Bull. Mater. Sci., Vol. 38, No. 4, August 2015, pp. 1033–1038. © Indian Academy of Sciences.

Effect of zinc oxide nanoparticles synthesized by a precipitation method on mechanical and morphological properties of the CR foam

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MS received 27 November 2014; accepted 8 January 2015

Abstract. **ZnO nanoparticles were synthesized by a precipitation method in aqueous media from zinc nitrate hexahydrate and sodium hydroxide. The synthesized ZnO nanoparticles exhibited a crystalline structure with hexagonal structure of the wurtzite. The morphology of the synthesized ZnO nanoparticles presented a spherical shape with the average primary size of 54.53 nm and the specific surface area of 20.28 $m^2\ g^{-1}$. The effect of the synthesized ZnO nanoparticles by the precipitation method as a crosslinking agent for chloroprene rubber foam (CR foam) on cure characteristics, mechanical properties and morphologies was investigated. The aim of this study is to vary the synthesized ZnO nanoparticles' level in the range of 0.5–5 parts per hundred parts of rubber (phr) compared with the conventional ZnO at 5 phr. The rheological characterization showed that the maximum torque (M_H), the minimum torque (M_L), the differential torque (M_H–M_L) and Mooney viscosity increased with the increase in synthesized ZnO nanoparticles' content, whereas the optimum cure time (t_{90}) and scorch time ($T5$) decreased. On the other hand, the mechanical properties such as hardness, tensile strength and specific gravity were improved. For CR foam, the results compared to the amount of conventional ZnO, only 60 wt% (3 phr) nano-ZnO was enough to obtain similar cure characteristics and mechanical properties. The synthesized ZnO nanoparticles showed the mechanical properties higher than conventional ZnO because of small particle size and large specific surface area which led to the increase in the degree of crosslinking.**

Keywords. **Zinc oxide; nanoparticles; synthesis; chloroprene rubber; CR foam.**

1. Introduction

Zinc oxide (ZnO) has attracted much attention because of its interest in basic study and its application aspects such as rubber, ceramics, electronics, paints, animal feed, cosmetics and pharmaceuticals.[1–3] In recent times, many applications need ZnO nanoparticles for high-quality products which include controlled processing from synthesis, forming and sintering. However, the synthesis of ZnO nanoparticles remains a challenge. Many methods for synthesis of ZnO nanoparticles have been reported in wet chemistry such as thermal decomposition,[4] sol–gel techniques[5] and precipitation.[6] Precipitation is one of the methods which can control the size, shape and morphology of particles at low temperature. Advantages of the aqueous precipitation method compared with other methods are low cost, simplicity and nontoxicity. Precipitate can be formed as nuclei and then nuclei grows to become particles.[7] Nuclei formation and growth of nuclei depend on the concentration of precursor solution and reactive time.[8] The precipitation method can control different parameters such as solution concentration and pH.[9,10] The synthesis of ZnO nanoparticles by the precipitation method involves the reaction of zinc salts such as $Zn(NO_3)_2$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $ZnSO_4$ with basic solutions containing LiOH, NH_4OH and NaOH.[3,11,12] Kumar *et al*[13] synthesized ZnO nanoparticles by the precipitation method from zinc sulphate heptahydrate and sodium hydrate as precursors. In rubber industry ZnO is used as an activator of rubber vulcanization. ZnO is important as it affects the vulcanization rate and properties of rubber products. Commonly, the conventional rubber grade uses ZnO particle size in the range of 0.1–0.4 μm and the specific surface area of around 10–20 $m^2\ g^{-1}$.[14,15] The tendency is to minimize the amount of ZnO in rubber compound because of its toxicity. Control of ZnO as activator is related to processing and properties of rubber. However, we expected that ZnO nanoparticles can reduce the amount of ZnO usage as activator. Kim *et al*[15] studied the effect of ZnO nanoparticles on the cure characteristics and mechanical properties of the silica-filled natural rubber/butadiene rubber compounds. With the increasing amount of ZnO nanoparticles, the cure characteristics and mechanical properties are increased. This is due to the increase in specific surface area of ZnO nanoparticles which leads to increase in the degree of crosslinking.

Chloroprene rubber (CR) is a polar rubber and contains chlorine atom attached to the backbone. Therefore, it has ozone and weather resistance, mineral and vegetable oil resistance and low flammability when compared with nonpolar rubbers such as natural rubber (NR), ethylene propylene diene monomer (EPDM), etc. Chloroprene rubber is

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vulcanized by metal oxides. The metal oxides often use ZnO as crosslinking agent with magnesium oxide (MgO), which is used as an acid acceptor. Generally, the conventional ZnO is used in chloroprene rubber formulation at 5 phr with magnesium oxide at 4 phr for the optimum cure state. The nanotechnology may be able to reduce the amount of usage of ZnO due to the decrease in particle size and increase of specific surface area. CR foam is produced with a blowing agent to create an air-filled matrix structure which is used in the automotive industry as well as in air conditioning fields. It is used for sealing, isolating, confinement and shock absorption.

In this study, ZnO nanoparticles are synthesized by the precipitation method using zinc nitrate hexahydrate and sodium hydroxide as precursors. The synthesized ZnO nanoparticles are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The specific surface area and particle size distribution are investigated by the Brunauer–Emmett–Teller (BET) and laser light scattering technique. Later, CR foam is prepared at various synthesized ZnO nanoparticles' levels in the range of 0.5–5 parts per hundred parts of rubber (phr) compared with the conventional ZnO at 5 phr. The influences of synthesized ZnO nanoparticles' content on the cure characteristics, Mooney viscosity and mechanical properties of the foam are investigated. Furthermore, a microscopic study is also performed to study the effect of the synthesized ZnO nanoparticles' content on the morphology of the CR foam.

2. Experimental

2.1 *Synthesis of ZnO nanoparticles*

ZnO nanoparticles were synthesized by the precipitation method using zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Qrec) and sodium hydroxide (NaOH, Qrec) as precursors. ZnO nanoparticles were produced by mixing aqueous solutions of zinc nitrate and sodium hydrate. ZnO nanoparticles were formed by the reaction between Zn^{2+} and hydroxide ions as shown by the following equations:[11]

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-, \quad (1)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2, \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O. \quad (3)$$

The aqueous solution was prepared by mixing zinc nitrate hexahydrate and sodium hydroxide aqueous solutions. In a typical procedure, 2.28 g of zinc nitrate hexahydrate was dissolved in 75 ml of deionized water and then, 0.6 g of NaOH in 150 ml of deionized water was added dropwise under magnetic stirring. After the addition was completed, the stirring was continued for 30 min and then cooled with cold water. The precipitates were filtered and washed by pure water several times. Then the obtained precipitates were dried at 60°C for 24 h and calcined at 200°C for 2 h. The crystalline and phase structure of the synthesized ZnO was studied by an X-ray diffractometer (XRD, D8-Advance, Bruker, CuKα radiation). FTIR spectra were studied in the range of 400–4000 cm^{-1}. Morphology and primary sizes of the synthesized ZnO were observed by a SEM (JSM-5410LV, JEOL). The specific surface areas were investigated by the Brunauer–Emmett–Teller (BET) technique. The particle size distribution was measured by a laser light scattering technique (Mastersizer 2000, Malvern Instruments). Morphology, particle size and specific surface area of the conventional ZnO were studied by SEM, BET and laser light scattering techniques, respectively.

2.2 *Preparation of the CR foam*

Formulation of the CR foam is shown in table 1. Compound was prepared in an internal mixer of 3 litre (fill factor 0.75 and rotor speed 30 rpm). The accelerator, blowing agent and curing agent were added on a two roll mill at

Table 1. Formulation of the CR foam.

Materials	cZnO-5 phr	nZnO-0.5 phr	nZnO-1 phr	nZnO-2 phr	nZnO-3 phr	nZnO-5 phr
Chloroprene rubber	100	100	100	100	100	100
Carbon black (N-774)	60	60	60	60	60	60
$CaCO_3$	30	30	30	30	30	30
Naphthenic oil	25	25	25	25	25	25
Stearic acid	1	1	1	1	1	1
MgO	4	4	4	4	4	4
Conventional ZnO	5	—	—	—	—	—
ZnO nanoparticles	—	0.5	1	2	3	5
Q-25	7	7	7	7	7	7
OBSH-75	3	3	3	3	3	3
ZDEC	1	1	1	1	1	1
TRA	0.8	0.8	0.8	0.8	0.8	0.8
DETU-80	1	1	1	1	1	1

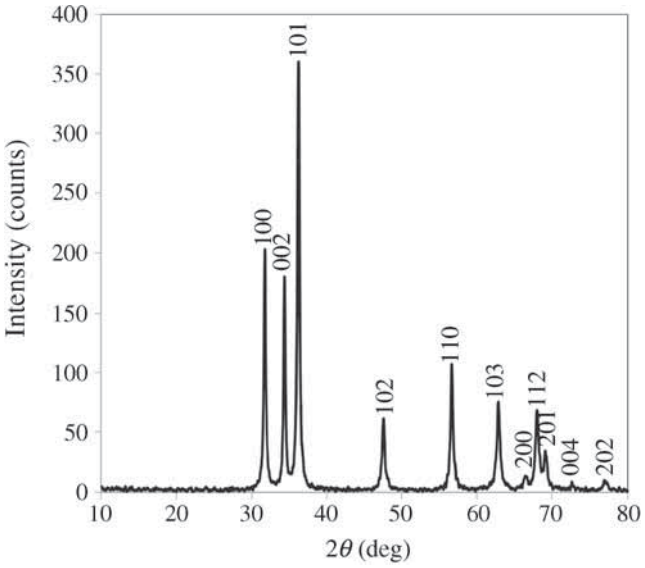

Figure 1. XRD pattern of the synthesized ZnO nanoparticles.

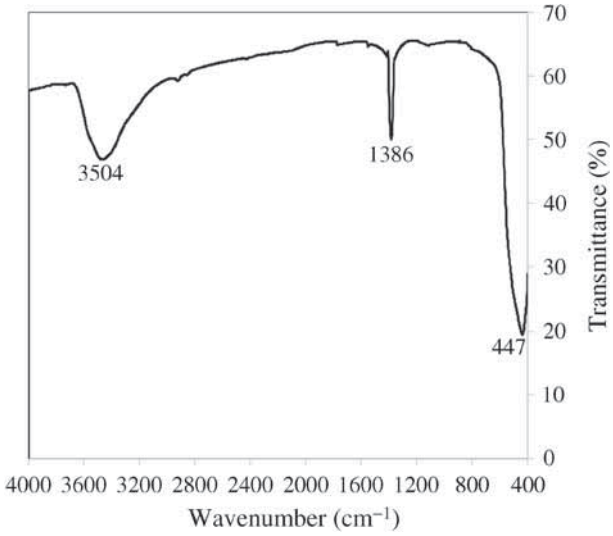

Figure 2. FTIR spectra of the synthesized ZnO nanoparticles.

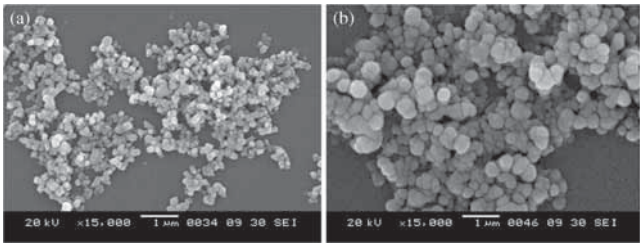

Figure 3. SEM images of ZnO particles (**a**) the synthesized ZnO nanoparticles and (**b**) the conventional ZnO.

room temperature (35°C) and sheeted off to a thickness of 8 mm.

2.3 *Characterization of the CR foam*

The cure characteristics of the CR foam were measured at 200°C for 10 min with a Moving Die Rheometer (MDR2000, Alpha Technologies). The maximum torque (M_H), the minimum torque (M_L), the differential torque (M_H–M_L) and the optimum cure time (t_{90}) were determined. Mooney viscosity (ML1 + 4) and scorch time ($T5$) were measured at 125°C for 6 min by a Mooney viscometer (MV2000, Alpha Technologies). Morphology of the CR foam was observed for the cell structure by a digital microscope (VHX-500F-Lens 450X, Keyence). The hardness test was performed using hardness tester (Teclock). The specimen was prepared by compression moulding at 165°C for 5 min (pre-vulcanization) and curing and foaming in air oven at 160°C for 30 min. Hardness scale was measured within 30 s after the full load was applied. The specific gravity of the CR foam was measured in accordance with ISO 1183. Finally, the tensile strength of the samples was measured using an autograph (AG-IS, Shimadzu) at a cross-head speed of 50 mm min^{-1} at 25 ± 5°C.

3. Results and discussion

3.1 *Characteristics of the synthesized ZnO nanoparticles*

The XRD pattern of the synthesized ZnO nanoparticles is shown in figure 1. The crystalline structure of synthesized ZnO nanoparticles exhibited a hexagonal structure of the wurtzite (JCPDS no. 36-1451). These planes correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202).[16] The average crystalline size of the synthesized ZnO was determined using Debye–Scherrer's formula.[7] The crystalline size analysis investigated from the highly intense and sharp diffraction peak corresponds to the (101) diffraction by the following equation:

$$\langle D\rangle = \frac{0.9\lambda}{\beta\cos\theta}, \tag{4}$$

where $\langle D\rangle$ is the average crystalline size, λ the CuKα radiation wavelength, i.e., 1.5414 Å, β the full-width at half-maximum in radians and θ the scattering angle in degree. The average crystalline size of the synthesized ZnO is 51.23 nm.

Figure 2 shows the FTIR spectra of the synthesized ZnO nanoparticles in the range of 4000–400 cm^{-1}. The broad band at 3504 cm^{-1} is the stretching vibration of O–H group. The peak at 1386 cm^{-1} is due to the O–H bending of water. The peak at 447 cm^{-1} is attributed to the Zn–O stretching of vibration which is consistent with the previously reported work.[11]

The SEM images of ZnO particles are shown in figure 3. The morphology of the synthesized ZnO nanoparticles is presented as a spherical shape with the average primary size of 54.35 nm (figure 3a). It was confirmed by Debye–Scherrer's formula that the morphology of the conventional ZnO showed a spherical shape with the average primary size of 218.98 nm in figure 3b. Table 2 shows the particle size and the specific surface area of the synthesized ZnO nanoparticles and the conventional ZnO.

Table 2. Average particle size and the specific surface area of ZnO particles.

Samples	Particle sizes (nm)	Specific surface area ($m^2\ g^{-1}$)
Synthesized ZnO nanoparticles	54.53	20.28
Conventional ZnO	218.98	1.33

Figure 4 shows particle size distribution of the synthesized ZnO nanoparticles and the conventional ZnO using laser light scattering technique. The synthesized ZnO nanoparticles showed particle size distribution of agglomerate nanoparticles. Most of the agglomerate sizes were in the range of 0.2–5 μm and some agglomerates around 20 μm. For the conventional ZnO, it showed the particle size distribution with agglomerated particles. Most of agglomerate sizes were in the range of 1.5–55 μm and some particles were in the range of 0.3–1.2 μm. The median particle size of the synthesized ZnO nanoparticles and the conventional ZnO was 2.39 and 7.00 μm, respectively.

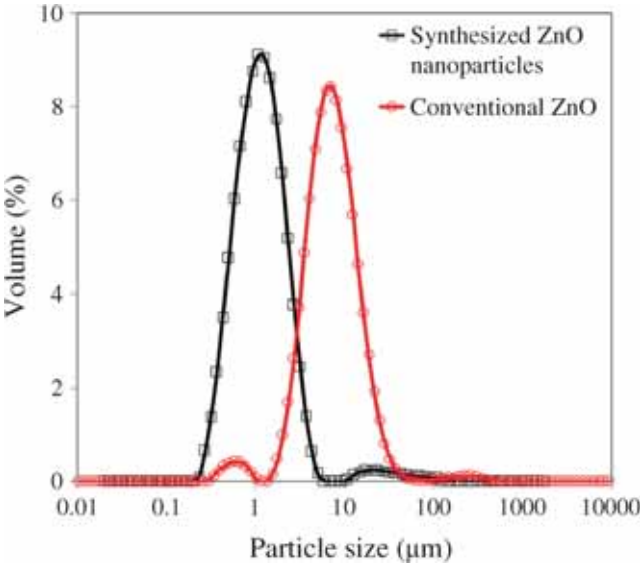

Figure 4. Particle size distribution of the synthesized ZnO nanoparticles and the conventional ZnO.

3.2 *Cure characteristics and Mooney viscosity of the CR foam*

The cure characteristics of the CR foam were measured by a Moving Die Rheometer (MDR2000) and Mooney viscosity was measured by a Mooney viscometer (MV2000) in which variation of synthesized ZnO nanoparticles' level in the range of 0.5–5 parts per hundred parts of rubber (phr) was compared with conventional ZnO 5 phr because of small particle size and large specific surface area. The test results showed that the maximum torque (M_H), the minimum torque (M_L) and the differential torque (M_H–M_L) were slightly increased with increasing synthesized ZnO nanoparticles' content, listed in table 3, indicating a higher degree of crosslink density in compound.

It was widely known that the differential torque (M_H–M_L) was directly related to the cure state or crosslink concentration of a network in compound.[17–19] The synthesized ZnO nanoparticles were often used as a curing agent with magnesium oxide (MgO) for vulcanization. It reacted with rubber molecular chain creating ether bond so as to completely crosslink in rubber as shown in figure 5.[20] A decreasing trend of the optimum cure time (t_{90}) and scorch time ($T5$) varied with the increase of the synthesized ZnO nanoparticles' content. This may be attributed to the $ZnCl_2$ formation in rubber vulcanization, which acts as a catalyst of vulcanization and accelerates the curing rate reaction. Furthermore, the increase of Mooney viscosity (ML1 + 4) was brought about by the increase in the synthesized ZnO nanoparticles' content because of faster scorch time ($T5$). Hence, at the 3 phr of the synthesized ZnO nanoparticles showed that the cure characteristics and Mooney viscosity were equivalent with the conventional ZnO at 5 phr, which indicate that it is similar to that of the cure state of rubber compound. The synthesized ZnO nanoparticles at 5 phr showed the highest degree of crosslink density in compound because of the highest differential torque (M_H–M_L).

3.3 *Mechanical properties of the CR foam*

The effect of the synthesized ZnO nanoparticles' content on the hardness and specific gravity of the CR foam is presented in figure 6. It was observed that the specific gravity of the CR foam gradually increased with the increase in the synthesized ZnO nanoparticles' content. This observation may be attributed to the decrease in foaming efficiency of rubber foam because of lower scorch time ($T5$). A

Table 3. Cure characteristics and Mooney viscosity of the CR foam.

Cure characteristics	cZnO-5 phr	nZnO-0.5 phr	nZnO-1 phr	nZnO-2 phr	nZnO-3 phr	nZnO-5 phr
The maximum torque (M_H), lb in	8.84	7.59	7.88	7.92	8.77	9.15
The minimum torque (M_L), lb in	0.77	0.74	0.78	0.79	0.85	0.86
The differential torque (M_H–M_L), lb in	8.07	6.85	7.10	7.13	7.92	8.29
The optimum cure time (t_{90}), min	3.45	4.32	4.19	3.86	3.51	3.32
Mooney viscosity (ML1 + 4 at 125°C), MU	31.48	26.17	28.97	31.22	32.50	33.12
Scorch time ($T5$), min	5.00	6.78	5.77	5.29	5.08	4.82

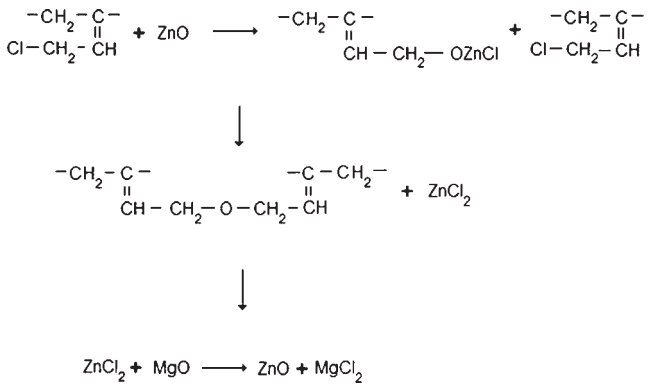

Figure 5. Mechanism of crosslinking by metal oxide.

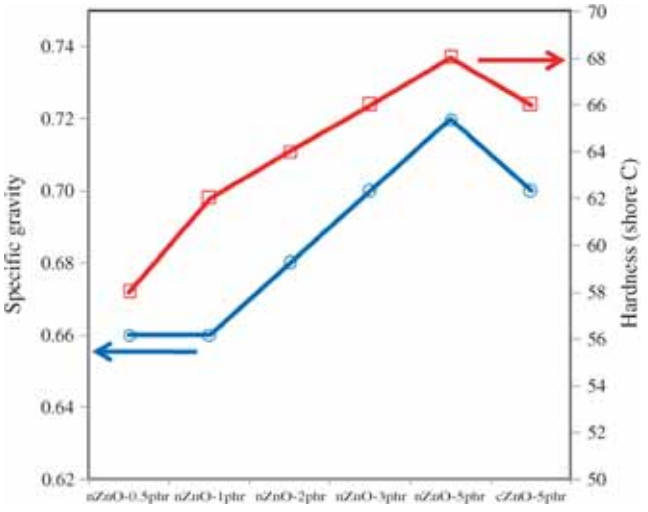

Figure 6. Specific gravity and hardness of the CR foam with various synthesized ZnO nanoparticles' content compared with conventional ZnO.

decreasing trend in scorch time ($T5$) with the increased synthesized ZnO nanoparticles' content in compound showed the low foam porosity and exhibited more rigid behaviour than the elastic behaviour, as later explained by a digital microscope. This result also corresponded to hardness of the rubber foam, which was similar to the result obtained for the specific gravity. It was obvious that the hardness and specific gravity directly corresponded to the particle size, specific surface area and amount of the synthesized ZnO nanoparticles. On the other hand, the tensile strength was also investigated with respect to the synthesized ZnO nanoparticles' content, as shown in figure 7. The tensile strength continuously increased with the increase in the synthesized ZnO nanoparticles' content. This observation is due to the reinforcement of crosslinking density which was affected by the increase of the differential torque (M_H–M_L), as previously mentioned in table 3. Moreover, the CR foam also showed the lowest foaming capability and exhibited better tensile properties.[21] From all the results mentioned above, the synthesized ZnO nanoparticles could be successfully reduced from 5 to 3 phr

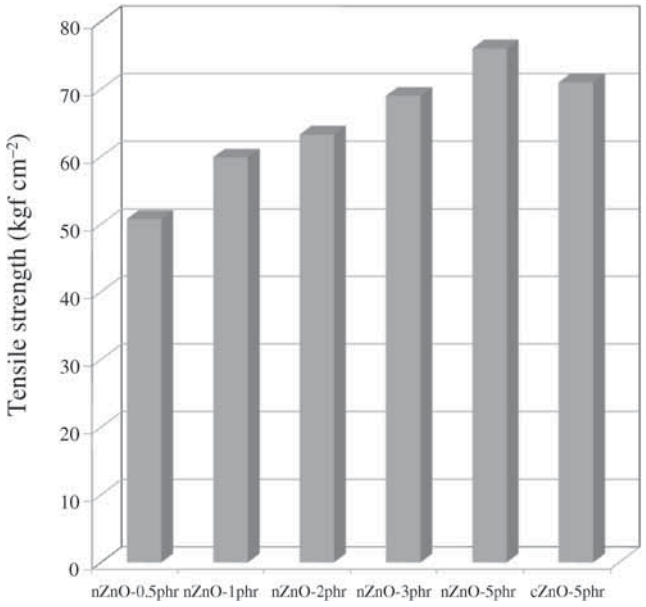

Figure 7. Tensile strength of the CR foam with various synthesized ZnO nanoparticles' content compared with conventional ZnO.

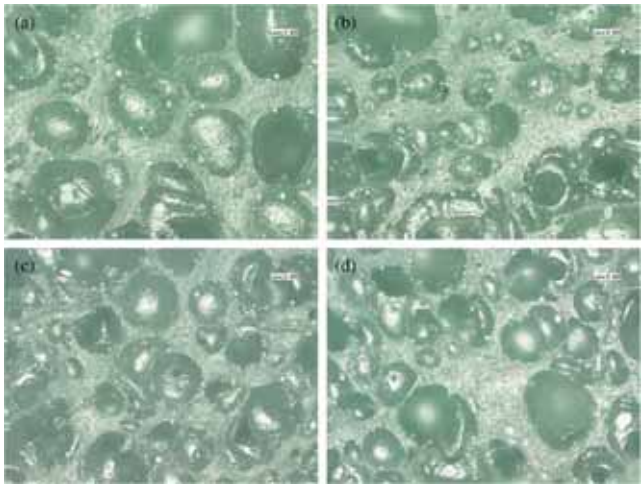

Figure 8. Morphology of the CR foam using (**a**) the synthesized ZnO nanoparticles at 1 phr, (**b**) the synthesized ZnO nanoparticles at 3 phr, (**c**) the synthesized ZnO nanoparticles at 5 phr and (**d**) the conventional ZnO at 5 phr.

because the particle sizes of ZnO are decreased, whereas, the specific surface area is increased. Moreover, it could be seen that the synthesized ZnO nanoparticles at 5 phr showed the highest mechanical properties.

3.4 *Morphological property of the CR foam*

The influence of the synthesized ZnO nanoparticles' content on the morphology and foam characteristics of the CR foam was evaluated by a digital microscope with 450 magnifications as illustrated in figure 8. The experimental result

showed that the cell size of the CR foam decreased with the increase in the synthesized ZnO nanoparticles' content. Moreover, the cell structure of the CR foam was a spherulite structure. This phenomenon was due to a decreasing trend of scorch time ($T5$) where the low expansion and foam porosity during the vulcanization process are affected. The cell morphology showed that the cell size of the CR foam directly corresponded to foam porosity and exhibited a closed cell structure because air was not free to pass through the cell.[22] It could be seen that cell structure of the CR foam at 5 phr of the conventional ZnO was similar to the cell size at 3 phr of the synthesized ZnO nanoparticles.

4. Conclusions

ZnO nanoparticles were synthesized by the precipitation method in an aqueous media from zinc nitrate hexahydrate and sodium hydroxide as precursors. The crystalline structure of the synthesized ZnO nanoparticles exhibited a hexagonal structure of wurtzite. TEM micrograph of the synthesized ZnO provided a spherical shape with the average primary size of 54.53 nm and the specific surface area of 20.28 $m^2\ g^{-1}$. The synthesized ZnO nanoparticles were used as a crosslinking agent compared with the conventional ZnO for the CR foam.

1. The maximum torque (M_H), the minimum torque (M_L), the differential torque (M_H–M_L) and Mooney viscosity are increased with the increase in the synthesized ZnO nanoparticles' content.
2. The optimum cure time (t_{90}) and Mooney scorch ($T5$) are decreased with the increase in the synthesized ZnO nanoparticles' content.
3. The hardness, tensile strength and specific gravity are increased with the increasing synthesized ZnO nanoparticles' content.
4. The cell size of the CR foam decreased with the increase in the synthesized ZnO nanoparticles.
5. For CR foam, the results compared to the amount of conventional ZnO at 5 phr, only a 60 wt% (3 phr) nano-ZnO was enough to obtain similar cure characteristics and mechanical properties.
6. The synthesized ZnO nanoparticles showed the mechanical properties higher than conventional ZnO because of the smaller particle size and larger specific surface area.

Acknowledgements

I gratefully acknowledge the financial support from the Research Promotion and Technology Transfer Center (RPTTC), Faculty of Liberal Arts and Science, Kasetsart University Kamphaeng Saen Campus and the Kasetsart University Research and Development Institute (KURDI).

References

1. Suntako R 2014 *Adv. Mater. Res.* **1025–1026** 525
2. Aimable A, Buscaglia M T, Buscaglia V and Bowen P 2010 *J. Eur. Ceram. Soc.* **30** 591
3. Faure B, Alvarez G S, Ahniyaz A, Villaluenga I, Berriozabal G, Miguel Y D and Bergstrom L 2013 *Sci. Technol. Adv. Mater.* **14** 1
4. Baskoutas S, Giabouranis P, Yannopoulos S N, Dracopoulos V, Toth L, Chrissanthopoulos A and Bouropoulos N 2007 *Thin Solid Films* **515** 8461
5. Rani S, Suri P, Shishodia P K and Mehra R M 2008 *Sol. Energy Mater. Sol. C* **92** 1639
6. Suntako R 2014 *Adv. Mater. Res.* **1044–1045** 23
7. Sangari N U and Devi S C 2013 *J. Solid State Chem.* **197** 483
8. Sharma D, Rajput J, Kaith B S, Kaur M and Sharma S 2010 *Thin Solid Films* **519** 1224
9. Suntako R 2014 *Appl. Mech. Mater.* **481** 60
10. Raoufi D 2013 *Renew. Energy* **50** 932
11. Nejati K, Rezvani Z and Pakizevand R 2011 *Int. Nano Lett.* **1** 75
12. Skapin S D, Drazic G and Orel Z C 2007 *Mater. Lett.* **61** 2783
13. Kumar S S, Venkateswarlu P, Rao V R and Rao G N 2013 *Int. Nano Lett.* **3** 30
14. Sahoo S, Maiti M, Ganguly A, George J J and Bhowmick A K 2007 *J. Appl. Polym. Sci.* **105** 2407
15. Kim I J, Kim W S, Lee D H, Kim W and Bae J W 2010 *J. Appl. Polym. Sci.* **117** 1535
16. Wang H, Li C, Zhao H, Li R and Liu J 2013 *Powder Technol.* **239** 266
17. Akhlaghi S, Kalaee M, Mazinani S, Jowdar E, Nouri A, Sharif A and Sedaghat N 2012 *Thermochim. Acta* **527** 91
18. Przybyszewska M, Zaborski M, Jakubowski B and Zawadiak J 2009 *Express Polym. Lett.* **3** 256
19. Tang M Z, Xing W, Wu J R, Huang G S, Li H and Wu S D 2014 *Chin. J. Polym. Sci.* **32** 658
20. Scott J C, White G D F, Thom D J, Whitny R A and Hopkins W 2003 *J. Polym. Sci. Part A* **41** 1915
21. Kim J H, Choi K C and Yoon J M 2006 *J. Ind. Eng. Chem.* **12** 795
22. Zhang B S, Lv X F, Zhang Z X, Liu Y, Kim J K and Xin Z X 2010 *Mater. Des.* **31** 3106