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Degradable Polyethylene/Rice Bran Film: Effect of Gylcerol

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In this study, a degradable film based on polyethylene (PE) and Rice bran (RB) as filler were developed. Low density polyethylene (LDPE) and rice bran (0 – 5 %) were prepared by using twin screw extruder and blown film machine. The effect of 3 phr of glycerol as plasticizer on the biodegradability, tensile properties and morphological properties of LDPE/RB films was evaluated. Increase in rice bran contents had an adverse effect on the tensile strength of LDPE/rice bran films. Incorporation of a glycerol as plasticizer had increased the tensile strength of LDPE/RB films. The addition of glycerol into the films enhanced the distribution and dispersion phase and thus, improved the tensile properties of the films. The SEM micrographs showed that the presence of glycerol in LDPE/RB films improved distribution and dispersion phase and the particle rice bran became smaller in LDPE matrix. The addition of rice bran in LDPE/RB films had increased their biodegradability due to microorganism soil attacks.

1. Introduction

Plastics are used around the world for various application in industry. The plastics widely use due to their properties such as light weight, low costs, good mechanical properties and easy processability. However, the difficulty to manage the plastic waste arise due to it takes a longer time to degrade or cannot degrade properly. Plastic waste also degrade into substances that are hazardous and polluting. Therefore it adversely affects the environmental, economic and ecological system, especially to a human being. Most of the plastic waste is dumped and let it degrade by itself. As a result, the availability of landfill area has decreased dramatically while the cost to provide for land filling for waste has increased drastically. Therefore, the recycling and incineration method had been done to minimize these problems. However, only a small percentage of plastic waste is recyclable and most of them are end up in the municipal landfill. On top of that, emission of corrosive gas, high capital cost, toxic gases and operating at high temperature make incineration less attractive (Moghadam et al., 2013). One of the solutions to tackle the problem of plastic waste management is the production and use of environmental friendly degradable polymers especially in the packaging applications (Monica et al., 2015). There are many renewable sources used to produce biodegradation polymer product such as starch, chitosan, wool and silk. There have been demands to use a biodegradable polymer that is comparable to substitute the growing use of non-biodegradable polymer (Tudorachi et al., 2000).

Most countries use rice as staple food especially Asian countries. The major rice growing countries are India, Thailand, Indonesia, China, Bangladesh, Vietnam, Burma, Philippines and the Japan (Hu et al., 2009). Rice bran is a byproduct of the rice milling process during the spread brown rice to white rice. The outer brown layer was called rice bran is composed of the rice germ and several sub-layers which account for approximately 8 % by weight of paddy rice and contain over 60 % of the nutrients found in each kernel of rice.

Today, the challenge of producing biodegradable polymer becomes the focus of research interest in order to overcome the problem of plastic waste management (Seggiani et al., 2015). Many researchers have been carried out to produce the degradable plastic film from LDPE and product from natural resources such as starch (Garg and Jana, 2006), flour (Morreale et al., 2008) and chitosan (Bourtoom and Chinnan, 2008). In this study, the rice bran from local producer will be used to produce degradable LDPE/rice bran film. The effect of rice bran

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content and plasticizer on the tensile properties, biodegradability and morphology were evaluated. The study on glycerol as plasticizer was adopted in order to enhance the compatibility between RB and LDPE.

2. Experimental

Materials

LDPE (LDF260GG; density: 0.922 g/cm^3) was purchased from TITAN Chemical, Malaysia. Rice bran with a particle size range of 100 – 500 µm was purchased from local rice mills in Kelantan, Malaysia. Glycerol ($C_3H_8O_3$) was purchased from Sigma-Aldrich (M) Sdn. Bhd. The glycerol was used as a plasticizer during blending between matrix and filler.

Experimental Procedure

Rice bran was dried in an oven at 60 ˚C for 24 h before using. Then, LDPE and rice bran with and without glycerol (3phr) were blended with different concentration of rice bran (0 – 4 %) by using Twin screw extruder with a temperature range of 150 – 190 ˚C while the speed was 50 rpm. The compound was pelletized by using pelletizer. The pellet of the compound was blowing into a film by using blown film machine (Tai King 42440) with temperature range 115 – 160 ˚C and the speed by 650 rpm. The mechanical properties of a biodegradable film of LDPE/Rice bran such as tensile strength and percentages of elongation at break were measured by using Lloyd Instruments testing machine. This speed of the machine was set at 50 mm/min and the sample film was prepared in a rectangular shape as ASTM D 882. The morphology of LDPE/RB film was analysed by using scanning electron microscopy (SEM). The soil burial test has been carried out to investigated biodegradability and the rate of biodegradation of the films that buried in the soil according to ASTM D1435. The samples of the films which was cut into uniform strip sheet (about 50 mm × 10 mm) were buried in a soil. The poly bag containing of soil and samples were exposed to environmental effects such as sunlight and rains for several months. The samples were collected following the schedule to determine the rate of biodegradation. The surfaces of the samples were cleaned with a tissue and dried. The weights of all samples were weighing measured and recorded. The percentage of degradation was determined by Eq(1).

$$\%\,Degradation = \frac{m_o - m_d}{m_o} x100\% \qquad (1)$$

Where m_o = initial weight of sample m_d = final weight after buried in soil.

3. Results and Discussion

Effect of Glycerol on LDPE/RB films

Glycerol was used as a plasticizer to improve the processibility and arrangement of distribution of RB in LDPE matrix and to reduce the agglomeration phenomenon. It is well known that improvement in the interfacial adhesion between two phases and the distribution of dispersion particles or phases are the main factors to enhance the mechanical properties such as tensile strength and elastic properties (Wang et al., 2004). Figure 3.1 shows the effect of glycerol on the tensile strength of LDPE/RB films. After the addition of glycerol, the tensile strength remarkably increased compared with the films without glycerol. The highest tensile strength was recorded at 4 wt % of RB content with 122.5 % increment. This is due to enhancement of distribution and dispersion phase of rice bran in LDPE matrix. The heterogeneous or immiscible phase between rice bran and LDPE matrix was caused stress concentration on the surface. In this case, the stress concentration leading to the formation of craze or microvoids on the surface and consequently accelerates the breaking process of the films (Wang et al., 2004). Hence, with the addition of glycerol in LDPE/RB films, the tensile strength increased due to the enhanced homogenous dispersion of rice bran in LDPE matrix which means decreasing the particle size of the dispersed phase. SEM micrographs in Figure 3.2 shows a better dispersion and smaller RB particles in LDPE/RB/Glycerol films compared to the films without glycerol (Figure 3.3 (a) and (b)). From the observation, it is shown that the surfaces of LDPE/RB/Glycerol films are smooth, with clear and uniform surfaces as compared to LDPE/RB films.

The maximum content of rice bran that can be used was 5 wt % due to the presence of glycerol and was only 4 wt% without glycerol. According to Laohakunjit and Noomhorm (2004), the addition of plasticizer can overcome the starch films brittleness and enhance the extensibility and flexibility. In addition, the plasticizer can also reduce the intermolecular forces between two phases and improves the molecular mobility of polymer chains. The presence of glycerol also improves interaction with starch molecules through hydrogen bonding which has significantly enhanced the mobility of polymer chains (Sabetzadeh et al., 2012). The effects of glycerol on polyethylene/starch blends had also been reported by Taguet et al. (2009) and they reported that the lack of glycerol in polyethylene/starch blends adversely affect the process of deformation of the tensile test.

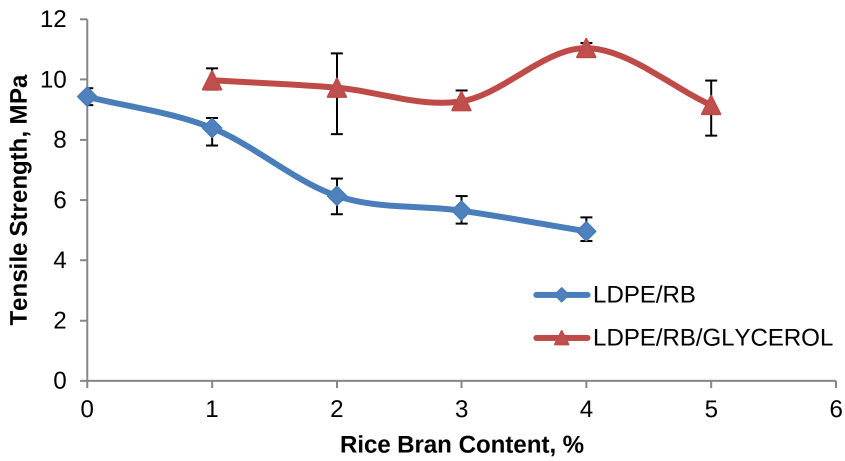
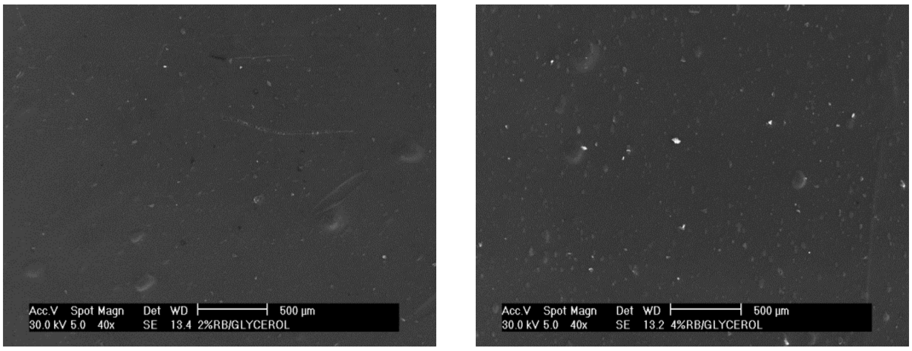


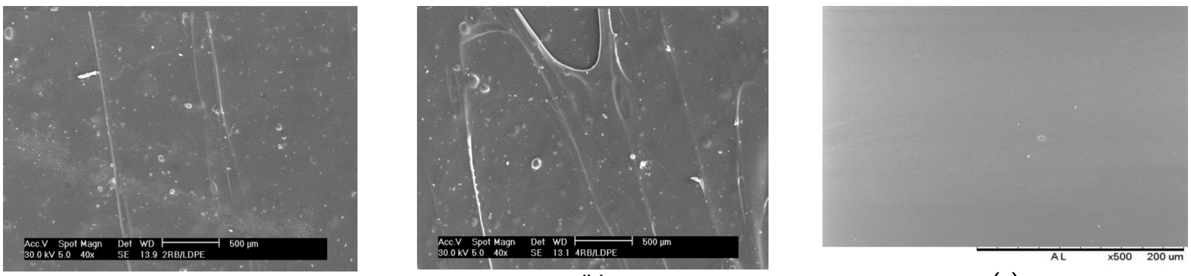
Figure 3.1: Effect of glycerol on tensile strength of LDPE/RB films and films at different RB content

In this study, the maximum tensile strength of LDPE/RB/Glycerol films obtained was 11.04 MPa at 4 wt % rice bran content. This is probably due to the adequate amount of glycerol to make full interaction with rice bran and thereby hydrogen bonding between rice bran and glycerol has resulted in the enhanced mobility of polymer chains and thus improving their mechanical properties, especially tensile strength (Garg and Jana, 2007).



(a) (b)

Figure 3.2: SEM micrographs of LDPE/RB films with addition glycerol: (a) 2 % rice bran + 3 phr glycerol, (b) 4 % rice bran + 3 phr glycerol



(a) (b) (c)

Figure 3.3: SEM micrographs of LDPE/RB films with different ratio of rice bran in LDPE content: (a) 2 %, (b) 4 % and (c) 0 %

Figure 3.4 shows the effect of rice bran concentration on elongation at break of LDPE/RB and LDPE/RB/Glycerol films. It can be seen that the percentage of elongation at break remarkably increased with the incorporation of glycerol in the LDPE/RB films. The highest value of elongation at break of LDPE/RB/Glycerol was 217.6 % for 3 % rice bran content. As expected, the existence of glycerol was capable of enhancing the ductility of gelatinized starch in RB thus increased the elongation at break. Glycerol is capable of enhancing the extensibility and flexibility of LDPE/RB films. The increase in RB content has decreased the elongation at break. This might due to the decreased compatibility of LDPE and RB at higher RB loading. According to Laohakunjit and Noomhorm (2004), the relative percentage of elongation at break increased with increasing plasticizer content for glycerol- and sorbitol-rice starch films. The dispersion of rice starch in LDPE has been improved and the agglomeration of starch has been reduced after the addition of glycerol. In addition, glycerol also enhances a macromolecular mobility causing a reduction in the apparent viscosity (Sabetzadeh et al., 2012).

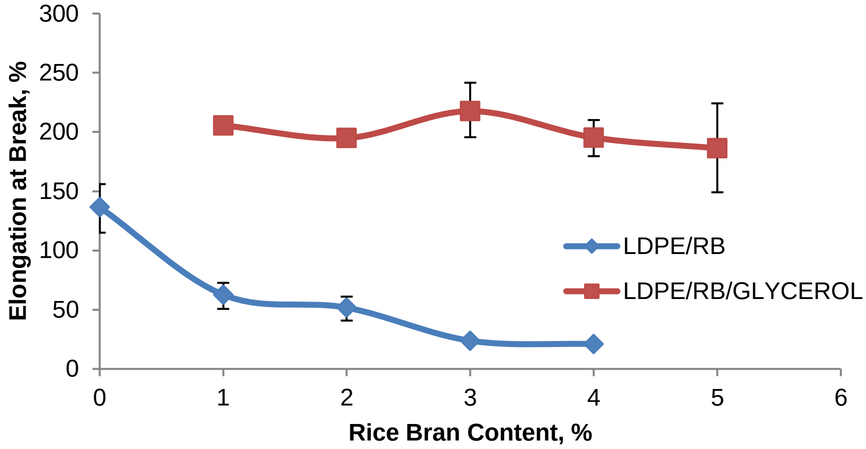


Figure 3.4: Effect of glycerol on elongation at break of LDPE/RB films at different RB loading

It is interesting to conclude that, the incorporation of glycerol in LDEP/RB films has improved the homogeneous distribution. In addition, incorporation of glycerol in LDPE/RB films also enhanced the dispersion of rice bran in LDPE matrix. From SEM micrographs of LDPE/RB/Glycerol films observation (Figure 3.3), the agglomeration of rice bran phenomenon was reduced instantly after the addition of glycerol. This is due to the interaction between glycerol and rice bran particle which becomes stronger and significantly, better appearance or surface of LDPE/RB/Glycerol was produced. The increasing dispersion particles were caused by the stronger interaction between glycerol and rice bran in the films compared to the interaction between rice bran granules and thus, reducing the rice bran agglomeration (Wang et al., 2004). In this study, the glycerol only improved the dispersion and distribution of rice bran in LDPE matrix but not much in interfacial adhesion between rice bran and LDPE. Therefore, the effective way to enhance the interfacial adhesion between rice bran and LDPE is with the addition of compatibilizer.

Soil burial Test

Soil burial test was carried out to determine the effect of rice bran (RB) content on the biodegradability properties of LDPE/RB films by the percentages of weight loss. The effect of plasticizer on the biodegradability of LDPE/RB films had been analyzed and presented in this section. Figure 3.5 shows that effect of time of buried to the percentages of weight loss for 2 % and 4 % of LDPE/RB films and LDPE/RB films with glycerol. The rice bran content had influenced the percentages of weight loss for LDPE/RB films. The percentage of weight loss was increased as increasing rice bran content in LDPE/RB films. The similar finding was reported by Soni and Saiyad (2011). Figure 3.5 showed, no significant effect on the percentage weight of pure LDPE films due to the bonding between C-C linkages in LDPE are not susceptible to microorganism attack. However, the incorporation of glycerol in LDPE/RB films has caused the increasing of weight with a negative value of percentages weight loss. From the observation, the sample of LDPE/RB films does not change color, indicating that no chemical interaction occurs during buried but only the reduction in weight. The microorganism of soil would attack the LDPE strips. These microorganisms possibly attack the rice bran content in LDPE matrix and it caused the LPDE chains was fractured or break. According to Borghei et al. (2010) reported the incorporation starch in LDPE matrix was cause attraction of microorganism soil to attack their blends. The capability of rice bran (hydrophilic) in LDPE films to absorb water was influenced their physicochemical properties and tendency to biodegradation and hydrolysis. The plastic such as LPDE is resistant to degradation in natural environment due to microorganism does not have any enzymes for degrading the synthetic polymer. Therefore, the presences of hydrophilic rice bran in LDPE films indirectly improve their ability of degradation and biodegradability. The similar discovery also reported by Khoramnejadian (2011).

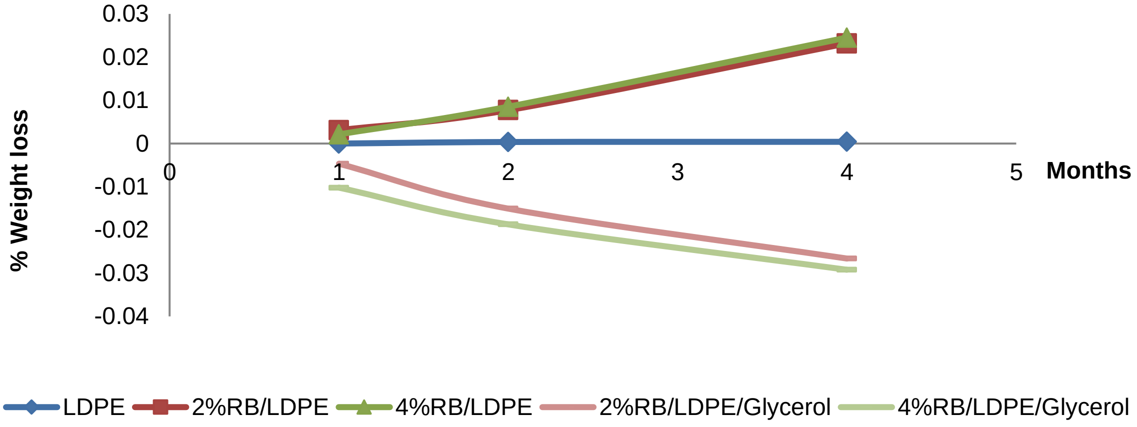


Figure 3.5: Effect of time immersion on the percentages of water absorption for LDPE/RB films

The incorporation of glycerol in LDPE/RB films probably has a negative effect on the rate of biodegradation. The negative percentages weight loss of LDPE/RB/Glycerol film shows the increment in their weight after a few months have been buried in the soil. This phenomenon occurred probably due to the presence of glycerol content which has the ability to absorb the water from the soil since glycerol is highly hydrophilic. The presence of glycerol in LDPE/RB films was formed the chemical interaction (hydrogen bonding) between rice bran and glycerol. It indirectly increased the rate of water absorption for the films. The presence of glycerol content in LDPE/RB films can increase their rate of biodegradation due to glycerol is hydrophilic nature and enhance the microorganism of soil activity (Ismail and Zaaba, 2012). In this case, the microorganisms of soil probably attack the rice bran content in LDPE/RB/Glycerol films but the effect of water absorption is higher than weight loss by biodegradation.

4. Conclusion

The rice bran content strongly affected the tensile properties, morphological and biodegradability properties of LDPE/RB film. The addition of rice bran content in LDPE films has decreased the tensile properties such as tensile strength and elongation at break of the films. The maximum ratio of rice bran loading can be incorporated to produce LDPE films by about 5 % without the addition of plasticizer. The tensile strength and elongation at break of LDPE/RB films increased with the addition of 3 phr glycerol. In addition, the presence of glycerol produced the chemical interaction of hydrogen bonding between rice bran and glycerol which has significantly increased the mobility of polymer chains and decreased the filler-filler interaction between rice bran molecules. The present study provides the valuable information on the underlying behaviour of the RB in the fabricated degradable LDPE/RB film. These findings enable the researchers to know more about the nature of RB, which, in turns, facilitates the future development of the degradable RB-based polymeric products.

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References

Borghei M., Karbassi A., Khoramnejadian S., Oromiehie A., Javid A.H., 2010, Microbial biodegradable potato starch based low density polyethylene, African Journal of Biotechnology 9 (26), 4075-4080.

Bourtoom T., Chinnan M.S., 2008, Preparation and properties of rice starch–chitosan blend biodegradable film. LWT - Food Science and Technology 41 (9), 1633-1641.

Garg S., Jana A.K., 2006, Effect of Starch Blends on Mechanical Properties of Low Density Polyethylene (LDPE) Film, Indian Chemical Engineering 48 (3), 185-189.

Hu G., Huang S., Cao S., Ma Z., 2009, Effect of enrichment with hemicellulose from rice bran on chemical and functional properties of bread, Food Chemistry 115 (3), 839-842.

Ismail H., Zaaba N.F., 2012, Tensile properties, degradation behavior, and water absorption of sago starch plastic films, Journal of Vinyl and Additive Technology 18 (4), 235-240.

Khoramnejadian S., 2011, Study of water absorption and biodegradation of potato starch based polyethylene, Advances in Environmental Biology 5 (10), 3156-3158.
Laohakunjit N., Noomhorm A., 2004, Effect of Plasticizers on Mechanical and Barrier Properties of Rice Starch Film, Starch – Stärke 56 (8), 348-356.
Moghadam R.A., Yusup S., Lam H.L, Shoaibi A.A., Ahmad M.M., 2013, Hydrogen Production from Mixture of Biomass and Polyethylene Waste in Fluidized Bed Catalytic Steam Co-Gasification Process, Chemical Engineering Transaction 35, 565-570.
Monica P., Seggiani M., Vitolo S., 2015, Polyethylene and Hydrolyzed Collagen Blend Films Produced by Blown Extrusion, Chemical Engineering Transaction 43, 1705-1710.
Morreale M., Scaffaro R., Maio A., La Mantia F. P., 2008, Effect of adding wood flour to the physical properties of a biodegradable polymer, Composites Part A: Applied Science and Manufacturing 39(3), 503-513.
Sabetzadeh M., Bagheri R., Masoomi M., 2012, Effect of corn starch content in thermoplastic starch/low-density polyethylene blends on their mechanical and flow properties, Journal of Applied Polymer Science 126, 63-69.
Seggiani M., Cinelli P., Verstichel S., Puccini M., Vitolo S., Anguillesi I., Lazzeri A., 2015, Development of Fibres-Reinforced Biodegradable Composites, Chemical Engineering Transaction 43, 1813-1818.
Soni D., Saiyad M., 2011, Biodegradable polyethylene bags, Proceeding of International Conference on Current Trends in Technology, 8-10 December, Institute of Technology, Nirma University, 382-481.
Taguet A., Huneault M.A., Favis B.D., 2009, Interface/morphology relationships in polymer blends with thermoplastic starch, Polymer 50 (24), 5733-5743.
Tudorachi N., Cascaval C.N., Rusu M., Pruteanu M., 2000, Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials, Polymer Testing 19 (7), 785-799.
Wang S., Yu J., Yu J., 2005, Compatible thermoplastic starch/polyethylene blends by one-step reactive extrusion, Polymer International 54 (2), 279-285.