

CHAPTER IV

ADMICELLAR POLYMERIZATION OF PCL-PLA ON NR LATEX PARTICLES

4.1 Abstract

Natural rubber is a soft polymer which almost consists with cis-polyisoprene. It was used for toughness modification. However, its molecular structure may cause immiscibility between 2 phases. So, surface modification is necessary for improve miscibility. This work, natural rubber was modified its surface by core-shell particle formation via admicellar polymerization by using polycaprolactone-poly lactide copolymer as shell layer. Optical microscope and TEM revealed that core-shell structure of admicelled particles. That mean core-shell particles of natural rubber can be prepared via admicellar polymerization. IR spectra of shell layer showed characteristic peaks of PCL and PLA and also showed pattern of copolymer. TGA thermograms showed only single decomposition of the admicelled particles despite there were three components with insignificant effect of monomers and initiator to monomers ratios. Similarly, particle size or shell thicknesses were hardly altered by both monomers and initiator to monomers ratios

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

4.2 Introduction

Natural rubber is polymer which almost consists with cis-polyisoprene. It is soft polymer with high toughness. So, it is useful polymer for toughening other rigid polymers. However, its chemical structure shows immiscible with some rigid polymer, such as polylactide. N. Bitinis and coworkers showed reduction of mechanical properties of, such as Young's modulus and tensile strength, when natural rubber was blended with polylactide because poor miscibility between natural rubber surface and polylactide (Bitinis, N. et al. 2011). So, surface modification is necessary to improve compatibility between surface of rubber particles and the polymer. Core-shell particles formation is a method that can modified surface of particles. The core material, such as rubber, is coated with shell material that is compatible with rigid polymer matrix, such as rigid polymer itself. G.D. Cai and coworkers showed that core-shell particles of polybutadiene-graft-polystyrene improved toughness of polystyrene with slight reduction of tensile strength (Cai, G.D. et al. 2012). Admicellar polymerization is a method for core-shell formation using surfactant as shell layer template.

This work aimed to prepared core-shell particles of natural rubber via admicellar polymerization for surface modification. Copolymer of polycaprolactone and polylactide was used as shell layer of synthesized particles. ϵ -Caprolactone to ladtide and initiator to monomers ratio was varied during synthesis. Then, morphology and thermal stability of synthesized rubber particles were determined.

4.3 Experimental

4.3.1 Materials

Concentrated natural rubber latex with 60% dried rubber contents was purchase from Rubber Research Institute of Thailand, Kasetsart University. ϵ -Caprolactone (CL), ethylene glycol 99.8% and tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) ~95% were purchase from SIGMA-ALDRICH. Chloroform AR grade was purchase form RCI LABSCAN. Cetyltrimethylammonium bromide (CTAB) $\geq 98\%$ was

purchase from MERCK MILLIPORE. Lactide monomer (LA) (99.5% purity) was purchased from Shenzhen Bright China Industrial Co., Ltd.

4.3.2 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 Sn(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.

4.3.3 Morphology

Optical microscope, LEICA DMRXP, and transmission electron microscope (TEM), JEOL JEM-2100, were used to determined morphology and size of synthesized particles. The samples for TEM were prepared by dropped and dried diluted synthesized latex on copper grid. For optical microscope, the samples were prepared by dropped and dried diluted synthesized latex on cover glass.

4.3.4 Chemical Function Groups

Shell layer polymer was characterized chemical function groups by using Fourier-transform infrared spectrometer, Thermo-Nicolet NEXUS 670. The synthesized latex was dried and extracted with chloroform for shell polymer. After that, shell polymer solutions were cast into thin films which used as specimens.

4.3.5 Thermogravimetric analysis

Thermogravimetric analysis of synthesized rubber was carried out with Perkin-Elmer Pyris Diamond TG/DTA instrument. The synthesized latex was dried into rubber bulk. Then, 3 to 7 mg of dried rubber was feed into platinum pan.

The samples were heated from 30 to 700 °C under nitrogen atmosphere with heating rate of 10 °C/min. Thermograms were determined for degradation temperature.

4.4 Results and Discussion

4.4.1 Morphology and Particle Size of Synthesized Particles

Optical microscope and TEM images were shown at figure 4.1 and 4.2. They showed difference both shape and size between natural rubber particles and synthesized particles. Synthesized particles image (figure 4.1a, 4.2a) showed transparent layer around murk core that different from dark circle particles of natural rubber (figure 4.1b, 4.2b), which mean core-shell structure occurred from admicellar polymerization. TEM image also showed particle size of synthesized particles about 2.2 microns that bigger than natural rubber particles with particle size about 0.8 microns. Particle size was not affected by CL to LA ratio and initiator to monomers ratio, as shown in figure 4.3 and 4.4 and table 4.1 and 4.2. However, TEM images of synthesized particles with initiator to monomers ratio (figure 4.4) revealed that initiator to monomer ratio showed slightly effect on shell thickness of the particles, shell thickness decreased from 0.75 microns to 0.55 microns when initiator to monomers ratio was changed from 0.5:100 to 2.0:100, as shown in table 4.2.

According to work of C. Hazara and coworkers (Hazra, C. et al. 2014) and A. Kongsinlark and coworkers (Kongsinlark, A. et al. 2012), size of core-shell particles were influenced by content of core and shell materials and surfactant content for admicelled particles. In this work, all of those factors were fixed. So, we observed similar results that the synthesized particles did not show change of their size due to monomers or initiator to monomers ratios.

4.4.2 Chemical Functional Groups of Shell Layer Polymer

IR spectra of shell layer were shown at figure 4.5 and 4.6. All of them showed peaks of carbonyl group of polylactide and polycarprolactone at 1737 and 1712 cm^{-1} respectively, and ester linkage at 1130, 1089 and 1037 cm^{-1} . Therefore, varied CL to LA ratio slightly affected intensity of IR spectra at carbonyl group, at 1737 and 1712 cm^{-1} , which changed followed variation. On the other hand, initiator to monomers ratio didn't had any effect on IR spectra of synthesized particles.

According to work of H. Qian and coworkers, pattern of IR spectra showed that polymer in shell layer was PCL-PLA block copolymer (Qian, H. et al. 2000).

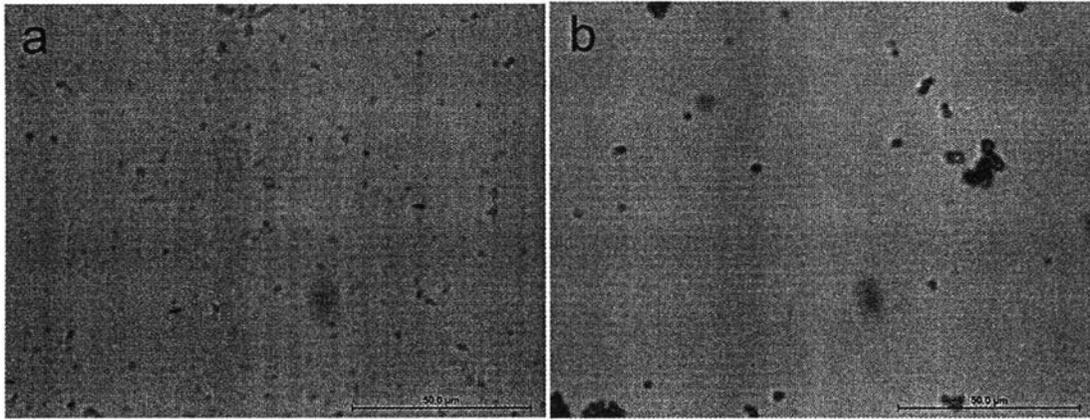


Figure 4.1 Optical microscope images of (a) natural rubber particles and (b) synthesized particles

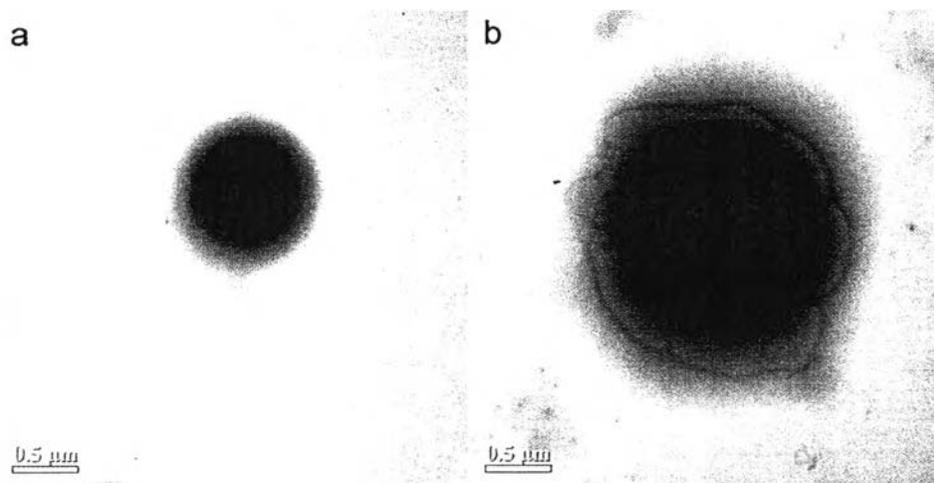


Figure 4.2 TEM images of (a) natural rubber particles and (b) synthesized particles

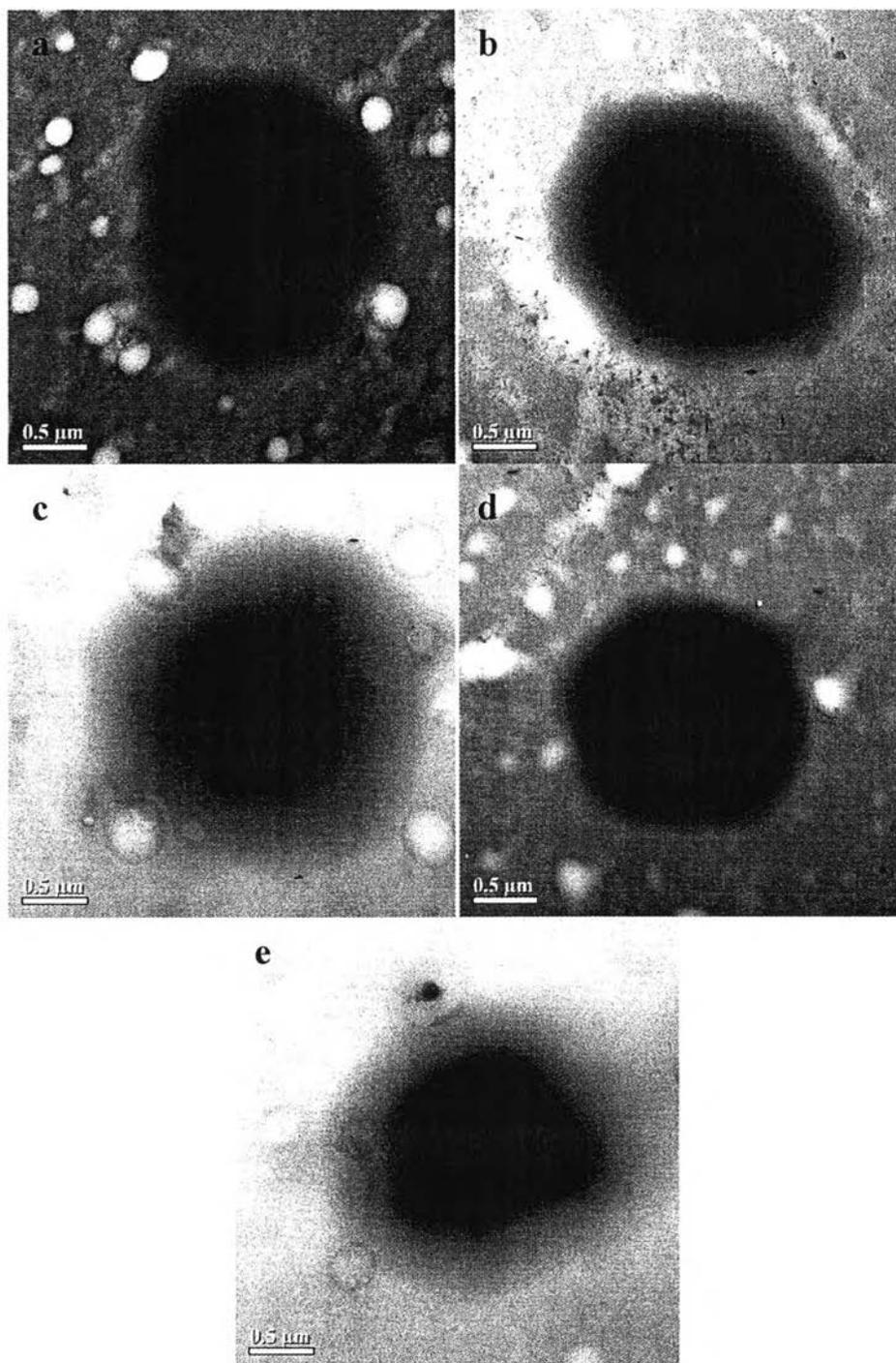


Figure 4.3 TEM image of synthesized particles with CL: LA monomers ratio variation; 30:70, b) 40:60, c) 50:50, d) 60:40 and e) 70:30, for initiator to monomer mole ratio of 0.5:100

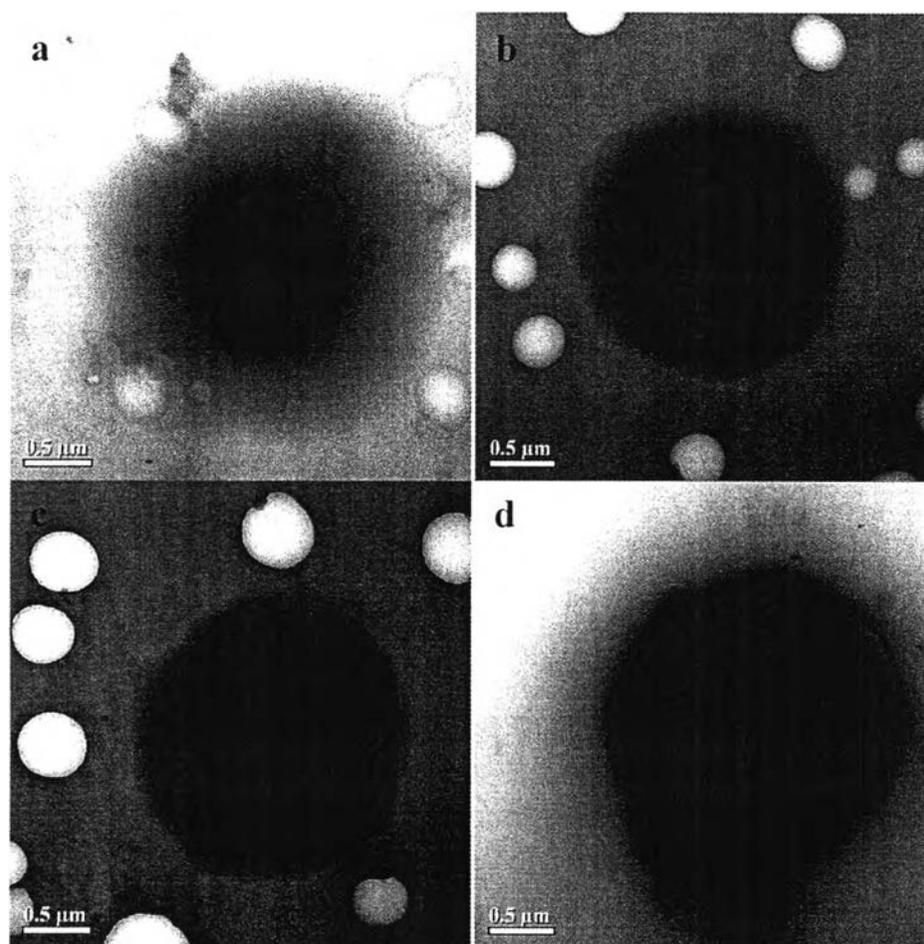


Figure 4.4 SEM image of synthesized particles with initiator to monomers ratio variation; a) 0.5:100, b) 1.0:100, c) 1.5:100 and d) 2.0:100 , for CL: LA monomer ratio = 50:50

Table 4.1 Size of synthesized particles with CL: LA monomers ratio variation for initiator to monomer mole ratio of 0.5:100, approximated from TEM images

Samples	Particle size (micron)	Core size (micron)	Shell Thickness (micron)
NR	-	1	-
307005	2.3	0.9	0.7
406005	2.3	0.9	0.7
505005	2.3	0.8	0.75
604005	2.1	0.9	0.6
703005	2.2	0.9	0.65

Table 4.2 Size of synthesized particles with initiator to monomers ratio variation for CL: LA monomer ratio = 50:50, approximated from TEM images

Samples	Particle size (micron)	Core size (micron)	Shell Thickness (micron)
NR	-	1	-
505005	2.3	0.8	0.75
505010	2.2	0.9	0.65
505015	2.1	0.9	0.6
505020	2	0.9	0.55

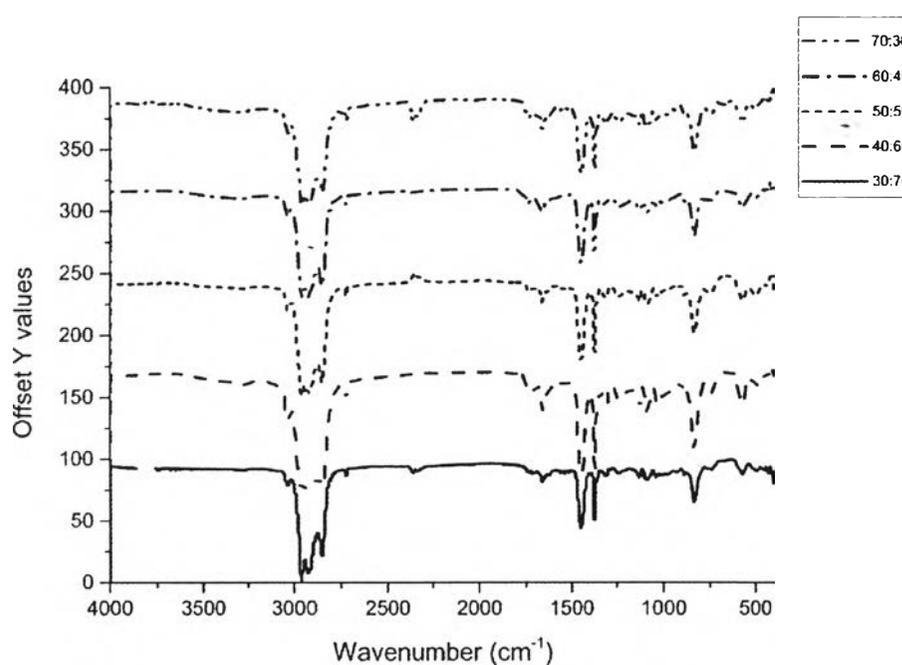


Figure 4.5 FTIR spectra of shell layer of synthesized particles with CL: LA monomers ratio variation for initiator to monomer mole ratio of 0.5:100

4.4.3 Thermogravimetric analysis of synthesized particles

TGA thermograms were shown at figure 4.7 and 4.8, and TGA results were shown at table 4.4 and 4.5. It showed that there is only one decomposition step although there are three components at content of 78-79 wt% NR, 5.6-13.2 wt% PCL and 7.2-16.4 wt% PLA, as shown in table 4.3. The admicellar polymerized particles had the onset decomposition temperature (T_d) about 347-350 °C, while natural

rubber had the onset T_d at 350.31 °C. Since the major component was NR, all three components could be decomposed together at temperature closed to decomposition temperature of NR. It is likely that the decomposition temperatures of the three components are closed despite that T_d of PCL is higher than that of PLA because of more ethyl group on the chain of PCL. This suggests good compatibility of the three components without adding any compatibilizer. The CL-LA ratio variation did not affect thermal stability of the admicellar polymerized particles defined by the onset temperature, but the residue was rather high for the one that had high PCL content. Similarly, initiator to monomers ratio variation did not show any effect on the onset thermal stability of the admicellar polymerized particles, but the residue was rather high for the one that had high initiator content. Moreover, the shell layer did not strongly improve thermal stability of natural rubber core, due to PCL and PLA have rather low T_d than NR, 353°C and 330°C respectively. (Pojanavaraphan, T. and Magaraphan, R. 2009)

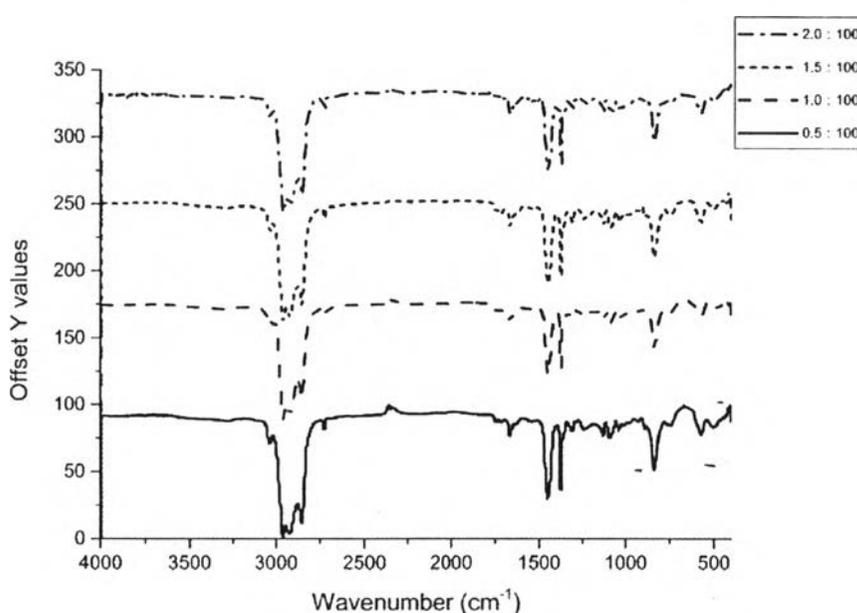
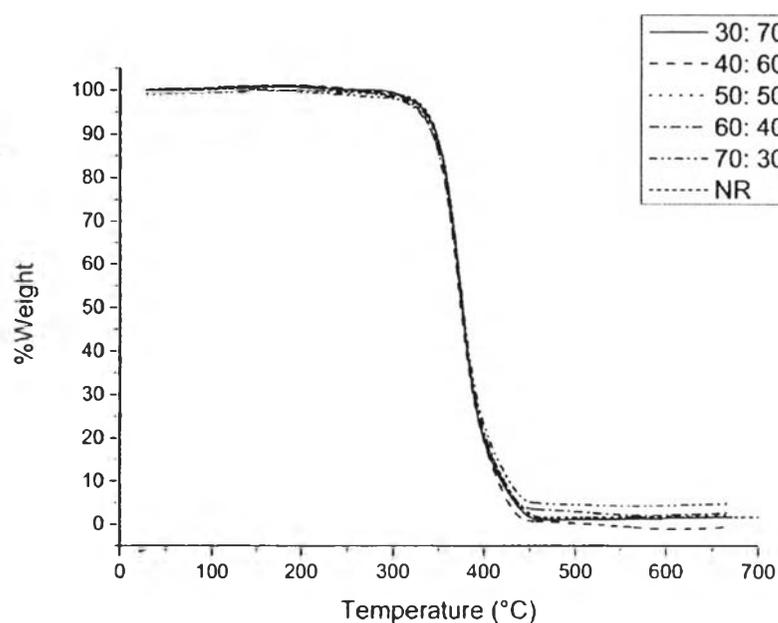


Figure 4.6 FTIR spectra of shell layer of synthesized particles with initiator to monomers ratio variation for CL: LA monomer ratio = 50:50

Table 4.3 Mass percentage of components in admicelled rubber.

Admicelled rubbers	NR Mass (g)	PCL mass (g)	PLA mass (g)	Overall mass (g)	%wt. of NR	%wt. of PCL	%wt. of PLA
307005	144.065	10.27	30.27	184.60	78.04	5.56	16.40
406005	144.065	13.70	25.94	183.71	78.42	7.46	14.12
505005	144.065	17.12	21.62	182.81	78.81	9.37	11.83
604005	144.065	20.55	17.30	181.91	79.20	11.29	9.51
703005	144.065	23.97	12.97	181.01	79.59	13.24	7.17

**Figure 4.7** TGA thermogram of synthesized particles with CL: LA monomers ratio variation for initiator to monomer mole ratio of 0.5:100

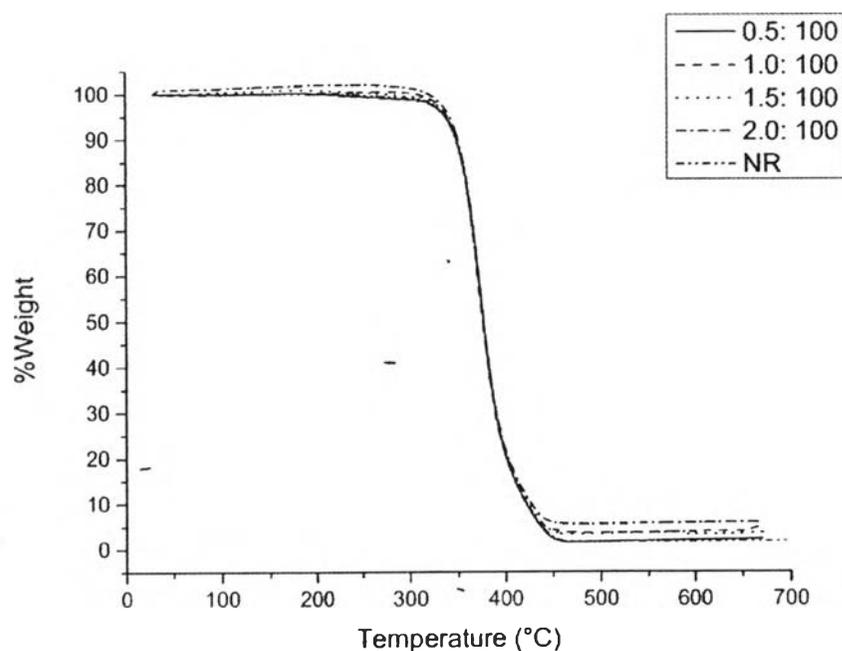


Figure 4.8 TGA thermogram of synthesized particles with initiator to monomers ratio variation for CL: LA monomer ratio = 50:50

Table 4.4 Degradation temperature of synthesized particles with CL: LA monomers ratio variation for initiator to monomer mole ratio of 0.5:100

Samples	T_d onset	$T_{d0.9}$	$T_{d0.5}$	$T_{d0.1}$	Residue
NR	350.31	348.25	376.54	422.86	1.72
PCL	353 ^a	332.5 ^a	-	-	-
PLA	330.41	326.66	348.18	363.82	0.74
307005	349.30	347.54	377.14	420.23	1.78
406005	347.05	343.46	375.29	416.31	0
505005	349.41	348.25	377.01	421.68	2.28
604005	347.04	343.45	376.38	422.87	2.74
703005	349.91	346.40	377.76	428.40	4.94

^a(Vilay, V. et al. 2010)

Table 4.5 Degradation temperature of synthesized particles with initiator to monomers ratio variation for CL: LA monomer ratio = 50:50

Samples	T _d onset	T _{d0.9}	T _{d0.5}	T _{d0.1}	Residue
NR	350.31	348.25	376.54	422.86	1.72
PCL	353 ^a	332.5 ^a	-	-	-
PLA	330.41	326.66	348.18	363.82	0.74
505005	349.41	348.25	377.24	421.68	2.28
505010	348.89	348.69	376.06	421.41	3.93
505015	349.38	348.89	377.24	424.56	3.55
505020	348.55	350.09	377.13	426.91	5.94

^a(Vilay, V. et al. 2010)

4.5 Conclusion

Core-shell particles of natural rubber fully covered by PCL-co-PLA were successfully prepared by admicellar polymerization. Moreover, it showed that the copolymer shell (not just homopolymer) could be prepared by admicellar polymerization as confirmed by ester linkage via FTIR absorption. The admicellar polymerized particles showed bigger size than natural rubber particles. The PCL-PLA shell did not sufficiently improve thermal stability of rubber core because they have rather low T_d than NR. There is only single decomposition which amazingly reveals good miscibility of the three components. The effect of CL to LA ratio and initiator to monomers ratio on size of particles, FTIR absorption patterns and decomposition temperatures were quite insignificant.

4.6 Acknowledgements

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4.7 References

- Bitinis, N., Verdejo, R., Cassagnau, P., and Lopez-Manchado, M.A. (2011) Structure and properties of polylactide/natural rubber blends. Materials Chemistry and Physics, 129(3), 823-831.
- 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.
- Hazra, C., Kundu, D., Chatterjee, A., Chaudhari, A., and Mishra, S. (2014) Poly(methyl methacrylate) (core)-biosurfactant (shell) nanoparticles: Size controlled sub-100 nm synthesis, characterization, antibacterial activity, cytotoxicity and sustained drug release behavior. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 449, 96-113.
- Kongsinlark, A., Rempel, G.L., and Prasassarakich, P. (2012) Synthesis of monodispersed polyisoprene-silica nanoparticles via differential microemulsion polymerization and mechanical properties of polyisoprene nanocomposite. Chemical Engineering Journal, 193-194, 215-226.
- Pojanavaraphan, T., and Magaraphan, R. (2009) Fabrication and characterization of new semiconducting nanomaterials composed of natural layered silicates (Na⁺-MMT), natural rubber (NR), and polypyrrole (PPy). Polymer, 51(5), 1111-1123.
- Qian, H., Bei, J., and Wang, S. (2000) Synthesis, characterization and degradation of ABA block copolymer of L-lactide and ϵ -caprolactone. Polymer Degradation and Stability, 68(3), 423-429.
- 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.
- Vilay, V., Mariatti, M., Ahmad, Z., Pasomsouk, K., and Todo, M. (2010) Improvement of microstructures and properties of biodegradable PLLA and PCL blends compatibilized with a triblock copolymer. Materials Science and Engineering: A, 527(26), 6930-6937.