

CHAPTER 5

CONCLUSIONS AND SUGGESTION FOR FURTHER RESEARCH

5.1 Conclusions

Palm stearin alkyd with excess hydroxyl groups in its chain was modified by incorporating acid anhydrides (PA and MA) to increase its carboxyl content. Presence of higher amount of carboxylic acid side chain has improved the ability of the alkyd to function as crosslinker when it is blended with ENR. This can be seen from the low swelling percentage of the blend after immersion in toluene and improved stability towards thermal degradation.

5.1.1 Modification of palm stearin alkyd

Modification of palm stearin alkyd to increase its carboxylic content was carried out through half ester formation at controlled reaction temperature. Results obtained show that the carboxyl content of the 3 modified alkyds (AlkydMA1, AlkydMA2 and AlkydPA1) synthesised are higher than the control alkyd and this accounts for the higher acid value of the modified alkyds. The incorporation of acid anhydrides proceeded through reaction with hydroxyl groups present in the control alkyd. This was confirmed following a decrease in the hydroxyl value and hydroxyl group peak absorbance observed from the FTIR analysis of the modified alkyds as compared to those of the control alkyd. As all the alkyds composed mainly of palm stearin, glycerol and PA, no significance difference were observed in their T_g . However, AlkydMA series can be differentiated from all the other alkyds as they exhibit additional peak at 1641 cm^{-1} (C=C stretching from the incorporated MA) in their IR spectra and 6.3 ppm

(resonance of vinyl protons from the incorporated MA, $-\text{OOC}-\text{CH}=\text{CH}-\text{COOH}$) in their $^1\text{H-NMR}$ spectra.

5.1.2 Reactions of palm-stearin alkyds with epoxidised natural rubber (ENR50)

This study consists of two parts. The first part focuses on the reaction between ENR50 and AlkydMA series. These alkyds were synthesised to contain different proportions of carboxyl: hydroxyl content through incorporation of different amount of MA as carboxylic acid side chain in the alkyd. The experimental results show that blend composed of modified alkyd with high amount of carboxylic acid side chain is more reactive towards rubber epoxy than that composed of unmodified alkyd. ENR50/AlkydCO blend that has been blended for 12 hours has < 10 % of gel content while ENR50/AlkydMA1 blend that was prepared under similar conditions contain as high as 50.6 % of gel after immersion in toluene. The difference observed is attributed to the higher carboxyl content in AlkydMA1, 7.8×10^{-4} mol of $-\text{COOH g}^{-1}$ of alkyd. The same reasoning explains why ENR50/AlkydMA2 blend has the highest T_g compared to the other two blends, ENR50/AlkydMA1 and ENR50/AlkydCO. Note that AlkydMA2 has 1.22×10^{-3} mol of $-\text{COOH g}^{-1}$ of alkyd. Thus, it can be concluded that the predominant crosslinking reaction in the blend is due to the reaction between the epoxy in ENR50 and carboxylic acid side chain from the incorporated MA in the alkyd.

The aim of the second part of this study is to compare the reactivity of MA-modified alkyd and PA-modified alkyd, having similar carboxyl content, towards reaction with epoxy groups of ENR50. It was found that ENR50/AlkydMA1 blend whose alkyd carries acid side chain in the form of $-\text{OOC}-\text{CH}=\text{CH}-\text{COOH}$ exhibit higher crosslink density compared to ENR50/AlkydPA1 blend that comprised of alkyd with acid side chain in the form of $-\text{OOC}-\text{Ph}-\text{COOH}$, where Ph = aromatic ring. Presumably,

presence of the bulky aromatic ring contributed to some steric hindrance in AlkydPA1 thus reduced the reactivity of the alkyd towards epoxy group of ENR50. The results also revealed that the highly crosslinked ENR50/AlkydMA1 blend has better tolerance towards thermal decomposition compared to ENR50/AlkydPA1 blend. E_d values of ENR50/AlkydMA1 blend series are higher compared to those of ENR50/AlkydPA1, reflecting the superiority of AlkydMA1 over AlkydPA1 as crosslinker in ENR50.

5.1.3 Enhancing crosslinking in ENR50/AlkydMA1 blend via UV-irradiation

Incorporation of benzophenone as UV photoinitiator has allowed ENR50/AlkydMA1 blend to undergo UV-induced crosslinking which enhanced the extent of crosslinking in the blend. The $-C=C-$ group from the grafted MA in the alkyd and isoprene unit in the ENR50 allow the blend to produce more crosslinked structure upon UV irradiation and consequently increased the thermal stability of the blend. Results from this work show that UV curing technology is an efficient and convenient way that could be used to increase the extent of crosslinking in ENR50/Alkyd blend. In an extension work of this study, TMPTA was incorporated into the blend to further enhance the crosslink density in the blend. TMPTA proves to be reactive additive which promotes formation of crosslink bridges via irradiation-induced free radical mechanism owing to its trifunctional nature. Blends produced are able to resist total dissolution when immersed in toluene, and have better tolerance towards thermal decomposition.

5.2 Suggestion for further research

In future, it would be of interest to investigate the mechanical properties of the crosslinked ENR50/Alkyd blend prepared via solvent casting technique at ambient temperature. It is expected that different blend compositions gave rise to different mechanical properties thus measurements of Young modulus and stress-strain behaviour would be necessary to design a simple self-vulcanised blend having optimum mechanical properties. In addition, these properties may be compared to those of ENR50 vulcanised via the classical sulphur vulcanisation in order to study the effectiveness of alkyd as 'green' crosslinker, alternative to the classical vulcanisation of NR which require sulphur and additives such as accelerators and zinc oxide.

The current scope of study is restricted to the reactions of ENR50 and alkyds at ambient temperature and a long blending time (up to 12 hours) was necessary to complete the reaction. It would be rather interesting to investigate the reactions at elevated temperature with the objective to accelerate the reaction between ENR50 and alkyds. Outcomes from the study such as change in percentage of swelling, T_g and extent of crosslink density with reaction temperature might be useful to establish the kinetics of the reaction mechanisms between the two blend components.