CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The model studies have demonstrated that crosslinked network at the rubber/silica interfaces can be obtained between vinyl-containing silica and natural rubber. It was also confirmed that the crosslinking really originated from reactions between vinyl groups on modified silica surface and double bonds of squalene. Previous attempts to prepare interfacial chemical bonding using radical initiators (*t*-butyl peroxide and AIBN) were not successful due to non-selective radical process towards unsaturated moieties of squalene. Instead of forming the interfacial crosslinked layer, surface oxidation was induced. In contrast, *p*-toluenesulfonic acid (*p*-TsOH) as a cationic initiator exhibited more desirable catalytic behavior. An interfacial crosslinked layer can be generated at both the VDMS-Si/SqE and TVS-Si/SqE interfaces. The network formation was also verified by XPS results: an attenuation of the Si signal from the substrate as well as a significant increase of carbon concentration were evidenced. The thickness of crosslinked layer increased as time, temperature and *p*-TsOH concentration increased. The rate of network formation was independent of vinyl group density (TVS-Si has 2.6 times of vinyl groups on the surface as compared to ones of VDMS-Si). A comparative study also indicated that the network can also be generated in the presence of sulfur and other necessary additives conventionally used for rubber vulcanization. The network

formation was quite rapid at 150°C, the same temperature used for a subsequent curing of silica-filled rubber composites.

The success of the preparation of NR composites filled with vinyl-modified silica using sulfur curing can be expressed as a decrease of cure time, scorch time without changing Mooney viscosity as well as exhibiting relatively high tensile strength. No significant difference in mechanical properties between composites filled with VDMS-Si and ones filled with TVS-Si was observed. In comparison with the composites filled with untreated silica and mixed with Si-69, the composites filled with vinyl-containing silica showed inferior tear strength and tensile modulus. In order to improve this weakness, the method of using VDMS-Si in combination with Si-69 was attempted. This method yielded composites with improved tear strength and tensile modulus while maintaining reasonably low cure time and scorch time. This data virtually complimented the model studies and suggest that it is feasible to use vinyl-containing silica as an alternative reinforced filler for natural rubber.

We are unable to distinguish the difference in silica distribution in all composites at the length scale that can be detected by SEM. This evidence implied that favorable curing charcateristic and mechanical properties of composites filled with vinyl-containing silica can be regarded as a consequence of chemical crosslinking at the silica/natural rubber interface.

5.2 Suggestion

In order to verify the formation of network at vinyl-containing silicon oxide/squalene interface in the presence of sulfur and additives, it is also necessary to characterize the crosslinked network using XPS technique. Detailed studies of S_{2p} peaks will allow us to assess the effectiveness of sulfur crosslinking in terms of the length of sulfide linkage and may led to the possibility to subsequently predict mechanical properties of the cured composites. It is also worth trying to analyze chemical bond formation at natural rubber/treated silica interface using attenuated total reflectance spectroscopy (ATR-IR). In addition, the effectiveness of interfacial crosslinking may be determined by bound rubber value of each rubber composites in order to test the concept of model studies.