Korea Polymer Journal, Vol. 9, No. 6, pp 297 – 302 (2001)

Korea Polymer Journal

Volume 9, Number 6 December 31, 2001

Mechanical Properties and Water Absorption of Rice Starch-Filled Linear Low Density Polyethylene

Mohammad A. Wahab

Polymer Technology Division, School of Industrial Technology, University Science Malaysia, 11800 Pulau Peneng, Malaysia

Mohammad A. Mottaleb*

Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh

Received March 20, 2001

Abstract : Rice starch was incorporated into linear low density polyethylene (LLDPE) using a Brabender Plastic-Corder internal mixer at a temperature of 140℃ and 40 rpm. The starch loading was varied from 0 to 30% with 5 intervals. Studies on brabender torque development, mechanical properties and water absorption were investigated. The starch loading did not influence the brabender torque significantly. With respect to mechanical properties; the tensile strength and elongation at break decrease with increasing starch loading. The Young's modulus also increases with the starch filling. Mechanical properties were deteriorated as the starch absorbed moisture. The rate of water absorption was dependent on the starch filling in the composites. The scanning electron microscope (SEM) analysis was performed for the tensile fracture surfaces and it revealed the starch agglomeration and a poor dispersion of starch in the LLDPE matrix.

Introduction

Biodegradable polymer has been a subject of interest for many years because of their potential to protect the environment by reducing non-biodegradable synthetic plastic waste.[1-4] Nowadays

Present and corresponding address:
Dr. Mohammad A. Mottaleb, NRC Postdoctoral Research Associate, Environmental Science Division, NERL, US Environmental Protection Agency, P.O.Box 93478, Las Vegas NV 89193-3478, USA. Fax: +702 798 2142
*e-mail : Mottaleb.Mohammad@epamail.epa.gov

plastic waste becomes a major concern and is considered to be a world wide environmental problem. Polyethylene, the largest volume plastic used in packaging, is the most offender since it is highly resistant to biodegradation. Products from agricultural sources with reference to starch especially constitute a good alternative in developing the degradable materials.[5] Starch is a promising raw material because it is readily available all year from many plants, with regard to current needs, low cost, stable price and is environmentally friendly.[6] It also satisfies the requirements of adequate thermal stability, minimum interference with flow properties and minimum disturbance with product quality.[7] Furthermore because of its low oxygen permeability, starch filled thermoplastic films are very attractive for food packaging.

The use of granular starch as a biodegradable filler for low density polyethylene was first reported by Griffin.[8] Amongst the application of the starch, it was first used as a filler in the production of polyethylene foam.[9] Starch was also utilized as a filler in PVC films[10] and when preparing cast films from the aqueous dispersion of starch in poly(vinyl alcohol), glycol, surfactant and formaldehyde.[11,13] Maize, wheat and tapioca starches have been incorporated into LDPE. Rice starch is produced in great abundance in Asia where it has been used in food and non-food formulations for long period of time. Now it is not surprising that starch has an enormous variability in quality. Despite this, it has many advantages over other fillers. This study will describe the mechanical properties, water absorption, and scanning electron micrographs for composites with different ratios of rice starch incor-porated into LLDPE.

Experimental

Materials. Rice starch was obtained from a local company in Malaysia. The average granule size of rice starch was in the range of 8-10 mm and its decomposition temperature was 230°C. The particle size of the granule was determined by MALVERN instrument, UK and unmodified granules were used in this study. LLDPE, ETILINAS LL0209SA grade, was obtained from Polyethylene (Malaysia) Sdn Bhd, and was used as the basin resin. The melting temperature of LLDPE was 128°C determined by differential scanning calorimetry (DSC) at the heating rate of 20 °C/min.

Sample Preparation. Rice starch was dried prior to compounding in a vacuum oven at 60°C for 24 h, essentially according to the method of Nikolov *et al.*[14] Before using the LLDPE with starch, the temperature of the oven was lowered down to the room temperature by switching off the power line and starch was kept in a desiccator for cooling. Followed by the cooling operation, the starch and LLDPE were compounded by Brabender Plasti-Corder internal mixer at a temperature of 140°C and 40 rpm for 13 min including 5 min preheating. The rice starch and LLDPE were mixed in a beaker before introducing them into the mixer for final compounding. Composites (45 g) containing starch loading 0, 5, 10, 15, 20, 25 and 30% were prepared.

Molding. The starch-LLDPE blends were molded with Kao Go Tech compression molding machine at 140°C for 5 min after 4 min preheating. The molding temperature and pressure were 140°C and 10 Mpa, respectively. After removing the blend from the molding machine, it was cooled for 4 min at the pressure of 10 Mpa. Samples were cut into dumb-bell specimens according to ASTM 638 and were used for all the tests.

Mechanical Properties. Tensile tests were carried out on an Instron machine (Model 1114) according to ASTM D638. A crossed-head speed of 50 mm/min, gauge length of 50 mm and a chart speed of 50 mm/min were used. Dumbbell specimens were conditioned at 30± 2% relative humidity for 24 h before testing. An average of 5 samples was used for each testing.

Morphology. The morphology of the tensile fracture surfaces of the blends was investigated using a scanning electron microscope (SEM) (Leica-Cambridge S-360). SEM was taken for sputter-coated with gold on the fractured surface.

Water Absorption. Water absorption studies were carried out according to ASTM D570. The dumbbell specimens of each composition were conditioned in an oven at 50°C for 24 h and were cooled in a desiccator before weighing. After cooling, it was weighed immediately by a nearest meter balance. The conditioned samples were immersed in a container of distilled water keeping constant temperature of 27°C. To perform the water absorption measurements, the samples were removed at every 24 h interval for the first one week and subsequently every one week (7× 24 h) from the water container. A tissue paper was used to remove the excess of water from the surface of the samples. The sample was then weighed immediately by a nearest meter balance and immersed in the water. The percentage increase in weight during re-immersion was calculated using following equation.

$$\%W_f = \frac{W_w - W_d}{W_d}$$

Where W_f, W_w and W_d represent the final increased weight percentage, wet weight and the conditioned weight of the testing samples, respectively.

Results and Discussion

Studies on Mixing Torque. The properties associated with the blending of starch and LLDPE have been investigated and the results are shown in Figure 1. This suggests that the stabilizing of torque was found to gain at 6 to 8 min. The constant torque values for LLDPE with different percentage of starch also indicate the completion of the mixing between filler and matrix. As starch loading increases, the torque value decreases. This may be due to the slippage between starch and LLDPE matrix. This is also due to the agglomeration of starch particles in the LLDPE matrix. These results are in close agreement with the investigated values[15] of the LLDPE/corn starch blend.

Tensile Strength. Figure 2 shows the effect of starch loading on the tensile strength of LLDPE composites. In general, it can be seen that there is an inverse relationship between starch loading and tensile strength. This means that the tensile strength of the composites decreases with increasing amount of starch filler. The drop of tensile strength became more significant when the concentration of starch loading was increased. One of the reasons could be the filler-filler interaction, which becomes more pronounced than that of the filler-matrix interaction. This was supported by SEM studies as the micrographs of starch granules shows a great tendency to form agglomerates especially at higher starch loading values. The other reason was the lack of the formation of strong interfacial bonds like hydrogen bonds between hydrophilic starch filler and hydrophobic LLDPE matrices. These results showed a good agreement with the work of Danjaji,[16] who carried out on sago starch-LLDPE composites. The results are in direct contrast to those presented by several research groups[15,17-19] because the increase in tensile strength of MA-g-LLDPE/starch blends

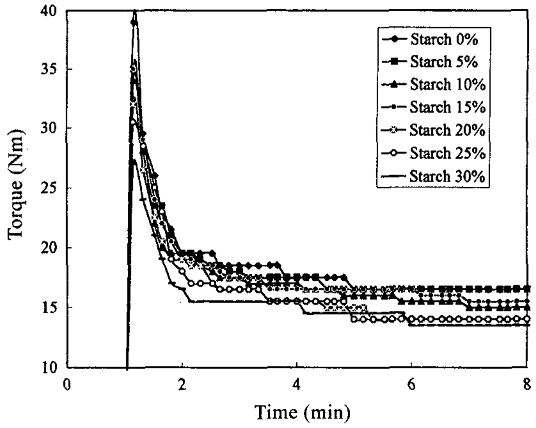

Figure 1. Mixing torque-time characteristics curves for different ratios of starch filler and LLDPE matrix.

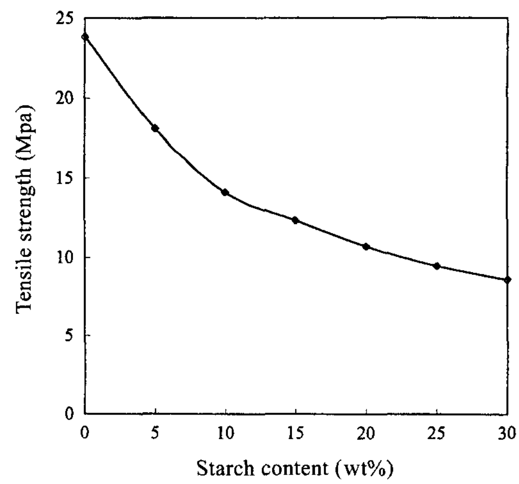

Figure 2. Effect of starch content on tensile strength of LLDPE composites.

could be due to increasing the interfacial adhesion resulting from the reaction between starch and MA-g-LLDPE.

Elongation at Break. Figure 3 depicts the elongation at break of the matrix (LLDPE) with the variation of starch loading. It can be seen that the elongation at break decreases with increasing starch loading as expected. Similar type of explanation can be made as for the tensile strength, which highly depends on the nature of the starch and LLDPE. As described earlier hydrogen bonds are not feasible between the starch and LLDPE, so the reduction of elongation at break is common. A dramatic reduction of elongation at break of the rice starch-LLDPE matrix was found when higher amount of starch was loaded. The reason for the dramatic reduction can be explained as; the starch granules do not elongate with the LLDPE, so the less strain was required to make the material fail.[20] In addition, the poor starch-LLDPE interaction led to the weak interfacial regions that permitted easier crack propagation. Thus the composite fracture at lower value of elongation was obtained with increasing starch loading. This agrees well with the work of Kang*et al.*[21] and Willet.[22]

Young's Modulus. Young's modulus is a measure of stiffness of a material. The effect of starch loading on the Young's modulus is shown in Figure 4. It can be seen that the modulus increases with the incorporation of the rice starch into LLDPE. This may be due to the stiffening effect that the starch granules are more stiffer than that of the LLDPE. The hydrogen bonding in starch gives higher modulus than that of a semi-crystalline polymer like LLDPE, which has no hydrogen bonding. Therefore, there is a direct relationship between the amount of starch in blends and the increase in the moduli. These results support with the works of Willet[22] for corn-LDPE and potato starch-LDPE filled matrix and Danjaji[16] for sago starch-LLDPE.

Morphology. Figure 5 and 6 show the SEM micrographs of tensile fracture surfaces of LLDPE (unfilled) and rice starchfilled LLDPE (15%). Figure 5 shows a ductile material with a very hard surface, whereas Figure 6 indicates a less ductile type with comparative poor surface. This also

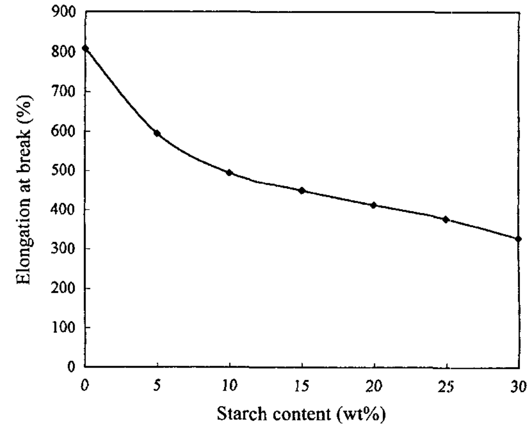

Figure 3. Effect of starch content on elongation at break of LLDPE composites.

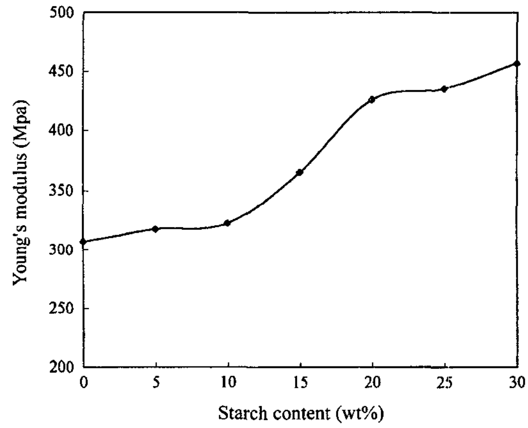

Figure 4. Effect of starch content on Young's modulus of LLDPE composites.

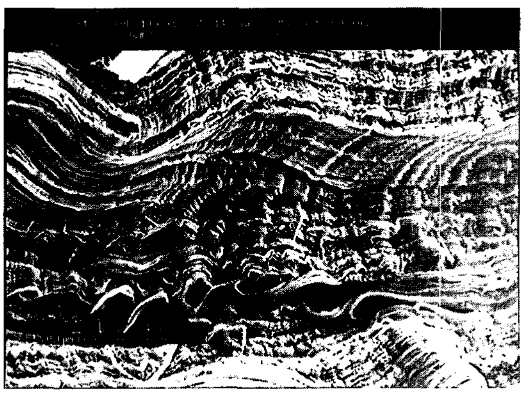

Figure 5. Scanning electron micrograph of the fractured surface of LLDPE.

depicts that the rice starch granules are of various shapes and also reveals that the starch granules serve as a particulate filler. The granules appeared as agglomerate and poor wetting was observed between the starch granules and LLDPE as void can be seen between the filler and matrix. It can also be observed that the distribution of the starch granules are not homogeneously dispersed in the polymer matrix because of poor adhesion between the starch and the synthetic polymer, as demonstrated by sharp interface between starch granules and the continuous phase. Hence the tensile strength and the elongation at break are expected to decrease with increase in the starch content.

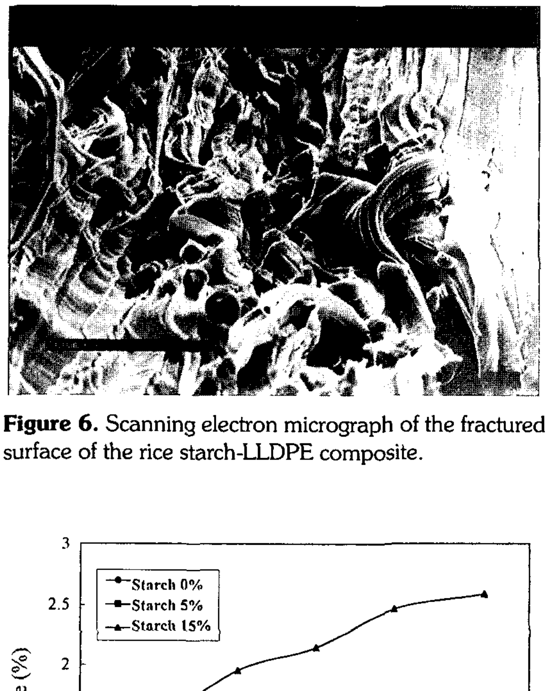

Figure 6. Scanning electron micrograph of the fractured surface of the rice starch-LLDPE composite.

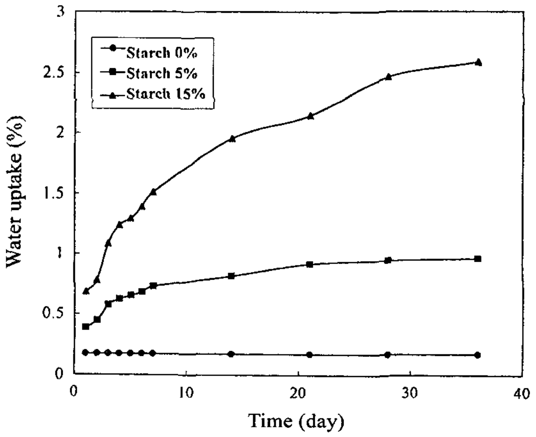

Figure 7. The variation of water uptake with time for LLDPE (starch %) and rice starch filled LLDPE composites.

This was found in the present investigation, as stated earlier.

Water Absorption. Figure 7 shows the water uptake of unfilled LLDPE and rice starch filled LLDPE. The unfilled LLDPE showed higher water resistance capability than the LLDPE/rice starch filled composite. The water absorption of the LLDPE/rice starch films increases proportionally with the starch content, which agrees well with the work of Nikolov *et al.*[14] This composite did not equilibrate even up to 36 days immersion in water. This satisfies the Willets observation[22] demonstrating that the equilibration time for starch-polyethylene composites is the period of months even when immersed in water. The water absorption did not change significantly in case of the lower starch content (5%). Because, less hydroxyl groups are available in the composites to form hydration with water. There was rapid water uptake during the first week of immersion and then gradually slowed down with time. It has also been found that the initial water addition to the starch strongly bound as hydrate and after all the available hydroxyl groups are used up in this fashion then it will lead to composite holding water less firmly thereafter.

Figure 8 and 9 show the effect of water on the tensile strength and elongation at break, which decrease with increasing the starch loading. The presence of moisture at the starch-LLDPE interface is believed to weaken the interfacial adhesion and leads to significant reduction in tensile

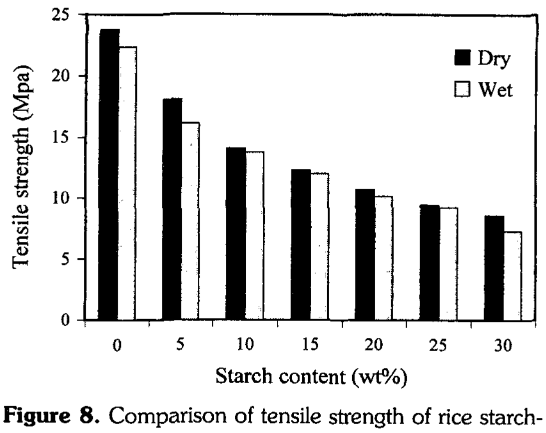

Figure 8. Comparison of tensile strength of rice starch-filled LLDPE composites.

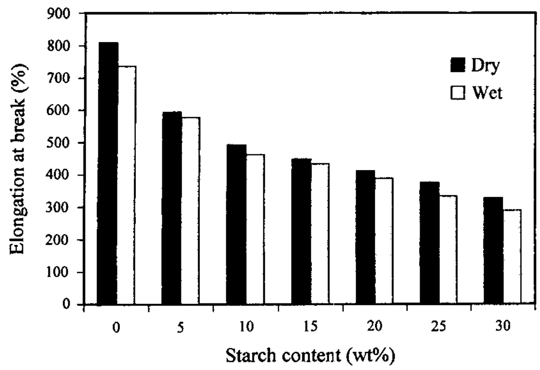

Figure 9. Comparison of elongation at break of rice starch- filled LLDPE composites.

properties of the composites. According to Otey *et al.*,[13] excessive of moisture could have a deteriorating effect and will lead to a reduction in tensile properties of starch-plastic composites. This statement supports our results.

Acknowledgements. The authors would like to thank Dr. A. Ariffin and Professor A. K. M. Omar, University Science Malaysia for providing the laboratory facilities and supplementary information to carry out the research work.

References

(1) Y. Doi and K. Fukuda, *Biodegradable Plastic and Polymers*, Elsevier, Amsterdam, 1994.
(2) W. M. Doane, C. L. Swanson, and G. F. Fanta*ACS Symposium Series*, **476**, 197 (1992).
(3) D. Raghavon, *Polym. Plast. Technol. Eng.*, **34**, 41 (1995).
(4) A. M. Thayer, *ACS Symposium Series,* **433**, 38 (1990).
(5) R. L. Shogren, G. F. Fanta, and W. M. Doane, *Starch/Starke,* **45,** 276 (1993).
(6) D. Loudin, V. G. Della, and P. Colonna, *Carbohydrate Polym.,* **27**, 261 (1995).
(7) T. M. Aminabhavi, R. H. Balundgi, and P. E. Cassiday, *Polym. Plast. Technol. Eng.,* **29,** 235 (1990).
(8) G. J. L. Griffin, *J. Am. Chem. Soc.,* **33,** 88 (1973).
(9) L. P. Dosmann and R. N. Steel, US Pat. 3334934 (1974).
(10) R. P. Westhoff, F. H. Otey, C. L. Mehltretter, andC. L. Russel, *Ind. Eng. Chem. Res. Dev.,* **13,** 123 (1974).
(11) F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res. Dev.,* **19**, 592 (1980).
(12) R. P. Westhoff, F. H. Otey, and C. L. Russel, *Ind. Eng. Chem. Res. Dev.,* **16,** 305 (1977).
(13) F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res.,* **26,** 1659 (1987).
(14) Z. L. Nikolov, R. L. Evangelista, W. Wung, J. L. Jone, and R. J. Gelina, *Ind. Eng. Chem. Res.,* **30,** 1841 (1990).
(15) R. Chandra and R. Rusgti, *Polym. Degrad. Stab.,* **56**, 185 (1997).
(16) Danjaji, Ph.D. Thesis, University Science Malaysis, 2000.
(17) J. L. Willet, US Pat. 5059642 (1991).
(18) J. L. Jane, A. W. Schwabacher, S. N. Ramarattan, and J. A. Moore, US Pat. 5115000 (1992).
(19) L. Mascia, *Thermoplastic: Materials Engineering; Applied Science,* Essex, England, 1982, pp 75.
(20) L. E. Nielson, *Comp. Matter,* **1,** 100 (1976).
(21) B. G. Kang, S. H. Yung, J. H. Yie, B. S. Yoon, and M. H. Soo, *J. Appl. Polym. Sci.,* **60**, 1977 (1996).
(22) J. L. Willet, *J. Appl. Polym. Sci.,* **54,** 685 (1994).