Improvement of the Mechanical and Thermal Properties of Silica-Filled Polychloroprene Vulcanizates Prepared from Latex System

Nittaya Rattanasom,[1,2] Pattana Kueseng,[3] Chudej Deeprasertkul[1,2]

[1]Institute of Molecular Biosciences, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand
[2]Research and Development Centre for Thai Rubber Industry, Faculty of Science, Mahidol University, Nakhon Pathom 73170, Thailand
[3]Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

ABSTRACT: In this work, well-dispersed silica suspension having excellent storage stability was prepared by using an ultrasonic probe. The obtained silica suspension and curatives were added into the polychloroprene (CR) latex for preparing silica-filled CR latex compounds having various silica loadings. Then, the silica-filled CR vulcanizates were prepared via a dipping process. The thermal and mechanical properties of the dipped CR vulcanizates containing silica dispersed by using an ultrasonic probe were compared with those of the dipped CR vulcanizates containing silica dispersed by using a mechanical stirrer. By using thermogravimetric analysis, it could be seen that thermal resistance of the dipped CR films having silica prepared by ultrasonic probe is greater than that prepared by using the mechanical stirrer. This result corresponds well with their tensile strength after aging in the hot-air oven. In addition, modulus, tensile strength, and tear strength of the vulcanizates prepared from CR latex compounds containing silica prepared by using the ultrasonic probe are obviously greater than those prepared by using the mechanical stirrer, especially at high silica loading. This is because the silica prepared using the ultrasonic probe is uniformly distributed and dispersed throughout the CR matrix, as can be observed in the scanning electron microscope micrographs. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2657–2668, 2012

Key words: polychloroprene; well-dispersed silica; thermal properties; mechanical properties; ultrasonic probe

INTRODUCTION

Polychloroprene (CR) is superior to natural rubber in that it is more resistant to heat, flame, ozone, weather, and chemicals.[1] Therefore, it can be used in applications where the products are in contact with solvents and oils, such as joint seals, hoses, and gloves.[1,2] In addition, the mechanical properties such as tensile strength, modulus, and hardness of solid CR have been reported to be improved by adding precipitated silica which is widely used for making colored products.[3] However, the mechanical properties of the silica-filled rubber can be also affected by several parameters such as particle size, surface area, aggregate structure and surface activity of silica, the distribution of silica in the rubber matrix, and rubber–silica interaction.[4–7] Some studies have been shown that the use of silica in latex is limited because silica tends to form agglomerates in the liquid. This leads to a lack of proper distribution of silica in the latex and a significant reduction in the mechanical properties of the dipped products containing silica compared with the unfilled ones.[8,9] To overcome this problem, both processing method and stabilizer are important parameters to be considered. An ultrasonic probe is rather expensive, but it is reported to be a tool with high potential to deagglomerate the powder such as Al_2O_3 and TiO_2 in liquid medium.[10,11] It is stated that dispersion of powder by using an ultrasonic probe is a consequence of microturbulences caused by fluctuation of pressure and cavitation.[12] When ultrasound is used for dispersing of high concentration batches, the liquid jets streams arising from ultrasonic cavitation make the particles collide with each other at velocities of up to 1000 km/h.[12] This leads to a very effective breakage of agglomerates and aggregates, especially for the particulates from several nanometers to couple of microns.[12] Thus, the ultrasonic probe is thought to be a practical tool for preparing the dispersed silica in the rubber. Additionally, it is well known that a mechanical stirrer is categorized as a high-shear device which is simple and inexpensive. Therefore, it is of our interest to compare the performance of these tools for preparing the silica

TABLE 1
List of Materials and Chemicals Used in This Study

Chemicals	Trade name/Grade	Supplier/Country
Chloroprene latex	Lipren T	Bayer Thai Co., Ltd./Thailand
Precipitated silica	Tokusil®233	Tokuyama Siam Silica Co., Ltd./Thailand
PEO–PPO–PEO triblock copolymers	Pluronic F127	BASF (Thai) Ltd./Thailand
Sodium hydroxide (NaOH)	AR	Fluka Co., Ltd./Thailand
50%w/w Sulphur dispersion	Commercial	Lucky Four Co., Ltd./Thailand
50%w/w Zinc oxide dispersion	Commercial	Lucky Four Co., Ltd./Thailand
Diphenyl guanidine (DPG)	Naftocit® DPG	Behn Meyer Chemical (T)/Thailand
Diphenyl-thiourea (DPTU)	Commercial	Bayer Thai Co., Ltd./Thailand
Calcium nitrate	AR	Cosan (Thailand) Co., Ltd./Thailand
Teric 16A16	AR	The East Asiatic (Thailand) Public Co., Ltd./Thailand
Corn powder	Food	Ocean foods (Thailand) Co., Ltd./Thailand

suspension. To overcome the bonding forces after wetting the silica as well as maintain the stability of the silica suspension during storage, a surfactant is also added in the system. In this work, polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymers (PEO–PPO–PEO triblock copolymers), consisting of two hydrophilic PEO chains and a hydrophobic PPO chain, are chosen because they generally give good stabilization ability.[13] The silica suspensions prepared by ultrasonic probe and mechanical stirrer are used for preparing silica/CR vulcanizates. Then, their mechanical and thermal properties are compared. Furthermore, fracture surfaces of silica/CR composites are examined using scanning electron microscope (SEM).

EXPERIMENTAL

Materials

Materials used in this experiment and their supplier are shown in Table I. PEO–PPO–PEO triblock copolymers having molecular weight of 12,600 g/mol were used as a surfactant. The curatives for preparing latex compound consisted of magnesium oxide, zinc oxide, diphenyl guanidine (DPG), and diphenyl-

thiourea (DPTU). Calcium nitrate solution containing Teric 16A16 was used as a coagulant in the dipping process.

Study of the effect of surfactant concentration, silica concentration, and sonication time on the particle size of silica suspension

The schematic diagram containing details for each study is depicted in Figure 1. Silica suspension was prepared by adding the precipitated silica in sodium hydroxide (NaOH) solution having pH 13. The amount of silica used depends on the study shown in Figure 1. Then, the mixture was manually stirred with a stirring rod before subjecting to sonication at 90% wave amplitude by using a Branson sonifier (W450; Hielscher Ultrasonics GmbH, Germany) operated at 20 kHz and equipped with a standard probe 13 mm in diameter. The experimental set-up is schematically shown in Figure 2. The silica suspension was prepared in a 150 mL beaker, covered with a piece of aluminum foil and placed in an ice bath. The sonication time for each experiment is also presented in the schematic diagram (Fig. 1). After sonicating, the surfactant was immediately added into the silica suspension and consequently stirred
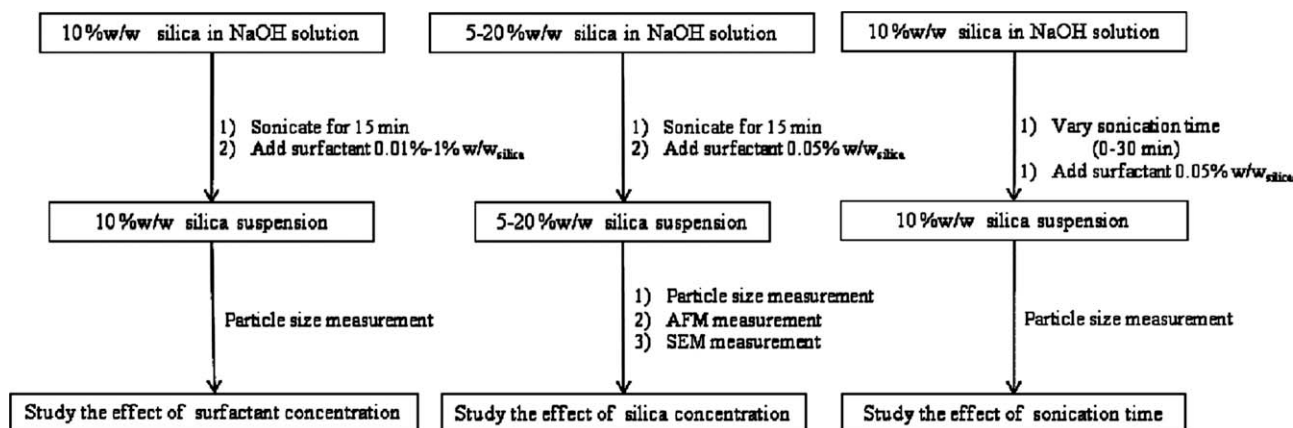

Figure 1 The schematic diagram for studying the effect of surfactant concentration, silica content and sonication time.
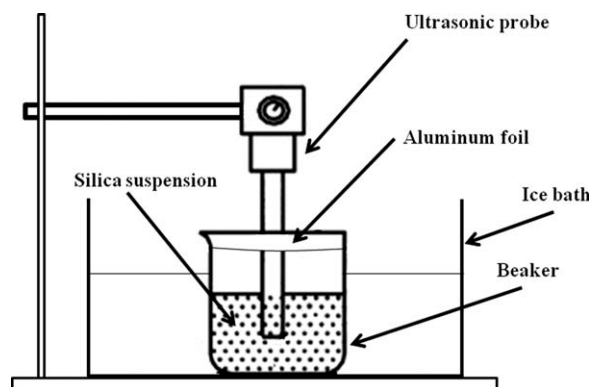
Figure 2 The schematic diagram of experimental set-up for preparing silica suspension by using ultrasonic probe.

with the magnetic stirrer for 4 min before determining the particle size distribution and average particle size at $d(0.5)$ by using a lazer particle size analyzer (Malvern 2000; Malvern Instruments, UK). For studying the effect of surfactant concentration on average particle size of silica suspension, the surfactant concentration was varied from 0.01 to 1% w/w_{silica}. The morphology of the silica at various concentrations was examined by using a SEM and an atomic force microscope (AFM).

Study of the effect of tool type on the particle size of silica suspension and the storage stability of the silica suspension

For studying the effect of the tool type on the dispersion performance, 10% w/w silica suspension was prepared by using different tools, which were the ultrasonic probe and mechanical stirrer. The silica added in NaOH solution was manually stirred with a stirring rod before subjecting to sonication at 90% wave amplitude by using a Branson sonifier, operated at 20 kHz. For the mechanical stirrer (Euro-St DS 2; IKA, Germany), a rotor speed of 400 rpm was used. The treatment time was varied from 0 to 30 min for both devices. A sampling of silica suspension was made at the interval of 5 min, and 0.05% w/w_{silica} surfactant solution was then added into the sampling for both cases before determining the average particle size at $d(0.5)$. For studying the storage stability, the

treatment time when using the ultrasonic probe and the mechanical stirrer was 15 and 30 min, respectively. After that, 0.05% w/w_{silica} surfactant solution was then added and stirred with the magnetic stirrer for 4 min. Thereafter, the silica suspensions were kept at 25°C, and the sampling was made at every 10 h for determining the average particle size of silica. The change in the stability of silica suspension was indicated by the change of its average particle size.

Preparation of silica/CR latex compounds and silica/CR vulcanizates

10% w/w silica suspension dispersed by using the ultrasonic probe and mechanical stirrer were used for preparing silica/CR latex compounds. The steps for preparing silica suspensions are schematically shown in Figure 3. After treating with either the ultrasonic bath or mechanical stirrer, 0.05% w/w_{silica} surfactant was instantly added into the obtained silica suspension and it was stirred for 4 min using a magnetic stirrer. The steps and details of the experiment for preparing silica/CR latex compounds and silica/CR vulcanizates are shown in Figure 4. The compound formulation is given in Table II. Then, the silica suspensions prepared above were added into the CR latex, and the mixture was stirred at room temperature using a magnetic stirrer. The silica suspension was added into the CR latex with various amount of silica ranging from 0 to 15 phr. Thereafter, the other chemicals functioning as curatives were added into the silica/CR latex, and the mixture was further stirred for 15 min. Finally, the silica/CR compounds were obtained. Afterward, silica/CR compounds containing various silica contents were used for preparing silica/CR vulcanizates via a coagulant dipping process using glove mold. The dipped samples were cured to 100% of complete cure in the hot-air oven at 100°C. Cure times of the dipped samples were determined at 100°C by using the moving die rheometer (RheoTECH MD+; Tech-Pro), according to ISO 6502 and they were in the range of 33–41 min depending on the formulation used. The corn powder was used for stripping the vulcanized silica/CR films from the mold. The vulcanized samples were left at 25°C for at least 1 day before determining the mechanical and thermal properties.
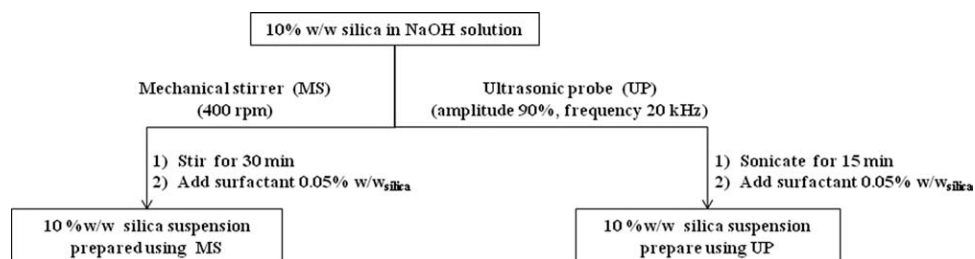

Figure 3 The schematic diagram for preparing silica suspensions using different devices.
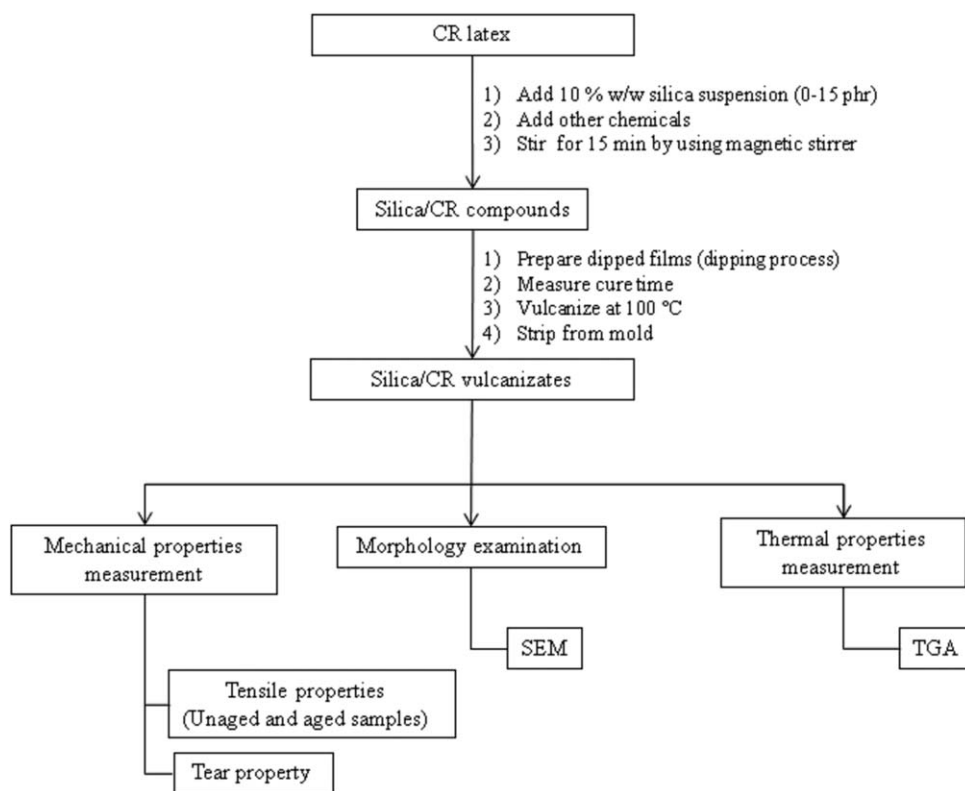
Figure 4 The schematic diagram of the experiment for preparing silica/CR latex compounds and silica/CR vulcanizates.

Measurement of the mechanical and thermal properties of silica/CR vulcanizates

All mechanical properties were measured using the universal testing machine (Instron extensometer 5566; Instron). Tensile properties were determined using the dumbbell-shaped specimens following ISO 37 Type 2 at a cross-head speed of 100 mm/min. Tensile properties after aging in the hot-air oven at 100°C for 22 h were also determined, and then the relative modulus and relative tensile strength were calculated by using eq. (1).[14]

$$\text{Relative tensile properties} = \frac{TP_a}{TP_u} \quad (1)$$

where TP_u and TP_a are the tensile properties (modulus or tensile strength) of unaged and aged samples. The measurement of tear strength was performed in accordance with ISO 34. The crescent test pieces were punched from the CR sheets by using die B. The values of tear and tensile properties were the average of 4–5 specimens. The decomposition temperatures of silica/CR vulcanizates were determined using the thermogravimetric analyzer (TGA/SDTA 851; Mettler-Toledo) with nonisothermal mode. Approximately 10 mg of the vulcanized CR were heated from 40°C to 600°C at a heating rate of 20°C/min with a continuous N_2 flow at 60 mL/min. Thereafter, the purge atmosphere was changed to

O_2, and the sample was continuously heated up to 850°C. The actual amount of silica in the vulcanized silica/CR samples could be also determined from TGA results by using eq. (2):

$$\text{Silica content (phr)} = \frac{(100 - R_f) \times (R_f - R_u)}{100} \quad (2)$$

where R_u and R_f are the residual weight (%) of unfilled CR film and silica-filled CR samples.

Morphology examination

The morphology of silica suspension was investigated by using a SEM and an AFM. The specimens were prepared by diluting the concentration of 10% w/w silica suspension to 6.7×10^{-4}% w/w.

TABLE II
Formulation of the CR Latex Compound

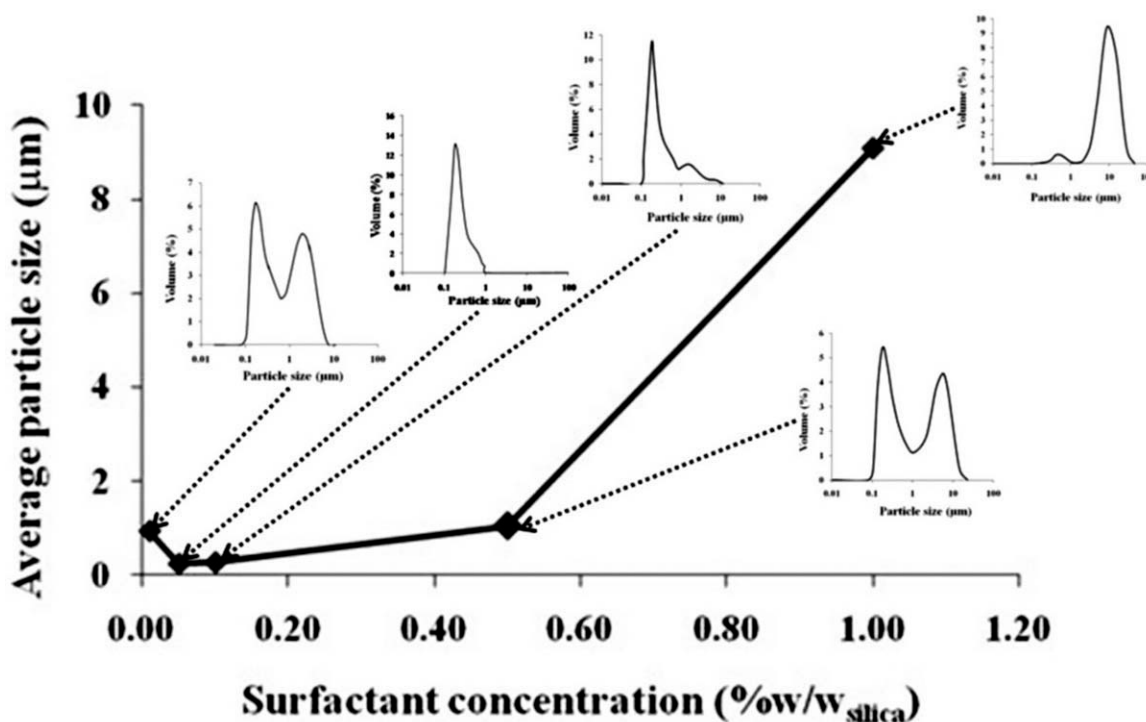| Ingredients	Wet weight (g)	Dry weight (g)
57% CR latex	175.4	100
33% Diphenyl guanidine (DPG) dispersion	1.52	0.5
10% Silica dispersion	0, 50, 100, 150	0, 5, 10, 15
50% Sulphur dispersion	2	1
50% Zinc oxide dispersion	10	5
10% N-N'-Diphenylthiourea (DPTU) dispersion	20	2

Figure 5 Effect of surfactant concentration on the average particle size of 10% w/w silica suspension.

Thereafter, it was dropped on the glass slides and dried in an oven at 60°C for 2 h. For SEM analysis, all samples were coated with platinum–palladium to prevent electron bombard on the sample surfaces before examining under SEM (S-2500; Hitachi, Japan) with 15 kV accelerating voltage. For AFM examination, the glass slide containing silica was placed on 100 μm cantilever, on which Si_3N_4 tip was mounted. The experiment was performed using the AFM (NS3a; Digital Instruments) in tapping mode. The oscillation frequency used was between 250 and 300 kHz, and tests were performed under hard tapping condition (set-point voltage was varied from 0.7 to 1.0 V). For the examination of the fracture surfaces, pieces of the silica/CR sheets were immersed in liquid nitrogen for 6 min, and they were then fractured. Thereafter, they were mounted on the stubs and subsequently gold-coated before examining under SEM using the same conditions as mentioned above.

RESULTS AND DISCUSSION

Effect of surfactant concentration, silica concentration, and sonication time on the particle size of silica suspension

The average particle size of silica suspension at various surfactant concentrations is depicted in Figure 5 together with the insets of their particle size distribution curves. The results reveal that the average

particle size of silica gradually reduces when the surfactant concentration is increased from 0.01% w/w_{silica} to 0.05% w/w_{silica}. This corresponds to an alteration of the particle size distribution from a bimodal peak to a narrow unimodal peak. Herein, it is also interesting to compare the particle size distribution curves of the silica suspension before and after sonication when containing 0.05% w/w_{silica} surfactant in Figure 6. The result indicates the existence of many small aggregates after sonication. This means that the energy locally injected in the suspension through the ultrasonic wave is large enough to break up the large agglomerates. Moreover, the separated particles can be shielded when the right quantity of surfactant is used so that the
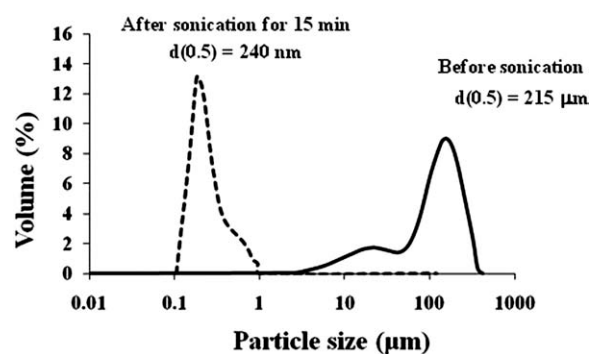

Figure 6 Particle size distribution of 10% w/w silica suspension in the presence of surfactant (0.05% w/w_{silica}), before and after sonication.
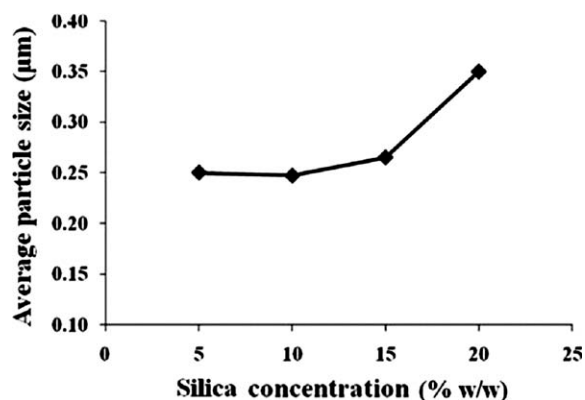
Figure 7 Effect of silica content on the average particle size of silica suspension.

reagglomeration is not possible. The average particle size at surfactant concentration 0.05% w/w$_{silica}$ is about 0.24 μm or 240 nm, and it is almost unchanged when surfactant concentration is increased up to 0.1% w/w$_{silica}$ as can be seen also in Figure 5. Nevertheless, the bimodal peak of bigger particle size is observed again when the concentration reaches 0.1% w/w$_{silica}$. This infers that the bigger silica aggregates start to form again in the suspension. In addition, when the surfactant concentration is greater than 0.1% w/w$_{silica}$, the average particle size gradually increases and it dramatically increases when the surfactant concentration is

higher than 0.5% w/w$_{silica}$. This is in good agreement with the appearance of the bimodal peak at even bigger particle size indicating the formation of many larger aggregates or agglomerates. It is believed that the bigger particle sizes are observed when the surfactant concentration is less than 0.05% w/w$_{silica}$ because the amount of surfactant is insufficient to completely cover the silica surface. Thus, the larger aggregates can be still formed through hydrogen bonding. Additionally, the bridging effect, that is, the surfactant molecule adsorbs on more than one silica particle is an explanation for the formation of the larger aggregates formed again when the surfactant concentration is greater than 0.1% w/w$_{silica}$.[15] The results obtained in this part show that 0.05% w/w$_{silica}$ of surfactant is suitable for preparing 10% w/w silica suspension, and it is chosen for further study.

The effect of silica concentration on the average particle size of silica dispersed by using the ultrasonic probe is depicted in Figure 7. It shows that the average particle size of silica is similar when silica concentration is less than 15% w/w, but it drastically increases when silica concentration is more than 15% w/w. This can be confirmed by SEM and AFM images illustrated in Figures 8 and 9, respectively. In addition, SEM and AFM images correspond well to each other. As can be seen in the images, most of the small silica clusters are individually distributed in the suspension when silica
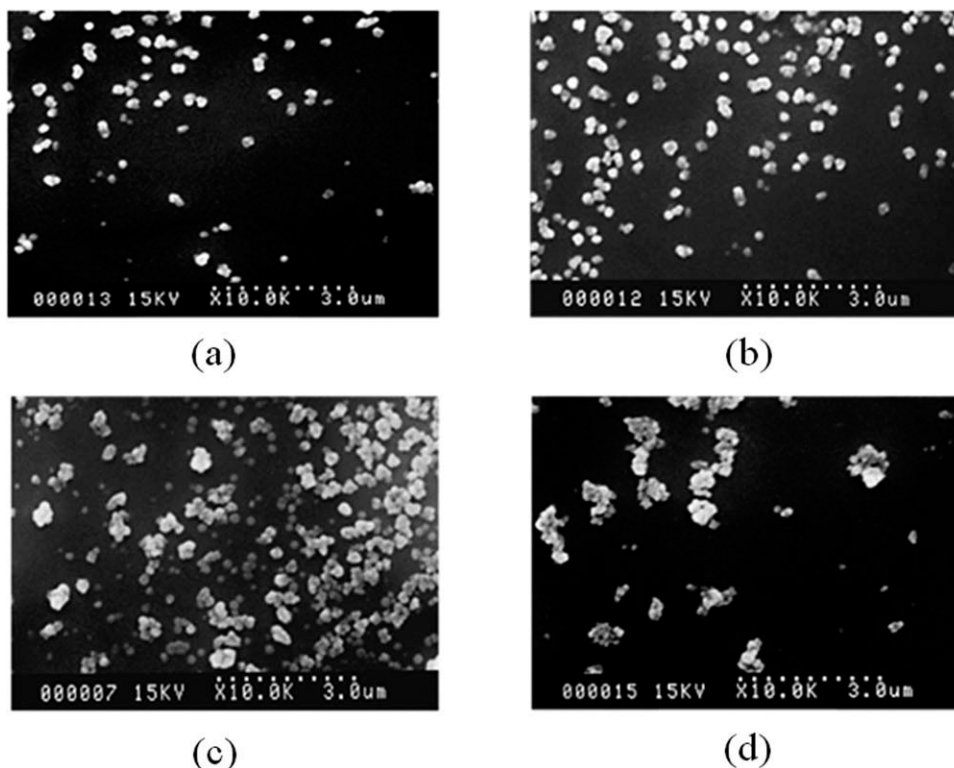

Figure 8 SEM micrographs of the dispersed silica prepared from silica suspension of various silica contents (% w/w): (a) 5%, (b) 10%, (c) 15%, and (d) 20%.
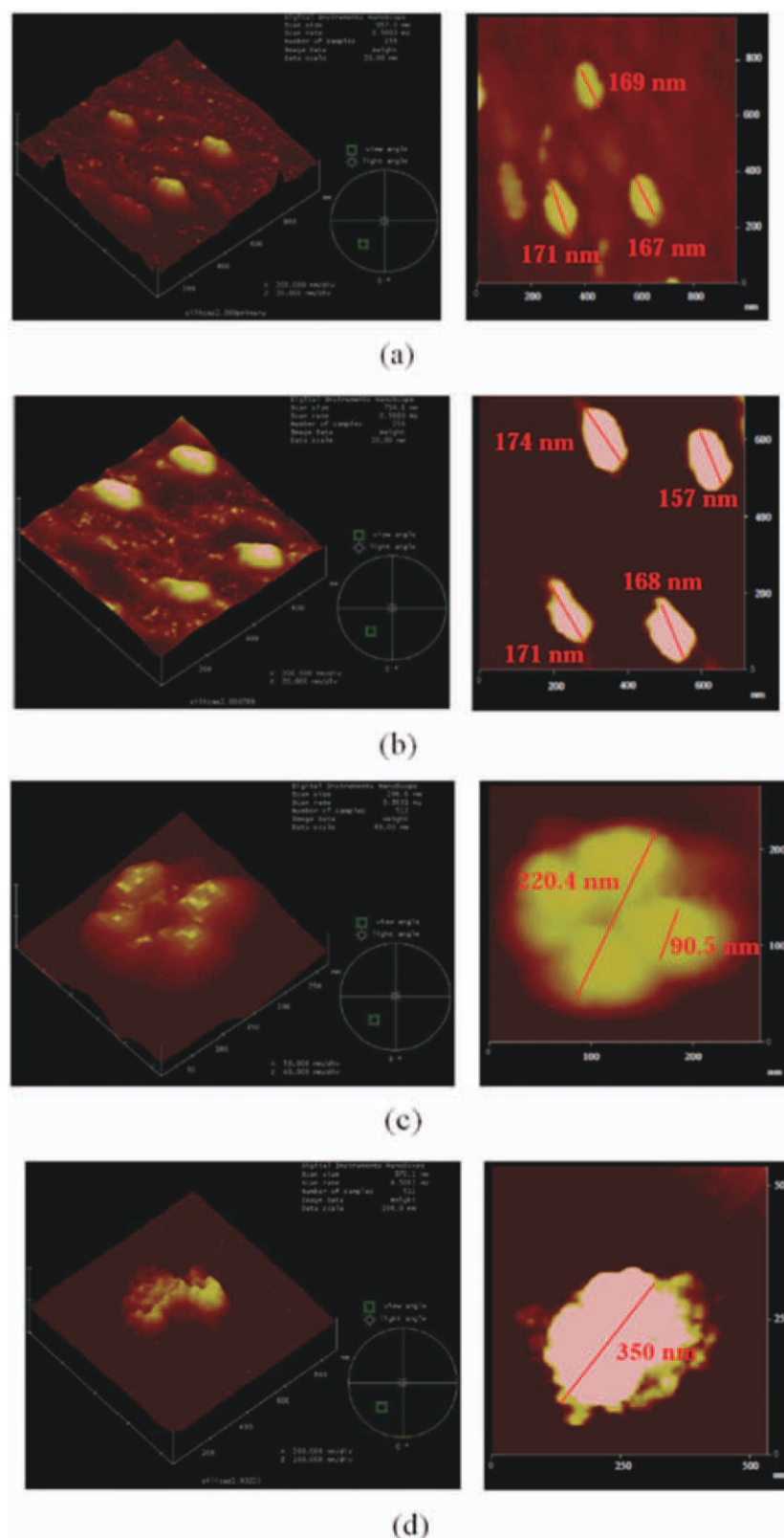
Figure 9 AFM images of the dispersed silica prepared from silica suspension of various silica contents (% w/w): (a) 5%, (b) 10%, (c) 15%, and (d) 20% [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com.]

concentration is less than 15% w/w. Then, the bigger silica clusters and bigger aggregates are observed when silica concentrations are 15 and 20% w/w, respectively. The average diameters of silica in 5, 10, 15, and 20% w/w silica suspension measured from the SEM micrographs are about 164, 175, 240,
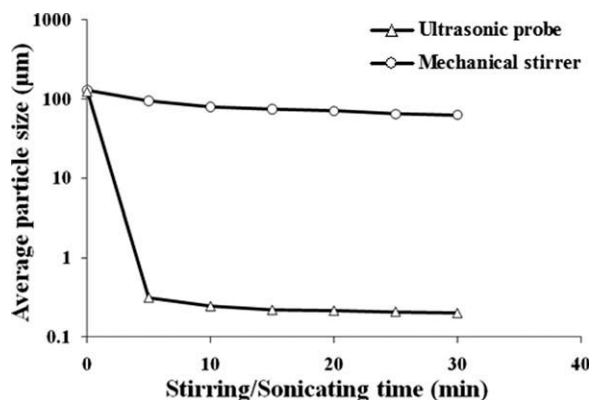
Figure 10 Average particle size of 10% w/w silica suspension as a function of stirring or sonicating time prepared by using different devices.

and 525 nm, respectively, while those shown in AFM images are about 167, 169, 220, and 350 nm, respectively. It appears that the average diameter of silica measured from SEM and AFM images is very similar when silica concentration is less than 20% w/w while the difference in size is large when silica concentration reaches 20% w/w. This may be due to the fact that when silica particles form bigger aggregates at 20% w/w silica suspension, the aggregate structures can be varied widely, either long or round shape which can greatly affect the measured diameter. In addition, the scan area in AFM is much less than that in SEM. Therefore, only one silica aggregate of high silica concentration system is observed in the AFM image which might not represent the average size of all silica aggregates in the system.

Effect of tool type on the average particle size of silica suspension and the storage stability of the silica suspension

Figure 10 shows the average particle size of the dispersed silica in 10% w/w silica suspension prepared by using the ultrasonic probe at various sonicating times, and it is compared with that prepared by using the mechanical stirrer. It is found that the average particle size of silica decreases with increasing time after treatment by both processing devices, though the characteristic of the reduction in particle size is rather different. The average particle size of silica prepared by using the mechanical stirrer gradually reduces with time while that prepared by using the ultrasonic probe dramatically decreases from 125.5 μm to 0.31 μm when sonicating for 5 min. Thereafter, it also slightly reduces with increasing time. At 15 and 30 min of treatment time, the average particle size of silica prepared by using the ultrasonic probe is about 0.24 and 0.20 μm, respectively, while that prepared by using the

mechanical stirrer is about 75 and 63 μm, respectively.

As the storage stability of silica suspension is one of the important parameters in dipping process, the storage stability of silica suspension prepared by both devices as a function of time is investigated and compared in Figure 11. As can be seen, the particle size of silica particles prepared by using the mechanical stirrer and ultrasonic probe does not change until the storage time reaches 63 and 1000 h, respectively. These results show that the triblock copolymers can provide stability for silica suspension prepared from both devices. Nevertheless, the silica suspension prepared using the ultrasonic probe exhibits the longer storage stability than that prepared by using the mechanical stirrer. This is because the stability of the suspension depends on the particle size of silica particles in the system.[16] From this result, it may be explained that the stabilization of silica suspension results from the adsorption of surfactant (PEO–PPO–PEO block copolymers) by the hydrogen bonding between the hydrophilic PEO groups and the silanol groups on silica surface.[13] As a consequence, the less polar PPO group points out in the solution and provide steric barrier between silica particles leading to the delay of large aggregation formation.[13] This means that the PEO–PPO–PEO copolymers are steric stabilizers for silica particles.

The mechanical and thermal properties of silica/CR vulcanizates

A total of 10% w/w silica suspension prepared by using mechanical stirrer and ultrasonic probe are added into CR latex for preparing silica/CR latex compounds with various silica contents. Then, the latex compounds are processed for preparing the
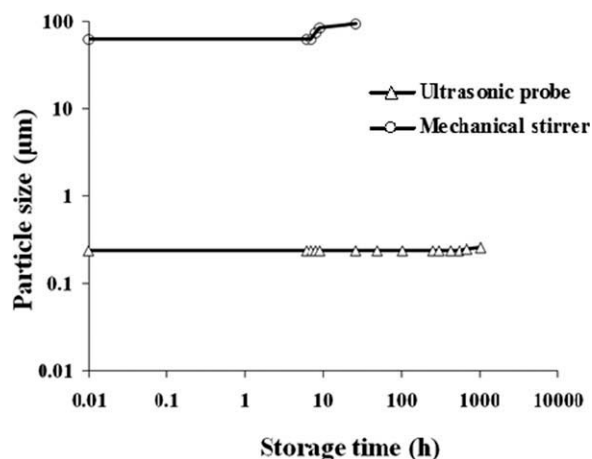

Figure 11 Average particle size of 10% w/w silica suspension as a function of storage time prepared by using different devices.

TABLE III
Mechanical Properties of Silica/CR Films Containing Various Silica Contents

Properties	Silica loading (phr)							
	Mechanical stirrer				Ultrasonic probe			
	0	5	10	15	0	5	10	15
300%Modulus (MPa)	0.94 ± 0.05	2.10 ± 0.02	2.30 ± 0.03	4.14 ± 0.02	0.94 ± 0.05	2.61 ± 0.03	3.17 ± 0.03	4.83 ± 0.01
Tensile strength (MPa)	5.5 ± 1.2	7.5 ± 1.0	10.2 ± 1.2	12.5 ± 0.5	5.5 ± 1.2	8.4 ± 0.8	13.1 ± 1.3	18.4 ± 0.3
Elongation at break (%)	1200 ± 24	748 ± 15	745 ± 19	690 ± 17	1200 ± 24	729 ± 14	749 ± 10	704 ± 15
Tear strength (kN/m)	23.4 ± 0.2	26.1 ± 0.3	37.4 ± 0.3	52.6 ± 1.6	23.4 ± 0.2	43 ± 2.5	71.2 ± 1.0	96.8 ± 0.4
Relative 300% modulus	1.07	1.11	1.16	1.18	1.07	1.09	1.15	1.17
Relative tensile strength	0.56	0.63	0.71	0.73	0.56	0.74	0.77	0.88

silica/CR vulcanizates, and the mechanical properties of the resulting vulcanizates are compared in Table III. It is apparent that 300% modulus, tensile strength, and tear strength increase with increasing silica loading while the elongation at break decreases markedly when only 5 phr of silica is added. Nevertheless, the elongation at break of the samples only slightly decreases when silica content is further increased. In addition, tensile strength and tear strength of the CR having silica prepared from ultrasonic probe are clearly greater than that prepared from the mechanical stirrer, especially at high silica loading. Tear strength of the samples containing 15 phr of silica prepared using the ultrasonic probe is about two times higher than that prepared by using the mechanical stirrer. This should be due to the better distribution and dispersion of the silica prepared using the ultrasonic probe as shown in Figure 12. On the other hand, the agglomeration of silica can be clearly observed in the specimens hav-

ing silica particles prepared by using the mechanical stirrer. These results also indicate that the silica deagglomerated by using ultrasonic probe still disperses well after adding into the CR latex. Thus, it is clear that the ultrasonic probe is more effective to disperse silica for using in the latex compared with the mechanical stirrer.

The thermal aging properties of all CR vulcanizates are also investigated by determining the tensile properties after aging at 100°C for 22 h. Then, the relative 300% modulus and relative tensile strength of the vulcanizates are calculated and given in Table III. The results clearly show that the relative 300% moduli of all samples are greater than one indicating the increase in the modulus of the CR films after being subjected to high temperature. The increase in modulus is thought to arise from the postcuring effect, which is commonly found in CR. The postcuring of CR is attributed to the formation of intermolecular crosslinking and/or intramolecular cyclization
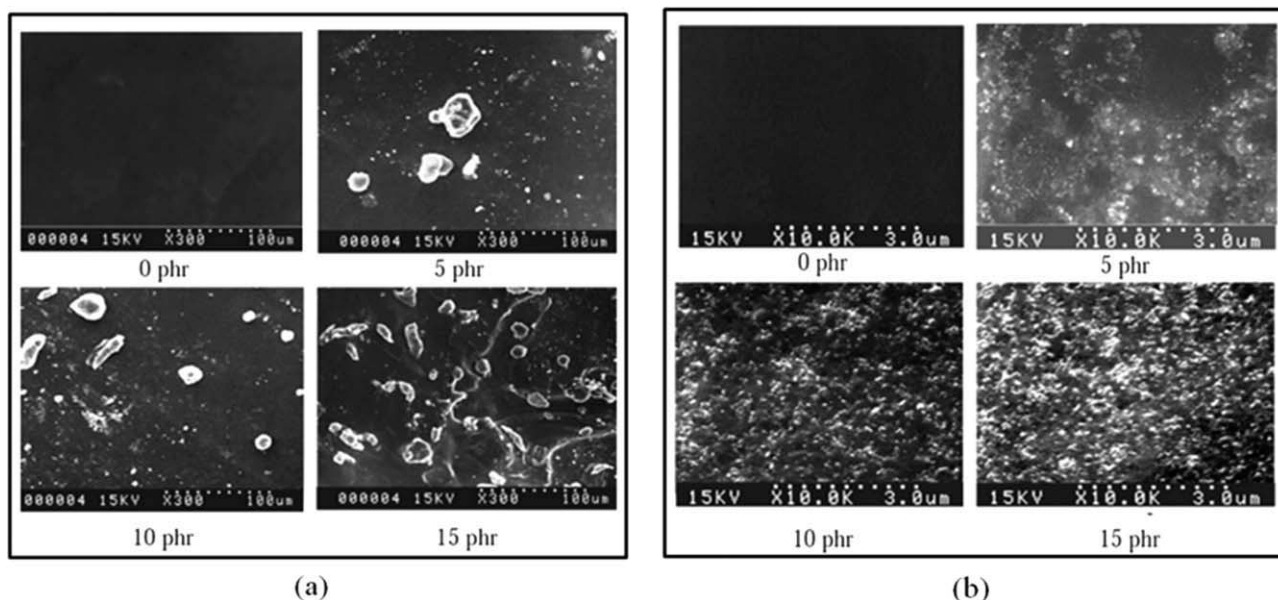

Figure 12 SEM micrographs of fracture surface of CR samples containing various silica contents prepared by using different devices: (a) mechanical stirrer and (b) ultrasonic probe.
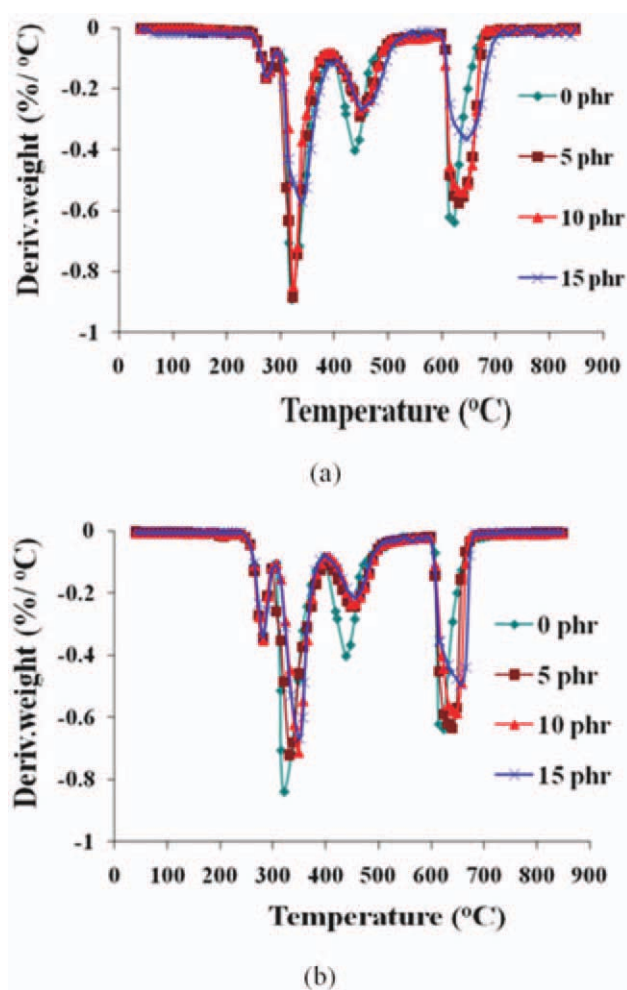
Figure 13 DTGA results of silica/CR composites having various silica contents prepared by using different devices: (a) mechanical stirrer and (b) ultrasonic probe [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com.]

between CR main chains.[17] In the previous study, the modulus of silica-filled CR/NR blend also increases after being subjected to high temperature, and the explanation is also given to the postcuring effect.[18]

Additionally, the relative modulus increases gradually with increasing silica loading implying that the degree of postcuring is also affected by the silica loading. The chemical reaction between the silanol group and the allylic chlorine atom in CR, which could take place at high temperature, could be the explanation for these results.[19,20] Table III also shows the increase in the relative tensile strength of the samples with increasing silica loading. Besides, the relative tensile strength of the specimens having silica prepared by using ultrasonic probe is higher than that of the mechanical stirrer. The result infers that the CR vulcanizates containing silica prepared by using ultrasonic probe exhibit the greater thermal aging resistance. Therefore, it can be concluded from this work that the improvement in thermal aging with increasing silica loading of the CR films prepared by using ultrasonic probe arises from the combination of dilution effect, enhanced crosslink density, and improved silica dispersion.

DTGA curves of the CR samples having various silica loadings prepared by using mechanical stirrer and ultrasonic probe are shown in Figure 13. It is evident that there are four decomposition steps. The first small decomposition peak (T_{max}^1) is caused by the decomposition of the corn powder used for stripping the dipped films from the molds. The second and third peaks (T_{max}^2 and T_{max}^3) are mainly resulted from the dehydrochlorination of chlorine atom in polymer chain of CR and the decomposition of the carbon atom, respectively. The fourth peak (T_{max}^4) corresponds to the decomposition of the carbon residues formed in the third stage.[21] It can also be seen that the second, third, and fourth decomposition peaks of the dipped CR films containing higher silica content shift to higher temperatures. The decomposition temperature at peak of the dipped films containing various silica loadings are compared in Table IV. It reveals that all decomposition temperatures at peaks, except for the T_{max}^1, tend to increase with increasing silica content for both

TABLE IV
DTGA Results of the Dipped CR Films Containing Various Silica Contents Prepared by Using Different Devices

| Method | Silica content (phr) | DTGA, temperature at which | | | |
		First peak (T_{max}^1); (°C)	Second peak (T_{max}^2); (°C)	Third peak (T_{max}^3); (°C)	Fourth peak (T_{max}^4); (°C)
Mechanical stirrer	0	273	321	438	623
	5	273	323	448	631
	10	273	327	454	640
	15	273	348	456	648
Ultrasonic probe	0	273	321	438	623
	5	273	331	450	640
	10	273	348	457	648
	15	273	350	466	655

TABLE V
Effect of Processing Methods on the Silica Content in the Dipped CR Film Determined from TGA Results

Device	Silica content (phr)	
	Compounded CR latex	Dipped CR film[a]
Mechanical stirrer	5	4.3 ± 0.9
	10	9.1 ± 1.4
	15	13.9 ± 1.7
Ultrasonic probe	5	4.7 ± 0.5
	10	9.3 ± 1.1
	15	14.2 ± 0.5

[a] Determined from TGA results.

processing methods. It has been reported that the improvement in thermal resistance of the CR containing silica is due to the migration of the inorganic nanoparticles to the surface of the composites at elevated temperature because of its relatively low surface potential energy.[22] This migration results in the formation of a silica/CR char, which acts as a heating barrier to protect the CR inside. Similar result was also found by Gilman et al.[23] Additionally, at a specific silica content, the samples having silica prepared by using ultrasonic probe gives the higher T_{max}^2, T_{max}^3, and T_{max}^4 than those having silica prepared by the mechanical stirrer. These results also correspond well with the thermal aging results discussed above.

As the CR films in this work were prepared from compounded CR latex containing various silica contents (0–15 phr) via a dipping process, it is likely that the actual amount of silica in the dipped films might be less than the amount of silica added into the CR latex. Therefore, the actual amount of silica in the dipped film is determined from the TGA results, and the data are summarized in Table V. Because the dipping process is performed while all silica/CR latex compounds have good stability, the result indicates the loss of silica particles by flowing back to the compounded latex tank during the dipping process. As the average particle size of CR latex which is about 130 nm is much smaller than that of silica particles, it is likely that some of the silica particles flow back to the compounded latex tank faster than the CR latex. As a consequence, the amount of silica in all dipped CR films is less than the amount of silica added into the CR latex. In addition, the amount of silica in the dipped CR films having silica prepared from ultrasonic probe is more than that of the corresponding CR films having silica prepared from mechanical stirrer. A possible explanation is that silica particles prepared by using ultrasonic probe are smaller than those prepared by mechanical stirrer. Thus, the smaller silica particles would flow back into the compounded latex tank less than the larger silica particles during the dipping process.

CONCLUSIONS

Well-dispersed silica suspension can be prepared by using the ultrasonic probe. At optimum conditions, which are 10% w/w silica suspension, 0.05% w/w surfactant concentration, and 15 min of sonication time, the silica suspension has the average particle size measured using the particle size analyzer of 240 nm. However, the average diameter of this silica determined by using SEM and AFM techniques are 175 and 169 nm, respectively. Additionally, the mechanical properties such as modulus and strengths, and thermal properties of silica/CR composites containing silica deagglomerated by the ultrasonic probe are obviously superior to those containing silica dispersed by the mechanical stirrer, especially at high silica loading. This is because the ultrasonic probe provides well distributed and dispersed silica suspension as well as the longer storage stability in the CR latex which gives rise to the better dispersion of silica in the CR vulcanizates. Fracture surfaces of the vulcanizates analyzed using SEM reveal that the silica particles deagglomerated by using ultrasonic probe still disperse well after adding into the CR latex. Thus, the silica suspension prepared in this work has high potential either for preparing the dipped rubber products such as gloves, or for preparing the silica/rubber masterbatch used for other applications.

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