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공학석사학위논문

Particle network formation in poly(lactic acid)/calcium carbonate composite with natural rubber and its effect of mechanical properties

천연 고무를 통한 폴리 락트산과 탄산 칼슘 복합체 내의 입자 구조 형성과 이에 따른 기계적 물성 변화에 관한 연구

2018 년 8 월

서울대학교 대학원

화학생물공학부

이 정 명

Abstract

Particle network formation in poly(lactic acid)/calcium carbonate composite with natural rubber and its effect of mechanical properties

Jung Myung Lee

School of Chemical and biological Engineering

The Graduate school

Seoul National University

Since poly(lactic acid) (PLA) has similar properties of commercial polymer, PLA has been received considerable attention as an alternative to petroleum based polymer. However, inherent brittleness of PLA is major drawback. Rubber toughening is common way to overcome brittleness of PLA. In the various studies, by controlling the morphology of rubber, brittleness of PLA could be compensated. However, rubber toughening caused decrease in stiffness. This property of polymer could be enhanced by adding nanoparticles to polymer. For effective improvement of stiffness, manipulating dispersion and structure of particles is major issue. In other word, for making stiffness–toughness well–balanced PLA/NR/particle composite, controlling not only morphology of dispersed phase but also dispersion and structure of particle is essential. In this study, PLA is blended with NR in order to compensate brittleness of PLA. Inorganic particles, calcium carbonate, are incorporated to this

polymer blend in order to not only minimize the decrease of strength but also improve the compatibility between two polymers. It is expected that the excess particles will not only play a role of being located at the interface of two polymer but also will deform the dispersed phase. It is also expected that the dispersion state of the particles will be changed because dispersed phase will induce the aggregation of the particles. We focus on the microstructure of ternary composite in terms of controlling both particle dispersion and dispersed phase morphology simultaneously. With changed an interaction between particle and dispersed phase, mutual effect of particle and dispersed phase was investigated. The effect of the content of particles, dispersed phase on morphology of ternary composites was also examined. To investigate dispersion and structure of particle and morphology of dispersed phase, rheological measurement and morphological observation were conducted.

Key words: Biopolymer, particle network, mechanical properties

Student Number: 2015–21078

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Chapter 1.

Introduction

Recently, various studies on biopolymer have been carried out to solve environmental problems such as lack of landfill [1] and marine ecosystem [2], caused by the use of commercial polymer. Poly(lactic acid) (PLA), as one of the biodegradable polymers, produced from plant-derived sources has received considerable amount of attention because it has properties similar to conventional petrochemical-based polymer [3]. However, the main disadvantage that limits the use of PLA is its inherent brittleness. One of the ways to compensate this brittleness is rubber toughening. Since ecofriendly natural rubber (NR) has good ductile property, studies have reported on blending NR with PLA to complement the brittle properties of PLA [4, 5]. The effect of NR morphology on mechanical properties, especially sizes of droplets, was investigated [4]. As content of NR was increase from 5 wt% to 20 wt%, more coalescence of NR occurs and droplets size also increase from 1.2 μm to 2 μm . Because the role as a homogeneous stress concentrator becomes ineffective and debonding does not occur homogeneously in the initial stage of stretching. Therefore, plastic deformation does not occur stably. In other words, controlling the morphology of the dispersed phase, especially the sizes of droplets, is a major issue in order to improve the brittleness with the rubber.

To control the morphology of the dispersed phase, thermodynamic approach of interfacial energy reduction have been proposed such as using copolymer [6, 7]. In recent years, studies have focused on role of a small amount of inorganic solid particles in polymer blend. [8]. Recent studies have been reported that compatibility of PLA/NR blend can be improved by adding clay. In ternary blend nanocomposite, clay can act as a compatibilizer because particles of clay which were located at the PLA/NR interface lower the interfacial energy and interrupt the coalescence of NR droplets [9]. Elongation at break of ternary blend nanocomposite can be increased since particles at the interface behave as stress homogenizers allowing slippage and redistribution of stress among polymer chain, hindering the growth of cracks [10]. In both of these studies, elongation at break was increased with rubber toughening,

but tensile strength decreased from approximately 40 MPa to 30 ~ 35 MPa. Since NR morphology and the dispersion state of the inorganic particles are important factors in NR toughening, the strategy of controlling these factors in the polymer blend nanocomposite will be a solution to the brittleness of PLA.

On the other hand, the drawback of this rubber toughening is a reduction in tensile strength. It is therefore essential to compensate for the strength of the polymer to minimize the decrease during rubber toughening. The most common way to compensate strength is adding nanoparticles in polymer [11, 12]. Dispersion and structure of particles in composites caused by the interaction between particle and polymer affect the mechanical properties of polymer composites. Therefore, researchers have reported to control the structure and dispersion of particles by changing various parameters such as morphology, surface treatment of particle, and addition of additives.

Two types of particles that have different shapes, nano-sized calcium carbonate (NPCC) and montmorillonite (MMT), were added to PLA, respectively, and the reinforcing and toughening effect by particles were investigated [13]. Since MMT has larger interfacial area and stronger interfacial interaction than NPCC, stress transfer to MMT platelets was increase and PLA/MMT composite has high tensile strength. On the other hand, massive crazing due to debonding at surface cause an increase in elongation at break of PLA/NPCC composite from 4 % to 13 %. Effect of particle coating with poly(ϵ -caprolactone) (PCL) on dispersion of particles and mechanical properties has been investigated [14]. PLA/CC composite has low tensile strength and elongation at break because uncoated CC particles are hydrophilic and have low compatibility with PLA. Coating CC particles with PCL resulted in homogenous dispersion of particle and less aggregation. Because coating increases interfacial interaction between CC and PLA, elongation at break of PLA/ coated CC(15 phr) was increased from 5% to 310 %. However, the tensile strength of PLA/coated CC was decreased more than that of PLA/uncoated CC because of

plasticizing effect of softened PCL. Recently, a research has been conducted to enhance the self-weld network structure of carbon fiber (CF) by adding poly(ether) urethane (PU) to PLA/carbon fiber composites [15]. The PU was located between the CFs due to the affinity between the PU and CF. The network of CF and PU can have stiffness of CF and ductility of PU, thus yield strength and elongation at break of PLA/CF/PU composite changed from 81.61 MPa to 83.18MPa and from 2% to 3.15%, respectively.

The morphology control of the ductile dispersed phase is most important to compensate for the brittleness of PLA. It is also essential to control the dispersion and structure of the particles in order to minimize the degradation of stiffness in rubber toughening. In other words, for inducing well-balanced stiffness-toughness in PLA composites, strategy of controlling both dispersion of particle and morphology of dispersed phase was essential.

In this study, PLA is blended with NR in order to compensate the brittleness of PLA. Inorganic particles, such as calcium carbonate, are incorporated to this polymer blend in order to not only minimize the decrease of strength but also improve the compatibility between two polymers.

Unlike the previous studies, which showed the effect of small amount of inorganic particles on the morphology of dispersed phase, excess particles (10 vol% ~) is added in this study. It is expected that the excess particles will not only play a role of being located at the interface but also will deform the dispersed phase. It is also expected that the dispersion state of the particles will be changed because dispersed phase will induce the aggregation of the particles. We focus on the microstructure of ternary composite in terms of controlling both particle dispersion and dispersed phase morphology simultaneously. The mutual effect of particle structure and morphology of dispersed phase is investigated by changing interfacial interaction between particle and dispersed phase through particle surface treatment. In addition, we investigated the effect of the content of particles and dispersed phase on

morphology of ternary composites, and tried to understand the role of each component.

Chapter 2.
Experimental methods

2.1 Material and sample preparation

Poly(lactic acid) (grade 4032D, $M_n = 90,000$ g/mol, $M_w = 181,000$ g/mol, PDI = 2.01) provided by Natureworks (USA) was used as the matrix. Two different types of precipitated calcium carbonate (PCC) were supplied by Imerys Mineral Ltd. One is PCC coated with fatty acid (grade socal312, Imersy, France) and the other is uncoated PCC (grade socal31, Imersy, France). Density and diameter of PCC particles are 2.77 g/ml and 80~100nm, respectively. Natural rubber (NR) (grade CSR5), which was used as the dispersed phase, was supplied by CRK Co. (Korea). Instead of NR, polypropylene (grade PP2150, Polymirea Co., Korea) was used as another dispersed polymer. All gradients were dried under vacuum at 80 °C for at least 8 hours before melt compounding. Internal mixer (Rheocomp mixer 600, MKE, Korea) was used for melt compounding. To exclude the influence of mixing sequence, all dried gradients were dry-mixed by hand and loaded into mixer at once. Samples were pre-molten at slow rotor speed of 10rpm for 2 minutes and then mixed at 100 rpm for 6 minutes at 190°C. Compositions of samples are shown in Table 1 as volume fraction. The content of NR is marked again based on the content of PLA/PCC composite which is regarded as 100 vol%. Each sample named referred to the composition of PCC and NR. For an example, if a composite was composed of 89% PLA, 10% PCC, and 1%NR, it named 10C1R. For coated particles, prefix c with C, and for uncoated particles, precede u with C.

Table 1 Compositions of PLA composites

Notation	Composition (v/v)		NR (phr)	NR/PCC
	PLA	PCC		
15cC, 15Uc	85	15	0	0
8R	100	0	8	–
10cC2R, 10uC2R	90	10	2	2/10
10Cc8R, 10uC8R	90	10	8	8/10
10cC19R, 10uC19R	90	10	19	19/10
12cC2R, 12uC2R	88	12	2	2/12
12cC8R, 12uC8R	88	12	8	8/12
12cC19R, 12uC19R	88	12	19	19/12
15cC2R, 15uC2R	85	15	2	2/15
15cC8R, 15uC8R	85	15	8	8/15
15cC19R, 15uC19R	85	15	19	19/15
1cC8R, 1uC8R	99	1	8	8/1
1cC19R, 1uC19R,	99	1	19	19/1
5cC8R, 5uC8R	95	5	8	8/5
5cC19R, 5uC19R	95	5	19	19/5

x (phr) = x/(100% composite + x)

2.2 Rheological and morphological characterization

Before measuring the rheological properties, a specimen with a diameter of 25 mm and a thickness of 1 mm was prepared using a hot press (CH4386, Carver). Rheological property was measured with a stress control type rheometer (DHR-3, TA instrument, USA). All measurements were carried out at 180 °C and an amplitude sweep test was performed before the frequency sweep test in order to find the linear viscoelastic region. Frequency sweep test was performed at 0.1 ~ 100 rad/s frequency.

Because rheological properties of ternary composites change with time, the data after waiting until it stabilized were used. It takes about 20 minutes to be stabilized, and we also checked that other samples, which do not changed with time, were thermally stable during rheological measurement for 20 minutes.

Morphological observation was investigated with Field-Emission Scanning Electron Microscope (SEM) (Carl Zeiss, Germany) and High Resolution-Transmission Electron Microscope (TEM) (JEOL Ltd, Japan). For the morphology observation through SEM, specimens were cut after being quenched with liquid nitrogen, and the surface was sputtered with a layer of platinum. Before TEM imaging, specimens were prepared using a Cryo Ultramicrotome (PT PC Ultramicrotome & Photographic) and Carbon coating was performed.

2.3 Mechanical test

Mechanical properties were measured using ASTM D638 type V with UTM (LF plus, Lloyd instruments Ltd). After a dumbbell-shaped specimen was prepared with hot press, measurements were carried out. The average data were obtained after at least 8 measurements.

Chapter 3.

Results and discussion

3.1 Effect of particle coating

As can be seen in Figure 1 (a), when 8 vol% of NR was added to 15cC, storage modulus was increased in low frequencies region. The slope of storage modulus was drastically changed from $G' \propto \omega^{0.81}$ for 15cC to $G' \propto \omega^{0.25}$ for 15cC8R. In the absence of NR, the storage modulus is less than the loss modulus at all frequencies. However, the storage modulus is greater than the loss modulus over the whole observation range of frequency for 15cC8R. In the case of composites with uncoated particles, even when NR was added, storage modulus slightly increased at low frequencies. This phenomenon occurs only when the coated particles are used, and the difference due to particle surface treatment is observed not only in rheological properties but also in morphology. SEM images of 15cC and 8R are given in Figure 2 (a), (b). In 15cC, particles are randomly dispersed in the matrix. For the 8R, the NR phase is dispersed in the PLA matrix with average size of 1.6 μm . According to 15uC8R, Figure 2 (d), it can be seen that there is almost no change in the size of the NR droplets, and the particles are randomly distributed in the matrix. However, SEM image of 15cC8R, Figure 2 (c), shows that the droplets of NR cannot be observed by SEM image. The compatibility between NR and PLA is increased with coated particle. The particle structure is difficult to figure out by using SEM. To figure out the distribution of particles, the TEM images of 15cC and 12cC8R are prepared. In Figure 3, TEM images of 15cC and 15cC8R are shown to compare the dispersion state of particle. It can be considered that the dispersion of particle is drastically changed due to the presence of rubber. In Figure 3 (a), the particles of 15cC are distributed randomly throughout the sample. On the other hand, in the case of 15cC8R, Figure 3 (b) shows that particles are lined up throughout the sample, or surrounding a small circle of 2–400 nm in size. The dispersed phase could be thought to play a role in aggregating particles. Particle percolation is formatted while aggregated particles are connected each other. At the same time, from the viewpoint of the

dispersed phase, particles prevent coalescence of NR droplets, which makes the droplets of NR remain in the size of several hundred nanometers. In other words, the percolation structure is formed due to the dispersed phase, and at the same time, the percolation structure makes the droplets size to several hundred nanometers.

In the ternary composite with coated particles, formation of percolation network and drastic decrease in the size of NR droplets occurred simultaneously. On the other hand, this phenomenon was not observed in the ternary composite containing uncoated particles. Due to the surface properties of the particles, the interactions between the components are varied and thus the locations of particles are changed in the ternary composites. The morphology changes according to particle location will be discussed further detail in the discussion section.

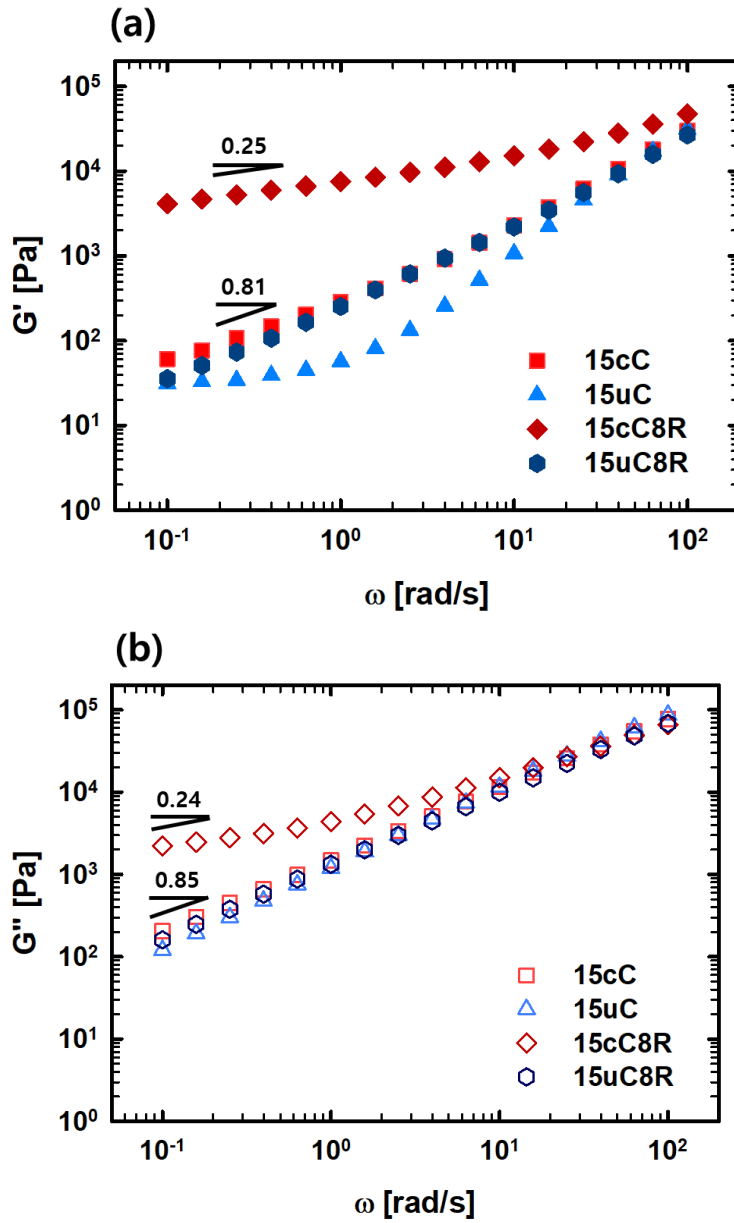


Figure 1 (a) Storage and (b) loss modulus of 15cC, 15uC, 15cC8R and 12uC8R as function of frequency

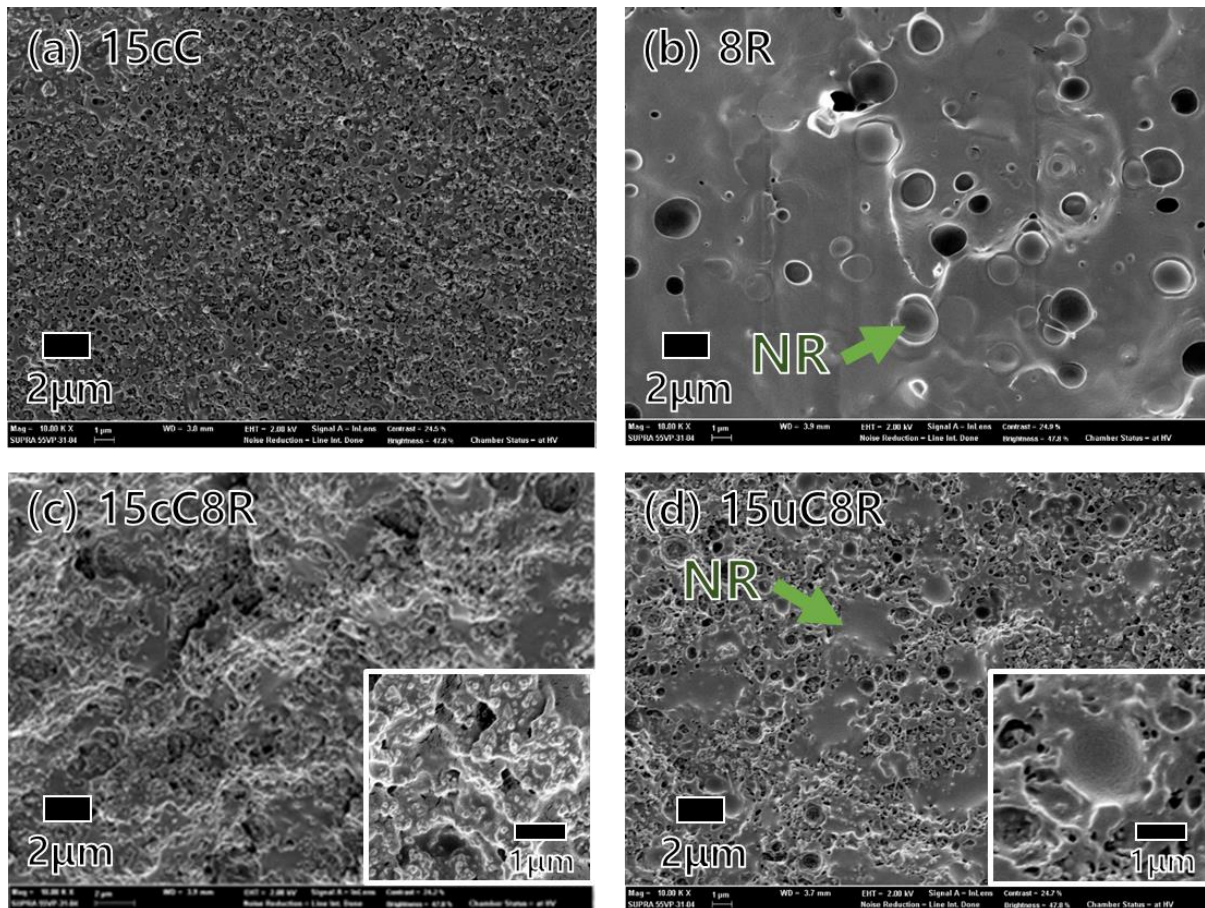


Figure 2 SEM images of (a) 15cC (b) 8R (c) 15cC8R (d) 15uC8R.

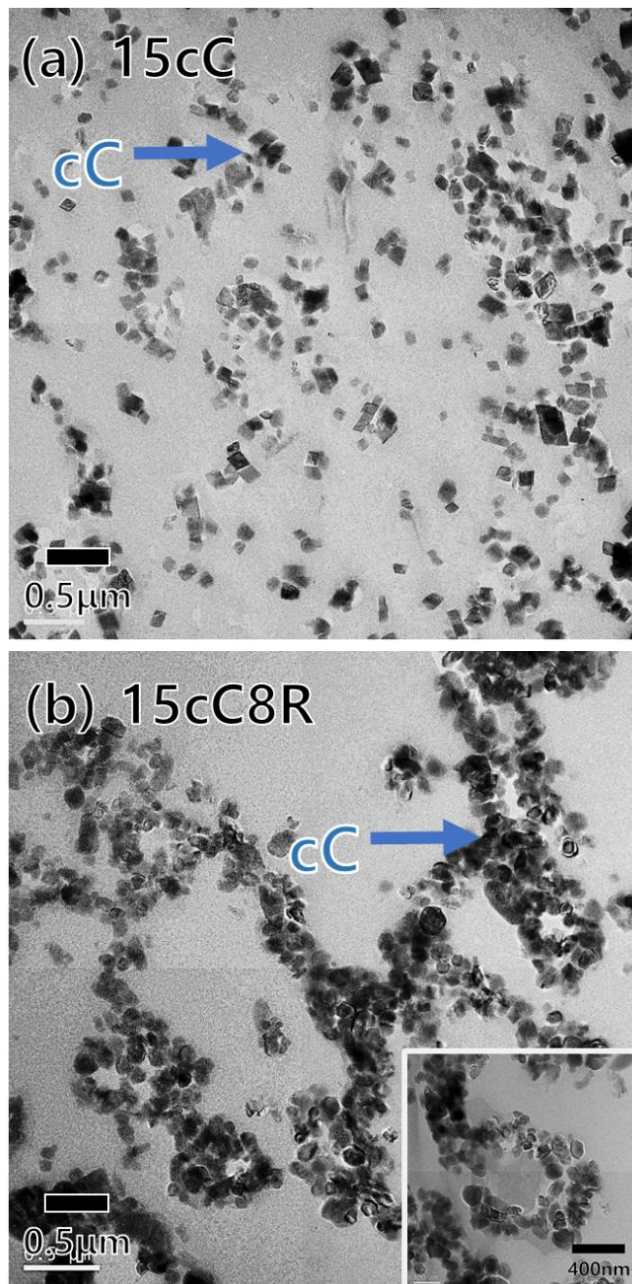


Figure 3 TEM pictures of 15cC and 15cC8R composites

3.2 Effect of coated PCC concentration

In order to clarify the effect of particle concentration to the network structure formation, the rheological properties and morphologies of composites with coated particle were observed by increasing the particle content from 1 to 15 vol% while the content of NR was fixed at 8 vol%. In Figure 4 (a), when the particle content is increased from 1 to 10 vol%, the storage modulus of the ternary composite with coated particles increase gradually, and when the particle content is increased further up to 12 vol%, the modulus increase more drastically. It turns out that the drastic increase in storage modulus overwhelm the loss modulus at 12 vol% of PCC.

On the other hand, storage and loss modulus of PLA/ucPCC/NR decrease as concentration of uncoated particles is increased. This decrease in rheology properties due to degradation during processing has been previously reported. Chain length reduction is caused by hydrolysis or alcoholysis reaction, which is caused by water or residual organometallic compounds used during polymerization [4].

In Figure 4 (b), the composites with up to 10 vol% of cPCC shows shear thinning behavior in the high frequency range. The complex viscosity of composites with 12 vol% or more of cPCC drastically increase in low frequency ranges.

As mentioned in Section 3.2, Percolation network was formed only in the composite with coated particle. Through rheological properties, it is considered that there is a transition point to form the particle percolation network. The percolation network was observed when the particle content was 12 vol% and higher for the composite containing 8 vol% NR. As shown in Figure 5 (a), the average size of NR droplets is 1.6 μm in the PLA/NR blend. Figure 7 (b) shows that the size of the NR droplets decreased to 1 μm with the addition of 1 vol% particles. It has been previously reported that a small amounts of particles located at the interface between the dispersed phase and the matrix prevent the coalescence of the dispersed phase and

maintain the size of the dispersed phase [9, 10]. It can be seen that 1 μm of the dispersed phase is still observed up to 5 vol% of the particles and more particles are on the matrix. However, with 12 vol% of the particles, the dispersed phase is too small to be clearly distinguished in the SEM image.

In Figure 5, Particle percolation network was formed above specific transition point. At the same particle concentration, the size of NR droplets is drastically changed. Due to a large amount of particle, NR deformed and remain in hundreds nanometer scale size. Deformed NR act as medium, which aggregate and line up a large amount of particles.

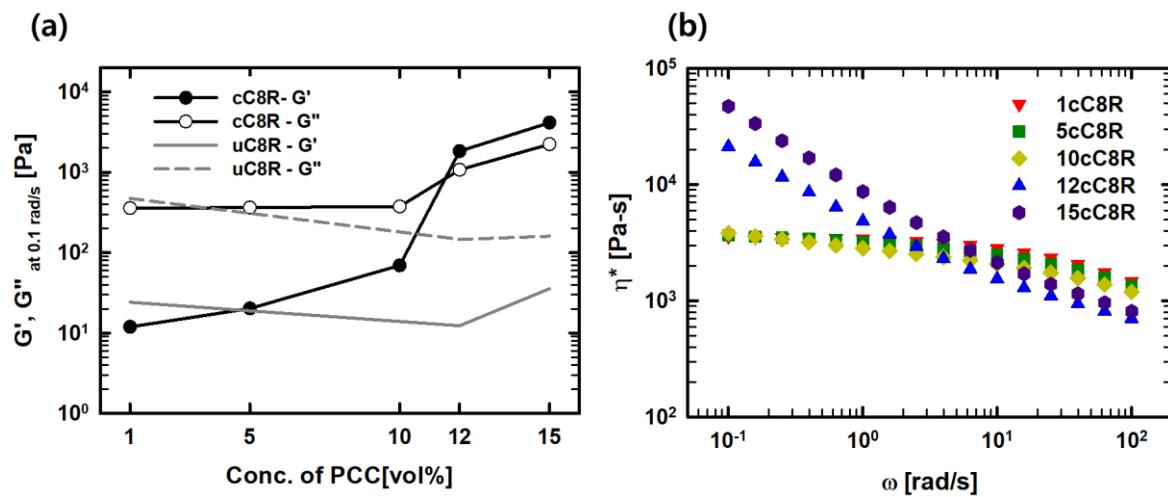


Figure 4 (a) Storage and loss modulus at 0.1 rad/s of PLA/cPCC/NR composites as function of Conc. of cPCC, (b) complex viscosity of PLA/cPCC/NR composites as function of frequency at 180 °C

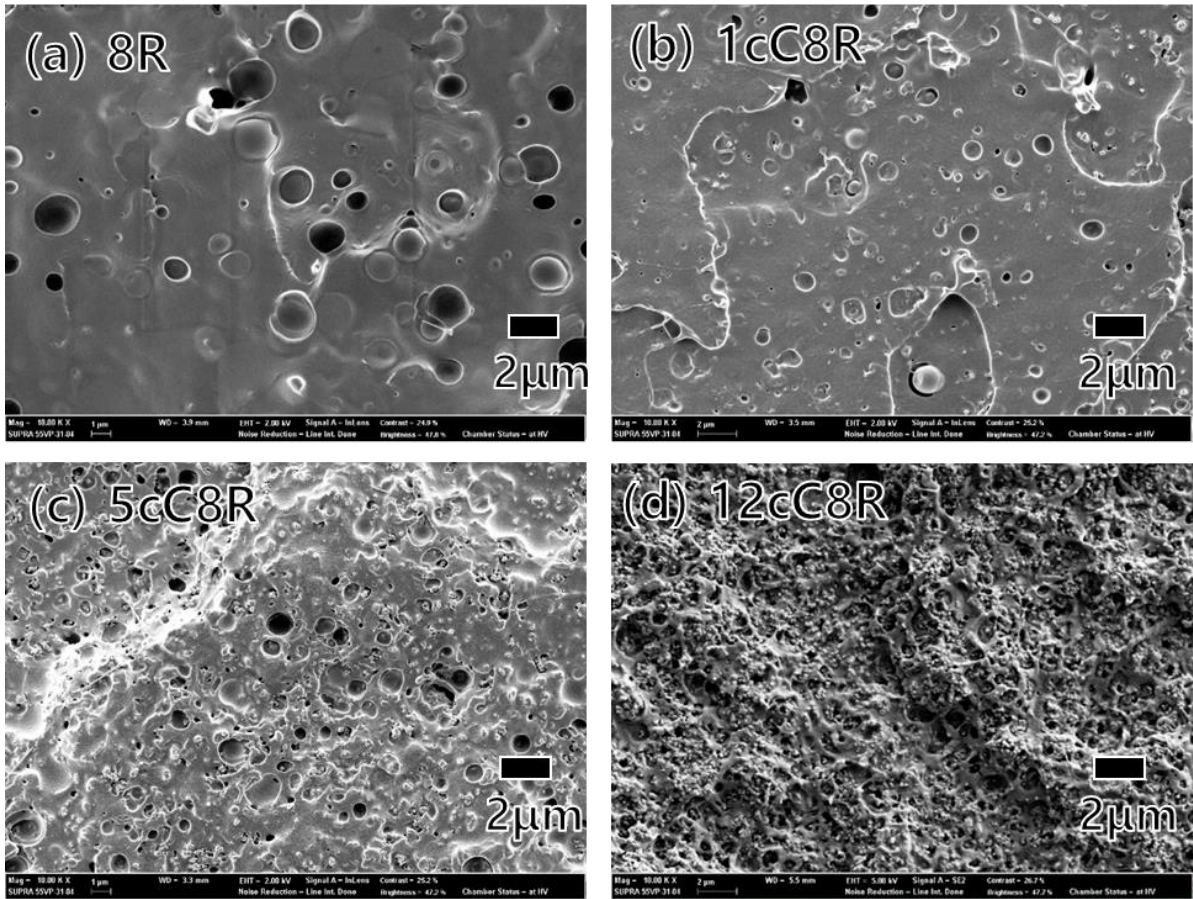


Figure 5 SEM images of (a) 8R, (b) 1cC8R, (c) 5cC8R and (d) 12cC8R

3.3 Effect of natural rubber concentration

Formation of particle percolation and decrease in droplets size of dispersed phase were competitively occurred. In order to understand the role of dispersed phase, rheological properties and morphology were observed while changing the NR content from 0 to 19 vol%. In Figure 6 (a), the slope of the storage modulus drastically changes when the content of particles increases from 15 vol% to 20 vol% for the composites without dispersed phase. However, when a small amount of NR is added, the abrupt change of this slope appears at the lower particle content. As 2 and 8 vol% of NR were added, the storage moduli goes through rapid increases when particle contents increased from 12 to 15 vol%, and 10 to 12 vol%, respectively. Figure 6 (b) shows that $\text{Tan}(\delta)$ has a value of less than 1 at the specific particle contents, in which slope of storage modulus was increased suddenly. Through these analyses, it can be concluded that there are some specific particle content where particle structures are changed, and that the increase of NR content shifts the percolation threshold to the lower particle content. The rheological properties in Figure 6 indicate that 12cC2R will not have percolation structure because its $\text{Tan}(\delta)$ is higher than 1. In Figure 7 (a), it is considered that the particle flocs are formed due to a small amount of NR but the flocs are not sufficiently connected to form a percolation network. During the mixing process, the dispersed phase, which is deformed, forms the aggregation of the particles. As the particle content increases, the aggregates are connected and the percolation structure is formed. On the other hand, as the dispersed phase increases, the amount of the medium to line up increases, heterogeneity increases, and percolation is formed.

On the other hand, TEM image of 12cC19R shows that the particles are arranged throughout whole sample and form a percolation network when the content of NR is larger than the content of particles.

Therefore, sufficient amount of particles and dispersion phase, which are mediators of particle structure, are complementary to form percolation.

As a result, dispersed phase induces the percolation network of the particles. Also, as the more NR is added, the more likely it is to form the particle network with the lower particle content.

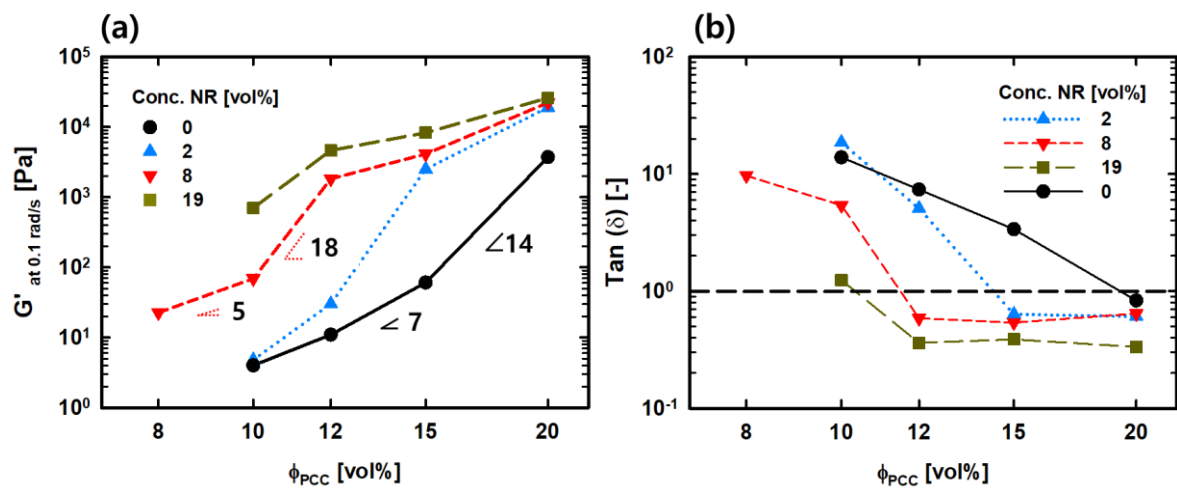


Figure 6 (a) Storage modulus at 0.1 rad/s of PLA/cPCC and PLA/cPCC/NR composite as function of Conc. of PCC

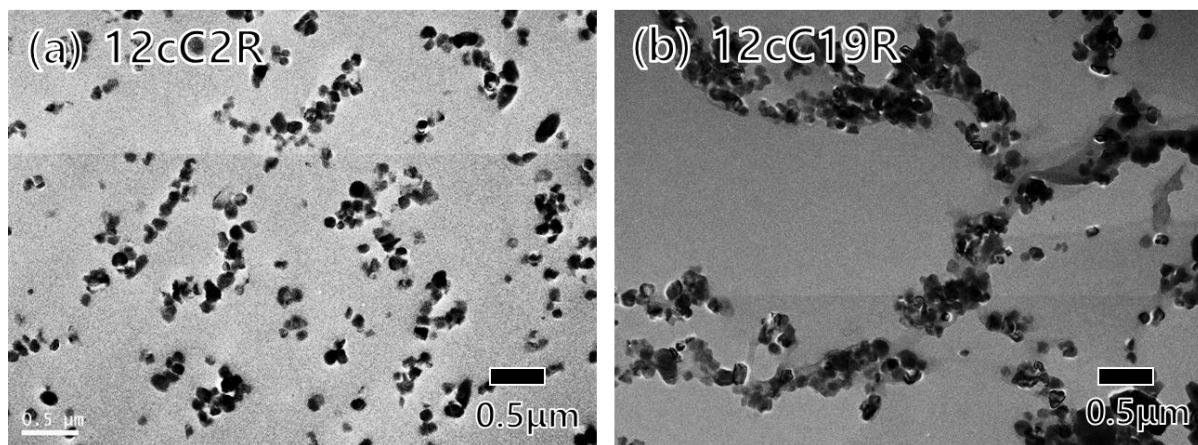


Figure 7 TEM images of (a) 12cC2R and (b) 12cC19R

3.4 Mechanical properties of PLA/PCC/NR

Mechanical properties of PLA/PCC and PLA/PCC/NR composites were shown in Figure 8, in which particle content was fixed at 12 vol% and NR content was varied. Although elongation at break of 12cC, 12uC are similar regardless of particle coating, elongation at break of ternary composites with 19 vol% of NR are drastically changed depending on particle coating.

With small amount of NR (8 vol% of NR), particles and NR changed the mechanical performance of PLA negligibly. Elongation at break of 12cC8R and 12uC8R increases to 17.9 and 16.7 %, respectively, and tensile strength of two composites decreases to 34.0 and 47.5 MPa, respectively. Although 8 vol% of NR is added, specimen of 12cC8R is fractured without necking or stress whitening [13] like the specimen of 12cC according to Figure 8 (c).

On the other hand, when 19 vol% of NR is added to 12cC and 12uC, the mechanical properties are drastically changed depending on the coating of particles. Elongation at break of 12cC19R increases to 86.4 %, more than 4 times compared to that of PLA. Tensile strength of this composite decrease to 23.4 MPa and stress whitening was observed in 12cC19R as shown in Figure 8 (c). When 19 vol% of NR is added to 12uC, elongation at break and tensile strength of 12uC19R are 17.7 % and 35.0 MPa, respectively. Compared with 12uC8R, mechanical properties of 12uC19R are deviate slightly. The above results show that the percolation network can be formed by the interaction of particles and NR. In addition, the size of the dispersed phase can be kept small due to the percolation network, which causes that the elongation at break is largely compensated for in result 3.4. This study gives a new strategy for controlling the particle dispersion and morphology of dispersed phase simultaneously, by which the mechanical properties of polymer could be improved.

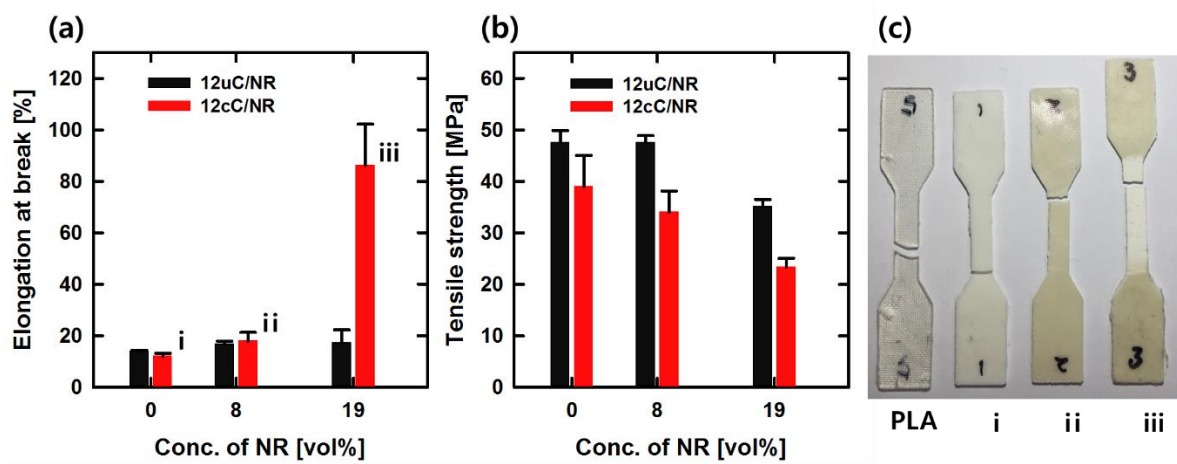


Figure 8 (a) Elongation at break (b) Tensile strength of PLA/cPCC/NR and PLA/ucPCC/NR and (c) specimens of PLA, PLA/cPCC (i), PLA/ucPCC/NR (ii) and PLA/cPCC/NR (iii)

Table 2 Mechanical properties of PLA, PLA/PCC/NR composites

	Elongation at break [%]	Tensile strength [MPa]	Young' s modulus [GPa]
PLA	22.2 ± 4.0	68.9 ± 2.8	2.1 ± 1.8
12cC	12.0 ± 1.2	39.0 ± 6.1	1.6 ± 1.1
12uC	13.9 ± 0.6	47.6 ± 2.3	1.4 ± 0.9
12cC8R	17.9 ± 3.4	34.0 ± 4.2	1.4 ± 0.9
12uC8R	16.7 ± 1.2	47.5 ± 1.3	1.2 ± 0.3
12cC19R	86.2 ± 16.0	23.4 ± 1.7	1.4 ± 0.3
12uC19R	17.1 ± 5.1	35.0 ± 1.4	1.3 ± 1.2

3.5 Estimation of particle location with wetting parameter

In section 3.1, depending on particle coating, particle structure and dispersed phase morphology were changed. Since the location of particles in ternary composites is related with surface energy of components, particle coating, which can change the particle surface energy, is a major factor in particle location. In previous study, particle location in ternary composite can be estimated by the wetting parameter, which can be calculated by surface energy of components [17]. Wetting parameter was defined by equation (1).

$$\omega_1 = \frac{\gamma_{p-2} - \gamma_{p-1}}{\gamma_{12}} \quad (1)$$

In this equation, γ_{p-i} is interfacial tension between particle and polymer and γ_{12} is interfacial tension between two polymers. The interfacial tension was calculated with equation (2), which was defined by Owens and Wendt equation.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \quad (2)$$

When wetting parameter, ω_1 , is bigger than 1, particles locate at polymer1. If ω_1 is smaller than -1 , particles locate at polymer2. If ω_1 has the other value, particles locate at interface of two polymer. The surface energy data of components were written on the Table 3 by using a reference paper [18–20]. The surface energy of all components at 180°C can be estimated by using $d\gamma/dT = -0.06 \text{ mJ/m}^2 \text{ K}^{-1}$ equation. Calculated interfacial tension and wetting parameter was marked at Table 4. Since wetting parameters of the coated and uncoated PCC are -0.5 and 5.2 , respectively, it can be considered that coated and uncoated PCC are located at the interface between two polymers and PLA matrix, respectively. This estimation through wetting parameter is in accordance with the location of particles in SEM and TEM images.

The coated particles that have high affinity with dispersed phase locate at interface between PLA and NR, preventing the coalescence of the dispersed phase and

stabilizing the morphology. In addition, when the content of the particles arranged at the interface is sufficiently increased, the percolation structure is formed by connecting the particles located at the interface. On the other hand, if the particles are preferred to be located in the matrix, they do not interact with the dispersed phase and the formation of percolation network do not occur.

Table 3 Surface energy data of PLA, NR, ucPCC and cPCC at 180°C [18–20]

	γ (mJ/m ²)	γ_d (mJ/m ²)	γ_p (mJ/m ²)
PLA	38.1	30.6	7.5
NR	22.4	18.1	4.3
ucPCC	84.3	–	–
cPCC	25.8	–	–

Table 4 Interfacial tension between PLA/NR, PCC/NR and PCC/PLA and wetting parameter

	$\gamma_{\text{PCC-NR}}$	$\gamma_{\text{PCC-PLA}}$	$\gamma_{\text{PLA-NR}}$	ω_{PLA}	Particle localization
cPCC	0.1	1.2	2.1	-0.5	Interface
ucPCC	19.8	9.0	2.1	5.2	PLA phase

Chapter 4.

Conclusion

In this study, the morphology of PLA/PCC/NR composite was controlled in order to improve the mechanical properties, especially brittleness. In controlling morphology, manipulating not only dispersion state of particles but also morphology of dispersed phase is a major issue. Therefore, we have studied a system that can control the morphology of the dispersed phase and the particle structure simultaneously. In order to understand our system fully, morphology and rheological properties of the ternary composites were investigated while changing particle coating, particle content, and dispersed phase content. Depending on particle coating, morphology of ternary composites were changed. Only in composites with coated particles, which are located at interface between PLA and NR, particles induced percolation network formation and size decrease of morphology droplets occurred simultaneously. On the other hand, in the ternary composite containing uncoated particles, the particles and the dispersed phase do not interact with each other and do not affect the morphology of the dispersed phase and the particles. In addition, the morphology of ternary composites was observed while increasing coated particle content. The particle percolation structure in ternary composites was formed above a specific amount of the particles, which means there is minimum particle content for the particle structure. As the content of NR was increased, the minimum content of particles for the above-mentioned phenomenon was decreased. In addition, through this system, the elongation at break of PLA/PCC composites increased from 12 % to 86 % by adding NR, which greatly improved the brittleness of PLA composite. This study gives a new strategy for controlling the particle dispersion and morphology of dispersed phase simultaneously, by which the mechanical properties of polymer could be improved.

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국문 요약

폴리 락트산은 상용 고분자와 비슷한 성질을 갖고 있기 때문에, 석유 원료의 고분자 대체할 수 있는 물질로써 상당한 관심을 받고 있다. 하지만 폴리 락트산이 가지고 있는 취성은 여러 산업의 적용에 걸림돌이 되고 있다. 천연 고무를 이용한 터프닝은 폴리락트산의 취성을 극복하기 위한 일반적인 방법으로 제시되고 있다. 최근의 많은 연구에서 천연 고무의 모폴로지를 제어함으로써 폴리 락트산의 취성을 보완할 수 있었다. 하지만 고무를 이용한 터프닝은 강도의 감소를 야기시킨다. 반면 고분자의 강도는 일반적으로 나노 입자를 고분자에 첨가하여 보완 할 수 있다. 강도의 효과적인 증가를 위해서 입자의 분산 상태 혹은 구조를 제어하는 것이 중요한 변수가 된다. 정리하여 보면 강도와 강성의 균형이 잘 잡힌 폴리 락트산 / 천연고무 / 입자 복합체를 만들기 위해서는 분산상의 모폴로지 뿐만 아니라 입자의 구조와 분산 상태를 제어하는 것이 필수적이다.

본 연구에서는 폴리 락트산의 취성을 보완하기 위하여 천연 고무와 블랜드 하였다. 또한 강도의 감소를 최소화 할 뿐만 아니라 두 고분자의 상용성을 증가시키기 위한 목적으로 무기 입자인 탄산 칼슘을 두 고분자 블랜드에 첨가하였다. 기존 대부분의 연구에서는 입자의 함량이 10wt%이하로 고정되나 본 연구에서는 10wt%이상의 과량의 입자를 첨가하였다. 이렇게 첨가된 과량의 입자가 분산상의 계면에 위치하고 분산상을 변형시키는 역할을 할 것으로 기대 되며, 분산상이 입자의 뭉침을 유도함으로써 입자의 분산 상태 또한 변화할 것으로 기대된다. 즉 본 연구에서는 3상 복합체 내의 입자 분산 상태와 분산상의 모폴로지를 동시에 제어할 수 있다는 관점에서 3상 복합체의 미세구조를 관찰 하였다. 구체적으로 입자와 분산상 사이의 상호작용을 변화시키며 입자와 분산상의 상호간의 역할에 대해 조사하였으며, 입자와 분산상의 함량이 3상 복합체의 모폴로지에 어떤 영향을 미치는지에 대해 연구되었다. 유변물성 측정과 모폴로지 관찰을 통해 분산상의 모폴로지와 입자의 분산상태를 조사할 수 있었다.

기존의 연구에서는 3상 복합체 내에서도 입자 혹은 분산상 중의 하나의 성분의 모폴로지를 제어하기 위한 연구가 주를 이루었다. 하지만 본 연구는 입자와 분산상의 모폴로지를 동시에 제어 하는 새로운 방법을 제시하였으며, 이를 이용하여 고분자의 물성 보완

가능성을 확인하였다는 점에서 의미가 있다.