Preparation and Properties of Spherical Natural Rubber/Silica Composite Powders via Spray Drying[†]

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Abstract

In this work, composite powders of natural rubber/silica (NR-SiO₂) were prepared via sol-gel and spray drying method. The morphology and physical properties of resultant rubber composite powders were characterized by scanning electron microscopy with energy dispersive X-ray spectrometry, laser light scattering particle sizer and thermogravimetric analyzer. The results showed that spray-dried NR-SiO₂ particles were spherical in shape with diameter of less than 10 μm, with silica on the outer layer. The particle size was found to increase gradually with the increase in NR/Si mass ratio. Marginal growth in particle size was observed with increasing feed flow rate. Increasing inlet air temperature improved the latex particle encapsulation by silica layer while maintaining the final particle size. The mechanical properties of NR-SiO₂ powders-filled polylactic acid (PLA) composite increase gradually with the addition of dried particles of higher rubber content. However, the composite exhibited relatively lower or reduced tensile strength and elongation at break compared to the host PLA polymer. This could be attributed to poor filler dispersion associated with weak filler/matrix interaction effect occurring during melt-compounding process.

Keywords: natural rubber, silica, composite powder, spray drying, sol-gel

1. Introduction

Natural rubber (NR) is an important natural plant polymer that is widely applied in various industrial sectors such as automobile, tires, aerospace, sports and consumer products. In recent years, there is growing research interest towards the preparation of ultrafine NR powders (NRP) with better physical and mechanical properties. NRP represents an attractive alternative to conventional rubber sheets in some applications, especially as additives or impact modifier. The use of fine NRP offers greater convenience in use and transportation compared to rubber sheets that require additional processing.

Numerous efforts have been made on the synthesis of

dried rubber-based particles ranging from micrometer to nanometer scale. For instance, Thill A. et al. demonstrated that it is possible to prepare nanoporous composite powder based on polybromostyrene and silica nanoparticles using ultrasonic spray system (Thill A. et al., 2005). Sae-Oui et al. reported the preparation of rubber powders via spray drying of pre-vulcanized NR followed by subsequent use as plastic additive in high-density polyethylene (HDPE) (Sae-Oui P. et al., 2010). Several powdered rubbers were successfully synthesized through gamma radiation crosslinking and spray drying of rubber lattices (Li D. et al., 2007; Peng J. et al., 2002; Wang Q. et al., 2011). It has been reported that the formation of nano-powdered rubbers is closely linked to the use of rubber latex with suitable crosslinking degree (Li D. et al., 2007).

Instead of irradiation technology, Paiva et al. described a methodology to produce composite spherical rubber powder by the modification of styrene-butadiene latex with methyl methacrylate and colloidal silica followed by spray drying (Paiva L.B.d. et al., 2014). Dried particulate rubber with particle sizes of 1 μm to 10 μm were obtained. On the other hand, the preparation of spray dried styrene-butadiene latex powder containing carbon

[†] Received 2 April 2019; Accepted 3 June 2019

J-STAGE Advance published online 29 June 2019

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nanotubes as reinforcing filler was demonstrated by Zhou et al. and his co-workers (Zhou X. et al., 2006). The above examples support the idea that spray drying is an attractive, yet efficient tool of producing dried rubber powders with controllable size and morphology. Spray drying is in fact a well-established technique used in pharmaceutical sectors (Lee D.-J. et al., 2013; Okamoto H. et al., 2002; Tong H.H.Y. et al., 2006). Although the rubber powders can be obtained by irradiation or latex modification in a prior step to spray drying, the drawback associated with these technologies are cost and safety problems.

Hence, we explored the possibility of producing composite rubber powder without the use of irradiation or modifying agents. We reported a methodology of natural rubber/silica (NR-SiO₂) composite powder preparation by spray drying a dispersion mixture containing silica sol and rubber latex. Silica is chosen because it is a kind of ceramic materials widely used in rubber reinforcement. In this study, the dried silica-coated rubber particles were formed via sol-gel reaction of siloxane on NR particles during spray drying. The effect of NR to silica mass ratio, spray-dryer feed rate and inlet air temperature on the properties of NR-SiO₂ powders was investigated. As part of study, the spray dried composite powders were melt-extruded and incorporated as filler into thermoplastic polylactic acid (PLA) in order to evaluate their thermal and mechanical properties. The findings of present study offer a simple method to fabricate NR-based powders with tailorable mechanical properties that may have useful application as impact modifier in chemical and plastic industries.

2. Materials and methods

2.1 Materials

Pre-vulcanized natural rubber latex with a total solid content of 60 wt% was obtained from Thai Rubber Latex Co. Ltd. Sodium silicate was procured from Fluka Chemicals, Germany. The host polymer in this study was polylactic acid (PLA) 2002D supplied by Nature Works, USA. All other chemicals were of analytical grade.

2.2 Preparation of NR-SiO₂ composite powders

The preparation of rubber composite powder was performed in 3 steps: (1) preparation of silica sol; (2) mixing of NR latex with silica sol; (3) spray drying process. First, silica sols were prepared by dispersing sodium silicate in a diluted aqueous solution of hydrochloric acid (HCl) at 50 °C for 5 min. The sodium silicate solution underwent hydrolysis and polycondensation reactions to form silica sols. Next, the as-prepared silica sols of 20 wt% silica

content were added to a diluted NR latex suspension and followed by sonication to constitute colloidal mixtures with varying NR/Si mass ratios ranging from 0.25:1 to 10:1. Finally, dry NR-SiO₂ powders were obtained by subjecting the mixture of silica sols and diluted NR to spray drying (mini-spray dryer, Buchi 190 model, Switzerland) at inlet air temperature of 160 °C and feed flow rate of 9 mL/min. The effect of feed rate and air inlet temperature on the final properties of resultant composite particles was also investigated.

2.3 Preparation of NR-SiO₂ particles filled PLA thermoplastic

The NR-SiO₂ filled PLA specimens were prepared according to the following procedure. A fixed 5.0 wt% of spray dried NR-SiO₂ powder was first blended and melt-compounded with PLA thermoplastic powder to obtain powdery mixture using a co-rotating twin screw extruder (LabTech LTE 20–40, LabTech Engineering Co., Ltd., Thailand) with temperature profile of 145–195 °C. The extrudates were then compression-molded at pressure of 50 bar and temperature of 165 °C for mechanical properties investigation.

2.4 Characterizations

The as-synthesized rubber composite powders were characterized in terms of particle size distribution, morphology, thermal stability and elemental composition. Particle size distribution was measured with laser diffraction analyzer (Mastersizer 2000, Malvern, UK). Prior to the size measurement, the NR-SiO₂ powder was dispersed in distilled water under sonication to obtain a homogeneous suspension without particle agglomeration. The morphological observation and elemental analysis of spray dried NR-SiO₂ particles were performed using scanning electron microscopy with energy dispersive X-ray spectrometer (SEM-EDX, JSM-6400, JEOL Ltd., Tokyo, Japan). The weight loss measurement of silica (control) and spray dried NR-SiO₂ particles was carried out in nitrogen gas with a thermogravimetric analyzer (TGA/DSC1, Mettler Toledo, Thailand).

The mechanical properties of the NR-SiO₂ particles filled PLA specimens were investigated using an electro-mechanical tensile tester (INSTRON 4206 universal testing machine, USA) in accordance with ASTM D256 and ASTM D638 Type 1.

3 Results and discussions

3.1 Characterization of NR-SiO₂ composite powders

3.1.1 Particle size distribution of NR-SiO₂ powders

Fig. 1 shows the particle size distributions and mean particle diameters of rubber composite powders prepared at different NR/Si mass ratios. As shown in **Fig. 1(a)**, there was no obvious change in the size distribution observed at the 3 lowest NR/Si ratios. The composite particles obtained at mass ratios of 0.25:1, 0.5:1, and 1:1 had very similar narrow size distributions with mean diameters centered at $\sim 0.6 \mu\text{m}$ (**Fig. 1(b)**). The size distribution curves became significantly broader and shifted to the bigger particle size region with further increase of NR/Si mass ratio from 2:1 (**Fig. 1(a)**). This observation could be attributed to the formation of a layer of silica around the NR latex particles. When the NR/Si mass ratio is smaller or equal to unity, the silica interacts well with rubber particles through cohesive forces to form a network in the suspensions, leading to crust formation after spray drying. However, when the value of this ratio reach 2:1 or silica amount is insufficiently lower than NR content, the particles tend to form this network in an aggregated form,

Fig. 1 (a) Particle size distribution and (b) mean particle diameter of NR-SiO₂ powders prepared at different NR/Si mass ratios. Reproduced by permission from Prachaya S. (2011).

causing latex-latex interparticle coalescence and agglomeration during drying process. It is worth mentioning that further increasing NR/Si mass ratio to 10:1 contributed to a more severe particle agglomeration, resulting in larger mean particle diameter as shown in **Fig. 1(b)**.

3.1.2 Morphology of NR-SiO₂ powders

It is well known that particle shape has a strong influence on the flow characteristics of powders (Ogata K., 2019; Talako T. et al., 2009). The morphology of spray dried rubber composite particles was characterized by SEM and the micrographs of the samples are presented in **Fig. 2**. As shown in **Fig. 2(a–f)**, all spray dried NR-SiO₂ particles were almost spherical in shape. However, large agglomerates were observed at higher NR/Si mass ratios. This observation substantiated our earlier findings on particle size measurement. The higher the NR/Si mass ratio, the more frequent the particles were aggregated in some regions. When a sufficiently high amount of silica was present, most of the rubber composite materials appeared as individual spherical particles (**Fig. 2(a–b)**). When silica content was significantly reduced, the drying process results in the formation of agglomerated clusters, as evidenced in **Fig. 2(f)**. It is clear that the composite particles aggregate greatly when there is insufficient silica to coat or encapsulate the rubber particle surface.

Fig. 2 SEM micrographs of NR-SiO₂ powders prepared at different NR/Si mass ratios: (a) 0.25:1, (b) 0.5:1, (c) 1:1, (d) 2:1, (e) 6:1, and (f) 10:1, respectively. Magnification 5 kx. Reproduced by permission from Prachaya S. (2011).

3.1.3 Elemental composition of NR-SiO₂ powders

The results of elemental sample analysis by EDX are presented in **Table 1**. The relative amount of silicon was decreased as the NR/Si mass ratio was increased. The results indicated that the amount of silica in the form of SiO₂ available for rubber particle encapsulation became insufficient at higher mass ratios. For NR/Si mass ratio of 0.25:1 and 0.5:1, the elemental ratio of C/Si was lower than 1 and most of the NR particles are sufficiently encapsulated within the silica shell. As expected, the elemental ratio of C/Si increased as the mass ratio rose from 0.25:1 to 6:1. In this case, the amount of silica required for coating rubber particles decreases significantly, leading to more particle aggregation as a result of insufficient surface coverage. It was considered that a plateau of silica encapsulation extent was reached at NR/Si mass ratio of 8:1, as evidenced by the essentially constant elemental ratio of C/Si.

3.1.4 Thermal stability of NR-SiO₂ powders

The TGA curves of spray dried NR-SiO₂ powders are shown in **Fig. 3**. All spray dried samples prepared at different NR/Si mass ratios showed a similar thermal deg-

Fig. 3 TGA curves of NR-SiO₂ powders prepared at different NR/Si mass ratios. Reproduced by permission from Prachaya S. (2011).

Table 1 Elemental composition of NR-SiO₂ powders prepared at different NR/Si mass ratios.

NR/Si mass ratio	% Element				C/Si ratio
	C	Si	O	Na	
0.25:1	13.14	28.11	44.77	13.98	0.47
0.5:1	17.29	24.00	45.38	13.33	0.72
1:1	29.47	18.07	42.39	10.07	1.63
2:1	56.10	9.28	29.03	5.59	6.04
4:1	65.27	5.38	25.49	3.40	12.13
6:1	71.33	5.14	20.39	2.78	13.88
8:1	75.58	3.53	18.64	1.99	21.41
10:1	76.36	3.59	17.45	2.29	21.27

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radation trend. There was an apparent thermal decomposition step for NR macromolecular chains. The onset temperature of decomposition with pronounced weight loss was observed in the range of 220 °C to 240 °C. When more silica was incorporated into the rubber composite matrix, the main decomposition profile gradually shifted to a higher temperature. This indicated that the spray dried composite powder gradually possessed a more complex thermo-oxidative decomposition associated with noticeable improvement of thermal ageing resistance. Similar observations were reported in the literature (Paiva L. B. d. et al., 2014; Peng Z. et al., 2007; Sen D. et al., 2006). The thermal stability of as-prepared composite powders was greatly governed by the effective silica coating of rubber particles.

3.1.5 Effect of feed rate

The effect of feed flow rate to the spray dryer on the NR-SiO₂ powder properties was determined. **Fig. 4** and **Table 2** show the effect on the particle size distribution and mean particle diameter of NR-SiO₂ powders prepared at fixed NR/Si mass ratio of 2:1 and constant inlet air temperature of 160 °C. The results showed that increasing the feed flow rate produced a mild gradual increase in powder particle size. By increasing the feed rate, more latex composite dispersion was introduced and atomized during spraying, thus resulting in larger liquid droplets and inducing more collisions and subsequent fusion of small particles into larger ones, as shown in **Fig. 5**. The thin uneven silica coating and uncoated NR surface can, respectively, be distinguished by looking at the distribution of Si

Fig. 4 Particle size distribution of NR-SiO₂ powders prepared at a different feed rates. Reproduced by permission from Prachaya S. (2011).

Table 2 Mean particle diameter (μm) of NR-SiO₂ powders at a different feed rates.

NR/Si mass ratio	Feed rate (mL/min)			
	7	9	11	13
2:1	6.93	7.65	8.15	8.28

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(see the tiny bright spots in **Fig. 6(b), (e), (h) and (k)**) and C elements (see the tiny bright spots in **Fig. 6(c), (f), (i) and (l)**). The composite particles prepared at a lower feed rate showed higher coverage of latex particles with silica,

possibly due to the increasing rate of heat transfer (Reineccius G.A., 2001).

3.1.6 Effect of inlet air temperature

Fig. 7 and **Table 3** show the effect of different inlet air temperature on particle size distribution and mean particle diameter of composite particles prepared at fixed NR/Si mass ratio of 2:1 and constant feed rate of 9 mL/min. It can be seen that increasing the inlet air temperature resulted in negligible changes in the particle size. As shown in **Fig. 8**, though the powder showed fractured particle surface with cracks or fissures, an increase in inlet air temperature produced more nearly smooth and hard particles. This is mainly due to fact that the increase in drying air temperature provided greater driving force for moisture evaporation, causing rapid drying and formation of rigid outer layer over rubber particles (**Fig. 9(g)**) (Alamilla-Beltrán L. et al., 2005; Finney J. et al., 2002). A relatively high drying temperature can accelerate both the hydrolysis and condensation processes of silanol groups, leading to higher conversion of silica sols into gelled particles (Wang S. et al., 2015). As a consequence, higher air inlet temperature favored the formation of more smooth and uniform layer of silica particles, as evidenced by the presence of high density of Si elements shown in **Fig. 9(h)**

Fig. 5 SEM micrographs of NR-SiO₂ powders prepared at a different feed rates: (a) 7 mL/min, (b) 9 mL/min, (c) 11 mL/min, and (d) 13 mL/min, respectively. Magnification 5 kx. Reproduced by permission from Prachaya S. (2011).

Fig. 6 SEM micrographs and EDS elemental X-ray maps showing silicon and carbon distribution within NR-SiO₂ powders prepared at different feed rates: (a–c) 7 mL/min, (d–f) 9 mL/min, (g–i) 11 mL/min, and (j–l) 13 mL/min respectively. Reproduced by permission from Prachaya S. (2011).

and (k). On the basis of obtained data, the optimum spray conditions for preparation of spherical rubber powders

containing fixed NR/Si mass ratio of 2:1 were determined as inlet air temperature of 160 °C and feed flow rate of 9 mL/min and therefore used in the subsequent study reported above.

Fig. 7 Particle size distribution of NR-SiO₂ powders prepared at different inlet air temperatures. Reproduced by permission from Prachaya S. (2011).

Table 3 Mean particle diameter (μm) of NR-SiO₂ powders at different inlet air temperatures.

NR/Si mass ratio	Inlet air temperature (°C)			
	120	140	160	180
2:1	7.53	7.66	7.65	7.68

Fig. 8 SEM micrographs of NR-SiO₂ powders prepared at different inlet air temperatures: (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C, respectively. Magnification 6 kx. Reproduced by permission from Prachaya S. (2011).

Fig. 9 SEM micrographs and EDS elemental X-ray maps showing silicon and carbon distribution within NR-SiO₂ powders prepared at different inlet air temperatures: (a–c) 120 °C, (d–f) 140 °C, (g–i) 160 °C and (j–l) 180 °C respectively. Reproduced by permission from Prachaya S. (2011).

3.2 Characterization of NR-SiO₂/PLA composite

3.2.1 Morphology of NR-SiO₂/PLA composite

SEM images of NR-SiO₂/PLA composite containing 5.0 wt% spray dried rubber powders as filler and prepared via melt compounding process are illustrated in **Fig. 10**. Based on **Fig. 10(b–d)**, the NR-SiO₂-loaded PLA composite showed a wrinkled and crumpled layer structure, possibly due to the strong filler-filler or particle-particle interactions resulting from fairly high mass ratio of NR to silica. When the amount of latex was more than that of silica layer, the rubber particles were not sufficiently covered by silica layer and thus agglomerated rapidly, leading to poor adhesion to and poor dispersion in polymer matrix. Individual NR-SiO₂ particles could be observed in the composite containing rubber powder of higher NR/Si mass ratio, as evidenced in **Fig. 10(d)**. In comparison, neat PLA exhibited little or no wrinkled appearance with a relatively homogeneous smooth surface. This morphological observation suggested that a better dispersion of rubber fillers in the polymer matrix was essential to yield an uniform NR-SiO₂/PLA composites.

3.2.2 Thermal and mechanical properties of NR-SiO₂/PLA composite

The DSC curves of NR-SiO₂/PLA composite and PLA polymer are presented in **Fig. 11**. The results showed that there is no significant variation of glass transition temperature ($T_g \sim 62^\circ\text{C}$) and melting temperature ($T_m \sim$

160°C) of all investigated composite specimens and neat PLA. The small variation ($< 1^\circ\text{C}$) could be primarily due to the restriction in the polymer chain mobility caused by the interaction between the powder filler and PLA matrix (De Falco A. et al., 2007; Paiva L.B.d. et al., 2014). **Table 4** summarizes the tensile strength, elongation at break and impact strength as a function of NR/Si mass ratio and spray drying conditions. Based on **Table 4**, one can observe that all the investigated mechanical properties exhibited a similar trend in which the addition of dried NR-SiO₂ powders led to an increase in the tensile strength and elongation at break as well as the impact strength values. However, all NR-SiO₂ powder-filled PLA specimens showed lower or reduced tensile strength and elongation at break than neat PLA, which reflected the poor dispersion and high agglomeration of filler particles within PLA matrix. This could be mainly ascribed to the presence of wrinkled surface as evidenced in **Fig. 10** and thus uneven residual stress distribution in the composite material. The wrinkled or crumpled morphology resulting from structural defects was caused by poor filler dispersion accompanied by weak filler/matrix interaction effect occurring during melt-compounding process. Similar observations on the effect of wrinkles on tensile properties and fracture stress were reported by Min et al. and Papageorgiou et al. (Min K. et al., 2011; Papageorgiou D.G. et al., 2017). Furthermore, it was reported that good dispersion control and the interaction between polymer-particle filler play a vital role in transferring properties from filler

Fig. 10 SEM micrographs of NR-SiO₂/PLA composite containing 5.0 wt% spray dried rubber powder prepared at different NR/Si mass ratios: (a) PLA (control), (b) 0.5:1, (c) 1:1, and (d) 2:1. Magnification 1 kx. Reproduced by permission from Prachaya S. (2011).

Fig. 11 DSC curves of NR-SiO₂/PLA composite containing 5.0 wt% spray dried rubber powders prepared at different NR/Si mass ratios. Reproduced by permission from Prachaya S. (2011).

Table 4 Mechanical properties of NR-SiO₂/PLA composite containing 5.0 wt% spray dried rubber powders prepared at different NR/Si mass ratios.

NR/Si mass ratio	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/m)
0.5:1	13.3 ± 3.8	0.98 ± 0.1	47.5 ± 3.5
1:1	18.5 ± 4.2	1.18 ± 0.3	51.7 ± 7.4
2:1	24.2 ± 2.7	1.49 ± 0.2	55.3 ± 5.6
PLA	45.1 ± 3.0	2.75 ± 0.1	48.9 ± 0.0

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to matrix (Blattmann C.O. et al., 2019; Nor N.A.M. et al., 2016; Song K., 2017; Tanno K., 1990).

4. Conclusions

In this study, we demonstrated a simple preparation of spherical NR-SiO₂ particles with diameter of less than 10 μm using sol-gel and spray drying. Our findings showed that the rubber particle size increased gradually with the increment of NR/Si mass ratio. Increasing feed flow rate induced the fusion of small particles with marginal increase in particle size. It was found that a low feed rate and high air inlet temperature led to more uniform encapsulation of rubber particles within the silica layer, as evidenced by high elemental C/Si ratio and SEM-EDX images. The incorporation of spray-dried powder of increasing rubber content gradually increased the mechanical strength of NR-SiO₂/PLA composite. However, both the tensile strength and elongation at break of the composites were relatively lower, compared to its neat polymer. It was deduced that poor particle dispersion

associated with poor filler-matrix interaction decreased the composite's mechanical strength; therefore, the melt-compounding process needs to be improved.

Acknowledgements

This scientific work was financially supported by the Centennial Fund of Chulalongkorn University.

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