The Effect of Different Compatibilizing Agents on Thermal Properties of Wheat Straw/Low Density Polyethylene Biocomposites

B. Tajeddin,[a,]* M. Rezaei,[b] and A. Mohammadi Sani [c]

Biocomposites of low density polyethylene (LDPE), wheat straw (WS), PEGs (polyethylene glycols), and MAPE (polyethylene-grafted-maleic anhydride) were blended by twin screw extruder at 145 $^{\circ}$C with a rotational speed of 60 rpm. Different ratios of the above materials were selected to create 30 formulations of treatments (T_1 to T_{30}). The effects of biocomposites' composition on the thermal properties of obtained biocomposites were then investigated using DSC instrument. Each sample of biocomposites was subjected to the heating cycles of 35 to 400°C. The results from DSC indicated that the melting temperature (t_m) of obtained biocomposites is more than that of WS (69.97°C) and they are almost as same as the t_m of pure LDPE (114.00°C). The degradation temperature (t_d) of composites is more than that of pure LDPE (420.41°C). This means that the resistance to thermal degradation of all samples is increased. Thus, adding WS to the LDPE matrix, in general, increased the t_d of composites. In addition, according to the statistics ranking model for all treatments, t_m and t_d data showed that treatments T_8:70%LDPE+30%WS+7%PEG600,T_9:70%LDPE+30%WS+10%PEG600,T_{13}:60%LDPE+40%WS+7%PEG400,andT_{22}:50%LDPE+50%WS+7%PEG600 illustrate almost the same thermal properties as pure LDPE. Therefore, PEG has a greater effect than MAPE does on the heat-tolerance of these biocomposites.

Contact information: a: Department of Food Engineering & Post Harvest Technology (Packaging Engineering), Agricultural Engineering Research Institute (AERI), P.O. Box: 31585-845, Karaj, Iran; b: MSc of Science and Technology, Zarrin Maedeh Sahar (Khaterkhah) Food Packaging Company, No. 23, Nourbakhsh Alley, Valiasr Square, Tehran, Iran; c: Associate Professor, Department of Food Science and Technology, Quchan Branch, Islamic Azad University, Quchan, Iran;
* Corresponding Author: behjat.tajeddin@yahoo.com

INTRODUCTION

There is increasing work on the manufacturing lignocellulosic materials/natural fibre-plastic composites because of their lower cost and environmental benefits. Nowadays, most materials used for packaging applications are petrochemical-based and non-biodegradable, leading to environmental pollution and serious ecological problems (Tharanathan 2003). Low density polyethylene (LDPE), a kind of polyethylene (PE), represents the majority of thermoplastics currently used as food packaging materials. It is one of the most usual synthetic polymers with highly hydrophobic nature and high

molecular weight. The most important application area of LDPE is the production of containers and blowing injection articles for production of storage and distribution containers, and its processing into films and pipes has been increasing (Brown 1992; Piringer and Baner 2000; Tajeddin *et al.* 2009; Tajeddin and Abdulah 2010). Since the packaging industry uses a lot of plastics, even a small reduction in the amount of plastic materials of each package would cause a significant polymer saving, and could improve solid waste problems. It is clear that the use of biodegradable polymers for packaging offers an alternative partial solution to the problem of gathering of solid waste composed of inert synthetic polymers (Tajeddin and Abdulah 2010; Jayasekara *et al.* 2003).

There is much current research focused on using biodegradable materials to produce bio-based plastics. Among bio-based polymers, lignocellulosic materials have gained importance in biocomposite formulations (Mohanty *et al.* 2005), and they are used as reinforcement fibers because of their high mechanical and thermal performances (Nishino 2004).

Lignocellulosic materials in powder (flour) form or fibers are used with thermoplastic polymers. The difference between fiber and the flour is in their *L/D* amount, *i.e.* their length-to-diameter ratio. To transfer the stress from continuous phase (matrix) to the dispersed phase, the length must be above a certain minimum value. The rigidity and strength of the composite increases when the value of *L/D* increases, however, it is often preferred a particulate form due to its easier process. In general, the particle sizes of 10 to 80 mesh are being used in the manufacture of plastic/natural materials composites (Mohanty *et al.* 2005; Clemons 2002; Klyosov 2007).

Moreover, in the preparation of biocomposites, various compatibilizer materials such as polyethylene glycol (PEG) and MAPE (polyethylene-graft-maleic anhydride) or additives are used for different purposes. PEG is a polyether compound with many applications from industrial manufacturing like packaging to medicine. MAPE is a polar material specifically designed to provide adhesion to inorganic fillers or additives, wood and paper fiber, glass, and the other materials.

Wheat is one of the oldest and most valuable plants on the land, and it has been found to be suitable for combining with other synthetic and natural materials. Chemical composition of wheat straw may vary according to genetics and plant growth conditions; however, the main ingredients of wheat straw are cellulose, hemicellulose, and lignin (Mckean and Jacobs 1997). Thus, wheat straw with the chemical composition of 72.9% holocellulose and 20.5% lignin (Misra 1987) is one of the cheap lignocellulosic materials that can be combined with synthetic polymers. On average, cellulose comprises one-half the dry mass of the wheat straw stems. Wheat straw mostly has long fibers with 0.015mm diameter and 1.5 mm length (fiber length is almost hundred times of their thickness), (Karimi 1992).

Sensitivity to temperature and water absorption is the important physical property of natural fibers, in which hemicellulose is the main factor to the water absorption and the heat degradation (Saheb and Jog 1999). Fibers are heat-sensitive materials. If they are exposed to high temperatures (above 200°C) for a long period, they will show some effects such as releasing volatiles and odor, discoloration, and the destruction of the fibers (Klyosov 2007; Lu *et al.* 2000; Caulfields *et al.* 2005).

The thermal behavior of a sample is usually a function of time as well as temperature. Thus, it is usually to carry out evaluations in a specified atmosphere, under programmed time and temperature conditions (Tajeddin and Abdulah 2010; Cowie 2008). Cellulosic materials present amorphous and crystalline domains and a high degree of organization. The crystallinity depends on the origin of the material. Crystallinity in cellulose partly results from hydrogen bonding between the cellulosic chains, but some hydrogen bonding also occurs in the amorphous phase, although its organization is low (Herrera *et al.* 2005). Due to the high degree of crystallinity of cellulose, plant fibers cannot be processed like thermoplastic polymers in general (Zhang *et al.* 2005).

Since the required processing methods (*e.g.* injection, extrusion, compression) for natural fiber-thermoplastic composites in packaging applications are all based on heating, understanding the thermal properties of such composites at their processing temperature is very important for studies on controlling and optimizing the manufacturing process (Li *et al.* 2008). For example, in an investigation of the influence of sisal fiber content on the thermal properties of LDPE-sisal composites using DSC and TGA, it was found that the presence of sisal fiber has an effect on the LDPE crystallinity and the thermal stability of the composites (Luyt and Malunka 2005). Additionally, Lei *et al.* (2007) showed that the thermal stability of recycled high density polyethylene (RHDPE)-wood and bagasse composites was lower than that of neat RHDPE. However, the results of TGA measurements by Yordanov and Minkova (2003) showed that the thermal stability of LDPE-PA6-2 pph Escor 5001 blends increases in the presence of 2 pph Escor 5001.

In general the DSC technique, used to characterize polymer thermal stability, has been further employed for assessment of comparative thermal stability of various polymer materials and prediction of material lifetimes (Dobkowski 2006). Heat flux DSC and power compensation DSC are two basic types of DSC systems. In the heat flux DSC that belongs to the class of heat-exchanging calorimeters, the sample and the reference are heated from the same source, and the temperature difference is measured. This signal is converted to a power difference using the calibration sensitivity (Suchitra 2004). Therefore, a study of the thermal properties of WS-LDPE composites using DSC based on heat flux is presented in this paper.

EXPERIMENTAL

Materials

The materials used in this work included LDPE (granules form, grade LF0200, density 0.92 g/cm^3, melt index 2 g/10min, supplied from Bandar Imam Khomaini Petrochemical Company, Iran); wheat straw, variety Pishtaz obtained from Seed and Plant Improvement Institute (SPII), Iran; PEGs (average molecular weight 400 and 600, liquid form, purchased from Ahoura Piam Company, Iran), and MAPE (granules form, viscosity 500cP (140°C), supplied from Ahoura Piam Company, Iran).

Biocomposites Preparation

To prepare the biocomposites, LDPE and the powder form (passed through 40 meshes (0.40 mm) of wheat straw were used at levels of 0, 30, 40, 50, and 60%. PEGs

and MAPE were applied in 0, 7, and 10% of LDPE. Therefore, predetermined amount of materials were mixed using twin screw extruder machine (model Dr. Collin-GmbH, d-8017, Germany) at 145°C with a rotor speed 60 rpm. The extruded compounds were then placed in the grinder (model Weiser WE-LS 200/200, Austrian) to be converted to the granular form, Fig. 1. The different ratios of all above materials resulted in the creation of 30 formulations of treatments (treatment number 1, T_1 to treatment number 30, T_{30}). Treatment number 1, T_1 is the pure polyethylene treatment as a control in this study.

Fig. 1. The Granule Form of Obtained LDPE/WS Biocomposites

Differential Scanning Calorimetric (DSC)

DSC is one of the applied methods to study of the thermal properties of polymers. The melting and decomposition behavior of the matrix polymer (LDPE) and the biocomposites were studied with a DSC (Mettler Toledo, Swiss) equipment, fitted with a cooler system using liquid nitrogen according to ASTM D3417 (2004). Instrument was first equilibrated in point of temperature and enthalpy with Indium ($T_{m.onset}$=156.6^{o}C, H=28.45J/g). Then 2 to 3 mg samples were weighed in aluminum pans (Crucible) and hermetically sealed; an empty pan was used as reference. The main heat flow from the furnace to the sample and reference containers (pans) passes symmetrically through a thermally conductive disk (Suchitra 2004).The scan was carried out for each sample at the heating rate of 10°C/min from temperature range of 35 to 400°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

As said, DSC is a technique that measures the difference in the heat flow to a sample and to a reference sample as a direct function of time or temperature under heating, cooling or isothermal conditions. As the temperature of the sample is increased,

the temperature is plotted on the x-axis and the difference in the heat flow between the sample and the reference on the y-axis (Suchitra 2004).

Therefore, the DSC curves were obtained for pure LDPE and all obtained biocomposites as a function of temperature and time against heat flow in this study. The DSC curves illustrate some of the main characteristics of the LDPE biocomposites such as degradation temperature and weight loss percentage. A typical DSC curve from the pure LDPE sample is shown in Fig. 2. The endothermic peak at 114.00^{o}C indicates the melting point and the other peak at 420.41^{o}C shows the degradation point.
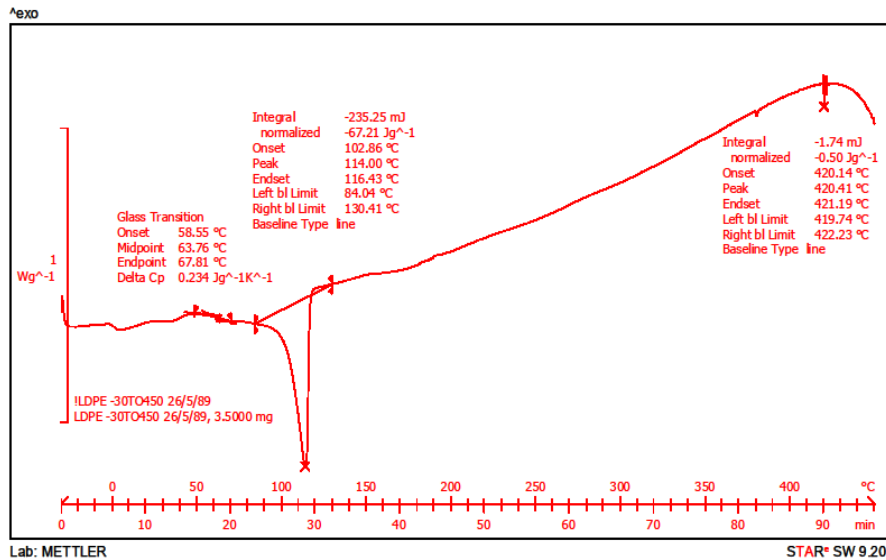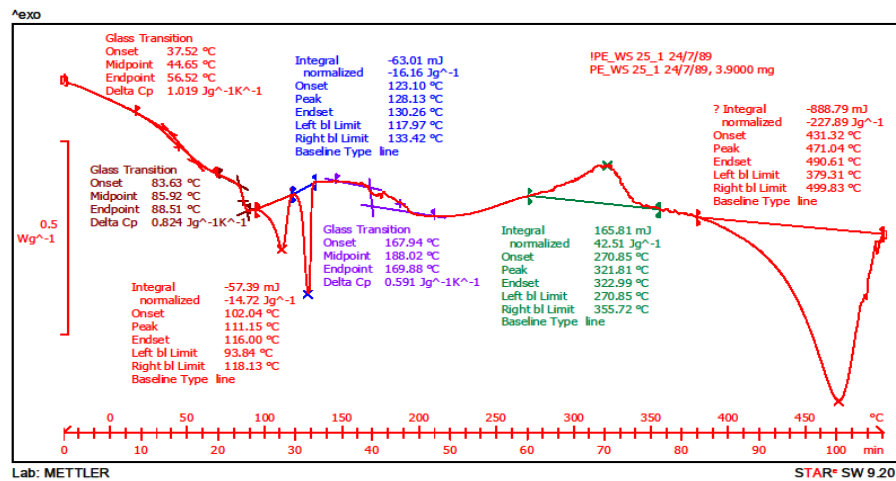

Fig. 2. DSC curve of pure LDPE Sample

Fig. 3. DSC Curve of T_{25} as a sample curve for LDPE-WS Biocomposites

A DSC curve for the 40%LDPE-60%WS composition (treatment number 25, T_{25}), as an instance, is also shown in Fig. 3. The endothermic peak at 111.15^{o}C illustrates the melting point of biocomposite, while the other peak appears at higher temperature, 471.04^{o}C, due to the degradation of the biocomposite.

Table 1 shows the experimental data for temperature changes and enthalpy (ΔH) for melting and decomposition of all treatments in the LDPE-WS composites. From this table, it is apparent that the thermal degradation began to occur only after the materials had absorbed significant amounts of the heat energy.

The heat initiated the degradation processes and the breaking down of the fibers and matrix structure. However, the melting temperature (t_m) for all composites was more than that of WS (69.97°C) and they are almost the same as the melting point of pure LDPE (114.00°C). This means that no significant difference was observed between melting temperatures as a result of incorporating WS to the LDPE matrix. In fact, for all LDPE-WS composites, two distinct endothermic peaks were obtained from DSC curves. The first peak, from the DSC curve of neat LDPE sample (Fig.1), indicates the melting temperature (114.00^{o}C), and the second peak (420.41^{o}C) shows the degradation temperature (t_d).

The t_d for all composites was more than that of pure LDPE (420.41^{o}C). This means that the thermal strength of all samples is increased. Thus, incorporating WS to the LDPE matrix, in general, increased the decomposition temperature of composites. This finding seems to be in agreement with Averous and Boquillon (2004) who found that the addition of cellulose fillers improved the thermal resistance of wheat starch-based biocomposites. However, this enhancement of thermal stability and properties can be attributed to an improvement in the interfacial adhesion and compatibility between the WS and matrix, due to the treatment of compatibilizing agent. Furthermore, ΔH (J/g) shows changes in the enthalpy (H) and describes whether the system absorbs or emits heat. When enthalpy is positive and ΔH is greater than zero, this indicates that a system absorbs heat (an endothermic reaction). In general, normalized ΔH (J/g) is measured in the DSC analysis that is shown in Table 1.

In addition, based on statistical ranking model, the results of t_m and t_d data for all treatments were ranked, and the results of such ranking are shown in Table 1. All samples were categorized to the four groups. In fact, the aim of ranking was to achieve the treatments that are placed with control (pure LDPE) in the same/different statistical group. The lowest t_m is for T_{11} with 111.12^{o}C (2.88^{o}C difference with control), and the highest t_m belongs to the T5 with 113.88^{o}C (0.12^{o}C difference with control). Among different treatments, T_4, T_8, T_9, T_{13}, T_{16}, and T_{22} treatments were placed in the same group with control (T_1) in point of t_d characteristic. Samples T_5, T_8, T_9, T_{13}, T_{22}, and T_{24} treatments were in the same group with control (T_1) in point of t_m property. Therefore, T_8, T_9, T_{13}, and T_{22} were found to have almost the same thermal properties as pure LDPE (T_1). All treatments 8, 9, 13, and 22 had PEG in their formulation. This finding means that, in comparison with MAPE, PEG had a more significant effect on resistance to thermal degradation by the biocomposites.

Table 1. DSC Data for LDPE-WS Composites and Their Thermal Properties Ranking

Treatments	t_m (^{o}C)	Normalized ΔH (J/g)	t_d (^{o}C)	Normalized ΔH (J/g)	Ranking t_m	Ranking t_d
T_1 (100LDPE)	114.00	67.21	420.41	0.50	4	1
T_2 (100WS)	69.97	151.30	476.90	4.85	1	2
T_3 (70LDPE+30WS)	112.90	24.74	468.74	384.36	3	2
T_4 (70LDPE+30WS+7MAPE)	113.27	45.86	452.43	1234.17	3	1
T_5 (70LDPE+30WS+10MAPE)	113.88	30.44	472.79	236.66	4	4
T_6 (70LDPE+30WS+7PEG400)	113.07	26.12	470.88	203.26	3	4
T_7 (70LDPE+30WS+10PEG400)	112.84	36.76	469.28	302.28	3	2
T_8 (70LDPE+30WS+7PEG600)	113.42	32.55	444.63	1439.81	4	1
T_9 (70LDPE+30WS+10PEG600)	113.29	106.68	447.76	2421.69	4	1
T_{10} (60LDPE+40WS)	111.52	24.21	468.82	298.00	1	2
T_{11} (60LDPE+40WS+7MAPE)	111.12	13.46	470.06	182.26	1	3
T_{12} (60LDPE+40WS+10MAPE)	111.74	48.85	470.90	423.55	1	4
T_{13} (60LDPE+40WS+7PEG400)	113.71	81.20	443.47	1079.50	4	1
T_{14} (60LDPE+40WS+10PEG400)	112.58	26.71	469.32	389.35	2	3
T_{15} (60LDPE+40WS+7PEG600)	113.07	29.55	468.73	246.10	3	2
T_{16} (60LDPE+40WS+10PEG600)	112.01	54.28	441.90	83.85	2	1
T_{17} (50LDPE+50WS)	112.75	54.87	473.17	300.75	3	4
T_{18} (50LDPE+50WS+7MAPE)	111.82	41.10	469.65	282.54	1	3
T_{19} (50LDPE+50WS+10MAPE)	111.85	28.23	468.23	329.98	1	2
T_{20} (50LDPE+50WS+7PEG400)	112.06	28.61	470.30	271.49	2	4
T_{21} (50LDPE+50WS+10PEG400)	112.95	37.55	469.75	371.76	3	3
T_{22} (50LDPE+50WS+7PEG600)	113.54	27.48	444.83	847.20	4	1
T_{23} (50LDPE+50WS+10PEG600)	112.50	24.59	464.59	187.72	2	2
T_{24} (40LDPE+60WS)	113.57	29.89	469.52	338.49	4	3
T_{25} (40LDPE+60WS+7MAPE)	111.15	14.72	471.04	227.89	1	4
T_{26} (40LDPE+60WS+10MAPE)	112.15	53.53	468.55	249.85	2	2
T_{27} (40LDPE+60WS+7PEG400)	112.30	56.77	470.27	265.39	2	3
T_{28} (40LDPE+60WS+10PEG400)	112.58	25.90	470.03	270.58	2	3
T_{29} (40LDPE+60WS+7PEG600)	112.90	36.30	470.57	336.81	3	4
T_{30} (40LDPE+60WS+10PEG600)	112.63	29.93	469.87	280.67	2	3

CONCLUSIONS

1. Adding PEGs to the LDPE matrix resulted in almost the same thermal properties as the pure LDPE. The effects of PEG addition were greater than those of MAPE.

2. In all treatments, melting temperature was more than the melting point of WS and it was almost is the same as that of pure LDPE.

3. In all cases, decomposition temperature of the composite was more than the decomposition point of LDPE.

4. Adding WS to the LDPE matrix, in general, improved the heat tolerance of composites.

5. Cellulose derivatives are typically used in the packaging industry. Since production of the cellulose derivatives need more costs and processes, the use of wheat straw directly in the biocomposites formulation can reduce the cost and decrease the use of chemical materials.

REFERENCES CITED

American Society for Testing and Material (ASTM). (2004). "Standard test method for enthalpies of fusion and crystalinity of polymers by diferencial scanning caloinetry (DSC)," (D3417-99).

Averous, L. and Boquillon, N. (2004). "Biocomposites based on plasticized starch: thermal and mechanical behaviours," *Carbohydrate Polymers* 56, 111-122.

Brown, W. E. (1992). *Plastics in Food Packaging: Properties, Design and Fabrication*, New York, Marcel Dekker, Inc.

Caulfields, D. F., Clemons, C., Jacobson, R. E., and Rowell, R. M. (2005). "Wood thermoplastic composites," in: *Handbook of Wood Chemistry & Wood Composites*, pp. 365-373.

Clemons, C. (2002). "Wood plastic composites in the USA," *Forest Products Journal* 52 (6), 10-18.

Cowie, J. M. G., and Arrighi, V. (2008). *Polymers: Chemistry & Physics of Modern Materials*, Taylor & Francis, Boca Raton.

Dobkowski, Z. (2006). "Thermal analysis techniques for characterization of polymer materials," *Polymer Degradation and Stability* 91, 488-493.

Herrera, F., Pedro, J., and Valadez-Gonzalez, A. (2005). in: *Natural Fibers, Biopolymers, and Biocomposites*, Mohanty, A.K., Misra, M., and Drzai, L.T. (eds.), pp. 177- 230, CRC Press.

Jayasekara, R., Harding, I., Bowater, I., Christie, G. B. Y., and Lonergan, G. T. (2003). "Preparation, surface modification and characterization of solution cast starch PVA blended films," *Environment and Biotechnology Centre*, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia.

Karimi, H. (1992). "Wheat," *University Publication Central*, Tehran, 599 pages. (In Persian)

Klyosov, A. A. (2007). *Wood Plastic Composites*, Wiley, London.

Mckean, W. T., and Jacobs, R. S. (1997). *Wheat Straw as a Paper Fiber Source*, The Clean Washington Center, 1997.

Misra, D. K. (1987). *Pulp and Paper Manufacture;Secondary Fibers and Nonwood Fibers*, Hamilton, F., and Leopold, B. (eds.), TAPPI, Atlanta, GA.

Mohanty, A. K., Misra, M., Drzal, L. T., Selke, S. E., Harte, B. R., and Hinrichsen, G. (2005). In: *Natural Fibers, Biopolymers, and Biocomposites*, Mohanty, A. K., Misra, M., and Drzal, L. T. (eds.), 1- 36, CRC Press.

Nishino, T. (2004). *Green Composites, Polymer Composites and the Environment*, Baillie, C. (ed.), pp. 49-80, CRC Press.

Lei, Y., Wu, Q., Yao, F., and Xu, Y. (2007). "Preparation and properties of recycled hdpe/natural fiber composites," *Composites, Part A: Applied Science and Manufacturing* 38, 1664-1674.

Li, X., Tabil, L.G., Oguocha, I. N., and Panigrahi, S. (2008). "Thermal diffusivity, thermal conductivity, and specific heat of flax fiber – HDPE biocomposites at processing temperatures," *Composites Science and Technology* 68, 1753-1758.

Lu, J. Z., Wu, Q., and Mchabb, H. S. J. (2000). "Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments," *Wood and Fiber Science* 32(1), 88-104.

Luyt, A. S. and Malunka, M. E. (2005). "Composites of low-density polyethylene and short sisal fibres: The effect of wax addition and peroxide treatment on thermal properties," *Thermochimica Acta* 426, 101-107.

Piringer, O. G., and Baner, A. L. (2000). *Plastic Packaging Materials for Food*, Wiley-Vch Press.

Saheb, D. N., and Jog, J. P. (1999). "Natural fiber polymer composites, A review," *Adv. Polym. Tech.* 18(4), 351-363.

Suchitra, M. (2004). in: *Advanced Topics in Characterization of Composites,* M. K. Kessler (ed.), Trafford Publishing, pp.11-33.

Tajeddin, B., and Abdulah, L. C. (2010). "Thermal properties of HDPE-kenaf cellulose composites," *Polymers & Polymer Composites* 18(5), 195- 199.

Tajeddin, B., Russly A. R., Luqman Chuah, A., Nor Azowa, I., and Yus Aniza, Y. (2009). "Thermal properties of low density polyethylene-filled kenaf cellulose composites," *Eur. J. Sci. Res.* 32(2), 223-230.

Tharanathan, R. N. (2003). "Biodegradable films and composite coatings: Past, present and future," *Trends Food Sci. Technol.* 14(3), 71-78.

Yordanov, H., and Minkova, L. (2003). "Microhardness and thermal stability of compatibilized LDPE/PA6 blends," *European Polymer Journal* 39, 951-958.

Zhang, M. Q., Rong, M. Z., and Lu, X. (2005). "Fully biodegradable natural fiber composites from renewable resources: All-plant fiber composites," *Composites Science and Technology* 65, 2514-2525.