TENSILE, BARRIER AND BIODEGRADATION STUDIES OF RICE HUSK/ORGANOCLAY HYBRID FILLER-FILLED LOW DENSITY POLYETHYLENE NANOCOMPOSITE FILMS

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Abstract

The objectives of this research are to investigate the effects of rice husk (RH) and compatibilizer content on tensile, barrier and biodegradation properties of hybrid RH/organically modified montmorillonite filled low density polyethylene nanocomposite films. Studies on the morphology were also conducted and structure-property relationship is discussed. Maleic anhydride modified polyethylene in various concentrations (from 0 to 9 parts per hundred contents) was used as compatibilizer. The formation of intercalated nanocomposites was observed in the presence of compatibilizer with the use of x-ray diffraction analysis. Increasing compatibilizer content increased the tensile and barrier properties. However, the tensile and barrier properties decreased with increasing RH content. The rate of biodegradation was observed to increase with the incorporation of RH.

1 Introduction

Film is the largest market segment for polyolefins and is extensively used for food-stuff and goods packaging; agricultural and merchandising [1, 2]. Low density polyethylenes (LDPE) have got a prominence over other polyolefin in flexible films because of its acceptable flexibility, easy processability, extensibility, easy to seal, resistant to moisture, impact toughness, stress crack resistance, microwavability and recyclability [3-5]. In fact, exploitation of these unique properties has made LDPE extremely useful to mankind and it is the widely used polymer for film packaging. It is pioneer PE family introduced commercially [4]; and having largest tonnage in the world with a continuous increase in per capita consumption despite an increase in their prices.

Nanocomposites, a fairly new class of engineered materials, are multiphase materials results from the combination of two or more distinctly dissimilar materials, including a matrix (continuous phase) and a filler/reinforcing material (dispersed phase) with at least one dimension is in the nanometer (10^{-9} m) range. This area emerged with the recognition that exfoliated silicate layers in polymer composites could yield enhanced mechanical, barrier and fire resistance properties as well as improved thermal stability as compared to microsized conventional fillers.

The incorporation of natural fibers in polymer matrices has become an emerging area of research and development owing to some specific properties of these natural fibre reinforced composites. However, the mixing of a polymer matrix with natural fibre does not lead to a composite with higher performance properties because of poor compatibility and wettability between the filler and the matrix. Polar hydroxyl groups on the surface of the lignocellulosic materials face difficulty in establishing a well bonded interface with the nonpolar matrix. The regents having functional groups that are capable of bridging and bonding the hydroxyl groups of the cellulosic materials with the matrix material are quite helpful in promoting adhesion. There have been some evidences in literature that the composites prepared by the incorporation of grfted co-polymers as compatibilizers had good interfacial adhesion and ultimately better performance properties than the uncompatibilized composites.

Hybrid composite materials are attractive as they result in a balance between performance properties and the cost of the composite that cannot be obtained with a single kind of reinforcement [6-8]. Previously, there have been studies regarding the hybridization of natural fibre with glass fibre [6, 8-10], carbon [11], and mica [12]; and have produced encouraging results. The present study entails optimization of MAPE loading level to obtain RH/Clay hybrid filler filled degradable nanocomposite films with acceptable tensile and barrier properties. Furthermore, the effect of the incorporation of the filler having different contents of the biomaterial on tensile, barrier and thermal properties; and degradability of the resulting nanocomposite films was investigated as well.

2 Materials and Methods

2.1 Materials

Rice husk (RH) was obtained from BERNAS (Padiberas Nasional Berhad), Malaysia. Organoclay (Nanomer® 1.44P) was used as reinforcing filler. It is natural montmorillonitre (MMT) modified with quarternary ammonium salt . Low density polyethylene (LDPE) is used as the polymer matrix with the grade LDF200GG. The characteristic properties of LDPE are given in Table 1. Maleic anhydride modified polyethylene (MAPE, OREVAC®18365) was used as a compatibilizer.

Material	Characteristic and its typical value	Supplier/manufacturer
LDPE	MFI = 2 g/10 min (ASTM D1238) Density = 0.922 g/cm^3 (ASTM D1505) Vicat softening point = 95 °C (ASTM D1525)	Titan Chemicals, Malaysia
MAPE	MFI = 2.5 g/10 min (ASTM D1238) Density = 0.916 g/cm^3 (ASTM D1505) Melting temperature = 120 °C Vicat softening point = 90 °C (ISO 306)	Arkema, Farance
Organoclay	MMT modified with quarternary ammonium salt Mean particle size = 15−20 µm	Nanocor® , USA

Table 1: Some of the characteristic properties of raw materials used in this study

2.2 Composite film processing

The RH flour was dried in an oven at 100 °C overnight prior to processing. RH/nanoclay hybrid filler, having various amounts of RH and 3 parts per hundred contents (phc) of RH and LDPE; was melt compounded with LDPE in a co-rotating Brabander twin screw extruder. The amount of clay was fixed to 3 phc as the said amount gives a good balance between performances and cost. MAPE was used as a coupling agent with various loading levels ranging from 0 to 9 phc, to investigate loading level effect on the dispersion/exfoliation of the hybrid filler. So the sample designation as 95/5/3/6 means 95 wt. % of LDPE and 5 wt.% of RH while nanoclay 3, and MAPE 6 phc of RH and LDPE. A detailed composition of the formulations prepared is summarized in Table 2. The extruded strands were air-dried in a cool air stream and pelletized. Finally, the resulting hybrid filler filled nanocomposite pellets as well as the neat LDPE and bio-filler filled LDPE biocomposite pellets were blown into films of around 75 µm thickness, using Extrusion blow film machine (Tai King, model: TK/HD, Tai King Machinery Factory Co. Ltd., Taiwan).

Sample designation	LDPE (wt. %)	RH (wt. %)	Nanoclay (phc)	MAPE (phc)
LDPE	100	0	0	0
95/5/0/0	95	5	0	0
95/5/3/3	95	5	3	3
95/5/3/6	95	5	3	6
95/5/3/9	95	5	3	9
97/3/3/9	97	3	3	9
96/4/3/9	96	4	3	9
94/6/3/9	94	6	3	9

Table 2: sample designation and their composition

2.3 Experimental techniques

2.3.1 X-ray diffraction analysis

Diffraction studies were carried out to investigate the delamination/exfoliation of organoclay in polymer matrix. A Bruker D8 Advance difractometer was used to measure the d-spacing of the hybrid filler-filled nanocomposite films.

2.3.2 Morphological analysis

The morphology of hybrid filler filled composite films' surface was evaluated using an electron microscope (TM 3000, Hitachi). Film samples were mounted onto copper stubs using double sided sticky tapes and the SEM micrographs were taken under different magnifications.

2.3.3 Tensile properties

Tensile testing was carried out by using Lloyds Universal Testing machine. Samples were prepared according to ASTM D882-10. At least eight different samples were tested for each sample composition and the values of tensile strength and elongation at break were obtained from stress-strain curves at a cross head speed of 50 mm/min.

2.3.4 Permeability measurements

The oxygen (O_2) permeability coefficient measurements for the films were carried out at room temperature in a constant pressure/variable volume type permeation cell designed according to ASTM D1434-82

2.3.5 Biodegradability test

The biodegradability test has been developed for the investigation and comparative evaluation of degradability of different materials. In this study, biocomposite samples have been subjected to soil burial test for 1, 2 and 3 months and the rate of biodegradation/disintegration of the buried samples of various compositions was studied as a function number of days, with the help of SEM micrographs. The soil used in these tests is a soil typically used in tree-nurseries.

3 Results and Discussion

3.1 X-ray diffraction analysis

In the present study, the clay intercalation was analysed by XRD and Figure 1 shows the difractogram of pristine oMMT and effect of the compatibilizer content on the intercalation of the nanocomposite films. The diffraction angles were used to calculate the interlayer distance (d-spacing) using Braggs' formula and the results are shown in Table 3. The diffractogram of oMMT has a peak maximum at $2\theta = 2.95$, corresponding to an interlayer distance of 2.99 nm. Increasing the MAPE content increased delamination and interlayer spacing between the clay platelets. Interestingly, the incorporation of different amounts of RH to the nanocomposite film did not affect the interlayer distance of oMMT as no significant change was observed in clay diffraction peak angles.

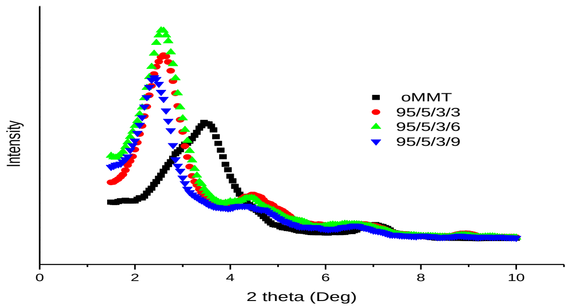

Figure 1: XRD pattern of pristine oMMT and nanocomposites of LDPE, 5 wt % RH and 3 phc of oMMT having different amounts of MAPE compatibilizer

sample	2θ(°)	Interlayer distance (nm)
oMMT	2.95	2.99
95/5/3/3	2.73	3.23
95/5/3/6	2.52	3.50
95/5/3/9	2.41	3.66
97/3/3/9	2.40	3.68
96/4/3/9	2.44	3.62
94/6/3/9	2.45	3.60

Table 3: Interlayer distances of neat oMMT and its nanocomposites

3.2 Morphological analysis

The SEM micrographs in Figure 2 compare the effect of compatibilizer content on the morphological properties of the hybrid composites. The micrographs show that increasing the MAPE content reduce the tendency of the RH to agglomerate; indicating an increase in the compatibility between the RH and the LDPE matrix.

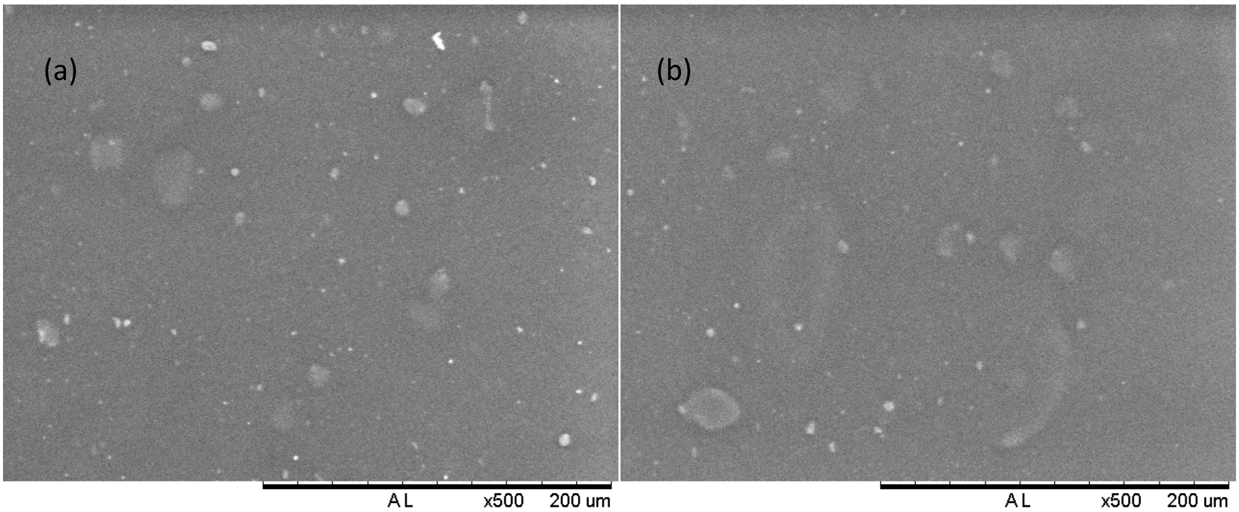

Figure 2: SEM micrographs of LDPE/RH/oMMT (95/5/3) nanocomposites with different contents of MAPE compatibilizer (a) 3 phc and (b) 9 phc.

3.3 Tensile properties

The results of tensile properties of RH/oMMT filled nanocomposite films are summarized in Table 4 and 5. The incorporation of 5 wt % RH to the LDPE matrix drastically reduced the tensile properties of the films. Tensile strength and elongation at break of the RH filled LDPE composite decreased from 18.8 to 6.8 MPa and 245 to 91 % respectively, in comparison to the neat LDPE. From Table 4, it is found that increasing the compatibilizer content improves the tensile strength and elongation at break. The results of increasing the compatibilizer content was found to support further the morphological observations. Increasing the RH content decreased the tensile strength and elongation at break of the composite films (Table 5).

Sample designation	Tensile strength (MPa)	Elongation at break (%)
95/5/3/3	8.9	81
95/5/3/6	8.6	106
95/5/3/9	10.1	109

Table 4: Effect of the compatibilizer loading level on tensile properties of LDPE/RH/oMMT 95/5/3 nanocomposite films

Sample designation	Tensile strength (MPa)	Elongation at break (%)
97/3/3/9	11.5	121
96/4/3/9	10.6	114
95/5/3/9	10.1	109
94/6/3/9	8.6	83

Table 5: Effect of the RH loading level on tensile properties of MAPE compatibilized (9 phc) LDPE/RH/oMMT nanocomposite films

3.4 Permeability measurements

The incorporation of 5 wt% of RH to the LDPE matrix drastically increased the O_2 permeability through the film (183.4 barrer) in comparison to the neat LDPE (3.4 barrer). Permeability results of the nanocomposite films having different contents of compatibilizer revealed that increasing the compatibilizer content appears to improve the O_2 barrier (Table 6). This improvement in barrier properties is due to the distribution of impermeable clay platelets that act as obstacles in the path of the diffusing molecules. These impermeable obstacles force the diffusing molecules to follow the tortuous path, which in turn, retard the diffusion of gas molecules. Furthermore, increasing the amount of MAPE content improves the delamination/intercalation of clay platelets that lead to the improvement of barrier properties. Increasing the RH content increased the oxygen permeability and the results are shown in Table 7.

Sample	95/5/3/3	95/5/3/6	95/5/3/9
Permeability (barrer)	147.3	17.3	9.4

Table 6: Effect of the Compatibilizer loading level on Oxygen Permeability of LDPE/RH/oMMT 95/5/3 nanocomposite films

Sample	97/3/3/9	96/4/3/9	95/5/3/9	94/6/3/9
Permeability (barrer)	5.4	5.7	9.4	16.4

Table 7: Effect of the RH loading level on tensile properties of 9 phc MAPE compatibilized LDPE/RH/oMMT nanocomposite films

3.5 Biodegradability studies

Figure 3 shows SEM micrographs of the LDPE/RH biocomposite films samples after 2 and 3 months of the soil burial. Many holes of different sizes and depths are seen in the samples under investigation showing the disintegration and breakup of the samples, indicating microorganisms attack. The numerous surface irregularities and the disintegration of the samples following the incorporation of RH can be attributed to biodegradability of the bio flour. There is no significant difference in degradability of LDPE/RH and LDPE/RH/clay composites.

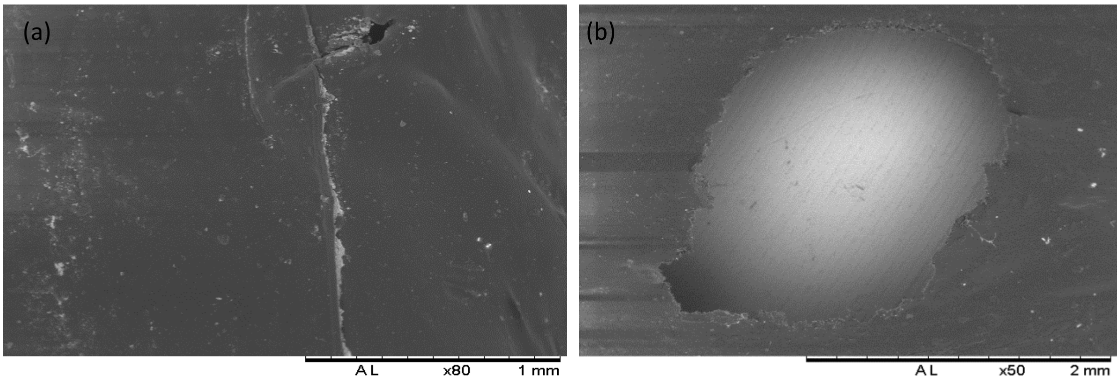

Figure 3: SEM micrographs of LDPE/RH 95:5 wt % composite showing the progression of biodegradation with time (a) 2 months and (b) 3 months

Conclusion

The objectives of this study are to determine the effect of RH and compatibilizer loading level on the tensile and oxygen barrier properties of MAPE compatibilized and RH/oMMT hybrid filler filled LDPE nanocomposite films. From the study, it can be concluded that tensile strength and elongation at break decreases as the RH loading level increases. The addition of MAPE resulted in an increase in the tensile strength and elongation at break. Increasing the RH content decreases oxygen barrier, while compatibilizer content increase the oxygen barrier. The study has also shown that the incorporation of RH into LDPE increase biodegradation significantly, which is an advantage from environmental point of view.

Acknowledgments

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