

CHAPTER V

TOUGHENING OF POLYLACTIDE WITH ADMICELLED NATURAL RUBBER PARTICLES AND ITS NANOCOMPOSITE

5.1 Abstract

Poly lactide (PLA) is a clear biodegradable polymer with good mechanical properties, but poor toughness. In this work, natural rubber (NR) was incorporated for toughness modification. However, natural rubber is a soft polymer which can cause the reduction of mechanical properties of the blends. So, NR was prepared as NR-PCL/PLA core-shell particles via admicellar polymerization. Then, the particles and its nanocomposites with nanoclay were blended with PLA. Effect of the-particle factors, caprolactone to lactide monomers ratios and initiator to monomers ratios of the shell polymer, and clay contents were observed for mechanical and thermal properties. DMA result showed that glass transition temperature (T_g) of the two components shifted close together, that means two components were more compatible. Impact testing showed that the particles with a high initiator to monomers ratio cause increasing of PLA's Impact force. Organoclay addition into admicelled rubber improved storage modulus in DMA, but impact force decreased severely. The monomers ratios did not show any significant effect on the impact properties of the blends.

Keywords: Admicellar polymerization, natural rubber, PCL-PLA copolymer.

5.2 Introduction

Poly lactide or polylactic acid (PLA) is a biodegradable polymer with good mechanical properties, high tensile strength and Young's modulus, that can compare with conventional plastics. Furthermore, it is clear plastic that suits for many applications. The disadvantage of PLA is brittleness, it has low toughness. So, toughness modification is necessary for practical application of PLA. There are 3 polymeric modification methods, stereochemistry, copolymerization and blending (Rasal, R.M. et al. 2009). However, blending is probably practical method. Natural rubber (NR) is a soft polymer that is used to modify toughness for brittle polymer. For simple blending of PLA and NR, problems may occur because chemical structure of NR causes immiscibility between rubber phase and polylactide matrix. So, surface modification is necessary for NR. Admicellar polymerization is a method for surface modification. By applying admicellar polymerization of any plastic to NR latex particles, the rubber-plastic core-shell particles are then obtained. Arends and coworkers revealed that rubber core-shell particles could modify toughness of brittle polymers (Arends, C.B. 1996). However, blending with soft polymer can cause reduction of mechanical properties. N. Bitinis and coworkers showed that introduction of nanocomposite into blends can compensate reduction of mechanical properties (Bitinis, N. et al. 2011; Koo, J.H. 2006).

This work aimed to modify toughness of PLA by blending with NR-polycaprolactone-polylactide copolymer (PCL/PLA) core-shell particles made by admicellar polymerization and mixing with the organoclay to obtain PLA/clay nanocomposite. Morphology, impact strength and thermomechanical properties were observed with the variation in particle compositions, such as shell monomers ratio, initiator content and organoclay content.

5.3 Experimental

5.3.1 Materials

Concentrated natural rubber latex with 60% dried rubber content was purchased from Rubber Research Institute of Thailand. ϵ -Caprolactone (CL), ethylene glycol 99.8% and tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) ~95% were purchased from Sigma-Aldrich. Polylactide 4032D was purchased from Naturework. Cetyltrimethylammonium bromide (CTAB) $\geq 98\%$ was purchased from Merck Millipore. Lactide monomer (LA) (99.5% purity) was purchased from Shenzhen Bright China Industrial Co., Ltd. Bentonite based organoclay was obtained from Thai Nippon Chemical Industry Co., Ltd.

5.3.2 Admicellar Polymerization

Concentrated NR latex was diluted to 5% dried rubber content. Then, 1 M CTAB solution was added into the diluted latex until concentration of CTAB was 2.8 mM. Ethylene glycol and $\text{Sn}(\text{Oct})_2$ were added into the mixture as initiator and catalyst respectively (Storey, R.F. and Sherman, J.W. 2002). The mixture was heated to 90 °C then CL and LA were sequentially starve-fed into mixture. The polymerization was allowed to continue for 9 hr. The synthesized particles were washed with distilled water and dried. Overall monomers content was fixed at 100 mM, mole ratio between ϵ -caprolactone and lactide was varied from 30:70 to 70:30. The initiator to monomers mole ratio was also varied from 0.5:100 to 2.0:100. The synthesized rubber was named with series of number following monomers ratio and initiator ratio, such as 505010 mean admicelled rubber with 50:50 CL to LA ratio and initiator at 1.0:100.

5.3.3 Nanocomposite Preparation

The admicellar synthesized latex (core-shell structure of NR-PCL/PLA) with monomer ratio of 50:50 and initiator to monomer ratio of 1.0:100 was chosen to incorporate with organoclay. The organoclay was dispersed in distilled water by vigorous stirring and mixed with the synthesized latex. Then, the mixture was vigorously sheared and dried into rubber–organoclay nanocomposites. The content of organoclay in the core-shell latex was varied from 5-20 %wt.

Nanocomposite was named as same as admicelled rubber following by number of clay content.

5.3.4 Blending and Specimens Preparation

The admicellar synthesized particles and its various nanocomposites of 10 wt% were blended with PLA pellets of 90 wt% in co-rotating twin-screw extruder (LABTECH) with temperature profile from feed hopper to die as following: 150,160 and 165 °C and screw speed at 25 rpm. Extrudate was cooled in water bath and cut into pellets. The blend nanocomposites had clay content of 0.5-2.0 wt%. Then, the pellets were compressed by LABTECH LP20 instruments using heating at 180 °C, pressure of 2000 psi for 10 min and then cooled to room temperature. Impact specimens were prepared followed ASTM D256, and dynamic mechanical analysis specimens were prepared with dimension 10 mm x 50 mm x 3 mm.

5.3.5 Mechanical Properties Measurement

Izod impact testing was carried out with Zwick 5113 pendulum impact tester. The specimens were notched before testing. Result was reported following ASTM D256.

Dynamic mechanical properties were evaluated by using GABO EPLEXOR 100 N dynamic mechanical analyzer. The specimens were tested with temperature scan mode; temperature was scanned from -100 to 100 °C with heating rate of 2 °C/min, frequency was fixed at 1 Hz. The results were analyzed for storage modulus, $\tan \delta$ and glass transition temperature.

5.3.6 Morphology of Blends

Cryo-fracture surface of blends was prepared in liquid nitrogen and coated with platinum. The cryo-fracture samples were observed for morphology of blends by using HITACHI TM 3000 scanning electron microscope (SEM).

5.3.7 D-spacing Measurement

D-spacing of clay layer in blends was measured by using Bruker D-8 Discover X-ray diffractometer (XRD) with X-ray wavelength at 0.154 nm. Specimens were prepared to be film with dimension 40 mm x 40 mm. 2-Theta values at the highest peak were calculated for d-spacing with bragg's law equation.

$$n\lambda = 2d \sin \theta$$

Where n is an integer determined by the order given, λ is the wavelength, d is distance between clay layers and θ is angle.

5.4 Results and Discussion

5.4.1 Effect of Admicelled Particle Variation on Morphology of Blends

SEM images of blends morphology showed in figure 5.1 and 5.2. The variation of ϵ -caprolactone to lactide ratios showed its effect on distribution of rubber particles as seen in figure 5.1. PLA blends with high mole ratio of caprolactone showed worse particle distribution than low mole ratio of caprolactone. Figure 5.1d-5.1e of blend with CL-LA 60:40 and 70:30 monomers ratio showed big agglomerated admicelled particles in PLA matrix. This effect is similar to the study of Cai and coworkers (Cai, G.D. et al. 2012) where increasing of polycaprolactone part in shell layer causes reducing miscibility between matrix and admicelled rubber.

Initiator content in admicelled particles also showed an effect on particle distribution. Admicelled particles perform good distribution and compatibility when initiator to monomer mole ratio was increased until it exceeded 1.5:100. As shown in figure 5.2d, agglomeration of rubber phase was observed when initiator to monomers mole ratio was 2.0:100. Increasing of initiator to monomers ratio also caused reduction of miscibility between 2 phases.

5.4.2 Effect of Admicelled Particle Variation on Thermomechanical Properties of Blends

Glass transition temperature (T_g) from DMA was shown in table 5.1. It showed that glass transition of PLA and NR shifted toward each other and became close together. T_g of PLA in blends decreased from 68.9 °C (T_g of pure PLA), while T_g of rubber part increased from T_g of NR at -66 °C (Bendahou, A. et al. 2009). This result showed compatibility between PLA and NR increased when NR was surface modified via admicellar polymerization (Zhang, W. et al. 2009). Otherwise, PLA/NR blends without surface modification also showed T_g shift, that revealed PLA and NR

had pretty compatibility. For the blends with high LA ratio in the shell, the increase in T_g of NR phase is more than the decrease in T_g of PLA phase. In addition, when initiator to monomer ratio increased, T_g of rubber phase also increased. Interestingly, with increasing organoclay content to the optimum value of 1.5 wt%, the nanocomposites showed greater shift of both T_g toward each other suggesting that organoclay contributes better compatibility between the two phases.

Area under $\tan \delta$, the represent of ability for force absorption of material, was shown in table 5.1. PLA/admicelled particles blends showed increasing of area under PLA's $\tan \delta$: That mean force absorption of PLA was improved when admicelled particles incorporated with PLA. The area under $\tan \delta$ slightly decreased when CL ratio in admicelled particles was increased, decreasing of compatibility caused decreasing of force absorption ability of material. Increasing of initiator ratio caused increasing of the area, it provide good compatibility between two phases. But, initiator ratio at 2.0:100 showed slightly decreased of the area because compatibility between two phases decreased. Clay adding caused severe decreasing of area under $\tan \delta$ of rubber part, from about 0.9-1.1 to about 0.7, while area of PLA part didn't change significantly. This results can concluded that clay embedded in rubber phase and disrupted force absorption of rubber with its stiffness.

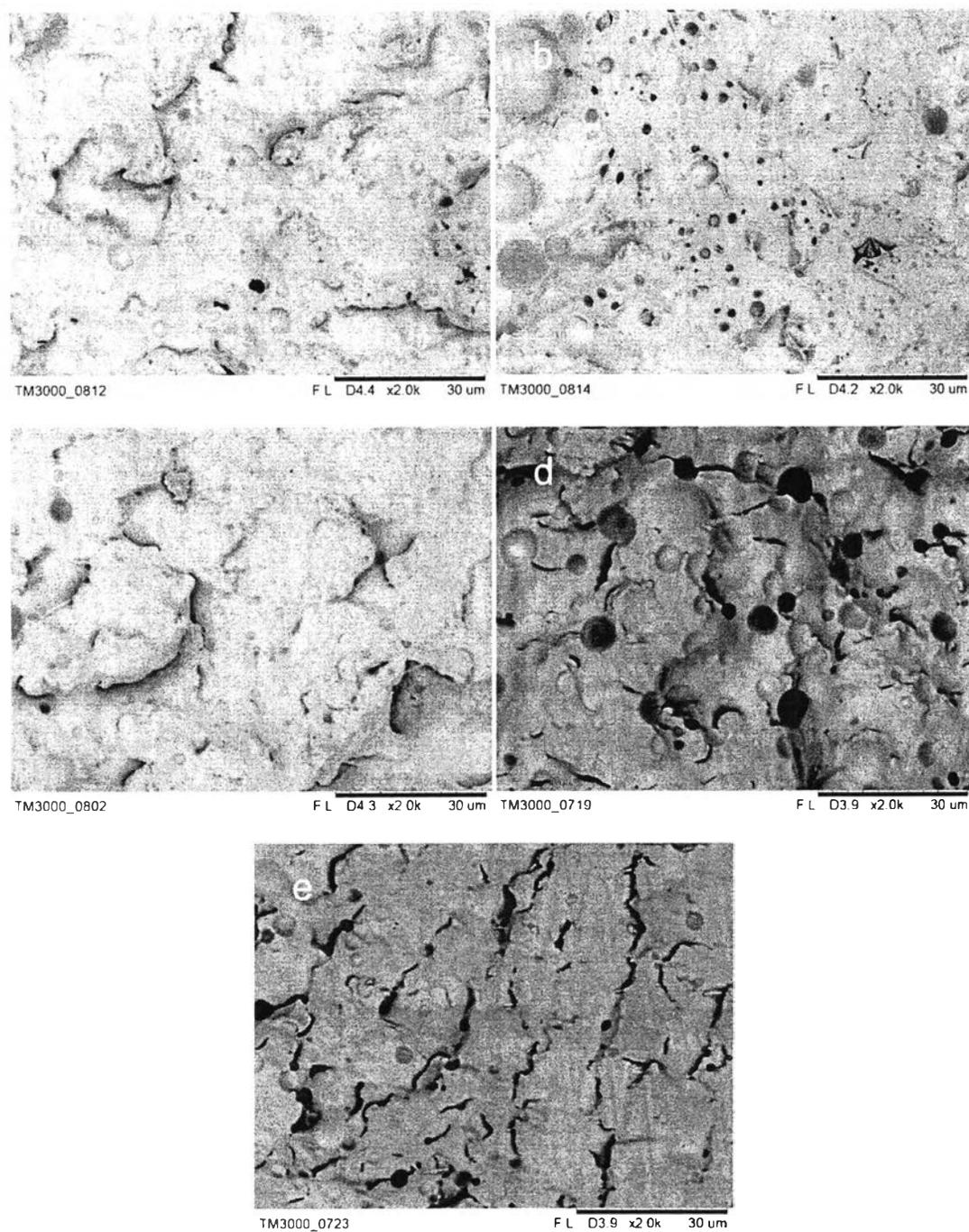


Figure 5.1 SEM images of 90/10 wt% PLA/admicelled rubber blends with CL-LA monomers ratio variation; a) 30:70, b) 40:60, c) 50:50, d) 60:40 and e) 70:30 for initiator to monomer mole ratio of 0.5:100

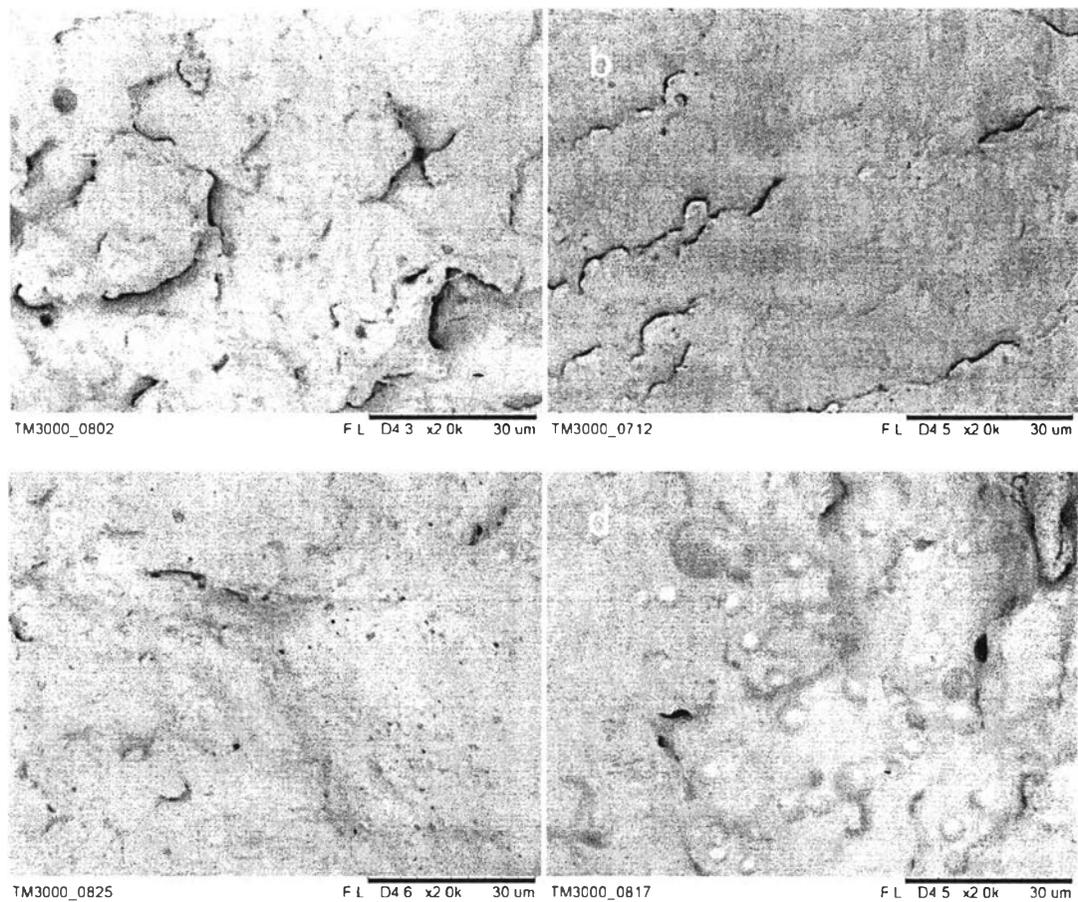


Figure 5.2 SEM image of 90/10 wt% PLA/admicelled rubber blends with initiator to monomers ratio variation; a) 0.5:100, b) 1.0:100, c) 1.5:100 and d) 2.0:100 for CL:LA monomer ratio = 50:50

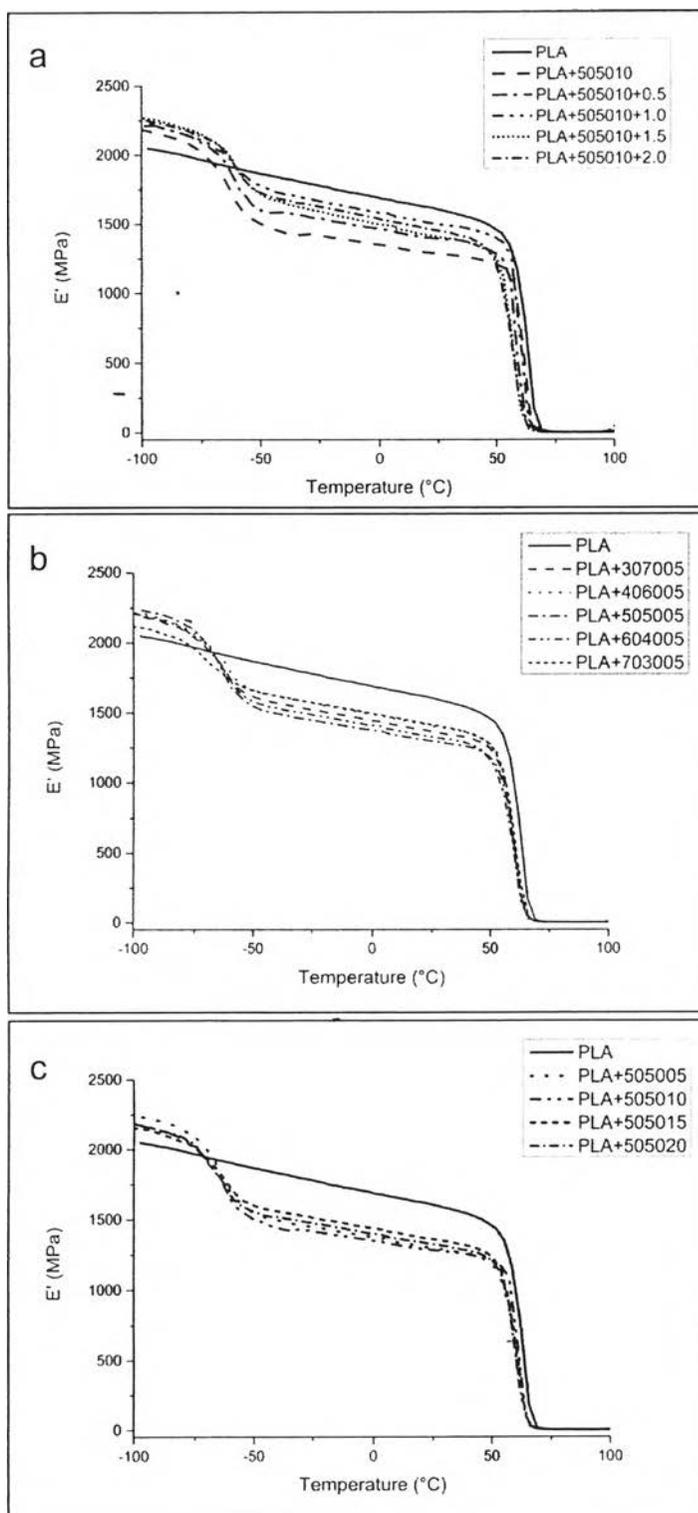


Figure 5.3 Storage modulus graph of blends with various factors; a) clay content, b) monomers ratio and c) initiator ratio

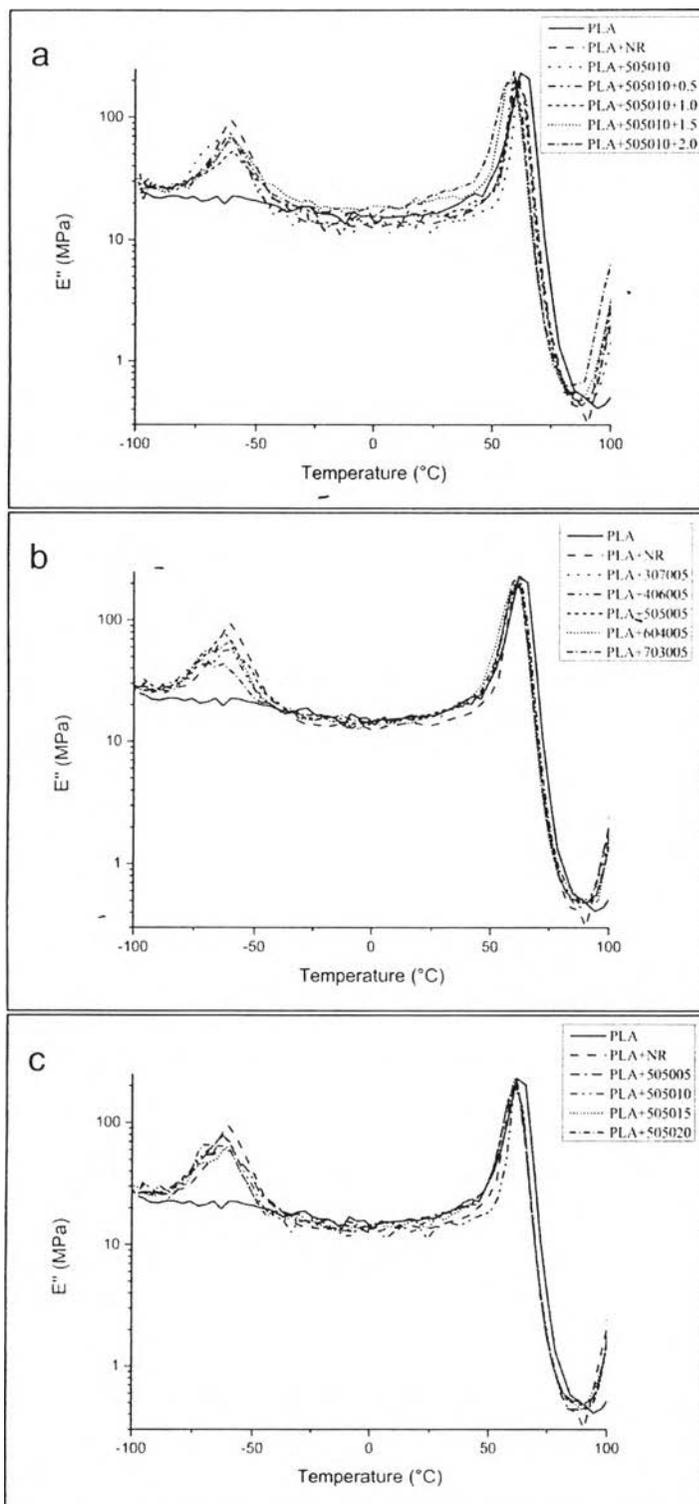


Figure 5.4 Loss modulus graph of blends with various factors; a) clay content, b) monomers ratio and c) initiator ratio

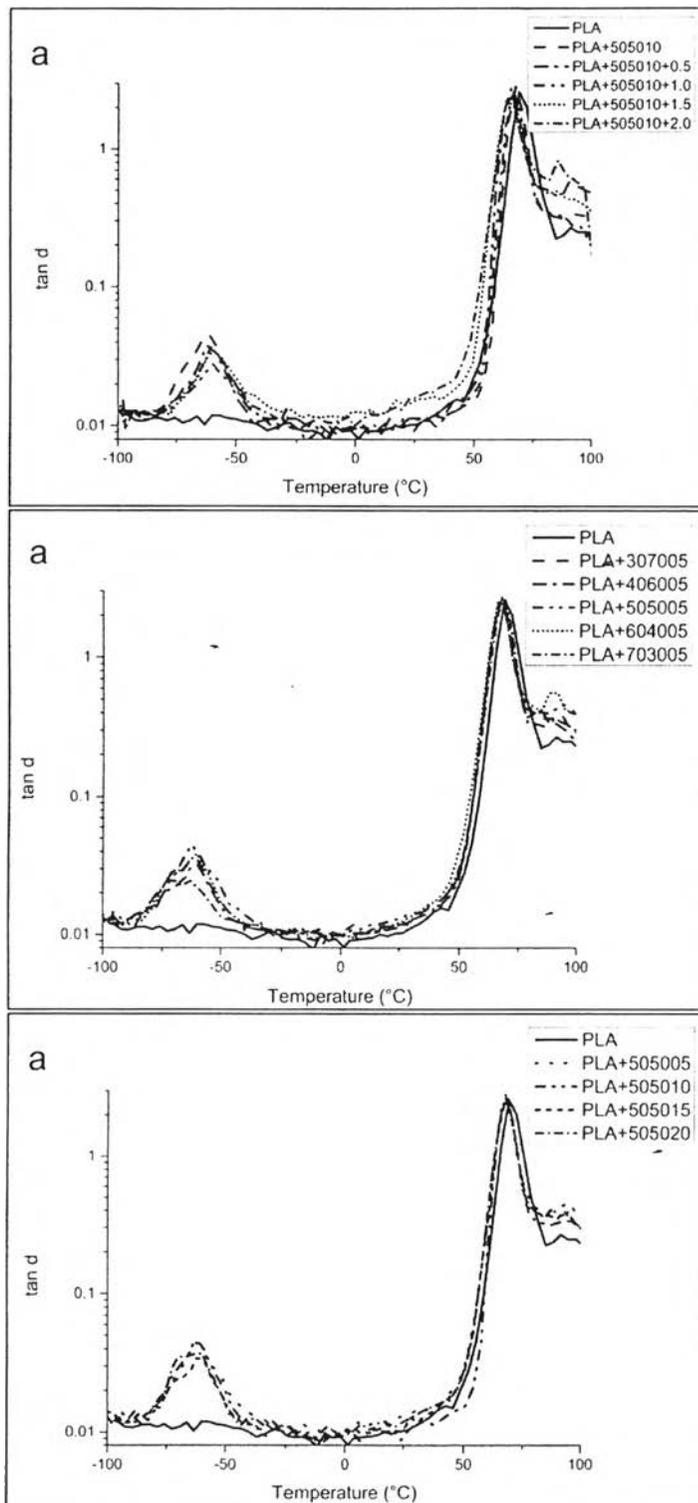


Figure 5.5 Tan δ (b, d and f) graph of blends with various factors; a) clay content, b) monomers ratio and c) initiator ratio

Table 5.1 Thermomechanical properties by DMA of PLA/admicelled rubber and PLA/admicelled rubber nanocomposite blends

Samples	Glass transition temperature (°C)		Area under tan δ	
	Rubber phase	PLA phase	Rubber phase	PLA phase
neat PLA	-	68.9	-	27.18
NR	-66.0 ^a	-	-	-
PLA/NR 90/10	-60.6	67.4	1.21	26.64
PLA+307005	-60.9	67.8	1.05	30.38
PLA+406005	-60.4	66.2	0.98	29.26
PLA+505005	-62.3	69.0	1.14	28.61
PLA+505010	-61.5	67.5	1.10	28.68
PLA+505010+0.5	-62.1	65.5	0.75	28.28
PLA+505010+1.0	-59.6	66.4	0.73	28.22
PLA+505010+1.5	-59.1	63.3	0.75	28.13
PLA+505010+2.0	-60.3	65.9	0.73	28.06
PLA+505015	-61.9	67.4	0.95	29.43
PLA+505020	-60.2	68.7	0.98	29.00
PLA+604005	-60.1	66.1	0.94	29.04
PLA+703005	-64.2	69.3	0.87	28.04

^a (Bendahou, A. et al. 2009)

5.4.3 D-spacing of Clay

Results from XRD were shown in table 5.2. After calculation of d-spacing with 2-theta value, it revealed that d-spacing increased when clay was incorporated with blends by using floss candy spinner. The neat organoclay showed d-spacing at 39.47 Å, while blends showed d-spacing more than 100 Å. That means clay was in intercalate state. However, 2-theta peak of blends with 1.5% clay did not

appear in testing range of instrument, that mean clay was in intercalate state with d-spacing more than 186.92 Å or it was exfoliated clay.

Table 5.2 2-Theta value from XRD and calculated d-spacing of organoclay in PLA blends

Samples	2-Theta (°)	D-spacing (Å)
Clay	6.2841	14.0535
Organoclay	2.2367	39.4667
PLA+505010+0.5	0.7871	112.1434
PLA+505010+1.0	0.6712	131.5149
PLA+505010+1.5	-	-
PLA+505010+2.0	0.4722	186.9226

5.4.4 Effect of Admicelled Particle Variation on Mechanical Properties

Impact testing results were shown in table 5.3. All PLA/admicelled rubber blends showed higher impact force than neat PLA. That means the blends had higher toughness than neat PLA. Otherwise, the blends also showed higher toughness than PLA/NR blends. This result revealed that surface modification, which increased compatibility between two phases, via admicellar polymerization caused increasing of toughness of material. Varied monomers ratios did not show effect on impact force that can be seen insignificant change of impact force when monomer ratio was varied, as seen in figure 5.4a. But, initiator to monomers ratio showed significant effect on impact force (figure 5.4b), increased initiator content caused increasing of impact force, because compatibility increased when initiator content was increased, as seen from SEM images results. Good compatibility caused good energy dissipation from PLA matrix to rubber phase. But, when initiator exceeded 1.5 %mole, impact force decreased because of decreasing of compatibility. Clay addition also affected impact force, impact force of PLA/admicelled nanocomposite blends decreased when clay content was increased as shown in figure 5.4c. This resulted of clay disrupted energy dissipation that caused higher brittle to PLA matrix (Nikkhah, S.J. et al. 2009).

Table 5.3 Impact testing result of PLA/admicelled rubber and PLA/admicelled rubber nanocomposite blends

Specimens	Impact Strength (J/m)
Neat PLA	59.24 ±0.909945
PLA+307005	61.6 ±0.282843
PLA+406005	61.52 ±0.798123
PLA+505005	61.72 ±0.109545
PLA+505010	61.28 ±0.363318
PLA+505010+0.5	44.82 ±0.248998
PLA+505010+1.0	44.62 ±0.204939
PLA+505010+1.5	44.48 ±0.109545
PLA+505010+2.0	44.16 ±0.151658
PLA+505015	76.06 ±2.025586
PLA+505020	70.32 ±0.931128
PLA+604005	61.36 ±0.167332
PLA+703005	61.24 ±0.45607

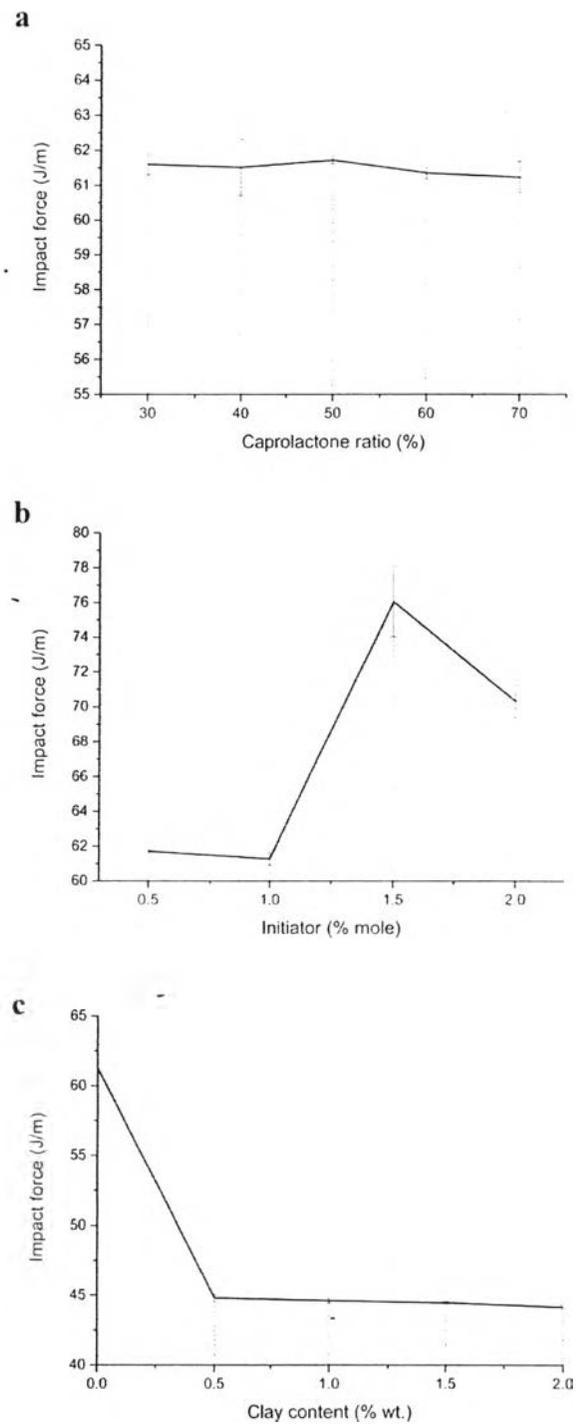


Figure 5.6 Effect of (a) caprolactone ratio, (b) initiator to monomers ratio and (c) clay content on impact strength of blends

5.5 Conclusion

Core-shell particles that were synthesized by using natural rubber as core and PCL/PLA as shell showed surface modification effect for natural rubber that increased compatibility in PLA/admicelled rubber blends. The result showed PLA/NR-PCL/PLA blends have their glass transition temperature shifted toward those of PLA and natural rubber. Clay content in nanocomposite also caused more compatibility to 2 phases. Monomers ratio of core-shell particles affected morphology of blends; large rubber domains was clearly observed when caprolactone component was increased. Initiator to monomers ratio affected impact strength; toughness increased when the ratio was increased until ratio exceeded 1.5:100 that showed decreasing of compatibility. PLA/admicelled rubber blends showed higher toughness than neat PLA and PLA/NR blend. Initiator to monomers ratio caused increasing impact strength by increasing compatibility between PLA and rubber phases. But clay generated brittleness or reducing impact strength to PLA. CL-LA ratios did not alter toughness of PLA.

5.6 Acknowledgements

The authors thank the partial scholarship provided by the Petroleum and Petrochemical College, Chulalongkorn University and the research funding by National Research Council of Thailand.

5.7 References

- Arends, C.B. (1996) Polymer Toughening. New York: Marcel Dekker, Inc.
- Bendahou, A., Kaddami, H., and Dufresne, A. (2009) Investigation on the effect of cellulosic nanoparticles' morphology on the properties of natural rubber based nanocomposites. European Polymer Journal, 46(4), 609-620.

- Bitinis, N., Verdejo, R., Maya, E.M., Espuche, E., Cassagnau, P., and Lopez-Manchado, M.A. (2011) Physicochemical properties of organoclay filled polylactic acid/natural rubber blend bionanocomposites. Composites Science and Technology, 72(2), 305-313.
- Cai, G.D., Yang, H.Y., Zhu, L.D., Liu, H., Wu, G.F., Zhang, M.Y., Zhou, C., Gao, G.H., and Zhang, H.X. (2012) Toughening polystyrene by core-shell grafting copolymer polybutadiene-graft-polystyrene with potassium persulfate as initiator. Journal of Industrial and Engineering Chemistry, 19(3), 823-828.
- Koo, J.H. (2006) Polymer Nanocomposites: Processing, Characterization, and Application New York: McGraw-Hill Companies
- Nikkhah, S.J., Ramazani S.A, A., Baniasadi, H., and Tavakolzadeh, F. (2009) Investigation of properties of polyethylene/clay nanocomposites prepared by new in situ Ziegler-Natta catalyst. Materials and Design, 30(7), 2309-2315.
- Rasal, R.M., Janorkar, A.V., and Hirt, D.E. (2009) Poly(lactic acid) modifications. Progress in Polymer Science, 35(3), 338-356.
- Storey, R.F., and Sherman, J.W. (2002) Kinetics and Mechanism of the Stannous Octoate-Catalyzed Bulk Polymerization of ϵ -Caprolactone. Macromolecules, 35(5), 1504-1512.
- Zhang, W., Chen, L., and Zhang, Y. (2009) Surprising shape-memory effect of polylactide resulted from toughening by polyamide elastomer. Polymer, 50(5), 1311-1315.