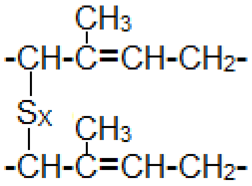
CHAPTER 2

LITERATURE REVIEWS

Oil palm tree is a great source of raw materials for the production of polymer. Almost every parts of the tree can be utilised in polymer synthesis. Whilst palm oil received great demands for the production of coatings, adhesives, and polyurethane foams, other parts of the oil palm tree such as trunk and empty fruit bunch serve well for the production of fiber board. In the current study, palm stearin is used to develop new oleochemical products. The ultimate aim of this work is to convert palm stearin into alkyd which could serve as crosslinking agent for ENR.

2.1 Known/ published works on ENR reactions and their applications

ENR is a semi-synthetic rubber, exhibiting double functionality for crosslinking, C=C and epoxide groups. Vulcanisation involving C=C group of ENR is usually associated with sulfur vulcanisation where sulfur-sulfur bond is inserted on α-carbon on the double bond, producing structure as shown in Figure 2.1. Gelling and Morrison (1985) had reported on the high efficiency of vulcanisation of ENR by sulfur alone. Sulfur reacts with the olefins by chain mechanism, and due to the random distribution of epoxide group in ENR, the chain cyclisation reaction between neighbouring double bonds is inhibited. Cure characteristic of unaccelerated sulfur vulcanisation of ENR having different epoxide content, i.e., ENR25 and ENR50 has been reported by Poh BT et al. (1996). It was found that the initial cure rate and maximum torque increases with increasing sulfur loading for both rubbers. However, vulcanised ENR50 exhibit higher value than ENR 25 due to the higher epoxide content in the former which provides greater activation of adjacent double bond.



where, x = 2, 4, 6, 8

Figure 2.1: Proposed crosslinking of ENR via sulfur vulcanisation

Generally, vulcanisation increases elasticity of rubber while it decreases plasticity (Coran, 2005). The plasticity of ENR vulcanisates can be improved by blending with thermoplastic to yield thermoplastic vulcanisate (TPV) which exhibits processing characteristic of thermoplastic and the functional performance of a conventional vulcanised rubber. TPV is prepared through dynamic vulcanisation, wherein the elastomer is vulcanised under dynamic shear to produce finely dispersed micron-sized elastomer particles with high crosslink density embedded in a thermoplastic matrix (Thitithammawong et al., 2007). TPVs based on ENR have been investigated through blending with polar thermoplastics such as PVC (Mousa et al., 1998), poly(ethylene-co-acrylic acid) (PEA) (Mohanty & Nando, 1997) and poly(methyl methacrylate) (PMMA) (Nakason et al., 2005).

The effect of vulcanisation system on the properties of thermoplastic vulcanisate based on ENR and semi-crystalline thermoplastic polyolefin; in particular polypropylene (PP) has been reported by Nakason et al. (2006). 3 types of curing systems, i.e., sulfur, peroxide and a mixture of sulfur and peroxide-cured systems were studied. It was found that TPV prepared using the mixed-cure system showed higher values of mixing torque, shear stress, shear viscosity, tensile strength and elongation at break compared to the other two curing systems. These increments may be attributed to the formation of S-S, C-S and the more stable C-C linkages in the ENR phase.

Utilisation of the epoxide groups in ENR as crosslinking sites were reviewed by Akiba and Hashim (1997). The rubber can be cured through reaction of epoxide groups with both acidic and nucleophilic reagents which results in ring opening of the highly strained 3-membered epoxy ring. Loo (1985) is among the earlier researchers who reported on the curing of ENR using molecule bearing an acid functionality. It was reported that vulcanisation of ENR with dibasic acids is generally slow, requiring 6-8 hours at elevated temperature of 160 °C. Curing of the rubber is characterised by the changes in physical properties, such as modulus, hardness and resilience, which are associated with significant increase in T_g of the ENR vulcanisates.

Findings from the crosslinking of ENR with dibasic acids have then captured the interest of Gan and Burfield (1989) to study the mode of action of dibasic crosslinking agents, in particular the cause of increase in T_g during vulcanisation of ENR. The studies were carried out by reacting ENR with a simple monobasic acid, benzoic acid. Since benzoic acid is monofunctional, the reaction of the acid with oxirane rings leads to formation of β-hydroxyester. T_g of the blend was found to increase proportionally with the benzoic acid loading. In other meaning, it shows that increase in T_g in ENR/benzoic acid blend is due to the reaction of the polar hydroxyl group, from the ring opened product, introducing inter- and intra- molecular hydrogen bonding. Therefore, it clarified that the dominant reason for the increase in T_g in the vulcanisation of ENR with dibasic acid is due to the hydrogen bonding induced by polar hydroxyl group from the ring opened structure of the rubber rather than crosslink formation.

However, Pire et. al (2010), in their studies of self-vulcanised blends based on ENR and dodecanedioic acid (DA) found that T_g of the cured blend increased non-linearly with the amount of DA. Comparison studies based on reaction of ENR and lauric acid showed that T_g of the grafted elastomer remain unchanged with all proportions of acid. Therefore, reaction of polar hydroxyl group from the ring opened structure could not explain the deviation from linearity in T_g of ENR/DA blends for high proportions of DA. The significant different results as compared to the work of Gan and companion (1989) may be due to the linear lauric acid used, which is less bulky than benzoic acid and does not interfere in the main chain mobility. The deviation in T_g of the blend at high amounts of DA is claimed to be due to the polar interactions induced by the pending chains in DA with other carboxylic groups (from pendant chains) and epoxide sites. In a recent work done by the same group, catalysis of the reaction of ENR with dicarboxylic acids was reported (Pire et al., 2011). 1,2-dimethylimidazole (DMI) were introduced in the blend to accelerate the crosslinking reaction at the same time as to weaken the detrimental effect of heat treatment and to subsequently improve the mechanical properties of the vulcanisates. DMI acts as an accelerator through formation of imidazolium dicarboxylate that enables the solubilisation and activation of the crosslinking agents.

Reaction of epoxide group in ENR with molecule bearing acid functionality has also led to the development of self-vulcanisable rubber blend system based on ENR and XNBR (Alex et al., 1989) where the blend constituents are vulcanisable by themselves without any curative or additive. The blend was prepared through blending of the masticated rubbers on a mill for 10 minutes followed by vulcanisation for 45 minutes at 140 °C. The rubber pairs complement each other by offering suitable functional groups for vulcanisation in the blend. Carboxyl group in XNBR are made available for vulcanisation of ENR while epoxide group of ENR are utilised as crosslinking agent for vulcanising XNBR. Besides, many chlorine containing polymers such as CSM (Mukhopadhyay & De, 1990b), CR (Alex & De, 1991a), and PVC (Ramesh & De, 1991) were found to form self-vulcanised blends with ENR. The proposed crosslinking reactions for these blends are shown in Figure 2.2. In ENR/ CSM blend, crosslinking in the form of sulfonate type of linkage is formed between epoxide group of ENR with

SO_2Cl group of CSM. While in ENR/CR blend, the blend components were linked together through an ether chain and a chlorine atom was attached at the carbon bearing the methyl group.

In the case of crosslinked PVC/ENR blends, the network structure consists of ether linkages and furanised ENR. It is proposed that crosslinking reaction between PVC and ENR occurs through attack of allylic chlorine of PVC on epoxide ring of ENR. Ratnam and Zaman (1997), have reported on modification of PVC/ENR blend by electron beam radiation. It was reported that the radiation had enhanced the homogeneity as well as the mechanical properties of the blend. Crosslinking of ENR50 phase upon exposure to irradiation has lead to the enhancement in tensile strength, elongation at break, hardness and aging properties of the blend. These irradiation-induced crosslinking in ENR are generally associated with the irradiation-induced ring opening side chain reaction of epoxy group and irradiation-induced oxidation at the *cis* double bond.

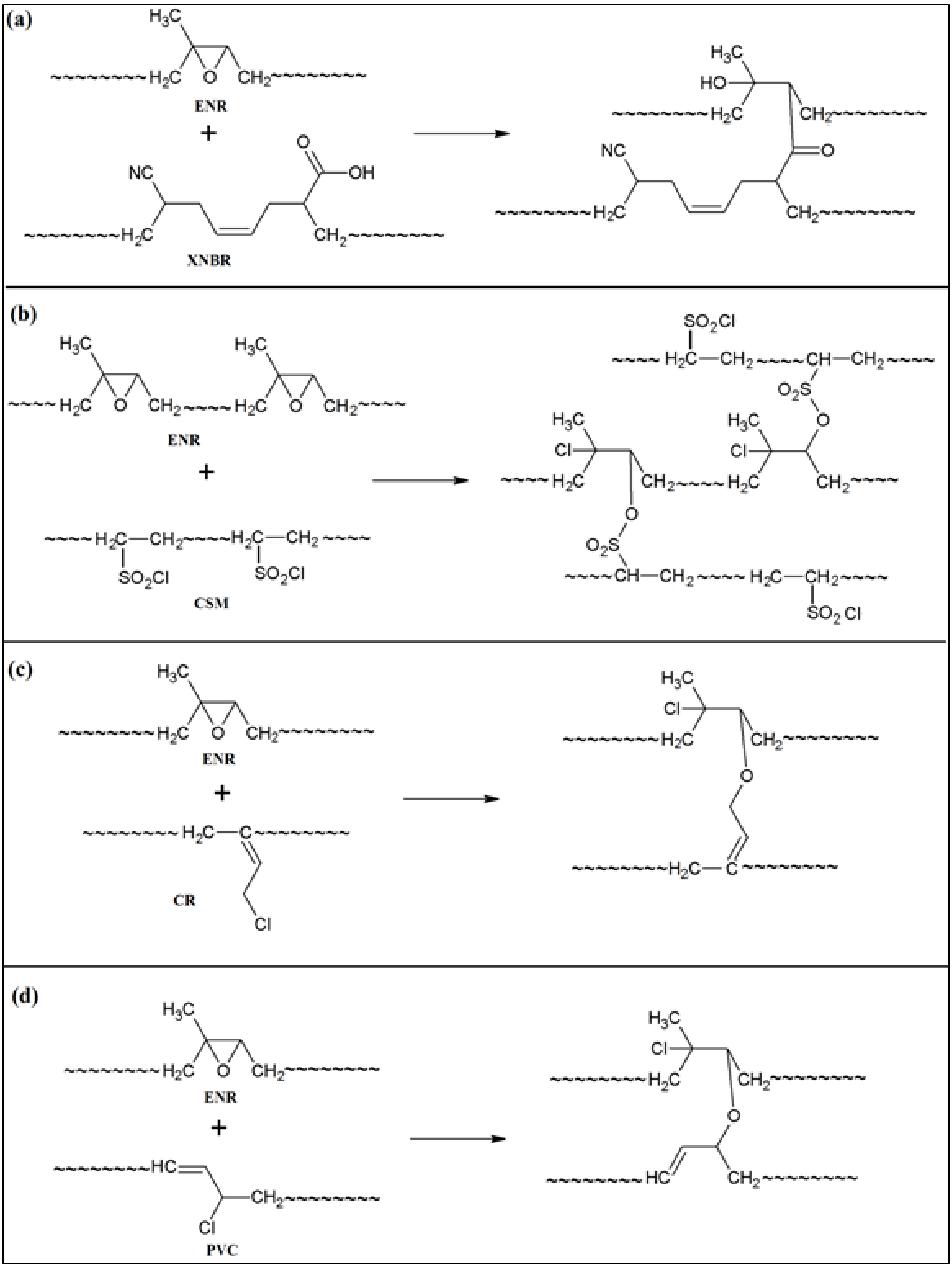


Figure 2.2: Probable crosslinking mechanism in (a) XNBR/ENR blends, (b) CSM/ENR blends, (c) CR/ENR blends, and (d) PVC/ENR blends

Curing reactions of ENR via the epoxide crosslinking sites with amine compounds and aminosilanes have also been reported. In the work of Hashim and Kohjiya (1994), curing of ENR with p-phenylenediamine catalysed by bisphenol-A was carried out at 180 °C. The curing reaction was found to be first order with respect to amine and activation energy for the reaction is in the region 67.5 kJ mol^{-1}, which is much higher compared to 36-52 kJ mol^{-1} in typical sulfur-cured ENRs. Reinforcement with carbon black has resulted in amine-cured vulcanisate with reasonably high tensile strength and relatively more rigid. Rigidity of the vulcanisate could be attributed to the bulkiness of the amine crosslinks and hydrogen bonding effect of bisphenol A.

From the works listed above, it shows that curing of ENR via reaction involving the epoxide groups is viable through blending with suitable molecules containing di- or multifiunctional carboxyl, chlorine or amine groups. Most of the blends were reported to be self-crosslinkable after exposure to specific temperature for prolonged time. However, in some blend, introduction of suitable catalysts or modification via exposure of irradiation on the ENR vulcanisates could be applied as a measure to enhance the extent of crosslinking in the blend.

2.2 Various alkyds (short, medium & long oil lengths) and their modification reactions

Alkyd serves as good binders for coating materials. Distinguished features of alkyds which include compatibility with many polymers and extremely wide formulating latitude made them suitable for production of broad range of coating materials. Except for PA which is of petrochemical origin, the other raw materials used in synthesis of alkyds are from renewable sources. Oil and fatty acids are the predominant renewable raw materials in alkyd resin. Selection of the right type of oil for the synthesis of alkyd are important as different oils may contain different amount of unsaturation which could influence the alkyd properties in terms of drying time and discoloration.

Most of the alkyds for surface coating applications were synthesised from drying oil such as tung oil, soya bean oil, linseed oil and sunflower oil (Guner et al., 2006). Alkyds synthesised from these oils, containing high amount of unsaturated fatty acids such as linolenic acid have shorter drying time as the unsaturation sites facilitate auto-oxidative curing mechanism in the alkyd. Besides that, the amount of oil incorporated in an alkyd formulation could influence the properties of alkyd as well. Reddy et al. (1986) have studied the effect oil length in linseed oil based alkyd towards the physico-chemicals properties of its coating. 4 types of alkyds with different oil length ranging from 50, 55, 60 and 66 % were prepared from linseed oil, glycerol and PA. Coatings formed from these alkyds were subsequently tested for its adhesion on a mild steel substrate together with determination of their mechanical properties such as tensile strength, percentage of elongation and toughness of the films. All the properties of the coatings were found to decrease with the increasing oil length of the alkyds.

Over the past decades, palm and palm kernel oils have become important raw materials in the world’s oils and fats scene (Kongsager & Reenberg, 2012). It is not surprising that palm oil has become one of the renewable sources of vegetable oils in the production of alkyd. Issam and Cheun (2009) have synthesised alkyds from palm oil. However, it was found that the alkyd coatings have limited drying ability, owing to the high amount of saturation in the oil. Generally, palm oil is fractionated to separate the liquid fraction, palm olein from the higher melting stearin. Both the liquid and solid fractions can be utilised as the sources of triglycerides in alkyd synthesis. For example, in the work of Ataei et al. (2011), non-drying palm oleic acid is used to synthesise alkyds and then modified into coatings with fast physical drying via copolymerisation of oleic acid based-alkyd with methyl methacrylate (MMA).

There are several works reported in the literature on the usage of palm stearin for alkyd synthesis. However, due to the reasonably inferior properties of palm stearin alkyd compared to other drying oil-alkyd, the alkyd synthesis is usually accompanied with some modifications to improve their properties. For example, in the work of Teo and Gan (1997a; 1997b), palm stearin alkyds were converted to water reducible resins that could produce coatings with good water reducibility. Besides that, in a separate work (Teo & Gan, 1999), they managed to form clear baking enamels with good film properties through mixing the water reducible palm stearin alkyd with methylated melamine resin. The drying ability of palm stearin alkyd was improved by Ang and Gan (2012) by converting the non-self-drying palm stearin alkyd into environment friendly ultraviolet-curable resin. Alkyd formulation was modified where unsaturated dibasic acid such as MA was used to partially substitute PA in the alkyd so as to increase the amount of unsaturation, thus rendering the alkyd coating UV-curable.

Palm stearin alkyds can be made as crosslinker for ENR by increasing -COOH content in the alkyd chains. Some chemists increased the –COOH content by incorporating acid anhydrides into the alkyd when the alkyd synthesis is near completion, where there are few unreacted carboxylic acids groups, but many unreacted hydroxyl groups. Such approach was carried out by Gan and Teo (1999) in their synthesis of water reducible alkyd from palm stearin. Trimellitic anhydride was incorporated into the alkyd cook when acid value of the alkyd has dropped to 20 mg KOH g^{-1} resin. Grafting of trimellitic anhydride on the alkyd chain through reaction between carboxyl group from the anhydride ring and free hydroxyl group in the alkyd chain resulted in alkyd with high acid value, approximately 50 mg KOH g^{-1} resin.

Wang et al. (2000) also produced water reducible coatings with good hydrolytic stability by increasing the carboxyl-functional group in the alkyds and using salts of their carboxyl groups to stabilise them as aqueous dispersions. Acrylic copolymer with two types of carboxyl groups, one derived from acrylic acid (AA) and one derived from methacrylic acid (MAA) is first prepared and then used as a polyacid to react with the monoglycerides in the synthesis of alkyd. The advantages of this approach lies in the greater functionality (reactive carboxyl groups per molecule) of the acrylic polyacid as compared to that of the difunctional acids or anhydrides typically used in alkyd synthesis. Besides, higher reactivity of carboxyl groups derived from AA to react with the monoglyceride unit as compared to those derived from MAA, helps in controlling the process, where acrylic-alkyd resin synthesis can be stopped after about half of the carboxyl groups have reacted.

The current work involves synthesis of palm stearin alkyd with high level of carboxyl-functional groups by incorporating acid anhydrides into alkyd, formulated with excess of hydroxyl groups. The modified alkyd is expected to act as crosslinker for ENR at ambient temperature.

2.3 Scopes of study

The main objective of this study is to investigate the potential of palm stearin alkyd with pendant –COOH groups as crosslinking agent in ENR50. The studies on the effect of concentration of –COOH group and type of acid side chain in alkyd on the properties of ENR50/Alkyd blend were investigated. Besides, effect of UV irradiation on the properties of the blend is also reported. The works done in this study include:

a) To synthesise alkyds with different –COOH content and different types of –COOH side chains via incorporation of anhydrides into a control alkyd, formulated with excess of hydroxyl group.
b) To find evidence on the incorporation of anhydrides as side chains in the alkyd by ^{1}H-NMR and FTIR analysis.

c) To establish the predominant reaction between the reactive functional groups of ENR50 and alkyd when blended at ambient temperature

d) To investigate the effect of –COOH content in alkyd on the extent of crosslinking in ENR50/Alkyd blends..

e) To investigate the effect of having alkyds with maleic acid side chains and phthalic acid side chains on the extent of crosslinking and properties of ENR50/Alkyd blends.

f) To enhance the extent of crosslinking in ENR50/Alkyd blends via introduction of photoinitiator (benzophenone) and crosslinking agent (TMPTA) into the blends and subsequently irradiated with UV light.