CHAPTER V

CONCLUSION AND FUTURE DIRECTION

5.1 Conclusion

In this study, the preparation of *in situ* silica was carried out by sol-gel reaction via rubber solution. The effects of reaction parameters i.e., solvent, catalyst type and concentration, mole ratio of TEOS to water, and reaction temperature on *in situ* silica formation were investigated. The effects of the *in situ* silica contents on the curing, mechanical, dynamic mechanical and thermal properties of the composite vulcanizate materials were also investigated in comparison conventional reinforcing filler (commercial silica, carbon black and calcium carbonate) with and without coupling agent.

THF was found to be the suitable solvent for the sol-gel reaction as it produced higher *in situ* silica contents in NR matrix when compared with $CHCl_3$ and CCl_4 by using the mole ratio of TEOS to H_2O at 1:1.8 and 0.093 M *n*-hexylamine at room temperature. *n*-hexylamine was the most efficient base catalyst to produce the high amount of *in situ* silica in rubbery matrix compared with *n*-butylamine. This may be explained by the longer chain of *n*-hexylamine which easily penetrated into NR matrix. The *in situ* silica contents in the rubber matrix increased with increasing catalyst concentration in both types of catalyst but the limitation of the catalyst solubility in water resulting in phase separation. The *in situ* silica content was significantly affected by the mole ratio of TEOS to water since the increase in TEOS:H_2O mole ratio promoted the rate of hydrolysis reaction in sol-gel process. To prevent the phase separation, the mole ratio of TEOS to H_2O should be less than 1:3. The long reaction time and high reaction temperature resulted in the high *in situ* silica yield in NR matrix.

The optimum condition that produced the high silica content (41 % or 70 phr) in rubbery matrix was the used of THF as the solvent, the mole ratio of TEOS to water 1:2.7 and use of 0.1395 M *n*-hexylamine as the catalyst at 50 °C for 7 days. At this condition, the good dispersion of *in situ* silica aggregates in rubbery matrix was observed. In comparison this sol-gel technique in rubber solution with the previous studied [17, 20], the results indicated that the generation of *in situ* silica in rubber solution produced *in situ* silica content 70 phr similar to the generation of *in situ* silica in solid rubber (71 phr) [20] and this was higher than that of the sol-gel technique in rubber latex which produced 23 phr of *in situ* silica [17].

Mooney viscosity and curing time increased with increasing *in situ* silica content. At the same filler content, Mooney viscosity and curing time of the NR filled samples increased as follows CB-30 < Ca-30 < In-30 < Si-30 due to the different surface properties of the filler.

The mechanical properties i.e., moduli and hardness of the composites were improved when the *in situ* silica content in NR vulcanizate increased. For the comparison of filler types, the moduli, compression set and abrasion resistance of *in situ* filled NR vulcanizate were improved compared with the Si-30 vulcanizate and Ca-30 vulcanizate. However, the mechanical properties of carbon black filled NR vulcanizate are higher than that of *in situ* silica filled NR vulcanizate. The addition of coupling agent into silica filled NR vulcanizates improved the mechanical properties.

From the dynamic mechanical properties analysis, the storage modulus (E′) at 25 °C suggested that the silica-silica interaction of *in situ* silica was weaker, resulting in better dispersion in the rubbery matrix, compared with the commercial silica. Additionally, the thermal stability of the *in situ* silica filled NR vulcanizate was improved resulting in the delayed decomposition process. Due to the characteristics of *in situ* silica prepared via NR solution, this sol-gel reaction method using TEOS is more useful and practical for industrial-scale synthesis than via NR latex.

5.2 Future Direction

Explore the use of other temperature in the sol-gel reaction with the aim to use shorter reaction time and get higher in situ silica content in NR matrix.

Study in more detail on the effect of reaction parameter such as catalyst types, catalyst concentration, silica precursor types, and mole ratio of TEOS to water on the mechanical properties and cure behavior of the rubber vulcanizate.

Investigate in the synthesis of *in situ* silica via the other rubber solution e.g. butadiene rubber.