CHAPTER 5

CONCLUSION AND SCOPE FOR FURTHER RESEARCH

5.1 Conclusion

Two types of palm oil-based polymers were allowed to react with ENR and the reactions were studied. The polymers were the palm oil modified polyfunctional polyester (alkyd) synthesized via esterification and the bacterial polyester (mcl-PHA) produced from palm oil derivatives.

5.1.1 The reactions between epoxidized natural rubber and palm-oil based alkyds

This study consists of two parts. The first part investigated the reactions between ENR and alkyds A1, A2 and A3 where these alkyds were synthesized with varying proportions of carboxylic and hydroxyl contents in order to establish the predominant reaction of these two functional groups with epoxy groups in ENR. These three alkyds, A1, A2 and A3, contain overwhelmingly more hydroxyl than carboxylic groups. They could react readily with ENR at ambient temperature to cause crosslinking of ENR. FTIR provides evidence of the chemical incorporation of these alkyds into ENR. The extent of crosslinking was determined through the percentage of swelling of the rubber in toluene and the results showed that A2 was more reactive than A1 or A3 towards rubber epoxy due to its higher carboxylic content. On the other hand, hydroxyl group does not appear to react with ENR at ambient temperature. The reason being A1 has 15% more –OH group than A3, and yet they showed similar reactivity due to their similar carboxylic content. Thus, it can be concluded that the predominant crosslinking reaction has occurred between the epoxy in ENR and the –COOH in alkyd.

The second part was the extension of the first study where alkyd A4 was synthesized under the same conditions as A2 (i.e. at 130°C within 540 minutes) but incorporated with higher carboxylic content than alkyds A1, A2 and A3. The subsequent reactions of A4 with ENR were then investigated. DSC result suggested that the blends of ENR and A4 were miscible over the whole composition ranges. Furthermore, the study also revealed that crosslinking reaction could occur in the blend at a faster rate when the blends contained either equimolar of –COOH to epoxy groups or with the epoxy group in excess.

5.1.2 The reactions between epoxidized natural rubber and palm oil-based medium-chain-length polyhydroxyalkanoates

Heating at 170°C for 30 minutes has caused very slight reduction in the molecular weight of ENR, due to minimum amount of chain scission via –C=C– bond of the isoprenyl unit, as ^{1}H-NMR result did not detect any change in epoxy content. On the other hand, when the mcl-PHA was heated under the same conditions, its number average molecular weight was reduced by half, and the amount of –COOH group has doubled. When about 10 parts of mcl-PHA was mixed with 100 parts of ENR at 170°C, there was an observable reaction, as shown by FTIR spectra, evidence of the conversion of free carboxylic acid to ester group with the shift of carbonyl peak from 1741 to 1737 cm^{-1}. ^{1}H-NMR result further confirmed the ring-opening of the epoxy group by the carboxylic terminal of the mcl-PHA. However, there was no noticeable reaction at ambient temperature for short reaction time.

DSC result suggested that the ENR/PHA blends were miscible over the whole composition ranges. This study indicated that there were strong interpolymer interactions occurred between ENR and mcl-PHA. Besides, mcl-PHA could contribute plasticizing effect in the blends and therefore low level of mcl-PHA, where less than 10 parts per hundred parts of ENR would be sufficient to improve the vulcanized ENR compound and suppress the reversion of the rubber[207].

5.1.3 Mechanical properties of the alkyd modified ENR and mcl-PHA modified ENR

Most of the mechanical testing work of the alkyd modified ENR and mcl-PHA modified ENR have been carried out by the researchers from SRI, Japan. Parts of the results have been published and presented[184,185,207,220].

5.2 Suggestions for further research

For future research, it would be of interest to investigate the higher percentage of half-esters of anhydride incorporated in A1 under the similar reaction conditions as applied during the preparation of alkyd A2. Alkyds incorporated with higher amount of half-esters would offer the opportunity to compare the extent of crosslinking upon reacting with ENR at ambient temperature. Further measurements of crosslink density, percentage of swelling, average molecular weight between crosslink and modulus of swollen crosslinked ENR in toluene would be thus necessary in order to have better understanding of the extent of crosslinking.

The work presented in the study of the reactions between ENR and alkyds was restricted to the reactions at ambient temperature. In future, it would be of interest to examine the reactions at elevated temperature with the possibility of the hydroxyl group also participating in the reaction with the epoxy groups in ENR. Compared with the reactions at ambient temperature, these reactions would lead to a change in the extent of crosslink density, percentage of swelling, average molecular weight between crosslink and modulus of swollen crosslinked ENR in toluene. Such outcomes might further add to our knowledge regarding the effect of temperature on the reaction mechanisms of ENR and alkyd.

For the study of the reactions between ENR and mcl-PHA, the work presented was restricted to the reactions at 170°C for 30 minutes, which was similar to the conditions adopted by the researchers at SRI, Japan for the vulcanization of ENR rubber compounds. Our study revealed that this reaction conditions were not sufficient for the reaction towards completion. In future, it would be of interest to prolong the reaction time and investigate the duration needed for the completion of reactions. Future research works can also look into the biodegradable properties of the mcl-PHA modified ENR.