

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Natural Rubber

Natural rubber is a natural polymer that obtains from juice of trees name *Hevea brasiliensis*. The juice is milk-white latex that contains polymer, sterols, proteins, fats and salt in colloid form. Rubber is obtained by coagulation with acid or evaporation. The polymer in natural rubber consists almost of cis-poly(isoprene) with molecular weight about 300,000 - 500,000 (Nicholson, J.W. 1991). Rubber is soft and flexible polymer. It has high toughness. So, it is used as toughness modifier for rigid polymer such as polystyrene and polylactide. A.P. Mathew and S. Thomas revealed that natural rubber modified toughness of polystyrene. The polystyrene/natural rubber blend showed higher impact strength than neat polystyrene (Mathew, A.P. and Thomas, S. 2010). V. Tanrattanakul and coworkers also showed that nylon 6/natural rubber blend showed toughness modification by increasing impact strength. But, epoxide natural rubber blend showed higher toughness, because epoxide natural rubber was compatible with nylon 6 better than natural rubber (Tanrattanakul, V. et al. 2008). That mean, good compatibility between phase affect to toughness improvement.

**Table 2.1** Cross-link density and izod impact strength values of IPNs.(Mathew, A.P. and Thomas, S. 2010)

Sample code	DVB content (wt.%)	NR/PS ratio	Cross-link density ( $\nu$ ) $\times 10^4$ (g mol/cm <sup>3</sup> )	Impact strength (J/m)	Resilience
PS	0	0:100	—	56	4.68
D <sub>0</sub> N <sub>20</sub>	0	30:70	7.43	167	17.65
D <sub>0</sub> N <sub>40</sub>	0	40:60	6.91	105	9.68
D <sub>0</sub> N <sub>60</sub>	0	50:50	6.07	102	9.12
D <sub>1</sub> N <sub>20</sub>	2	30:70	9.81	183	17.05
D <sub>1</sub> N <sub>40</sub>	2	40:60	7.63	154	15.38
D <sub>1</sub> N <sub>60</sub>	2	50:50	6.74	76.7	7.62
D <sub>2</sub> N <sub>20</sub>	4	30:70	12.35	127	11.82
D <sub>2</sub> N <sub>40</sub>	4	40:60	10.91	201	17.95
D <sub>2</sub> N <sub>60</sub>	4	50:50	9.96	142	12.71
D <sub>3</sub> N <sub>20</sub>	6	30:70	18.33	47	4.67
D <sub>3</sub> N <sub>40</sub>	6	40:60	16.81	209	20.28
D <sub>3</sub> N <sub>60</sub>	6	50:50	15.09	114	10.22

**Table 2.2** Cross-link Effect of rubber type on tensile properties and impact strength of the blends containing 30% uncompounded rubber.(Tanrattanakul, V. et al. 2008)

Rubber	$\sigma_y$ (MPa)	$\varepsilon_y$ (%)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Impact strength (kJ/m <sup>2</sup> )
–	81.97 ± 4.56	19 ± 1	74.37 ± 11.59	45 ± 13	6.38 ± 2.43
ENR	23.64 ± 0.82	11 ± 1	28.35 ± 4.00	60 ± 10	34.51 ± 6.97
NR	39.47 ± 2.09	12 ± 1	45.26 ± 2.43	51 ± 8	6.80 ± 1.55

## 2.2 Core-shell Particles

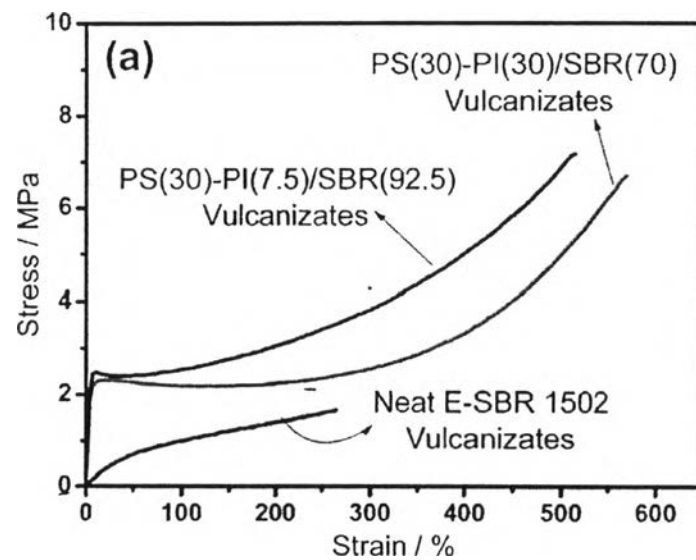
Core-shell particles are synthesized particles consist different of properties between inner core and outer shell. These particles can be blended with matrix for properties improvement, especially mechanical properties(Paul, D.R. and Bucknall, C.B. 2000). Core-shell can be produced by coating shell polymer on core substance's surface, such as natural rubber and silica, via grafting, emulsion and admicellar polymerization. Parameters for properties improvement of core-shell particles are particle diameter, shell thickness, properties of core and shell and interaction between shell and matrix materials(Arends, C.B. 1996). These particles can be classified to 2 type, stiff core and soft core particles.

### 2.2.1 Stiff core particles

Core of these particles is inorganic particles and rigid polymers, such as silica(Wang, Q. et al. 2011), titania(Meng, B. et al. 2010) and polystyrene(Lu, M. et al. 2012). Core materials, called seeds, are encapsulated with thin film soft or rubbery polymer. Purposes of these particles addition are improvement tensile strength and modulus to blends(Adeli, M. 2008).

### 2.2.2 Soft core particles

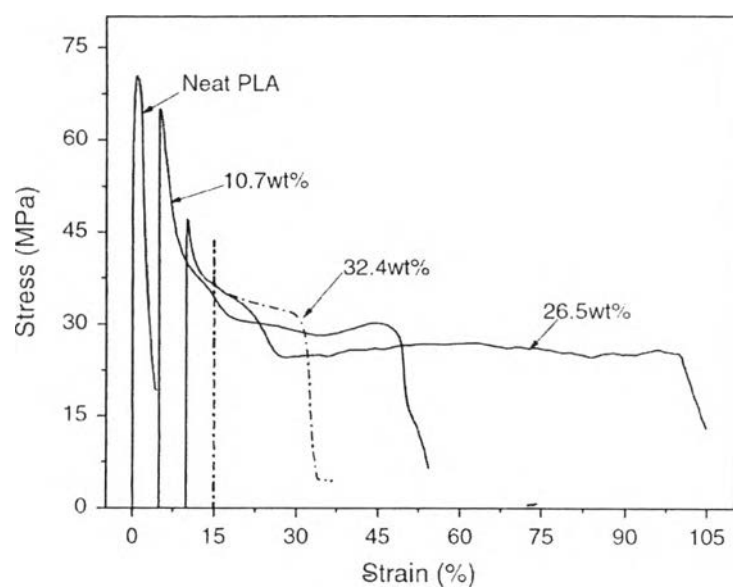
These particles consist with soft and rubbery polymeric core, such as natural rubber(Pojanavaraphan, T. and Magaraphan, R. 2009) and polybutadiene(Cai, G.D. et al. 2012), those are surrounded by rigid polymeric shell, such as polystyrene and polypyrrole. Addition these particles cause toughness and elongation at break improvement to blends(Collier, A.A. 1994).



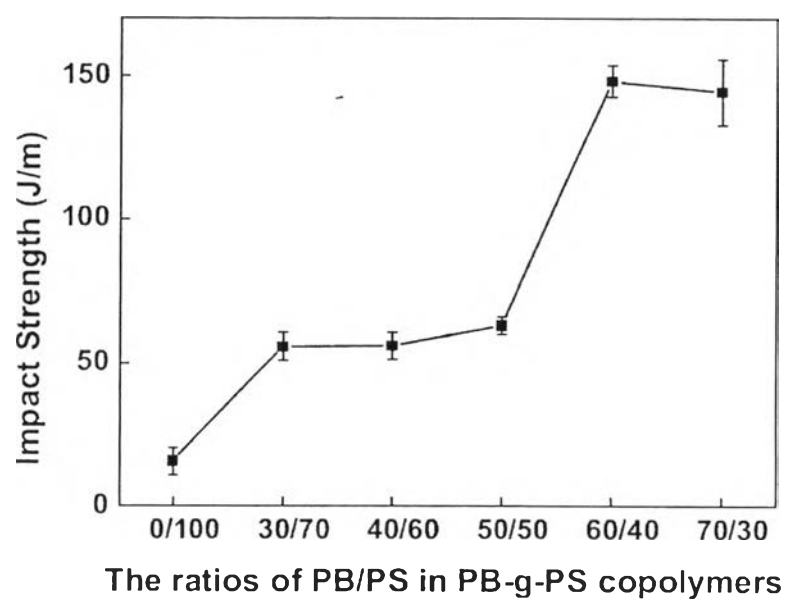
**Figure 2.1** Mechanical properties of the PS-PI nanoparticles filled SBR composites.(Lu, M. et al. 2012)

**Table 2.3** Tensile properties of pure NR and its nanocomposites ( $\text{SiO}_2/\text{NR} = 2/100$  w/w).(Wang, Q. et al. 2011)

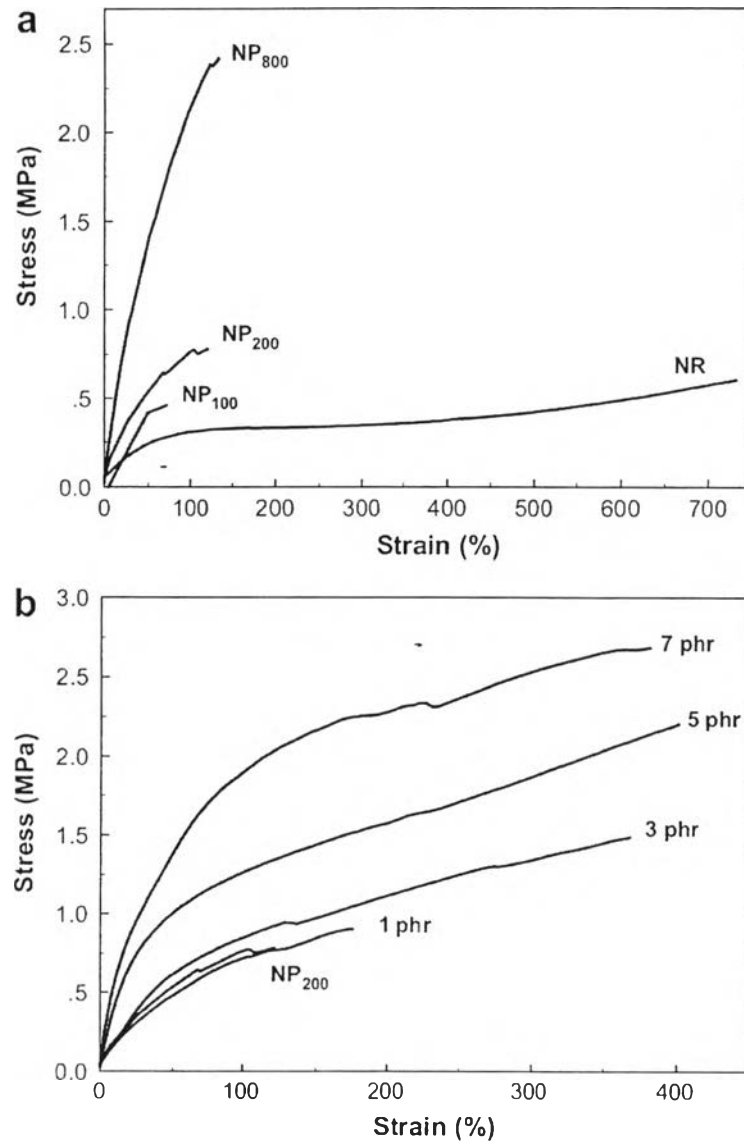
Samples	NR	NR-PMMA	NR-PMMA/ $\text{SiO}_2$	NR-PMMA/ $\text{SiO}_2$ -PMMA
Tensile strength/MPa	6.99	7.23	8.95	10.65
Elongation at break/%	835	823	772	773
Tensile modulus/MPa				
300% elongation	0.92	0.82	1.22	1.95
500% elongation	1.00	0.94	1.46	2.32
700% elongation	1.58	2.06	2.96	3.37



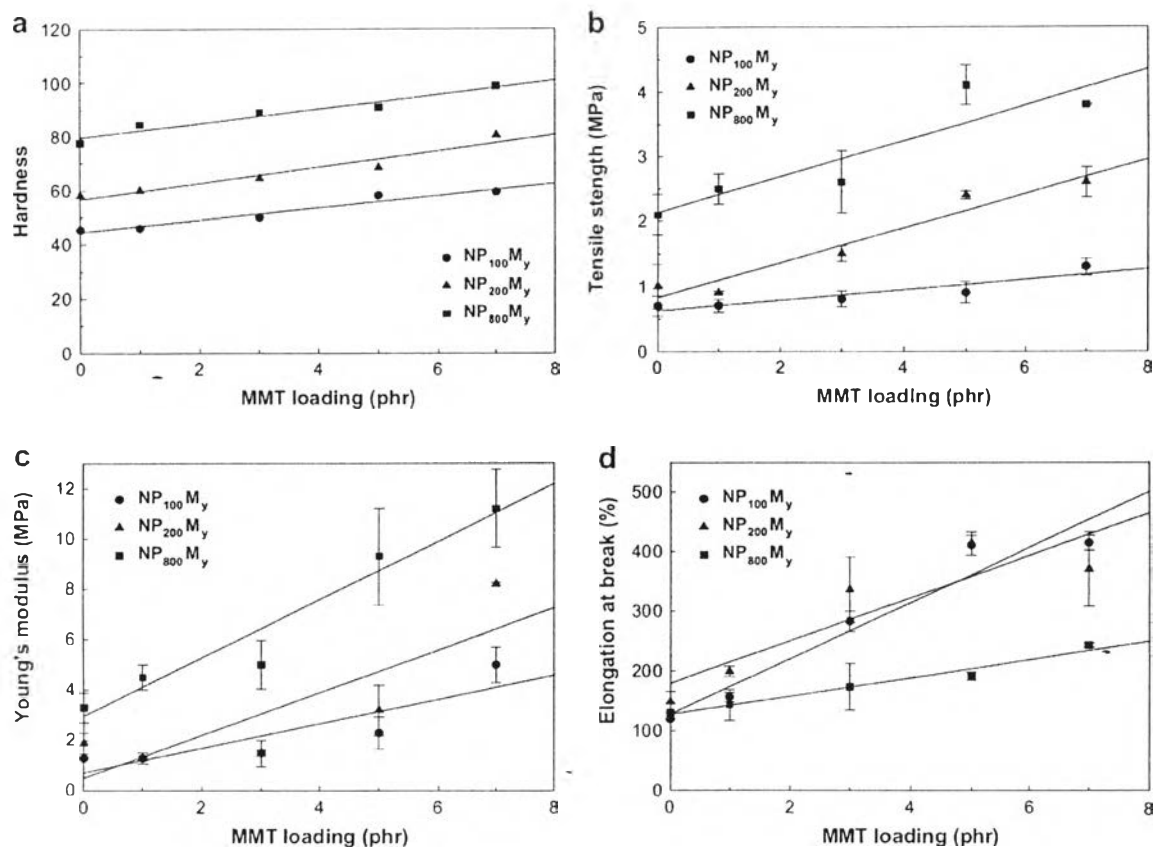
**Figure 2.2** Stress–train curves of different C-TiO<sub>2</sub> contents; curves were shifted along the strain axis (increments of 5%) for clarity.(Meng, B. et al. 2010)



**Figure 2.3** The impact strength of PS/PB-g-PS blends with various compositions of PB-g-PS copolymers.(Cai, G.D. et al. 2012)



**Figure 2.4** Typical stress–strain curves of (a) pure NR and NP<sub>x</sub> composites, and (b) NP<sub>200</sub> and NP<sub>200M</sub>, series. (Pojanavaraphan, T. and Magaraphan, R. 2009)



**Figure 2.5** Dependence of the mechanical properties of the NP100My, NP200My, and NP800My series on clay loading: (a) hardness, (b) tensile strength, (c) Young's modulus, and (d) elongation at break. (Pojanavaraphan, T. and Magaraphan, R. 2009)

### 2.3 Admicellar Polymerization

Admicellar polymerization is a surface modification method by coating thin layer of polymer on substrate surface, such as rubber particle and fiber. Surfactants are key substance for this method. Surfactants form into bilayer and surround substrate's surface, then they act as template for thin layer polymer by limit area of polymerization. Admicellar polymerization is carried out with 4 steps (Genetti, W.B. et al. 1998).

### 2.3.1 Admicelle Formation

Surfactant molecules form bilayer and adsorb on substrate surface to be admicelle. Concentration of surfactant is below the critical micelle concentration but sufficient for admicelle formation.

### 2.3.2 Solubilization

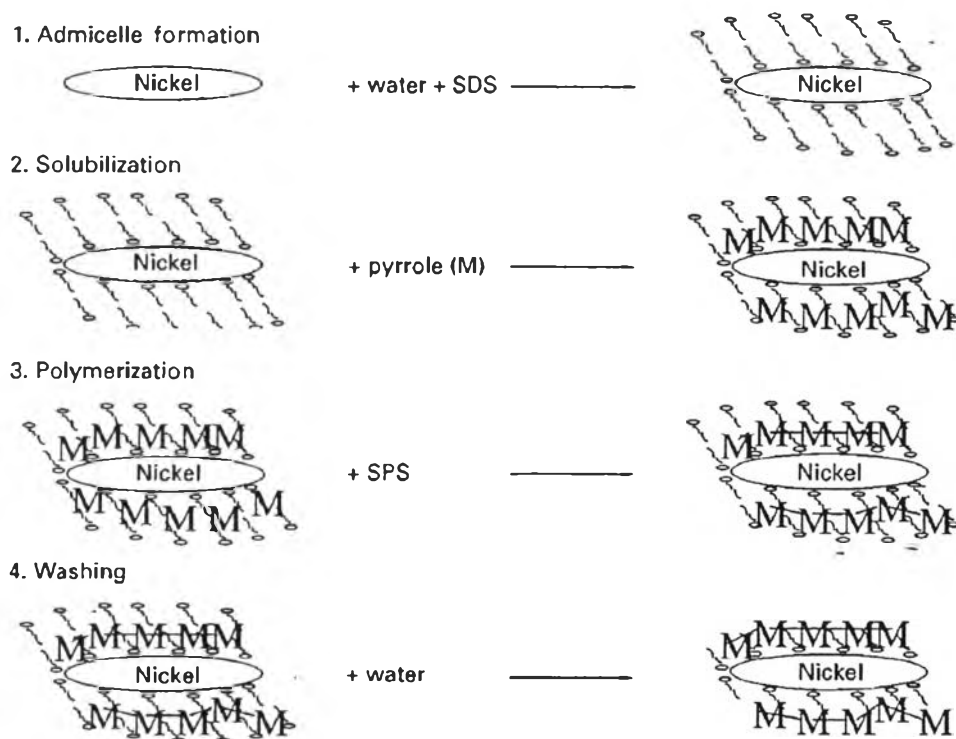
Monomers are added and dissolve into admicelle layer. Admicelle bilayer cage monomers and force them to surround substrate particles.

### 2.3.3 Polymerization

Monomers are polymerized when initiator and catalyst appear in admicelle system. Thin films are formed and coated on substrate surface.

### 2.3.4 Washing

Outer layer of admicelle is washed out with water.



**Figure 2.6** Steps in admicellar polymerization.(Genetti, W.B. et al. 1998)

## 2.4 Polylactide

Polylactide or polylactic acid is biodegradable polyester that is produced from renewable resource. Biomass is fertilized and becomes lactic acid or lactide monomer, after those monomers are polymerized to be polylactide by condensation or ring-opening polymerization (Lasprilla, A.J.R. et al. 2011; Rasal, R.M. et al. 2009).

Advantage of polylactide

1. Eco-friendly
2. Biocompatibility
3. Processibility
4. Energy saving

Although polylactide has many advantages, it also has some limitations.

1. Poor toughness
2. Slow degradation rate
3. Hydrophobicity
4. Lack of reactive side-chain group

These disadvantages restrict many applications. So, toughness modifications are necessary for polylactide before usage.

## 2.5 Toughness Modifications of Polylactide

Polylactide has low toughness and cause problem for many applications. That mean toughness modification is necessary to polylactic acid. Approaches for toughness improvement can separate to 3 ways (Rasal, R.M. et al. 2009).

### 2.5.1 Stereochemical

Lactide has three stereoisomers; L-lactide, D-lactide and meso-lactide. These isomers composition can cause different properties of material. Mixture of pure poly(L-lactide) and poly(D-lactide) with ratio 1:1 show better mechanical properties than pure polymer because of 'Stereocomplex' (Tsuji, H. and Ikada, Y. 1999). Polylactide chain with some meso-lactide has lower crystalline rate than pure poly(L-lactide), that cause more amorphous part and more toughness in material.

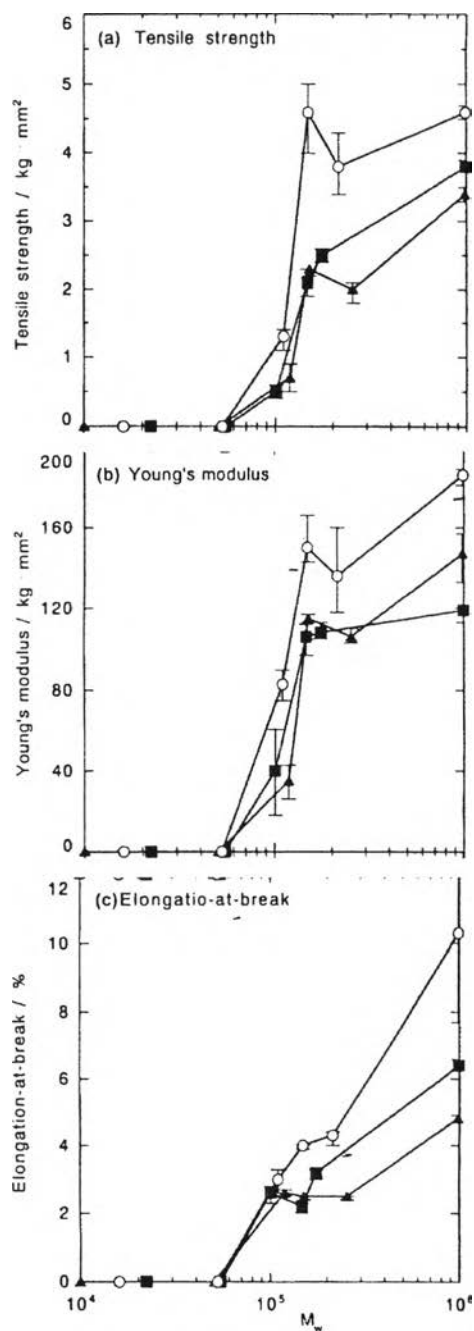


### 2.5.2 Copolymerization

Poly lactide can copolymerize with other polymers or monomers by both polycondensation and ring-opening copolymerization. Poly lactide can copolymerize with both diol or diacid monomers and acid-end or hydroxyl-end polymers via condensation copolymerization (Yoon, J.-S. et al. 1999). This approach's advantage is control of chain's end groups, either hydroxyl or carboxyl groups. But disadvantage is low molecular weight (Huh, K.M. and Bae, Y.H. 1999). This disadvantage can be solved by using chain extender such as diisocyanate. Poly lactide can copolymerize with ring monomer, such as  $\epsilon$ -caprolactone, via ring opening polymerization with catalyst. This approach give high molecular weight and precisely chemistry control polymer chain (Huang, M.-H. et al. 2004; Qian, H. et al. 2000). Copolymerization decrease crystalline of poly lactide and increase toughness of material, but phase separation can occurs and decrease mechanical properties.

### 2.5.3 Blending

This approach is the most extensive way for poly lactic acid toughening. There are 3 types of substance for blending. Plasticizers are low molecular weight substance for blending. Plasticizers can reduce stiffness of poly lactide, increase ductility and productivity. M. Murariu et al. founded that poly lactic acid with ester-like plasticizers had more elongation at break than neat poly lactide (Murariu, M. et al. 2008).



**Figure 2.7** (a) Tensile strength, (b) Young's modulus, and (c) elongation-at-break of 1:1 blend films (W), non-blended PLLA films (O), and nonblended PDLA films (B) as a function of  $M_w$ . (Tsuji, H. and Ikada, Y. 1999)

Disadvantage of plasticizers was severe decreasing of tensile strength and Young's modulus and plasticizer migration that can deteriorate polylactide. Second blending substance is non-biodegradable fillers, such as soft non-biodegradable polymers and inorganic particles. Soft non-biodegradable polymers show impact strength and toughness improvement when they are added to polylactide. Q. Zhou and coworkers study to modified toughness of polylactide with ultrafine full-vulcanized powdered rubber and found that both tensile and impact toughness increased with rubber content (Zhao, Q. et al. 2013). Although, addition inorganic particles, such as calcium carbonate and nanoclays, to polylactide increase tensile strength and modulus because stiffness of particles, but B. Li et al. and L. Jiang et al. showed that small amount of particles in polylactide matrix can improved toughness of polylactide (Jiang, L. et al. 2007; Li, B. et al. 2009). Disadvantages for these blending substances are polylactide's biodegradability disruption and mechanical properties reduction at high content of clay. Last blending substance is other biodegradable polymers. This substance improves toughness of polylactide without compromise biodegradability. Z. Xiong et al. blended polylactide with starch and epoxidized soybean oil, and found that toughness of polylactide was improved(Xiong, Z. et al. 2012). But miscibility between polylactide and added polymers must be concerned, If they are immiscible blend, mechanical properties, such as modulus and tensile strength, are reduced because phase separation. This problem can be solved by addition compatibilizers, such as copolymer between polylactide and added polymers(Imre, B. and Pukánszky, B. 2013).

**Table 2.4** Tensile properties of the PLLA–EVA85 blends.(Yoon, J.-S. et al. 1999)

Sample	Stress at break (kg mm <sup>-2</sup> )	Tensile modulus (kg mm <sup>-2</sup> )	Strain at break (%)
PLLA100	5.7	219	4.5
PLLA90	4.6	184	4.7
PLLA70	3.3	134	6.9
PLLA50	1.7	130	10.2
PLLA30	1.7	131	9.0
PLLA10	1.4	64	208.9
EVA85	1.4	62	244.9

**Table 2.5** Molecular weight, molecular weight distribution and block ratio of PEG/PLLA multiblock copolymers. nd: not determined.(Huh, K.M. and Bae, Y.H. 1999)

Block length (PEG/PLLA)	Yield (%)	$M_n^a$	$M_w^a$	$M_w/D^a$	Block ratio <sup>b</sup> (PEG/PLLA)
1000:1690	82	19 400	26 100	1.35	1.02
1500:1690	nd	14 000	23 100	1.65	1.05
2000:820 <sup>c</sup>	77	8800	15 300	1.74	1.25
2000:1130 <sup>c</sup>	80	14 800	21 900	1.48	0.95
2000:1130	nd	31 100	40 100	1.29	1.07
2000:1430 <sup>c</sup>	nd	9300	13 200	1.42	1.60
2000:1480	nd	31 400	41 400	1.32	1.13
2000:1690	86	33 100	41 300	1.25	1.10
2000:1990	84	25 000	33 400	1.34	0.97
2000:2170	87	15 700	23 800	1.52	0.94
2000:3150	90	12 300	21 000	1.71	1.18

<sup>a</sup> Determined by GPC.

<sup>b</sup> Calculated from <sup>1</sup>H-NMR spectra

<sup>c</sup> Water-soluble block copolymers

**Table 2.6** Thermal properties, mechanical properties, and water absorption of the block copolymers.(Qian, H. et al. 2000)

Sample	LA/CL (mol/mol)	$T_m$ (CL) (°C)	$T_m$ (LA) (°C)	$\Delta H_m$ (CL) (J/g)	$\sigma$ (MPa)	$\epsilon$ (%)	Water absorption (%)
C-1	90/10	44.9		1.55	63.2	Brittle	1.09
C-2	80/20	51.1	155.1	3.86			
C-3	70/30	51.1	153.4	6.68	40.2	443	1.12
C-4	60/40	52.3	152.9	11.3			
C-5	50/50	53.9	152.0	21.8	37.8	791	0.24
C-6	30/70	53.4	149.7	32.6	22.1	661	0.48

**Table 2.7** Block copolymers of different compositions.(Qian, H. et al. 2000)

Sample	Initiator: $\epsilon$ -CL (mol/mol)	L-LA/ $\epsilon$ -CL <sup>a</sup> (mol/mol)	Yield (%)	L-LA/ $\epsilon$ -CL <sup>b</sup> (mol/mol)	$[\eta]$ (dl/g)	$M_w^c$ ( $10^{-4}$ )
P-1	1:100	0:100	94.1	0:100	0.45	
P-2	0.5:100	0:100	95.2	0:100	0.75	
C-1	0.5:100	90:10	97.0	89:11	2.84	15.6
C-2	0.5:100	80:20	93.0	79:21	1.61	9.68
C-3	0.5:100	70:30	94.8	70:30	1.44	8.67
C-4	0.5:100	60:40	92.8	60:40	1.16	8.67
C-5	0.5:100	50:50	94.5	50:50	0.97	6.93
C-6	0.5:100	30:70	95.0	28:72	0.83	6.37

<sup>a</sup> Feed ratio of L-LA and  $\epsilon$ -CL.

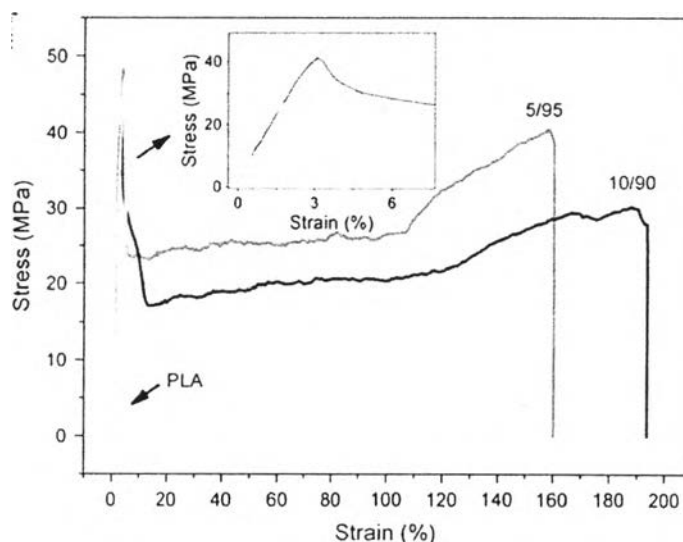
<sup>b</sup> Compositions of copolymers obtained.

<sup>c</sup>  $M_w$  from GPC measurement

**Table 2.8** Tensile properties of different PLA compositions (standard deviations are given in brackets).(Murariu, M. et al. 2008)

Compositions (% by weight)	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Young's modulus (MPa)	Nominal strain at break (%)
PLA	66 (2)	65 (3)	1000 (100)	11 (3)
PLA-40% AII	-	57 (3)	1600 (150)	6 (1)
PLA-40% AII-10% DOA	18 (1)	15 (1)	1150 (300)	8 (3)
PLA-40% AII-10% GTA	26 (1)	14 (1)	700 (50)	75 (34)
PLA-40% AII-10% Glyp3	31 (2)	27 (2)	960 (60)	6 (1)
PLA-40% AII-10% Glyp7	31 (1)	27 (3)	950 (60)	7 (1)

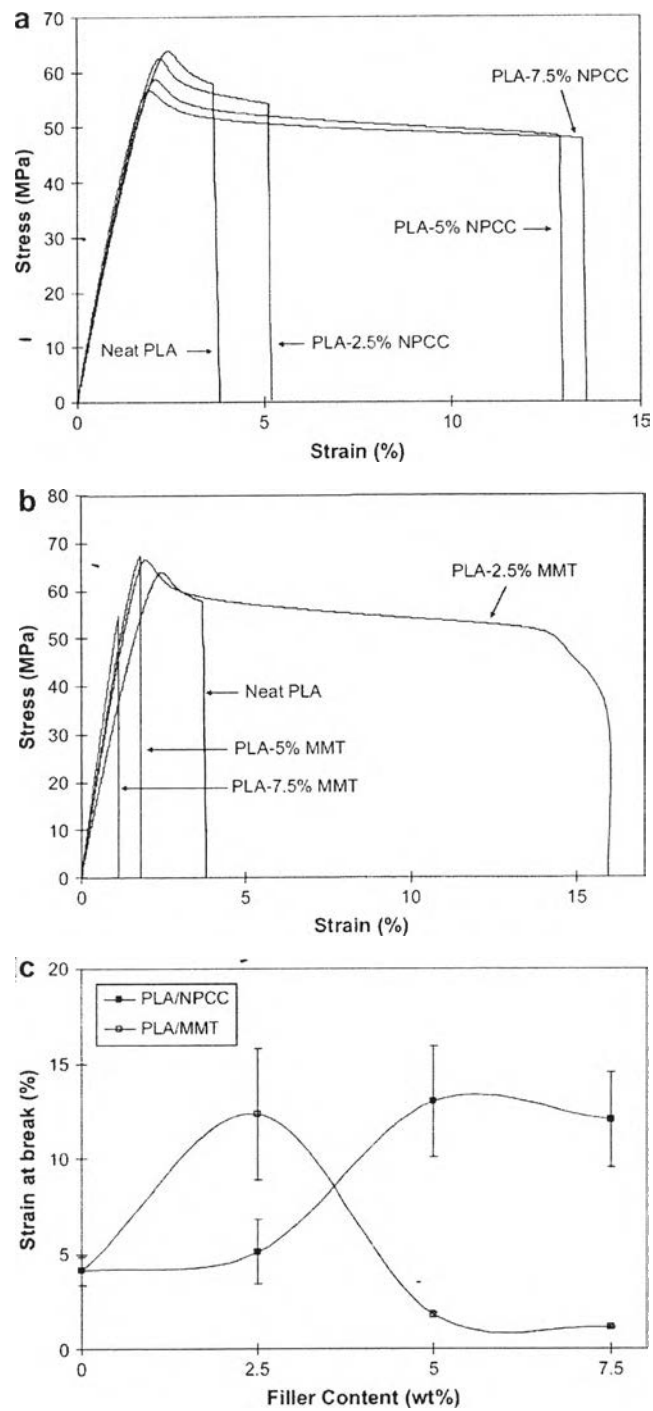
\* Gauge length of 25.4 mm.



**Figure 2.8** Tensile stress–strain curves of the blends with various PAE/PLA weight compositions.(Zhang, W. et al. 2009)

**Table 2.9** Mechanical properties of Neat PLA and PLA-UFPRx as a foundation of UFPR contents.(Zhao, Q. et al. 2013)

Samples	Elongation at break (%)	Tensile strength (Mpa)	Tensile modulus (Mpa)	Impact strength (KJ/m <sup>2</sup> )
PLA	6.08 ± 0.36	68.05 ± 1.06	2062 ± 12	1.60 ± 0.21
PLA-UFPR0.5	106.60 ± 15.08	67.53 ± 0.17	1922 ± 66	2.00 ± 0.15
PLA-UFPR1	219.93 ± 2.64	66.26 ± 1.36	1896 ± 2	2.20 ± 0.23
PLA-UFPR3	231.45 ± 20.55	65.67 ± 0.76	1768 ± 54	2.60 ± 0.37
PLA-UFPR5	215.63 ± 12.21	65.39 ± 0.70	2029 ± 129	3.20 ± 0.19



**Figure 2.9** Stress-strain curves of (a) PLA/NPCC, (b) PLA/MMT nanocomposites and (c) the comparison of their strain-at-break values. (Jiang, L. et al. 2007)

**Table 2.10** Mechanical properties of neat PLA and PLAOR nanocomposites.(Li, B. et al. 2009)

Samples	Clay content (wt.%)	Tensile modulus (GPa)	Tensile strength at yield (MPa)	Elongation at break (%)
Neat PLA	0	1.1 ± 0.1	68.8 ± 0.6	7.9 ± 0.8
PLAOR0.5	0.5	1.2 ± 0.1	55.8 ± 1.9	58.7 ± 9.0
PLAOR1	1	1.3 ± 0.1	58.7 ± 1.0	209.7 ± 25.7
PLAOR2	2	1.3 ± 0.1	54.1 ± 2.6	106.1 ± 28.1
PLAOR3	3	1.3 ± 0.2	46.1 ± 1.4	47.9 ± 3.8
PLAOR5	5	1.5 ± 0.1	36.8 ± 3.6	25.2 ± 3.8

**Table 2.11** Mechanical properties of neat PLA and PLA blends with different DS in MGST, various content of MGST3, and different content of ESO.(Xiong, Z. et al. 2012)

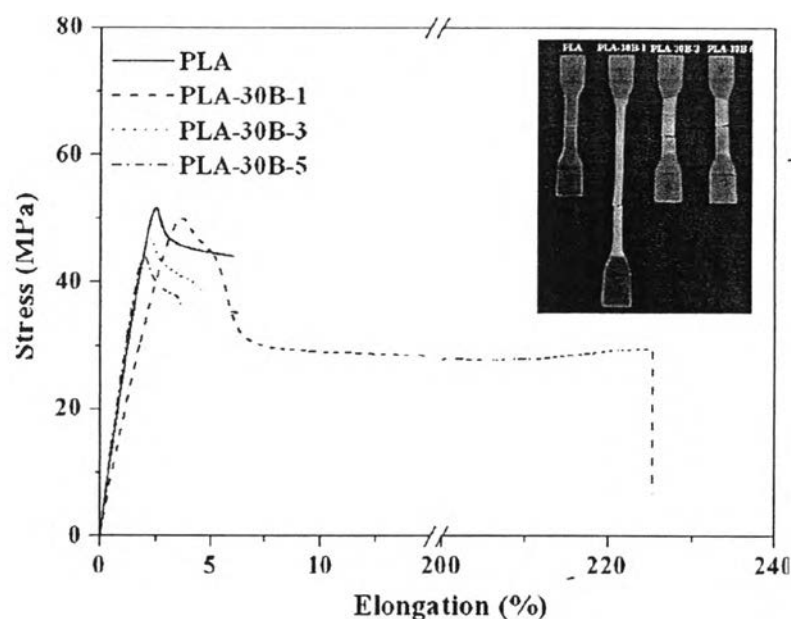
Composition	Impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
Neat PLA	18(±1.0)	69(±1)	5(±1)	3018(±50)
PLA/ESO (90/10)	19(±0.5)	62(±2)	6(±2)	2727(±15)
PLA/starch (90/10)	14(±1.0)	57(±2)	6(±1)	2855(±20)
PLA/native starch/ESO (80/10/10)	30(±1.0)	38(±2)	64(±5)	2406(±10)
PLA/MGST1/ESO (80/10/10)	34(±0.5)	36(±1)	78(±5)	2264(±13)
PLA/MGST2/ESO (80/10/10)	38(±0.7)	41(±1)	112(±10)	2412(±30)
PLA/MGST3/ESO (80/10/10)	42(±1.0)	43(±2)	140(±10)	2510(±20)
PLA/MGST3/ESO (70/20/10)	36(±1.2)	35(±1)	96(±6)	2318(±18)
PLA/MGST3/ESO (60/30/10)	31(±1.0)	25(±2)	63(±5)	1769(±20)
PLA/MGST3/ESO (65/30/5)	28(±1.0)	32(±1)	56(±5)	2063(±15)
PLA/MGST3/ESO (58/30/12)	36(±0.8)	19(±1)	68(±3)	1366(±10)
PLA/MGST3/ESO (55/30/15)	23(±1.0)	16(±2)	32(±5)	1057(±25)

\* Values reported here are averages of four tensile bar tests according to the test standard. IS, TS, EB and TM represented the impact strength, tensile strength, elongation at break and tensile modulus, respectively.

## 2.6 Polymer-clay Nanocomposite

Composite materials are materials that contain 2 phases, major phase and minor phase, and minor phase reinforces properties for major phase. If dispersed phase is in nano-scale, material can be called nanocomposite material. It is well known that addition of dispersed phase into matrix can improve mechanical properties of material, especially nano-scale particles that have high aspect ratio. Polymer-clay nanocomposite is incorporation between polymer and clay with exfoliate or intercalate state(Koo, J.H. 2006). Added clay can increase mechanical properties, especially modulus, for polymer matrix. H. Zhao and coworkers studied characteristic of polylactide/polyhydroxybutyrate-co-valerate/clay nanocomposite. They found that storage and Young's modulus of the

polylactide/polyhydroxybutyrate-co-valerate blends increased when the blends were incorporated with clay, but tensile strength and elongation at break decreased (Zhao, H. et al. 2013). S. Lai and coworkers studied mechanical properties of PLA/clay nanocomposite. They also found the increasing of modulus and decreasing of tensile strength and elongation at break when polymer matrix was mixed with clay (Lai, S.-M. et al. 2013).



**Figure 2.10** Tensile stress–elongation curves of the PLA and PLA–30B (1, 3, and 5 phr) nanocomposites. The inset is the sample photo of dumbbell specimens after tensile break. (Lai, S.-M. et al. 2013)

**Table 2.12** Tensile mechanical properties including initial modulus ( $E$ ), yield stress ( $\sigma_y$ ), tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) along with the predicted moduli by Halpin–Tsai and Mori–Tanaka equations of the PLA–30B nanocomposites. (Lai, S.-M. et al. 2013)

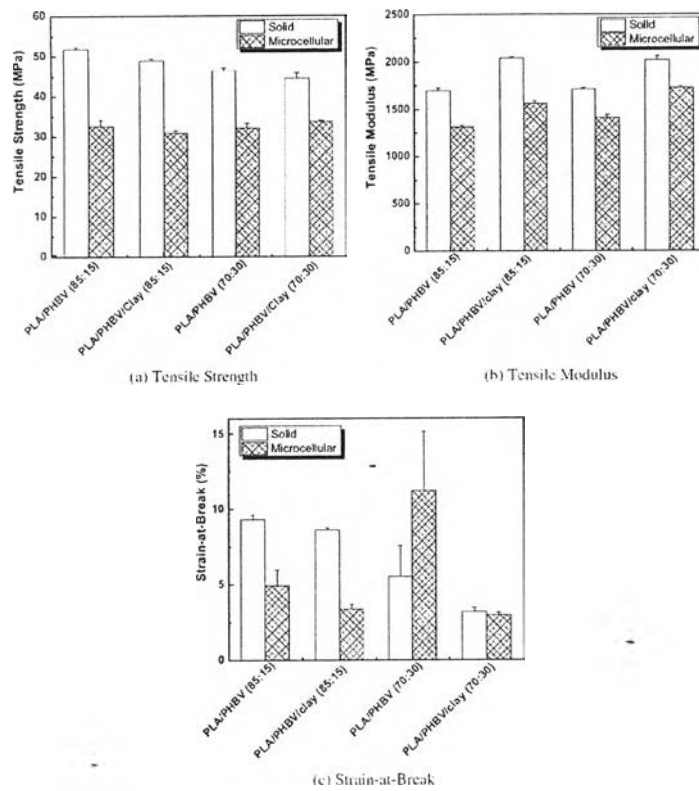
Sample	$E$ (GPa)	$\sigma_y$ (MPa)	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$E_{H-T}$ (GPa) <sup>a</sup>	$E_{M-T}$ (GPa) <sup>b</sup>
PLA	$2.35 \pm 0.03^c$	$51.7 \pm 0.6$	$44.4 \pm 0.9$	$5.61 \pm 0.91$	2.35	2.35
PLA-30B-1	$1.64 \pm 0.07$	$50.8 \pm 0.8$	$29.2 \pm 0.8$	$208 \pm 45$	2.54	2.48
PLA-30B-3	$2.47 \pm 0.05$	$46.4 \pm 1.1$	$38.5 \pm 1.5$	$4.43 \pm 1.09$	2.75	2.59
PLA-30B-5	$2.68 \pm 0.08$	$44.8 \pm 1.2$	$37.9 \pm 1.0$	$3.35 \pm 0.75$	3.04	2.77

<sup>a</sup>  $E_{H-T}$ : Predicted modulus from the Halpin–Tsai equation.

<sup>b</sup>  $E_{M-T}$ : Predicted modulus from the Mori–Tanaka equation.

<sup>c</sup> Mean and standard deviation from five determinations.





**Figure 2.11** Mechanical properties of solid and microcellular PLA/PHBV blends and PLA/PHBV/clay nanocomposites: (a) tensile strength, (b) tensile modulus, and (c) strain-at-break. (Zhao, H. et al. 2013)