

Mechanical properties and morphology of poly(lactic acid)/modified natural rubber blends

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Abstract

The blending of poly(lactic acid) (PLLA) with 2 types of modified natural rubber, namely: hydroxyl epoxidized natural rubber (HENR) and hydroxyl natural rubber (ONR), was investigated. The study was carried out using low molecular weight poly(lactic acid)-g-hydroxyl liquid natural rubber (LMW.PLA-g-HLNR) and DL-lactide-g-hydroxyl liquid natural rubber (lactide-g-HLNR) as compatibilizers. The PLLA blends were compounded using an internal mixer and compression moulded into specimens for mechanical testing. Tensile tests and impact tests were performed in order to compare and contrast the mechanical properties of the blends. It was found that the tensile strength and impact strength of the PLLA/HENR blend (70:30) without compatibilizer decreased markedly compared with PLLA, while the elongation at break increased slightly. The addition of 2 wt% LMW.PLA-g-HLNR increased the impact strength and elongation at break but slightly lowered the tensile strength relative to virgin PLLA. In contrast, the PLLA/HNR blends of all compositions did not show any clear improvement of mechanical properties. The effects of the addition of starch and glycerol were also studied from which it was found that the elongation at break increased but the tensile strength decreased compare with PLLA.

Keywords: Poly(lactic acid); Polymer blend; Modified natural rubber; Compatibilizer

Introduction

Plastic materials are widely used in everyday life and this trend is continuing due to their ease of production and because they are lightweight and affordable. However, as the rates of their production and consumption increase, so does the problem of plastic waste. Consequently, the use of materials derived from natural resources that have properties similar to plastic but are biodegradable are of increasing interest. These materials include lignin (Davis, 2003), cellulose (Davis, 2003), chitosan (Kumar *et al.*, 2004), starch (Preechawong *et al.*, 2005), poly(hydroxybutyrate (PHB) (Zhang *et al.*, 1996) and poly(lactic acid) (PLA) (Yew *et al.*, 2005).

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polymer produced from renewable resources. It has a broad range of applications, as biomedical and pharmaceutical materials and as a biodegradable substitute for traditional petrochemical-based thermoplastics (De Jong *et al.*, 2001; Rhim *et al.*, 2007; Hanafi *et al.*, 2000). However, PLA has a relatively high glass transition temperature ($T_g \sim 55^\circ\text{C}$) (Cohn and Salomon, 2005) which limits its applications at room temperature. As a result, there have been several reports describing the improvement of the

mechanical properties of PLA by blending with flexible polymers such as natural rubber. However, physical blending resulted in phase separation between the PLA and the second component (Jin *et al.*, 2000). One way to overcome this problem has been to copolymerize a flexible polymer with either PLA or another polymer that is compatible with PLA and to then use this copolymer as a blend compatibilizer. The copolymerization can be carried out via various techniques such as ring-opening copolymerization with lactide (Ouchi *et al.*, 2006), copolycondensation of lactic acid (Ajioka *et al.*, 1998) and copolymerization of low molecular weight poly(lactic acid) (LMW.PLA) (De Jong *et al.*, 2001). These reactions can be carried out using appropriate initiators or catalysts either in bulk or in solution in an organic solvent.

Many researchers have described the use of rubber or modified rubber in the preparation of polymer blends with PLA. For example, Jin *et al.* (2000) prepared polymer blends of poly(L-lactic acid) (PLLA) with poly(*cis*-1,4-isoprene) (PIP) and polyisoprene-g-poly(vinylacetate) (PIP-g-PVAc) containing 40% poly(vinyl acetate). The experimental results showed that specimens prepared from PLLA-PIP 80:20 blend had lower tensile strength, elongation at break and toughness in comparison with pure PLLA due to phase separation in the blend. When PLLA was blended with PIP-g-PVAc instead, an 80:20 blend showed more compatibility resulting in an increase in toughness and elongation at break. However, the tensile strength was still slightly lower than that of pure PLLA.

Yew *et al.* (2005) reduced the cost of PLA by mixing with rice starch (RS). The results showed that the modulus increased with increasing starch content but so did the brittleness. When epoxidized natural rubber (ENR: 50% epoxide content) was chosen to enhance the toughness and elongation of the blend, it was found that the addition of 20% starch and 5% ENR gave the best results with properties comparable with pure PLLA.

This present article now describes the preparation of polymer blends of PLLA with two types of modified natural rubber, namely: hydroxyl epoxidized natural rubber (HENR) and hydroxyl natural rubber (HNR). The effects of compatibilizers prepared from grafting low molecular weight poly(DL-lactic acid) on hydroxyl liquid natural rubber (LMW.PDLLA-g-HLNR) and DL-lactide on hydroxyl liquid natural rubber (DL-lactide-g-HLNR) are studied. Since these graft copolymers have similarities with the structures of both PLA and modified natural rubber, they can be expected to increase blend compatibility. In order to reduce the cost of PLA, this paper also includes the effect of adding starch as a blends component.

Experimental

Materials

Poly(L-lactic acid) (PLLA) grade 4042D was purchased from NatureWorks. Modified natural rubbers were prepared by the Rubber Research Group in Naresuan University, Thailand. Hydroxyl epoxidized natural rubber (HENR) was prepared with 50% epoxide and 10% hydroxyl contents while the hydroxyl natural rubber (HNR) had 70% hydroxyl content. The graft copolymer compatibilizers were also prepared in Naresuan from 2 different viscosity-average molecular weight, \bar{M}_v , hydroxyl liquid natural rubber (HLNR), with $\bar{M}_v = 14,400$ g/mol and $\bar{M}_v = 30,500$

g/mol, and low molecular weight poly(DL-lactic acid) (LMW.PLA) and DL-lactide (Pray-in and Phetphaisit, 2009). These four materials were designated as LMW.PLA-g-HLNR (14400), LMW.PLA-g-HLNR(30500), Lactide-g-HLNR(14400) and Lactide-g-HLNR(30500). Chemical structures of graft compatibilizers were demonstrated in Figure 1. Epoxide and hydroxyl contents, T_g and average molecular weight of PLLA/modified natural rubber blends were presented in Table 1. Cassava starch was purchased from Thai Wah Food Product Public Co., Ltd. The glycerol (Glycerine-Colgate-Chemical) used was commercial grade.

Table 1 Epoxide and hydroxyl contents, T_g and average molecular weight of PLLA/modified natural rubber blends

Formulation	Epoxide unit (%)	Hydroxyl unit (%)	T_g (at mid point) ($^{\circ}\text{C}$)	\bar{M}_v (g/mol)	\bar{M}_n (g/mol)
PLLA	-	-	63.63	-	-
HENR	50	10	15.19	-	-
HNR	-	70	23.66	-	-
LMW.PLA	-	-	22.96	-	534
HLNR(14400)	-	21	29.56	14,400	-
HLNR(30500)	-	26	-13.67	30,500	-
LMW.PLA-g-HLNR(14400)	-	-	41.78	-	-
LMW.PLA-g-HLNR(30500)	-	-	23.50	-	-
Lactide-g-HLNR(14400)	-	-	42.22	-	-
Lactide-g-HLNR(30500)	-	-	-5.18	-	-

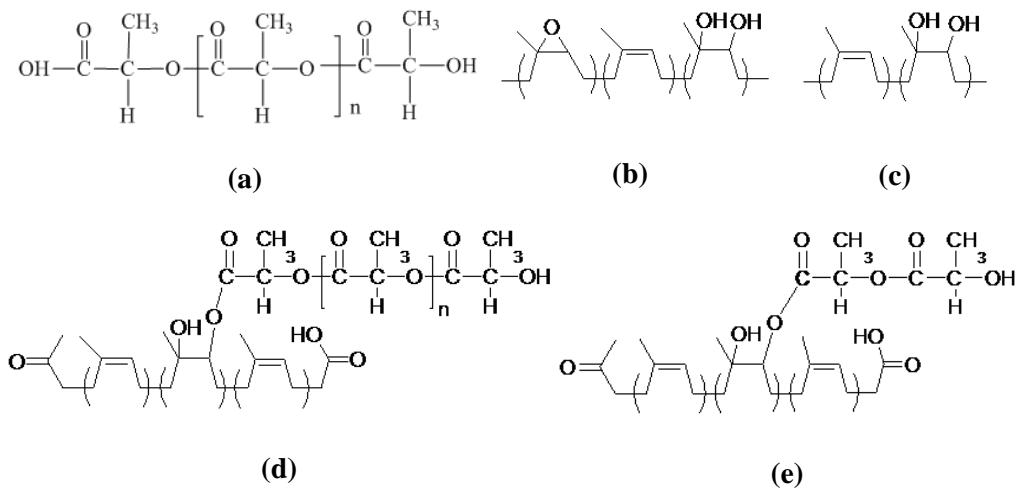


Figure 1 Chemical structures of (a) PLLA (b) HENR (c) HNR (d) LMW.PLA-g-HLNR and (e) Lactide-g-HLNR

Sample preparation

The relative amounts of the various ingredients which were used to prepare the polymer blends of PLLA, modified natural rubber (HENR/HNR), graft compatibilizer, cassava and glycerol are shown in Table 2. In the preparation of the polymer blends of PLLA, modified natural rubber and compatibilizer, the PLLA was first coated with a grafted compatibilizer by solution coating. Thereafter, the coated PLLAs and the modified natural rubber were blended in an internal mixer at 165°C using a rotor speed of 100 rpm for 15 min. After cooling to room temperature, each compound was cut into small pieces. In the preparation of the polymer blends between the PLLA, modified natural rubber, compatibilizer, cassava and glycerol, the coated PLLA was blended with modified natural rubber in an internal mixer at 165°C using a rotor speed of 100 rpm for 5 min. The cassava and glycerol was then added and the compound mixed for a further 15 min under the same conditions. After cooling to room temperature, the compound was cut into small pieces.

The compound granules were processed by compression moulding at 180°C using a pressure of 2,100 psi for 10 min following which dumbbell-shaped specimens (25 mm x 165 mm x 1 mm) for tensile testing according to ASTM D638 and rectangular-shaped specimens (10 mm x 50 mm x 5 mm) for impact testing were prepared.

Mechanical properties

Tensile strength and elongation at break were measured according to ASTM D638 by a Universal Testing Machine (WD-5E). The crosshead speed was set at 50 mm/min with a force of 5 kN. All tests were performed at room temperature and the average of five repeat measurements recorded for each composition.

Impact strength was measured using a Charpy Impact Tester (JB-300). The rectangular-shaped test specimens were tested using a pendulum of size 4 J.

Morphological studies

Scanning electron microscopy (SEM: LEO 1455 VP) was used to study the phase distribution of the modified natural rubber in the PLLA matrix. Test samples were cut from the fracture surfaces of the tensile test specimens. The specimens were sputter-coated with gold in order to prevent electrical discharge SEM examination.

Table 2 Compositions of the PLLA/modified natural rubber blends

Sample	PLLA (%)	HENR (%)	HNR (%)	LMW.PLA-g-HLNR (wt%)	Lactide-g-HLNR (wt%)	Starch (wt%)	Glycerol (wt%)
1	70	30	-	-	-	-	-
2	70	30	-	2 ^{1,2}	-	-	-
3	70	30	-	4 ¹	-	-	-
4	70	30	-	-	2 ^{1,2}	-	-
5	70	-	30	2 ²	-	-	-
6	50	-	50	2 ²	-	-	-
7	30	-	70	2 ²	-	-	-
8	50	-	50	2 ²	-	20	20
9	50	-	50	2 ²	-	40	20

¹ graft compatibilizer prepared from HLNR $\overline{M}_v = 14400$ g/mol

² graft compatibilizer prepared from HLNR $\overline{M}_v = 30500$ g/mol

Results and Discussion

Effect of epoxidized natural rubber polyol (OENR)

In the first study, PLLA and HENR (50% epoxide and 10% hydroxyl contents) were mixed in PLLA:HENR ratios of 90:10, 80:20 and 70:30 in the internal mixer. The blend specimens after compression were found to be opaque. The blend containing only 10% HENR gave a brittle plastic like virgin PLLA. As the HENR content was increased to 20-30%, the blend became tougher and more flexible. At a PLLA:HENR ratio of 70:30, the tensile strength and impact strength of the PLLA/HENR blend were both significantly lower than those of virgin PLLA while the elongation at break was only slightly higher (Table 3). From these results, it appears that the addition of HENR, increases flexibility but otherwise decrease mechanical strength compared with pure PLLA. This may be due to the incompatibility of PLLA and HENR. It also may be due to the many small air bubbles in the specimens prepared for tensile testing which, for pure PLLA, was not a problem. From the SEM micrographs, it was observed that the surface of PLLA was smooth and gave a brittle fracture whereas the surface of polymer blends showed coarse phase morphology with small pores and larger cavities across the surface cross-section (Figure 2).

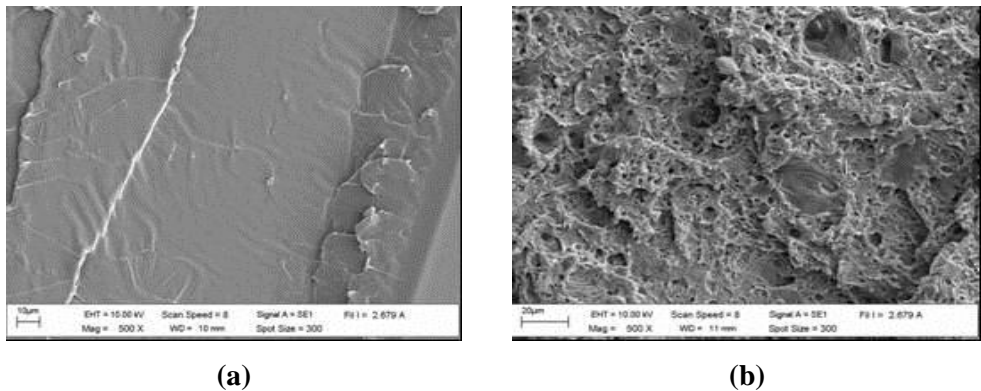


Figure 2 SEM micrographs of the tensile fracture surfaces of (a) virgin PLLA and (b) PLLA:HENR blend (70:30) (Sample 1)

Table 3 Tensile and impact properties of virgin PLLA and the PLLA/OENR blends

Sample	Tensile strength [MPa]	Elongation at break [%]	Impact strength [kJ/m ²]
PLLA (grade 4042D)	49.50 ± 1.58	5.33 ± 0.87	27.08 ± 0.85
1	22.80 ± 1.87	6.55 ± 1.34	18.20 ± 3.34

Effects of type and amount of compatibilizer

Four types of compatibilizers: LMW.PLA-g-HLNR(14400), LMW.PLA -g-HLNR(30500), Lactide-g-HLNR(14400) and Lactide-g-HLNR(30500) were used to increase the compatibility of the PLLA/HENR 70:30 blend. The tensile and impact properties of the blends are shown in Table 4. The tensile strength, elongation at break and impact strength of the PLLA/HENR blend was increased by the addition of 2% LMW.PLA-g-HLNR(14400). The SEM micrograph of the tensile fracture surface of the PLLA/HENR blend with added 2 % LMW.PLA-g-HLNR(14400) showed a smoother surface than that of the starting blend. A stretching out of the polymer matrix generated under tension was also noted (Figure 3 (a)).

The elongation at break of the polymer blend, increased with increasing molecular weight of the HLNR in the compatibilizer (2% LMW.PLA-g-HLNR (30500)) while the tensile and impact strengths were lower. The SEM micrograph of the tensile fracture surface of the PLLA/HENR blend containing 2% LMW.PLA-g-HLNR(30500) shows a smooth surface (Figure 3 (b)). Also, the pore size is smaller compared to the blend without compatibilizer. Furthermore, it was found that stretching of the polymer matrix was different from that using of 2% LMW.PLA-g-HLNR(14400). This may be due to their different glass transition temperatures. Whereas LMW.PLA-g-HLNR(14400) has a $T_g = 41.78^\circ\text{C}$, resulting in a matrix that was solid and sticky at room temperature, the LMW.PLA-g-HLNR(30500) has a $T_g = 23.50^\circ\text{C}$ which is lower than room temperature, resulting in a matrix showing rubbery behavior leading to a decrease in both tensile and impact strength.

However, although the addition of LMW.PLA-g-HLNR(14400) increased toughness and elongation at break, adding more graft compatibilizer (4%) resulted in a decrease of the mechanical properties. This may be due to the high T_g of LMW.PLA-g-HLNR(14400) giving a polymer blend with behavior intermediate between glassy and rubbery states. The flexibility and the toughness of the blend polymer are decreased.

The addition of Lactide-g-HLNR compatibilizer gave a different result from LMW.PLA-g-HLNR. The use of Lactide-g-HLNR(30500) ($T_g = -5.18^\circ\text{C}$) gave superior tensile and impact properties than Lactide-g-HLNR(14400) ($T_g = 42.22^\circ\text{C}$). This may be due to the Lactide-g-HLNR having one unit of lactic acid per one position of grafting site while LMW.PLA-g-HLNR contain about six units of lactic acid. Thus in the case of Lactide-g-HLNR, the molecular weight of HLNR is an important factor in promoting compatibility between the PLLA and HENR. The advantage of using LMW.PLA-g-HLNR is that it contains both lactic acid oligomer and modified liquid rubber, both of which can improve the compatibility and properties of polymer blend. This may be due to the long chain of LMW.PLA may entanglement with PLLA better than lactile that contain one unit of lactic acid per one position of grafting site. While, the moderate molecular weight of HLNR (14400 g/mol) help the compatibiliser migrate to the phase boundaries between PLLA and HENR preferable than the high molecular weight HLNR (30500 g/mol). Apart from the compatibilization between HLNR and HENR, there might be the interaction of hydroxyl group on HLNR and carbonyl group of PLLA. Then, the

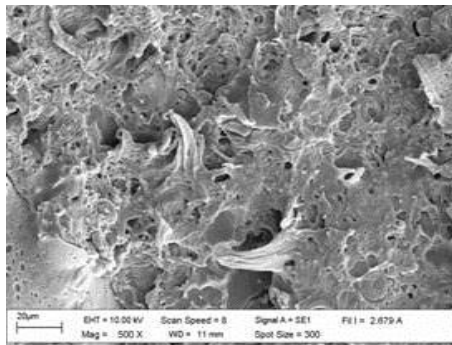
PLLA blended with HENR having LMW.PLA-g-HLNR(14400) as a compatibiliser showed the superior physical properties than the other compatibiliser.

Table 4 Tensile and impact properties of PLLA/HENR blends with various types and amounts of compatibilizer

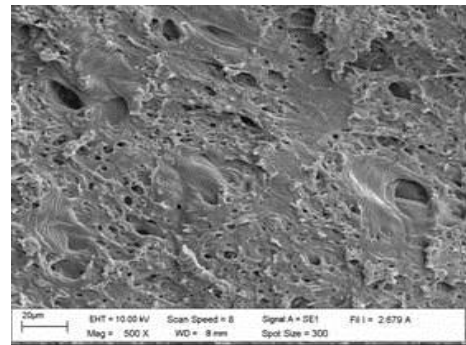
Sample	Tensile strength [MPa]	Elongation at break [%]	Impact strength [kJ/m ²]
2 ¹	30.00 ± 1.41	8.83 ± 1.50	30.54 ± 5.68
2 ²	20.71 ± 1.45	14.60 ± 0.96	13.88 ± 2.83
3	24.67 ± 0.58	3.80 ± 0.89	16.44 ± 2.66
4 ¹	15.29 ± 1.80	4.08 ± 0.58	9.59 ± 1.82
4 ²	23.71 ± 1.60	4.44 ± 0.42	17.18 ± 3.02

¹ graft compatibilizer prepared from HLNR $\overline{M}_v = 14400$ g/mol

² graft compatibilizer prepared from HLNR $\overline{M}_v = 30500$ g/mol



(a)



(b)

Figure 3 SEM micrographs of the tensile fracture surfaces of PLLA:HENR blends (70:30) with different compatibilizers molecular weights: (a) 2% LMW.PLA-g-HLNR(14400) (Sample 2¹) and (b) 2%LMW.PLA-g-HLNR(30500) (Sample 2²)

Effects of hydroxyl content on modified natural rubber

Increasing the hydroxyl content on the modified natural rubber from 10% (HENR) to 70% (HNR) was of interest since, generally, a higher hydroxyl content result in more opportunity to react with the carboxylic acid groups of the PLA during shear mixing at high temperature. This, in turn, may lead to an increase in the compatibility of the polymer blend. However, the results show that the polymer

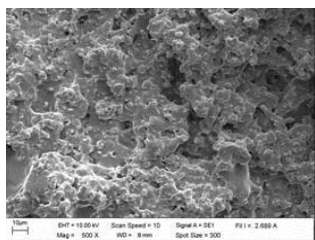
blends prepared from PLLA and HNR using 2% LMW.PLA-g-HLNR(30500) as a compatibilizer are brittle. Tensile test piece could not be cut even when the ratio of HNR was increased from 30% to 70%. The impact strengths of polymer blends of PLLA:HNR = 70:30 (Sample 5), 50:50 (Sample 6) and 30:70 (Sample 7) were 15.04 ± 3.38 , 10.94 ± 1.28 and 12.06 ± 3.33 kJ/m² respectively. The brittle behavior of these polymer blend may be due to the high glass transition temperature of HNR ($T_g = 23.66^\circ\text{C}$) resulting in glassy rather than elastic behavior.

Effect of cassava starch

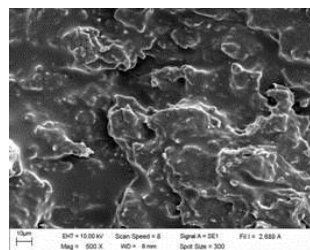
The variations in tensile strength and elongation at break with cassava starch loading in the polymer blend PLLA/HNR with 2% LMW.PLA-g-HLNR (30500) and 20% glycerol as compatibilizer and processing aid are shown in Table 5. The addition of 20% starch and 20% glycerol to PLLA/HNR changed the characteristic of the blend from being brittle to being a soft and flexible plastic. Although the specimen could stretch more that the starting PLLA and PLLA/HNR blend, the tensile strength decreased significantly. Moreover, adding excessive amounts of starch (40 wt%) decreased both the elongation at break and tensile strength. Figure 4 shows the SEM micrographs of the PLLA/HNR blend containing 20 wt% and 40 wt% starch. It was observed that adding 40 wt% starch produced larger aggregated particles than 20 wt%. (Figure 4) This aggregation may have decreased the interfacial bonding between the starch particles and the polymer matrix leading to a deterioration in the physical properties of the blend.

Table 5 Tensile properties of PLLA/HNR blends with various amounts of cassava starch

Sample	Tensile strength [MPa]	Elongation at break [%]
8	6.50 ± 0.50	31.53 ± 5.70
9	4.33 ± 0.52	4.67 ± 1.13



(a)



(b)

Figure 4 SEM micrographs of the tensile fracture surfaces of the PLLA:HNR blend (50:50) with different amounts of starch (a) 20 wt% starch (Sample 8) and (b) 40 wt% starch (Sample 9)

Conclusions

A comparison of the mechanical properties of polymer blends prepared from PLLA and 2 types of modified natural rubber (Hydroxyl epoxidized natural rubber (HENR) and hydroxyl natural rubber (HNR)) found that blending with HENR decreased both the tensile strength and impact strength of PLLA significantly, while the elongation at break was slightly increased. The addition of 2% LMW.PLA-g-HLNR graft compatibilizer increased the tensile strength, impact strength and elongation at break of PLLA/HENR. However, a larger amount (4%) of LMW.PLA-g-HLNR or Lactide-g-HLNR as compatibilizer did not improve the tensile properties and decreased the impact strength. Blends of PLLA with HNR in all ratios showed dramatic decreases in both tensile and impact properties even with the addition of a graft compatibilizer. In addition, it was found that specimens prepared from the PLLA/HNR blends gave brittle plastics, whereas those from PLLA/HENR blends exhibited more flexibility.

The addition of 20% starch and 20% glycerol improved the flexibility and elongation at break of the PLLA/HNR blend. However, the tensile strength showed a significant decrease compared to virgin PLLA.

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References

- Ajioka, M., Suizu, H. and Kashima, T. (1998) Aliphatic polyesters and their copolymers synthesized through direct condensation polymerization. *Polymer Degradation and Stability*, 59, 137-143.
- Cohn, D. and Salomon, A.H. (2005) Designing biodegradable multiblock PCL/PLA thermoplastic elastomers. *Biomaterials*, 26, 2297-2305.
- Davis, G. (2003). Characterization and characteristics of degradable polymer sack. *Materials Characterization*, 51, 147-157.
- De Jong, S.J., De Smedt, S.C., Demeester, J., Van Nostrum, C.F., Kettenes-van den Bosch, J.J. and Hennink, W.E. (2001) Biodegradable hydrogels based on stereocomplex formation between lactic acid oligomers grafted to dextran. *Journal of Controlled Release*, 72, 47-56.
- Hanafi, M.M., Eltaib, S.M. and Ahmad, M.B. (2000) Physical and chemical characteristics of controlled release compound fertilizer. *European Polymer Journal*, 36, 2081-2088.
- Jin, H.J., Chin, I.J., Kim, M.N., Kim, S.H and Yoon, J.S. (2000) Blending of poly(L-lactic acid) with poly (*cis*-1,4-isoprene). *European Polymer Journal*, 36, 165-169.

- Kumar, R.M., Muzzarelli, R.A., Sashiwa, H. and Domb, A.J. (2004). Chitosan chemistry and pharmaceutical perspectives. *Chemical Review*, 104, 6017-6084.
- Ouchi, T., Ichimura, S. and Ohya, Y. (2006) Synthesis of branched poly(lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film. *Polymer*, 47, 429-434.
- Pray-in, Y. and Phetphaisit, C.W. (2009) Polylactic acid-g-Modified Natural Rubber: Synthesis and Characterization In: Proceedings of the Pure and Applied Chemistry International Conference (PACCON), Phitsanulok, Thailand, January 14-16 2009; 630-633.
- Preechawong, D., Peesan, M., Supaphol, P. and Rujiravanit, R. (2005). Preparation and characterization of starch/poly(L-lactic acid) hybrid foams. *Carbohydrate Polymers*, 59, 329-337.
- Rhim, J.W., Lee, J.H. and Perry, K.W. (2007) Mechanical and barrier properties of biodegradable soy protein isolate-based films coated with polylactic acid. *LWT*, 40, 232-238.
- Yew, G.H., Chow, W.S., Mohd Ishak, Z.A. and Mohd Yusof, A.M. (2005) Natural weathering of poly(lactic acid): effects of rice starch and epoxidized natural rubber. *Journal of Elastomers and Plastics*, 41, 369-382.
- Yew, G.H., Mohd Yusof, A.M., Mohd Ishak, Z.A. and Ishiaku, U.S. (2005) Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites. *Polymer Degradation and Stability*, 90, 488-500.
- Zhang, L., Xiong, C. and Deng, X. (1996). Miscibility, crystallization and morphology of poly (hydroxybutyrate)/poly(*d,l*-lactide)blends. *Polymer*, 37, 235-241.