of poly (propylene-stat-ethylene) fractions, *Polymer*, vol. 38, pp 361-369, 1997.
- [19] Tabatabaei, A., Mark, L. H., & Park, C. B., Visualization of polypropylene crystallites formed from a stressed melt in extrusion. *Polymer*, vol 101, pp 48-58, 2016.