



LLDPE film development surface with nucleating agents to reduce fat stains from food adherence on the film surface for easy rinsing before recycling

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Abstract

The purpose of this research was to enhance the surface of linear low-density polyethylene (LLDPE) film by using single and hybrid nucleating agents to reduce fat stains from food adherence on the film surface for easy rinsing before recycling, consequently reducing energy consumption before recycling. The process begins with the preparation of a high-concentration masterbatch of LLDPE with nucleating agents and polyethylene glycol (PEG), followed by blown film and test analysis. The results showed that both single and hybrid nucleating agents resulted in substantial modifications in the surface characteristics of the film. The altered surface texture of the film makes fat stains easy to remove. In addition, the use of hybrid nucleating agents resulted in considerable roughness on the film's surface. It can calculate the average roughness (R_a) from atomic force microscopy (AFM) images, which is very low at 4.7 nm, and the roughness is consistent. The contact angle was 99.17 degrees, and the percentage of crystallinity was clearly higher than that of a single nucleating agent. As a result, the fat stains on the film surface are easier to remove. The visual appearance, morphology, functional group, and mechanical properties of the films, on the other hand, were not significantly different. In summary, using a nucleating agent helped to rinse fat stains from the film easily.

1. Introduction

In recent years, the food industry has grown significantly compared to the past. As a result, the volume of packaging film used is large [1]. Particularly in the field of food bags, which are often made of polyolefin plastics such as linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP), which have excellent strength and outstanding durability in use [2]. However, LLDPE plastics are more commonly used than other polymers due to their toughness and flexibility, as well as their ability to be utilized in a range of applications, especially in food bags [3]. Normally, food bags are often comprised of two layers of plastic: "LDPE" on the outside and "LLDPE" on the inside, which must come into contact with food. As a result, the LLDPE inside the bag is important because it often adheres to contact with food, making it difficult to clean before recycling, resulting in water and energy waste. Since food contains fat stains, they tend to adhere to the LLDPE coating and are difficult to wash away. To address this issue, LLDPE film must be developed to reduce fat stains from food adherence on the film surface, decrease the impact of water and energy waste, and facilitate the recycling of food bags.

Even today, there are technologies that can reduce water adherence on various surfaces, such as coating and surface treatment technology

[4]. However, these technologies are incapable of resolving the issue of fat stain adherence to LLDPE film. Furthermore, waterproof coatings frequently include highly hazardous chemicals. As a result, it is not suited for LLDPE film that has come into contact with food. It was also shown that waterproof coatings had no effect on the adherence of fat stains, a component of food. Therefore, it will fail to decrease the fat stain's adherence to the LLDPE film. To solve this problem while keeping safety in mind. The use of nucleating agent additions that are non-toxic and safe appears to be a suitable and reasonable alternative. A nucleating agent is a crystalline agent that is very important in the polymer industry, particularly in packaging film, because it improves the film's stability, such as its thermal and mechanical properties [5,6]. In addition, the use of nucleating agents may result in the formation of nanometer-sized crystals on the film surface [7]. As a result, the surface area of the film exhibits a high degree of crystallinity and a shift in roughness. For the reasons mentioned above, it is possible that the use of nucleating agents reduces fat stain adherence on LLDPE film.

Nucleating agents such as calcium carbonate and kaolin are commonly utilized as crystallization agents nowadays [8,9]. It is safe to use and inexpensive when compared to other nucleating agents. Calcium carbonate is a calcium salt with the formula CaCO_3 [10]. It is insoluble in water and appears as a white, odorless powder

or colorless crystals [10]. It is commonly used in food coloring, food firming, and fertilizer [10]. It combines a calcium salt, a carbonate salt, a one-carbon molecule, and an inorganic calcium salt [10]. Kaolin is a colorless, odorless powder that ranges from white to yellowish to grayish [11]. It is mostly composed of the clay mineral kaolinite ($\text{Al}_2\text{O}_3(\text{SiO}_2)_2(\text{H}_2\text{O})_2$), a hydrous aluminosilicate [11]. It is not insoluble in water [11]. In addition, it has applications in the paper, rubber, and plastic industries [11]. According to the calcium carbonate and kaolin information provided above, As can be seen, calcium carbonate and kaolin should be harmless and non-toxic if they were utilized in this research. Furthermore, a mixing aid and plasticizer must be used to achieve excellent mixing between LLDPE and the nucleating agent. Polyethylene glycol (PEG) functions as a mixing aid and a plasticizer [12]. It is a crystalline white powder, non-toxic, and widely utilized in a range of industries, including polymers and pharmaceuticals [12]. It has the chemical formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ and a rather wide range of molecular weights that will vary depending on the application [13]. Y. D. Zhu *et al.* [14] investigated the dispersion of CaCO_3 in polypropylene (PP) film. The results revealed that the addition of a modest amount of CaCO_3 caused alterations to several properties. In particular, the surface roughness of the film has increased significantly. The rough surface is formed by CaCO_3 , which produces crystalline in the film. However, the fat adherence of food on the film was not tested in this research. A. Mallik *et al.* [15] discovered that using kaolin as an ingredient in low-density polyethylene (LDPE) film increased mechanical properties such as Young's modulus, shore hardness, and water absorption. However, this research did not investigate the ability of fat stains to adhere to the surface of the film. In summary, no research has been conducted on the use of nucleating agents, both single and hybrid, to study fat stains adherence on the surface of LLDPE film. As a result, this will be the first study to investigate the possibility of reducing fat stain adherence on the surface of LLDPE film for the benefit of the recycling industry.

This research focuses on the development of the LLDPE film surface, which is the layer that comes into contact with food, by using single and hybrid nucleating agents to reduce fat stain adherence on the film surface for easy rinsing before recycling. In the first step, a highly concentrated masterbatch is prepared by combining LLDPE resin with a nucleating agent and PEG. In the second step, the masterbatch is combined with LLDPE resin and then blown into film. Finally, the physical and chemical properties of the film are analyzed. Including testing for fat stains from food adherence on the film surface with coconut milk as an indicator. Coconut milk represents food stains that tend to adhere to the film well, making rinsing difficult.

2. Experimental

2.1 Materials

LLDPE (L2009F blown film grade, SCG Chemical, Thailand) with a melt flow rate of $1.0 \text{ g} \cdot 10 \text{ min}^{-1}$ at 190°C . Calcium carbonate with particle sizes ranging from $1 \mu\text{m}$ to $5 \mu\text{m}$ was purchased from Chemipan Corporation Co., Ltd. (Thailand). Kaolin with particle sizes ranging from $1 \mu\text{m}$ to $8 \mu\text{m}$ was purchased from Vicker Pigment Co., Ltd.

(Thailand), and polyethylene glycol (food grade, molecular weight = 4000) was purchased from Talad Chemie Co., Ltd. (Thailand).

2.2 Preparation of masterbatch compounds

The LLDPE/10 wt% calcium carbonate or LLDPE/10 wt% kaolin composites with 1 wt% PEG 4000 are prepared using a twin-screw extruder (Prism USALAB 16, Thermo Electron Co., UK). The diameter of the screws is 16 mm, and the L/D is 25. The temperature profile from the hopper to the die was 130, 140, 150, 160, 170, 180, and 190°C , and the screw speed was 200 rpm. Finally, a masterbatch with a high concentration of nucleating agents (10%) was obtained. Figure 1 demonstrates the masterbatch production process.

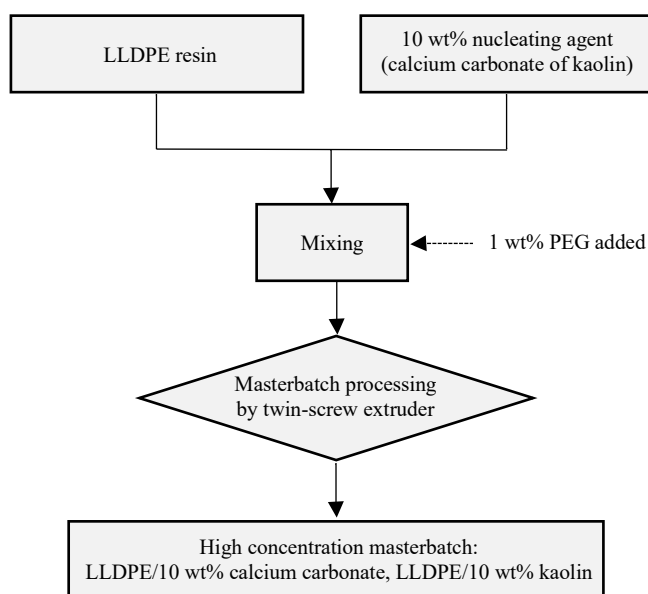


Figure 1. Masterbatch production process.

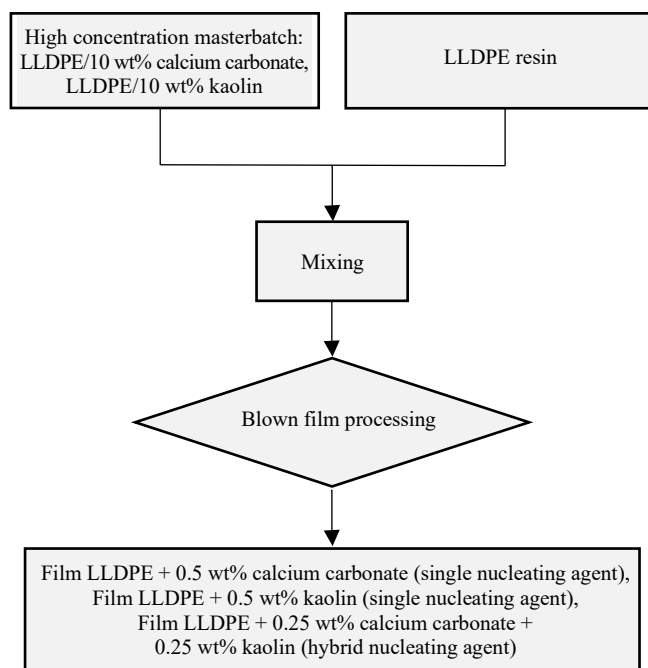


Figure 2. Film production process.

Table 1. Weight and volume fractions of nucleating agent in LLDPE film.

Films formula	LLDPE resin (virgin) (g)	LLDPE/10 wt% calcium carbonate (masterbatch) (g)	LLDPE/10 wt% kaolin (masterbatch) (g)
LLDPE (control)	200	0	0
LLDPE/0.5 wt% calcium carbonate	190	10	0
LLDPE/0.5 wt% kaolin	190	0	10
LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin	190	5	5

2.3 Preparation of blown film process

Figure 2 shows the film production process. To produce a film containing 0.5 wt% nucleating agent, it starts with a high-concentration masterbatch (10 wt% of nucleating agent) that is, afterwards, diluted with more LLDPE resin and produced into films using a blown film extruder (Salee Color Lab, Samut Prakan, Thailand) with a screw diameter of 25 mm connected to an O-ring die. The compound resin was extruded at temperature profiles of 140°C/150°C/160°C/170°C with a die temperature of 165°C and a 35 rpm to 40 rpm screw speed with take-up and take-down speeds were set to 4.5 m·min⁻¹ and 5.5 m·min⁻¹, respectively. The films were collected and stored in ziploc bags containing silica gel sachets and kept at 25°C until required for measurement. Film thickness was measured using an ID-C112BS micrometer (accuracy ± 0.005 mm, Mitutoyo, Japan). The weight and volume fractions of the prepared LLDPE (control), LLDPE/calcium carbonate, LLDPE/kaolin, and LLDPE/calcium carbonate/kaolin films are listed in Table 1.

2.4 Characterization

The capability to prepare the masterbatch and films to assess color, consistency, and dispersion was captured with a Nikon DSLR Camera (D850, Japan). The ability to flow of the masterbatch was tested using a Melt Flow Index Tester (QC-652S, USA) according to ASTM D1238. Surface characterization of the film was conducted using scanning electron microscopy (JEOL, USA) and atomic force microscopy (AFMSPA 400, Seiko Instruments, Japan). The contact angle of the film was assessed using a contact angle instrument (Dataphysics brand tension meter, model PSL 250, USA). The functional groups of the film before and after modification with the nucleating agent were examined by a Fourier-transform infrared spectrometer (Perkin Elmer, USA). The crystal structure of the film was investigated using an X-ray diffractometer (Bruker, SRS-3400, Germany) to determine the correlation between crystallinity and film smoothness. The mechanical properties of the film were measured using a Universal Testing Machine (Lloyd Instrument, Hampshire, UK) according to ASTM standard method D882-18 (2018). The fat stain on the film was examined with the ImageJ program. Statistical analysis was performed with an SPSS software system (Origin Pro 8.5 Version 2020, USA). Each experiment was repeated at least three times. The experimental data were subjected to a one-way analysis of variance (ANOVA). The mean comparisons were run by Duncan's multiple range test, with the level of significance set at $p < 0.05$.

3. Results and discussion

3.1 Masterbatch characteristics

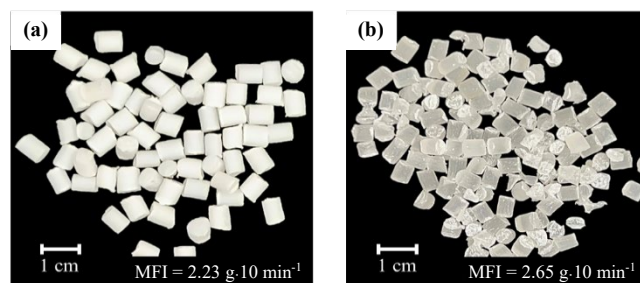


Figure 3. The visual appearance of the masterbatch: (a) LLDPE/calcium carbonate, and (b) LLDPE/kaolin at a concentration of 10%wt nucleating agent, taken with a Nikon DSLR Camera (D850).

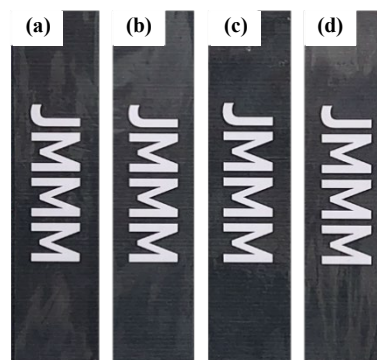


Figure 4. The visual appearance of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin, taken with a Nikon DSLR Camera (D850).

The optical microscope examination of the masterbatch LLDPE/calcium carbonate (Figure 3(a)) and LLDPE/kaolin (Figure 3(b)) containing 10 wt% nucleating agent demonstrated consistent color, dispersibility, and excellent homogeneity. In addition, the melt flow index (MFI) of masterbatch revealed that LLDPE/10 wt% calcium carbonate was 2.23 g·10 min⁻¹ and LLDPE/10 wt% kaolin was 2.65 g·10 min⁻¹. This demonstrated that the masterbatch preparation was effective because the MFI achieved was very low, indicating good compatibility between LLDPE and the nucleating agent. After that, the masterbatch was diluted with LLDPE virgin pellets and formed by the blown film process.

3.2 The visual appearance of the films

Considering the film in each formulation, it can be noted that LLDPE (control) (Figure 4(a)) is quite transparent, with excellent light transmission and the letters "JMMMM" clearly observable. The film characteristics of LLDPE/0.5 wt% calcium carbonate (Figure 4(b)) and LLDPE/0.5 wt% kaolin (Figure 4(c)) containing

the single nucleating agent were similar to those of the LLDPE (control), except that the films had slightly more turbidity. This is due to the nucleating agent, which is visible as a white powder. As a result, when dispersed in the film, the film becomes slightly turbid. When LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin (Figure 4(d)) containing the hybrid nucleating agent was examined, it was obvious that the film was similar to that of the single nucleating agent and did not change considerably. The explanation for this is that the film has the same amount of single and hybrid nucleating agents. As a result, the outcome is identical. In summary, the films containing the nucleating agent still maintain sufficient light transmission to allow the letters "JMMM" to be clearly visible despite the film's minor turbidity.

3.3 SEM surface morphology of the films

Figure 5 shows SEM images of the surface of the film. The surface of the LLDPE (control) (Figure 5(a)) was found to be relatively smooth based on SEM images. While LLDPE/0.5 wt% calcium carbonate (Figure 5(b)) and LLDPE/0.5 wt% kaolin (Figure 5(c)) films containing a single nucleating agent had the same smoothness as the LLDPE (control). However, the crystallizing agent dispersion on film was only marginally noticed. The surface of the hybrid nucleating agent-containing LLDPE/0.25 wt% calcium carbonate/ 0.25 wt% kaolin film (Figure 5(d)) was identical to that of the single nucleating agent-containing film. Finally, the surface characteristics of the film cannot be readily compared when analyzed using the SEM technique.

3.4 Surface topography of the films

To thoroughly examine the surface characteristics of the film, the AFM images must be used to generate topography. The topography shows the smoothness, roughness, and crystal of the surface of the film, as well as the narrow gap between the roughness on the surface.

Importantly, the surface roughness of the film can be calculated from the topography and reported as the average roughness (R_a), resulting in an assessment of the film's ability to adhere to fat stains when it comes into contact with food. Figure 6 shows the two-dimensional (2D) and three-dimensional (3D) AFM images of the surface topography of the films. The surface of LLDPE (control) (Figure 6(a)) was found to have a rough surface and a different level surface with a R_a value of 12.5 nm. While LLDPE/0.5 wt% calcium carbonate (Figure 6(b)) and LLDPE/0.5 wt% kaolin (Figure 6(c)) films containing a single nucleating agent showed a uniformly roughness surface, had a small size crystal, and the narrow gap between the roughness on the surface was discovered to be narrow and close together, the R_a values were 6.2 and 5.9, respectively. When compared to LLDPE (control), the R_a values of films added with a single nucleating agent decreased because the nucleating agent contributed to the modification of the surface of the film by systematically arranging the surface characteristics until the film finished identical to the roughness of very smooth surfaces [16]. The LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin film (Figure 6(d)) containing a hybrid nucleating agent exhibited consistent roughness, had a very small size crystal, and had a narrow gap between the roughness on the surface aligned. It is nearly interlinked between the gaps on the film surface and has a very low R_a value of 4.7 nm, indicating fine and symmetrical roughness on the film surface. In summary, different R_a values have influenced the surface roughness of the film. This may also have an effect on the film's contact angle value, crystallinity percentage, fat stain adherence to the film surface, and film rinsing.

Furthermore, when compared to the research of M. Li *et al.* [17], which used a single nucleating agent such as kaolin as a crystallizing agent in the film to improve the surface. The surface of the film was found to be rather smooth, with no narrow gaps between the roughness on the surface. In addition, when the R_a values on the surface of the film were examined, it was discovered to be as high as 2.74 μm . As a result of the huge gap on the surface, it may be difficult to remove fat stains on the film.

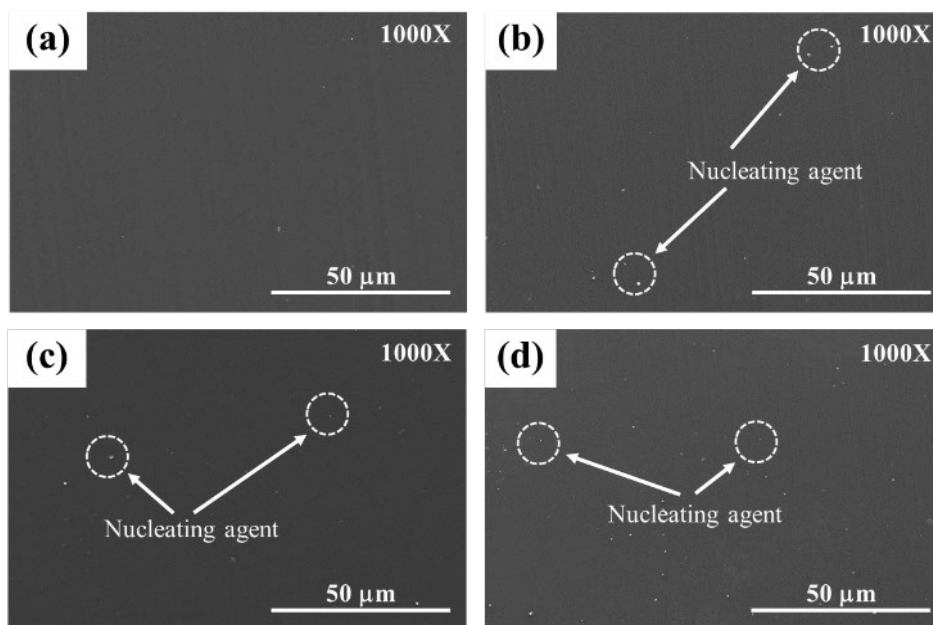


Figure 5. SEM surface of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin under magnification of 1000X.

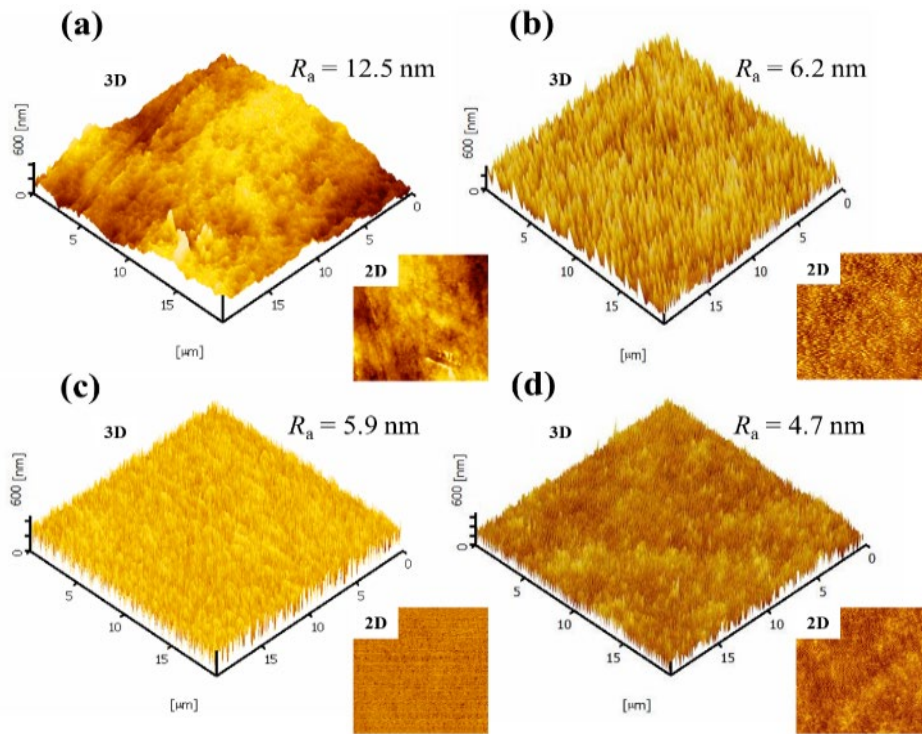


Figure 6. 2D and 3D AFM images of the surface topography of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/ 0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin.

3.5 The crystal structure of the films

The XRD pattern of the films in the range 10° to 50° is shown in Figure 7. The XRD pattern of LLDPE (control) (Figure 7(a)) shows three main peaks at 21.62° , 23.73° , and 36.22° of the 2-theta angle, which corresponds to the (110), (220), and (020) planes [18]. The plane peak of the LLDPE/0.5 wt% calcium carbonate (Figure 7(b)) and LLDPE/0.5 wt% kaolin (Figure 7(c)) films containing a single nucleating agent is the same as that of LLDPE, except that the 2-theta angle shifts for LLDPE/0.5 wt% calcium carbonate are 21.43° , 23.66° , and 36.32° , and for LLDPE/0.5 wt% kaolin are 21.56° , 23.85° , and 36.35° , respectively. Further investigation revealed a significant difference in the height of the main peak when compared to LLDPE (control). This revealed a trend toward increased crystallinity. The plane peak of LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin (Figure 7(d)) film containing a hybrid nucleating agent is the same as that of LLDPE (control) and LLDPE having a single nucleating agent. However, the main peaks with a slight shift in the 2-theta angle are 21.50° , 23.79° , and 36.29° . Importantly, the height of the main peak appears to be significantly higher when compared to LLDPE (control) and LLDPE containing the single nucleating agent.

In addition, the crystallinity was calculated by dividing the total area of the polymer crystalline peaks by the total area under the diffraction curve and summarized in Table 2. The LLDPE (control) had a percent crystallinity of 28.24%. The percent crystallinity of the LLDPE/0.5 wt% calcium carbonate was 36.33%, while the LLDPE/0.5 wt% kaolin had a percent crystallinity of 38.52%. LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin had a percent crystallinity of 42.61%. Notably, the percent crystallinity increased in all cases when compared to the crystallinity of the LDPE (control), implying that nucleating agents work to induce crystallinity and are the cause of

the slight shift in the XRD pattern [19]. Meanwhile, compared to a single nucleating agent, the addition of hybrid nucleating agents considerably increased the percentage of crystallinity. This is possibly due to the induced of the two types of nucleating agents, which differ in density and molecular weight. As a result of the different crystallization periods of the polymer, the amount of crystals in the film increases. Overall, a high percentage of crystallinity makes it easier to rinse upward coconut milk that has adhered to the film. The high crystallinity produces changes at the film's surface, affecting the crystallinity of the surface topography and possibly increasing the contact angle.

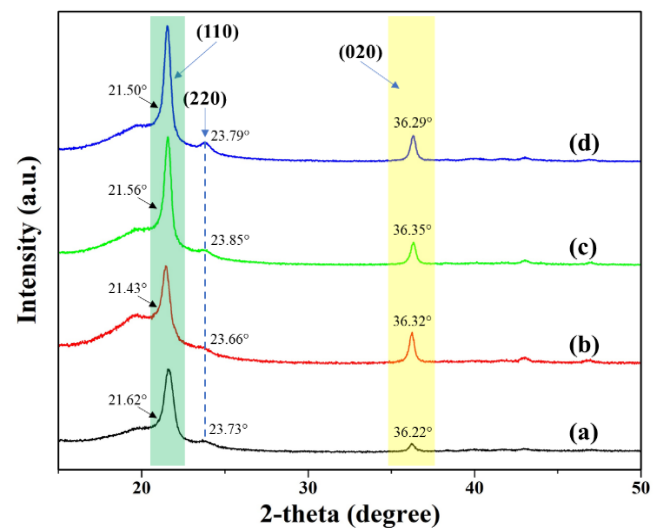


Figure 7. The crystal structure of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin.

3.6 The contact angle of the films

The contact angle was measured with the films, as shown in Figure 8. According to the findings of the experiments, the LLDPE (control) (Figure 8(a)) had a contact angle of 73.66° , which was quite low. While the contact angles of the LLDPE/0.5 wt% calcium carbonate (Figure 8(b)) and LLDPE/0.5 wt% kaolin (Figure 8(c)) films, which were composed of a single nucleating agent, are 85.52° and 86.45° , respectively. It can be observed that the contact angle is significantly higher compared to the LLDPE (control). The reason for this is that the nucleating agent may be able to improve the surface of the film, specifically the crystallinity and density [20]. When considering the LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin (Figure 8(d)) film containing a hybrid nucleating agent, the contact angle was greatly raised to 99.17° . This is because the employment of different nucleating agents might enhance their interaction and lead to a significantly higher crystallinity of the film, which is confirmed by XRD revealing a significant rise in the percentage of crystallinity. Therefore, the higher crystallinity of the film may increase the contact angle [21]. As a result, fat stain adherence on the surface of LLDPE film may be less easy to remove.

3.7 Fat stain adherence to the films and one-time rinsing

To test the film, coconut milk was utilized to represent the fat stains that will adhere to the LLDPE film. The findings of the experiments showed that when the film was dipped in coconut milk, the coconut milk adhered rather nicely to it. This phenomenon occurs in every formula film, as illustrated in Figure 9. This is due to the fact that coconut milk has several components, including not only water but also a variety of oils, lipids, and minerals, which help it adhere nicely to the film. Especially, when the coconut milky film was rinsed with water one time, it was discovered that the LDPE (control) (Figure 9(a)) still had the fat stains adhered to it and could not be rinsed off. Importantly, as compared to the LLDPE (control), the LLDPE/0.5 wt% calcium carbonate (Figure 9(b)) and LLDPE/0.5 wt% kaolin (Figure 9(c)) films containing a single nucleating agent reduced the fat stains on the film better when rinsed with water one time. This is because it is quite likely that the nucleating agent aids in the formation of small crystals on the film surface [22], aiding the rinsing of fat stains from the film. This result is correlated with surface topography from AFM analysis. Furthermore, it was discovered that LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin (Figure 9(d)) film containing a hybrid nucleating agent offered extremely excellent outcomes when rinsed with water one time, revealing that fat stains could be easily removed. The interaction

between the two nucleating agents could create different crystals [23], increasing fat stains rinsing from the film. Therefore, the crystals on the film surface, the narrow gap between the roughness on the surface, and the high contact angle can aid in rinsing fat stains from the film surface. As a result, the fat stain from coconut milk on the film will be easy to remove. This saves energy and helps with recycling. Furthermore, areas with and without fat stains were clearly evident when fat stains on the film were analyzed with the ImageJ program.

The reason for the easy rinsing of coconut milk drops from the film is predicted in Figure 10. It is possible that a nucleating agent causes consistent roughness on the film surface and a nanoscale gap on the surface [24], resulting in the Wenzel state phenomenon when a coconut milk drop comes into contact with the film. However, some fat stains remained on the film surface after rinsing the coconut milk drop with water. It is possible that the fat stains adherence remains in narrow gaps, making removal difficult and leaving some fat stains on the film surface.

3.8 Functional group of the films

Based on FTIR analysis in Figure 11, LLDPE has been shown to be the main component of all film formulations (Figure 11(a-d)). The wave numbers at the position 2910 cm^{-1} indicate CH_2 asymmetric stretching, 2850 cm^{-1} indicate CH_2 symmetric stretching, 1470 cm^{-1} indicate bending deformation, and 730 cm^{-1} indicate rocking deformation, which represents the function group in the LLDPE polymer [25]. Despite the addition of single and hybrid nucleating agents to the films, no new functional groups formed because the amount added was just 0.5 wt%, and the FTIR cannot be analyzed. Importantly, the FTIR spectral does not shift in all formulations. It demonstrates that the nucleating agents do not react chemically with the films and so cannot alter the functional group.

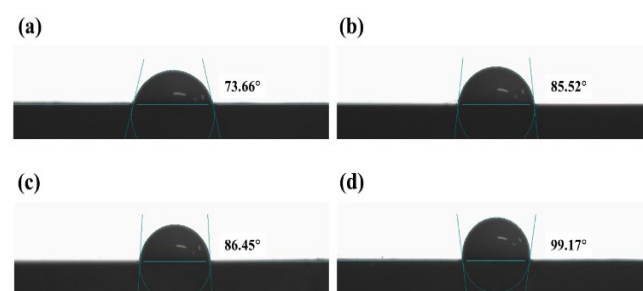


Figure 8. The contact angle of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin.

Table 2. Crystallinity percentage, mechanical properties and thickness of the films.

Films formula	Percentage of crystallinity (%) ^a	Tensile strength (MPa) ^{b,d}	Elongation at break (%) ^{b,d}	Thickness (mm) ^{c,d}
LLDPE (control)	28.24	15.15 ± 1.12	800.23 ± 30.43	0.51 ± 0.11
LLDPE/0.5 wt% calcium carbonate	36.33	18.92 ± 1.47	762.31 ± 25.51	0.51 ± 0.13
LLDPE/0.5 wt% kaolin	38.52	19.56 ± 1.36	758.87 ± 14.96	0.51 ± 0.17
LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin	42.61	22.17 ± 1.22	722.64 ± 18.72	0.51 ± 0.14

^a The percentage of crystallinity was calculated in the 15 to 40 range of two theta, ^b Mean of ten replicates \pm standard deviations, ^c Mean of six replicates \pm standard deviations,

^d Data reported are average values \pm standard deviations. Values within each column with different letters are significantly different ($p < 0.05$).

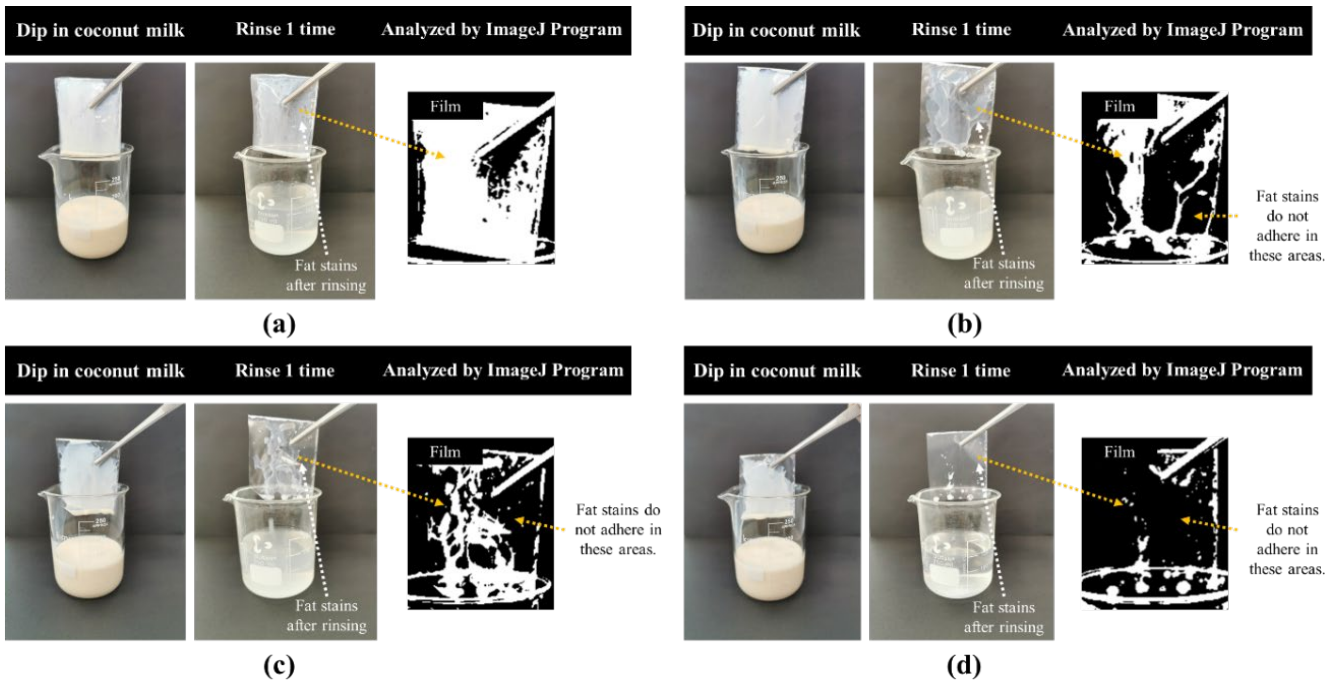


Figure 9. Coconut milk adherence to the films, one-time rinsing, and ImageJ analysis program: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin.

(Note: The coconut milk used in the testing was "ROI THAI BRAND" from Thailand, which is an ingredient in Thai cuisine, and the tested film size is 4 x 6 cm.)

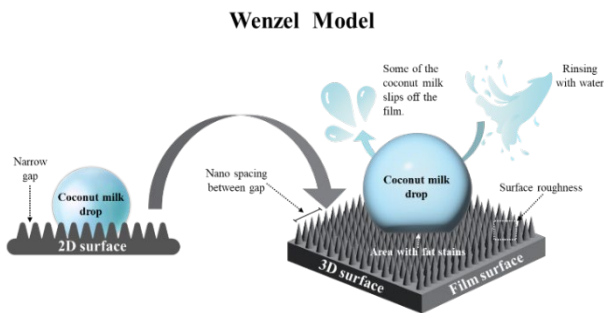


Figure 10. The Wenzel model and the process for rinsing coconut milk drops.

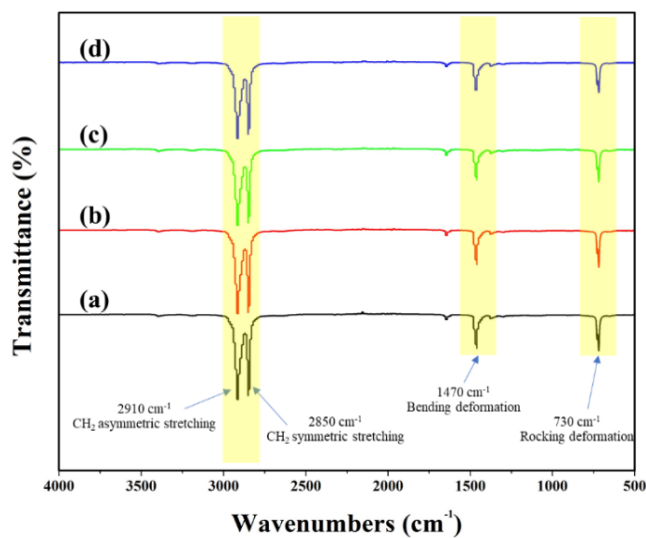


Figure 11. Functional group of the films: (a) LLDPE (control), (b) LLDPE/0.5 wt% calcium carbonate, (c) LLDPE/0.5 wt% kaolin, and (d) LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin.

3.9 Mechanical properties of the films

Mechanical properties are another vital property to describe because they determine how to sustain loads when utilized in food packaging film. The mechanical properties of the films were analyzed in terms of tensile strength and elongation at break, as shown in Table 2. According to the test results, LLDPE (control) had a tensile strength of 15.15 ± 1.12 MPa and an elongation at break of $800.23 \pm 30.43\%$. However, LLDPE/0.5 wt% calcium carbonate and LLDPE/0.5 wt% kaolin films with a single nucleating agent added produced a slightly higher tensile strength than LLDPE (control). The enhanced tensile strength may be due to the high crystallinity of the film and the nucleating agents appearing as rigid fillers compatible with LLDPE, resulting in higher tensile strength [26]. The tensile strength of LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin film with added hybrid nucleating agents was higher than that of LLDPE (control) and LLDPE with single nucleating agents added. This is due to the film's increased crystallinity, as demonstrated by the XRD results. As a result, it may result in a dense film with an increased probability of stronger tensile strength. Furthermore, while analyzing elongation at break, it was discovered that the addition of single and hybrid nucleating agents reduced the elongation at break of LLDPE/0.5 wt% calcium carbonate, LLDPE/0.5 wt% kaolin, and LLDPE/0.25 wt% calcium carbonate/0.25 wt% kaolin films compared to LLDPE (control). The reason for the decrease in elongation at break is that the polymer chain in the structure of LLDPE has a reduced free volume due to higher crystallinity [27,28]. As a result, the film has become even more solid. However, the changes in mechanical properties had no effect on the usage of film for food packaging because both tensile strength and elongation at break remained within acceptable limits. In general, commercial LLDPE films have tensile strength and elongation at

break values ranging from 7.30 MPa to 42.0 MPa and 460% to 1100%, respectively. As a result, the films obtained in this research have attributes that are acceptable when compared to commercial films. Finally, the thickness of the film (Table 2) is not significantly different in every example. As a result, it will not be considered when comparing mechanical properties.

4. Conclusion

The results of this research show that utilizing both types of nucleating agents, single and hybrid nucleating agents, at a concentration of 0.5 wt% can aid in the rinsing of fat stains on the LLDPE film surface. Furthermore, the employment of nucleating agents does not significantly affect the physical and chemical properties of the film. In conclusion, this research will be beneficial to the private sector in making films with easier-to-clean properties at a low cost and with simple preparation.

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Reference

- [1] E. Tito, J. S. dos Passos, S. Bensaid, R. Pirone, and P. Biller, "Multilayer plastic film chemical recycling via sequential hydrothermal liquefaction," *Resources, Conservation and Recycling*, vol. 197, pp. 107067, 2023.
- [2] N. Pinpru, and S. Woramongkolchai, "Crosslinking effects on alginate/carboxymethyl cellulose packaging film properties," *Chiang Mai Journal of Science*, vol. 47, no. 4, pp. 712-722, 2020.
- [3] A. Khumkomgool, T. Saneluksana, and N. Harnkarnsujarit, "Active meat packaging from thermoplastic cassava starch containing sappan and cinnamon herbal extracts via LLDPE blown-film extrusion," *Food Packaging and Shelf Life*, vol. 26, p. 100557, 2020.
- [4] Y. Shen, F. Hu, X. X. Zhang, K. Thakur, K. R. R. Rengasamy, M. R. Khan, R. Busquets, and Z. J. Wei, "Fortification of polysaccharide-based packaging films and coatings with essential oils: A review of their preparation and use in meat preservation," *International Journal of Biological Macromolecules*, vol. 242, pp. 124767, 2023.
- [5] T. Tábi, T. Ageyeva, and J. G. Kovács, "The influence of nucleating agents, plasticizers, and molding conditions on the properties of injection molded PLA products," *Materials Today Communications*, vol. 32, p. 103936, 2022.
- [6] Y. Phuphuak, Y. Miao, P. Zinck, and S. Chirachanchai, "Balancing crystalline and amorphous domains in PLA through star-structured polylactides with dual plasticizer/nucleating agent functionality," *Polymer*, vol. 54, no. 26, pp. 7058-7070, 2013.
- [7] X. Liu, X. Miao, X. Cai, J. Shao, F. Zou, W. Song, J. Qiao, and C. Wu, "The orientation of the dispersed phase and crystals in an injection-molded impact polypropylene copolymer," *Polymer Testing*, vol. 90, pp. 106658, 2020.
- [8] Y. Huang, G. Chen, Z. Yao, H. Li, and Y. Wu, "Non-isothermal crystallization behavior of polypropylene with nucleating agents and nano-calcium carbonate," *European Polymer Journal*, vol. 41, no. 11, pp. 2753-2760, 2005.
- [9] A. Anam, N. Gamit, V. Prajapati, and B. Z. Dholakiya, "An overview of kaolin and its potential application in thermosetting polymers," *Materials Today Communications*, vol. 36, p 106827, 2023.
- [10] S. C. S. Teixeira, M. M. Moreira, A. P. Lima, L. S. Santos, B. M. da Rocha, E. S. de Lima, R. A. A. F. da Costa, A. L. N. da Silva, M. C. G. Rocha, and F. M. B. Coutinho, "Study of blends of HDPE and different grades of CaCO₃. Part I. Factorial experimental design," *Polymer Testing*, vol. 24, no. 8, pp. 983-987, 2005.
- [11] Z. A. Nur Hanani, F. Reich, T. Tolksdorf, H. Siemen, and N. Bandick, "Monitoring the effect of active packaging films with silver-kaolinite using different packaging systems on the quality of beef meat," *Heliyon*, vol. 8, no. 10, pp. e11019, 2022.
- [12] S. Kormin, F. Kormin, and M. D. H. Beg, "Effect of plasticizer on physical and mechanical properties of LDPE/sago starch blend," *Journal of Physics: Conference Series*, vol. 1150, p. 012032, 2019.
- [13] B. M. Tselana, S. Muniyasamy, V. O. Ojijo, and W. Mhike, "Melt processible biodegradable blends of polyethylene glycol plasticized cellulose diacetate with polylactic acid and polybutylene adipate-co-terephthalate," *Journal of Polymers and the Environment*, pp. 1-18, 2023.
- [14] Y. D. Zhu, G. C. Allen, P. G. Jones, J. M. Adams, D. I. Gittins, P.J. Heard, and D.R. Skuse, "Dispersion characterisation of CaCO₃ particles in PP/CaCO₃ composites," *Composites Part A: Applied Science and Manufacturing*, vol. 60, pp. 38-43, 2014.
- [15] A. Mallik, A. K. Barikb, and B. Palb, "Comparative studies on physico-mechanical properties of compositematerials of low density polyethylene and raw/calced kaolin," *Journal of Asian Ceramic Societies*, vol. 3, pp. 212-216, 2015.
- [16] Q. Chen, Z. Wang, S. Zhang, Y. Cao, and J. Chen, "Structure evolution and deformation behavior of polyethylene film during biaxial stretching," *ACS Omega*, vol. 5, no. 1, pp. 655-666, 2020.
- [17] M. Li, Y. Chen, L. Wu, Z. Zhang, and K. Mai, "A novel polypropylene composite filled by kaolin particles with β -nucleation," *Journal of Thermal Analysis and Calorimetry*, vol. 135, no. 4, pp. 2137-2145, 2018.
- [18] M. Irani, H. Ismail, and Z. Ahmad, "Preparation and properties of linear low-density polyethylene-g-poly(acrylic acid)/ organo-montmorillonite superabsorbent hydrogel composites," *Polymer Testing*, vol. 32, no. 3, pp. 502-512, 2013.
- [19] Z. Zhang, C. Wang, J. Zhang, and K. Mai, "The β -nucleation of polypropylene random copolymer filled by nano-CaCO₃ supported β -nucleating agent," *Journal of Thermal Analysis and Calorimetry*, vol. 109, no. 3, pp. 1587-1596, 2011.
- [20] Y. An, S. Wang, R. Li, D. Shi, Y. Gao, and L. Song, "Effect of different nucleating agent on crystallization kinetics and morphology of polypropylene," *e-Polymers* vol. 19, pp. 32-39, 2019.

- [21] S. M. Davachi, B. S. Heidari, R. Sahraeian, and A. Abbaspourrad, "The effect of nanoperlite and its silane treatment on the crystallinity, rheological, optical, and surface properties of polypropylene/nanoperlite nanocomposite films," *Composites Part B: Engineering*, vol. 175, p. 107088, 2019.
- [22] A. G. Simanke, A. P. d. Azeredo, C. d. Lemos, and R. S. Mauler, "Influence of nucleating agent on the crystallization kinetics and morphology of polypropylene," *Polímeros*, vol. 26, no. 2, pp. 152-160, 2016.
- [23] V. Krmelová, M. Gavendová, T. Zatroch, J. Krmela, A. Dubec, B. Bizubová, M. Kleščík, and A. Balogová, "Structure and properties of nucleated polypropylene fibres," *IOP Conference Series: Materials Science and Engineering*, vol. 776, p. 012096, 2020.
- [24] H. Haham, M. Y. Shen, S. L. Billington, and C. W. Frank, "Comparison of nanocrystalline cellulose dispersion versus surface nucleation in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) crystallization," *SPE Polymers*, vol. 1, no. 1, pp. 15-25, 2020.
- [25] M. Ghozali, E. Triwulandari, A. Haryono, and E. Yuanita, "Effect of lignin on morphology, biodegradability, mechanical and thermal properties of low linear density polyethylene/lignin biocomposites," *IOP Conference Series: Materials Science and Engineering*, vol. 223, p. 012022, 2017.
- [26] Z.-Z. Liu, G.-Q. Zheng, H.-H. Shi, C.-T. Liu, L.-W. Mi, Q. Li, and X.-H. Liu, "simultaneous enhancement of toughness and strength of stretched ipp film via tiny amount of β -nucleating agent under "shear-free" Melt-extrusion," *Chinese Journal of Polymer Science*, vol. 39, no. 11, pp. 1481-1488, 2021.
- [27] F. Ö. Özmihçi and D. Balköse, "Effects of particle size and electrical resistivity of filler on mechanical, electrical, and thermal properties of linear low-density polyethylene-zinc oxide composites," *Journal of Applied Polymer Science*, vol. 130, no. 4, pp. 2734-2743, 2013.
- [28] Y. Wang, Y. Shi, W. Shao, Y. Ren, W. Dong, F. Zhang, and L. Z. Liu, "Crystallization, structures, and properties of different polyolefins with similar grafting degree of maleic anhydride," *Polymers (Basel)*, vol. 12, no. 3, 2020.