

THE DEVELOPMENT OF BIODEGRADABLE PLASTIC WITH NATURAL COLOURANT AS PACKAGING MATERIAL

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Abstract.

The aim of this study is to develop biodegradable plastic with natural colourants as packaging material. Blends of anthocyanin and bromocresol purple (BCP) as biological and chemical colourants respectively, tapioca starch, glycerol, polyethylene grafted maleic anhydride (PE-g-MA), clay nanocomposites and low density polyethylene (LDPE) with different formulation contents for five types of blends were prepared using a lab scale twin screw extruder. A series of low density polyethylene (LDPE) with different blends formulation were developed via blow film extrusion. The morphology and properties of the blends were evaluated by using a scanning electron microscope (SEM). The dispersion of tapioca starch in the LDPE matrix was homogeneous and mechanical properties of the films were improved with the addition of glycerol. The interfacial adhesion between tapioca starch and LDPE was further improved by the addition of PEG-MA according to the morphological structure shown by SEM micrographs, thus enhanced the mechanical properties of the films. Formulations containing 35 % tapioca starch with fairly high concentrations of additives indicate the importance of the concentration of starch and the presence of additives on the biodegradability of tapioca starch-LDPE film blends.

Keywords: Biodegradable, LDPE, tapioca starch, blow film extrusion, packaging film

Abstrak. Kajian ini dilakukan bertujuan untuk menghasilkan plastik terbiodegradasi dengan bahan pewarna natural sebagai bahan pembungkusan. Campuran anthocyanin dan bromokresol ungu (BCP) sebagai bahan pewarna biologi dan kimia, kanji ubi kayu, gliserol, polyethylene grafted maleic anhydride (PE-g-MA), tanah liat nanokomposit dan polyethylene berketumpatan rendah (LDPE) dengan kandungan formulasi yang berbeza bagi lima jenis campuran yang berlainan disediakan dengan menggunakan twin screw extruder berskala makmal. Beberapa siri LDPE dengan campuran formulasi yang berlainan dihasilkan dengan menggunakan blow film extrusion. Morfologi dan sifat setiap campuran akan dikaji dengan menggunakan mikroskop peneliti elektron (SEM). Penyebaran kanji ubi kayu dalam matriks LDPE adalah sekata dan sifat mekanikal plastik filem telah diperelokkan selepas penambahan gliserol. Permukaan lekatan antara kanji tepung ubi dan LDPE telah diperelokkan dengan penambahan PE-g-MA bersarkan struktur morfologi melalui SEM, dengan itu memperbaiki sifat mekanikal filem. Formulasi yang mengandungi 35% kanji tepung ubi dengan konsentrasi bahan pengaruh yang tinggi menunjukkan kepentingan konsentrasi kanji dan kewujudan bahan pengaruh terhadap biodegradasi campuran kanji-LDPE.

1.0 INTRODUCTION

Today's plastics are designed with little consideration for their ultimate disposability. Plastics are strong, easily processable, inexpensive, light-weight and energy efficient. They are disposable, very durable and have excellent barrier properties. However, they also have several disadvantages. One of the largest being that plastic does not break down in the environment. They are not readily broken down by the natural elements in the environment or composting to become a part of the biological carbon cycle of our ecosystem.

According to Narayan (1993), plastics are resistant to biological degradation because microorganisms do not have enzymes capable of degrading and utilizing most man made polymers. The hydrophobic character of plastics inhibits enzyme activity and the low surface area of plastics with their inherent high molecular weight further compounds the problem. Biodegradable plastics should have the needed performance characteristic in their intended use, but after use should undergo biodegradation in appropriate waste management infrastructures to environmentally compatible constituents. For example, a truly biodegradable plastic will be converted to CO_2 , H_2O , and compost in a composting infrastructure leaving no persistent or toxic residue (Narayan, 1993).

The addition of biodegradable additives to the formulation of plastics can be enhanced the biodegradability of synthetic polymers like polyethylene. Starch is one of the most common degradable fillers used in plastic formulations. Raw starch is considered to be a cost effective additive and meets the requirement of high thermal stability, minimum interference with flow properties, and minimum disturbance of product (Shah et al., 1995). In plastics containing blends of polyethylene with starch, microbes initially attack starch resulting in an increase in the porosity and surface to volume ratio of the polymer blend and a consequent enhancement of its biodegradability (Nikazar et al., 2005).

The microbes should first adhere to the surface of the polymer in order to attack the starch, so polymers that have a rougher surface finish are more prone to microbial attack. The increase in the starch content and decrease in the starch granule size enhance the biodegradability of the plastic blends.

The biodegradability of the polyethylene-starch blends can be further enhanced by the addition of other additives such as autooxidants (for example unsaturated fatty acids and their derivatives), photo degraders (for example aromatic or aliphatic ketone), chemical degraders (for example an aliphatic polyhydroxy carboxylic acid) and various compatibilizers (Downie, 2002).

The incorporation of pro-oxidant which consisted of metal salts and unsaturated elastomer enhanced the thermo-oxidative degradation rate of sago starch filled LLDPE composites (Sharma et al., 2001). Lee et al. (1991) found that the degradation of polyethylene molecules by lignin degrading bacteria in those films containing starch and pro-oxidants. The use of plasticized starch such as glycerol has also been found to affect the degradability of the plastic blends. The plasticizers content is directly relates to the mechanical properties of the material.

However, the addition of starch to polyolefin blends results in a reduction in their mechanical strength. Besides, the amount of starch in the blend also affects its mechanical properties. This will necessitates an increase in the thickness of bags made from this blends. These measures include the chemical modification of starch, the use of compatibilizers, such as oxidized polyethylene, fatty acids, and ethylene-co-acrylic acid (Bikiaris et al., 1998). Increaseing the starch content is shown to worsen the mechanical and rheological properties and the processability of the system (Willet et. al, 1994). Mani and Bhattacharya (Mani et al., 1998) found that amylose to amylopectin ratio of starch affect the physical properties of starch/PE blends. The size and type of starch in the starch based PE films also affects its physical properties. For example Lee (1994) found a strong negative correlation between tensile and yield strength values of the films and average starch granule diameter.

In this study the incorporation of additives in the tapioca starch based LDPE blends has been considered as a means of improving the mechanical properties and biodegradability of plastic films made form these blends. Antocyanin and Bromocresol Purple as biological and chemical colourants was incorporated into blends to evaluate their stability as natural colourants for packaging material. The addition of plasticizer such as glycerol can improve the strengthens of the plastics characteristics. Glycerol is often used as a plasticizer in polymer blends to increase softness and pliability. Maleic anhydride-grafted Polyethylene (PE-g-MA) was used as compatibilizer for the immiscible system. Maleic anhydride-grafted Polyethylene (PE-g-MA) enhanced the interfacial interaction between the LDPE and starch phases, makes them more compatible with each other. The effect of the concentration of tapioca starch and the addition PE-g-MA as a coupling agent on the mechanical properties and biodegradability of starch-LDPE blends has been investigated. This results in an increase in the stability of the morphology in the mixing process and it is also enhances the mechanical properties.

2.0 METHODOLOGY

2.1 Materials

Low-density polyethylene (LDPE) was a product of Titanlene, LDF 200 yy, with a melt flow index of 2g/10min. Tapioca starch was dried at 120°C for 24 hr to a moisture content of less than 1% prior to specimen preparation. Anthocyanin was obtained from Laboratory of Bioprocess. Bromocresol purple and calcium hydroxide were obtained from Merck KgaA, Germany. PEg-MA with an approximate maleic anhydride content of 3wt %, glycerol and clay nanocomposite were obtained from Laboratory of Polimer (N14)

2.2 Preparation of LDPE Blends

Tapioca starch, glycerol (1% of LDPE weight), PE-g-MA ratios of 10% and 20%, of LDPE weight), clay nanocomposites, anthocyanin, bromocresol purple and LDPE were blended at room temperature with a high speed mixer at tapioca starch to LDPE ratios of 0%, 15%, 25%, and 35% (w/w) for five different formulation. These blends which in five different formulation were then melt-blended in a lab-scale twin screw extruder. The plastic film were developed via blow film extrusion at a processing temperature of 170°C.

2.3 Morphology Observation

The blend samples were fractured in liquid nitrogen and the fracture surface of the samples was observed using a Hitachi S-2300 Scanning Electron Microscope (Tokyo, Japan) at an accelerating voltage of 25KV.

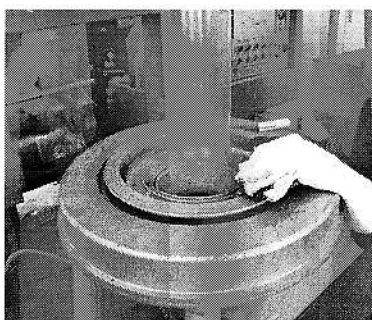


Figure 1: Picture shown the extrusion.



Figure 2: Picture shown the blow film twin screw extruder.

3.0 RESULT AND DISCUSSION

3.1 Packaging film formation

A series of low density polyethylene (LDPE) with different formulation of blend were prepared by twin screw extrusion. Different percentage of tapioca starch in LDPE sheets were then produced by blow film extrusion. The presence of high starch contents had an adverse effect on the mechanical properties of LDPE/tapioca starch blends. However, the addition of processing aids to the blends improved the interfacial adhesion between the two materials, hence, improved the mechanical properties of the films. High content of starch amount also was found to increase the rate of biodegradability of LDPE/tapioca starch films.

3.2 Packaging film appearance

In figures which follow, blend morphologies are presented by plastic film development via blow film extrusion. Each figure pertains morphologies for the LDPE with volume compositions of 0%, 15%, 25%, and 35% weight fraction of tapioca starch to LDPE. Antocyanin and bromocresol purple (BCP) as a biological and chemical colourants are incorporated into blend morphologies to indicate their stability as natural colourants for plastic packaging. Progressive morphology development can be discerned by sequentially inspecting micrographs of each figure corresponding to a particular composition.

As discussed in relation to Figure 3, the incorporation of calcium hydroxide (Ca(OH)_2) and bromocresol purple (BCP) in the polymer matrix which has a negative influence on the stretching properties of the plastic. This two additives cannot be joined together with LDPE without the addition of plasticizers. This plastic film formulation is unable to blow and it shows the chaotic layered configuration.



Figure 3: Plastic packaging of LDPE/Calcium Hydroxide/Bromocresol Purple

Therefore, for the second formulation, glycerol was added into the blends. The addition of plasticizer such as glycerol can improve the strengthens of the plastics characteristics. Glycerol is often used as a plasticizer in polymer blends to increase softness and pliability. The result presented in Figure 4(a) that the blends was able to blow in order to form a plastic film via blow film extrusion. Figure 4.6 shows the SEM micrographs of LDPE/Calcium hydroxide/Bromocresol Purple/Glycerol. It had been reported that the dispersion of those blends in LDPE matrix was inhomogeneous. The glycerol might have increased the interaction between LDPE/calcium hydroxide/bromocresol purple, which in turn hindered the dispersion in LDPE matrix.

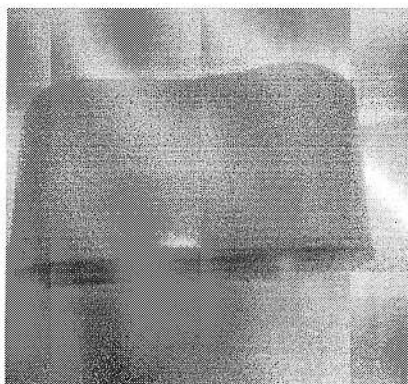


Figure 4 (a): Plastic packaging of LDPE/Calcium Hydroxide/glycerol/Bromocresol Purple

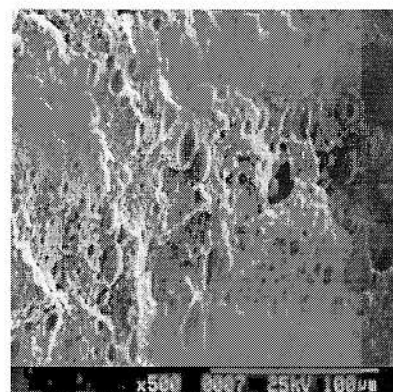


Figure 4.2(b): SEM micrographos of fracture surface of LDPE/Ca(OH)₂/glycerol/BCP

Two undesirable effects of the incorporation of starch into plastic films are the reduction in the yield stress and elongation-at-break values of the films. The latter case is the result of the incorporation of starch granules in the polymer matrix, which has a negative influence on the stretching properties of the plastic. The blend that contains the lowest amount of starch (formulation 3) exhibits a fairly low tensile strength. These problems of starch can be decreased by homogeneous incorporation of sheet-like non-permeable barrier elements such as clay minerals by mix-melting. The nanoclays are the potential ingredient in this application as they are environmentally acceptable, naturally abundant minerals that are toxin-free and can be used as one of the components for food packaging. However, the addition of clay nanocomposites has increase the tensile strength of the plastic films. Even at 4% clay loading, the permeability of the nanocomposite was reduced. Figure 5 show the result that the blends formulation was unable to blow at 4% clay nanocomposites loading. This observation suggests that clay nanocomposites contributes to the worsening of mechanical properties under when the clay loading exceeds 4% and above.

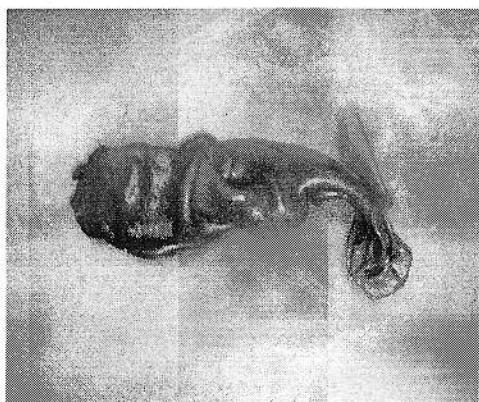


Figure 5: Plastic packaging of LDPE/tapioca starch/glycerol/Anthocyanin/Clay nanocomposites with 15% weight fraction of starch to LDPE.

The homogeneous dispersion of tapioca starch in LDPE matrix would reduce the chance of a significant stress concentration. Consequently, materials were fractured at higher ultimate strength and displacement. From Figure 6(a), it shows that the blend (formulation 4) was able to blow it forms the brown coloured plastic film. This means that the tensile strength of LDPE/tapioca starch/ bromocresol purple/glycerol/PE-g-MA blends was significantly greater than that of LDPE/tapioca starch blends. It was believed that PE-g-MA increased adhesion between the LDPE matrix and the starch filler because PE-g-MA was situated at the interface between starch and LDPE and intergated with both constituents based on SEM results showed in Figure 6(b). The improved interfacial adhesion played an important role in the stress transfer, thus reducing the chance of interfacial debonding and leading to improved tensile strength. In addition, these results also supported the finding that the interaction between starch and PE-g-MA was similar to that between hydroxyl groups in tapioca starch and anhydride groups in PE-g-MA (Bikiaris and Panayiotou, 1998). However the coloured of BCP was easily degrade at the temperature higher than 120°C. Therefore it shows that the colour of plastic film is brown (which from tapioca starch) because the blue colour of BCP has degrade itself at the higher temperature above 100°C.

and the interfacial adhesion between dispersed phase and matrix are key factors to determine the mechanical properties (Paul, 1978).

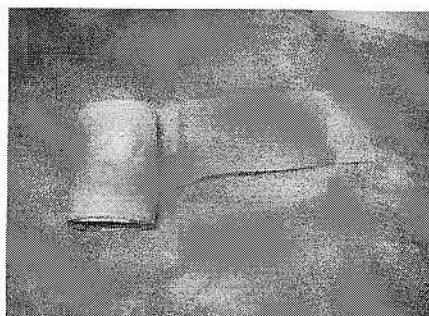


Figure 7(a): Plastic packaging of LDPE/tapioca starch/glycerol/Anthocyanin/PE-g-MA with 35% weight fraction of starch to LDPE.

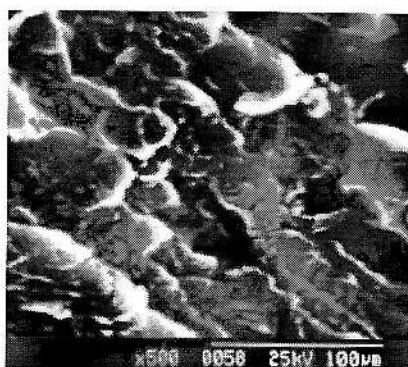


Figure 7(b): SEM micrographos of fracture surface of LDPE/tapioca starch/glycerol/PE-g-MA with 35% weight fraction of starch to LDPE.

From this study, the best quantity 80% LDPE, 20% PE-g-MA (compatibilizer), 35% tapioca starch with antocyanin (nanoencapsulation) 1% glycerol for biodegradable with natural colourants as packaging material. This indicates the importance of both the starch concentration and the presence of the appropriate additives in the composition of starch based biodegradable LDPE films.

3.3 Natural colourants

From figure 8 and 9 shows that the antocyanin is more stable than bromocresol purple. The percentage of stability of BCP is lower than anthocyanin and had easily degrade itself at the high temperature. The stability of anthocyanin shows a good

potential as a natural colourant. Therefore, from the results indicate that anthocyanin can replace bromocresol purple as a natural colourant.

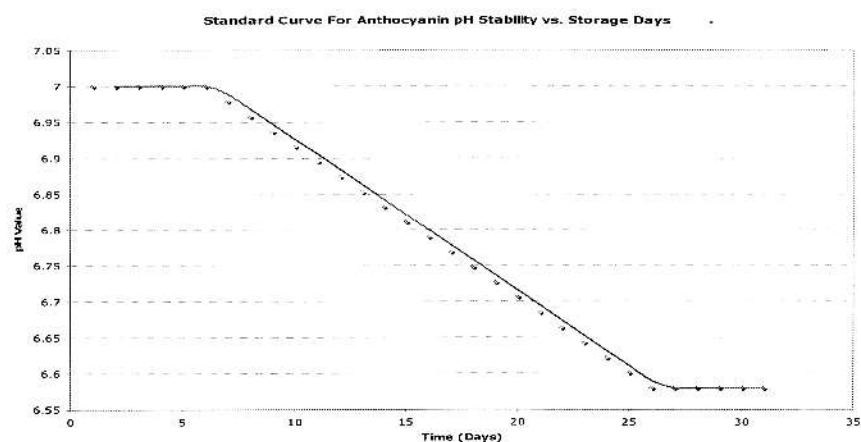


Figure 8: Standard Curve For Anthocyanin in pH Stability vs. Storage Days.

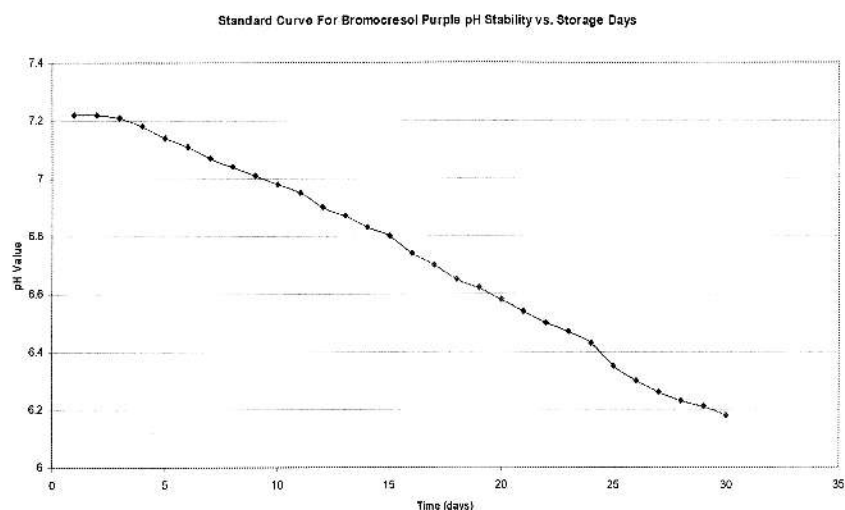


Figure 9: Standard Curve For Bromocresol Purple in pH Stability vs. Storage Days.

4.0 CONCLUSIONS

From this project, it can be concluded that the stability of tapioca starch and anthocyanin incorporated into Low Density Polyethylene (LDPE) shows a good potential as a biodegradable plastic with natural colourant. The best formulation contain 35% tapioca starch with anthocyanin (nanoencapsulation), 20% PE-g-maleic anhydride (compatibilizer) and 1% glycerol incorporated into LDPE to create biodegradable plastic. PE-g-MA improved the interfacial properties between tapioca starch and LDPE.

Bromocresol purple can easily degrade itself at the high temperature above than 100°C, while anthocyanin maintain its stability during at high temperature. Therefore, anthocyanin can replace bromocresol purple as a natural colourant.

5.0 ACKNOWLEDGEMENT

The financial contribution from Ministry of Higher Education Malaysia (MOHE), Ministry of Science, Technology And Innovation (MOSTI) and Research Management Centre UTM was greatly appreciated.

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