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## MECHANICAL PERFORMANCE OF EPOXIDIZED PALM OLEIN-EPOXY COATINGS ON METAL SURFACE

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### ABSTRACT

*Epoxy coatings are valued for their excellent adhesive strength and toughness, which are contributing factors in determining a coating life in aggressive environments. It has been shown in another study that epoxidized palm oil (EPO) can partially substitute diglycidyl ether of bisphenol A (DGEBA) in an epoxy coating formulation. Due to the presence of one epoxy ring per molecule of EPO, it is theorized that the cured EPO-DGEBA-amine network has a lower crosslinking density than a DGEBA-amine network, resulting in lower mechanical properties. However, it is expected that impact resistance would be enhanced due to the aliphatic chain present in EPO. This study aims to investigate the effect of EPO on the coating's adhesive strength and impact resistance. EPO-modified epoxy coatings were formulated using 30 wt% EPO in the resin system and cured using a cycloaliphatic amine adduct. Coatings were applied on mild steel specimens and heated to 100, 130 and 150°C for 90 minutes. Adhesion tests were done using the pull-off method and impact resistance tests were carried out using a falling dart of known weight from a fixed height. Test results showed that EPO-epoxy coating shows excellent adhesive strength and good impact strength when cured at 150°C for 90 minutes.*

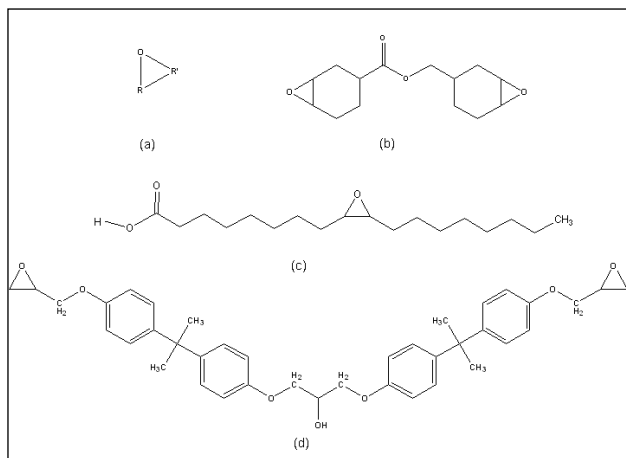
*Keywords: EPO, coating, corrosion, epoxidized, bio-blend*

### INTRODUCTION

Coatings are the most widely used method used to protect metallic substrates against corrosion (Roberge, 2000). Corrosion control by organic coatings is achieved by a combination of barrier effect and resistance of current flow. There are three main constituents in any organic coating formulation, namely (a) binder, (b) solvent, and (c) pigment. The main component contributing a coating's barrier properties is the binder. A binder 'holds' the different components together by "forming a continuous polymeric phase in which all other components can be incorporated" (Schweitzer, 2006). Binders are classified according to their film-forming mechanisms. The most common processes involved in the formation of a continuous solid film are solvent evaporation, oxidative crosslinking, chemical curing or a combination of the processes. Epoxy coatings are chemically cured as crosslinking takes place between compounds with epoxy moieties with a curing agent. In general, epoxy curing agents are hydrogen donors.

There are three types of epoxy compounds, namely (a) cycloaliphatic epoxy, (b) epoxidized oils and (c) glycidated resins. These compounds contain one or more oxirane ring (Fig. 1). Most epoxy coatings today are based on diglycidyl ether of bisphenol A (DGEBA), a glycidated resin produced from reacting bisphenol A (BPA) and Epichlorohydrin (ECH), both of which are synthesized from petroleum products (Paul, 1996). In order to reduce the industry's dependence on petroleum, researchers are now targeting epoxidized oils as potential raw materials in epoxy coatings (Raquez, 2010; Seniha Güner, 2006). Many researchers have reported encouraging findings from their studies on various epoxidized oils such as epoxidized *Annona squamosa* oil (Ahmad, 2006), epoxidized linseed oil (Earls, 2007) and epoxidized soybean oil (Jin and Park, 2008). In fact, coatings based on epoxidized soybean oil are already commercially available. It is practical to note that the selection of plant oil is influenced by two factors; economy and geography. The best option for our region is palm oil, based on its high yield and availability (Salimon, Salih, and Yousif; Yap, Gan, and Ng, 2010).

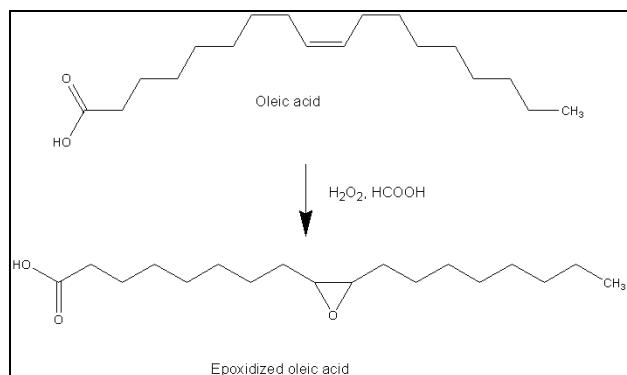
Figure 1. Molecular structure of (a) a compound with epoxy moieties (general), (b) a cycloaliphatic epoxy, (c) a long-chain epoxy, and (d) a bisphenol-A epoxy.



Globally, oil palm generates about 4–5 tonnes of oil/ha/year, about 10 times the yield of soybean oil (Choo Y. M., 2005). Currently, palm olein is used to produce a wide range of products such as cooking oil, soaps, biodiesel, drilling mud and skincare products. Epoxidized plant oils maintain most of their original molecule structures, except that their double bonds are replaced by oxirane rings. Epoxidation of plant oils have been successfully carried out via two methods (a) in-situ chemical oxidation using peracid or (b) enzyme-catalyzed epoxidation. Examples of plant oils that have been successfully epoxidized are linseed oil (Sharmin, Ashraf, and Ahmad, 2007), nahar seed (*Messua ferra L.*) oil (Das and Karak, 2009), soybean oil, jatropha oil (Meyer, November 2008) and palm oil (Derawi and Salimon, 2010). Epoxidation of palm olein can be represented by the epoxidation of oleic acid (Fig. 2). Epoxidized palm olein (EPO) is now commercially available and utilized in the production of polyurethane foam and polyester (Lye, 2006). Theoretically, an oxirane ring readily undergoes reactions with other compounds due to the high degree of strain within it (Nicholson, 1991). Consequently, it can be expected that different methods can be used to generate a solid film using EPO. One of the earliest studies done on EPO is a study of curing of EPO-cycloaliphatic diepoxide system using UV radiation (Wan Rosli, 2003). It reported evidence of the epoxy ring opening, indicating that chemical curing took place.

Other studies suggested that chemical curing of EPO may also be achieved by using common epoxy curing agents. Epoxy resins cure through nucleophilic addition, during which oxirane ring opens and protons are donated by the curing agent, forming covalent bonds between the macromolecules (Ravve, 1995). Based on the presence of oxirane rings in EPO and commercial epoxy resins, as well as the knowledge that commercial liquid epoxy resins cure through the oxirane ring opening (Bauer, Marx, and Watkins, 1995), researchers expect EPO to react with common epoxy curing agents to form solid, polymeric films suitable for coating application. However, the approach so far has been to introduce EPO to conventional epoxy resin in order to maintain the latter's excellent physical and chemical properties. A study of biodegradable polymers using epoxidized soybean oil-modified resin used N-Benxylpyrazinium hexafluoroantimonate (BPH) (Jin and Park, 2008). Other studies used an anhydride curing agent (Tan and Chow, 2010) and m-xylylenediamine (Sarwono, 2009) to cure epoxy blends consisting of EPO and DGEBA. These studies proved that it is possible to generate EPO-modified epoxy polymer materials by using common epoxy curing agents.

Figure 2: Epoxidation of oleic acid



A key observation from these studies is the effect of oil content to the oil-modified epoxy resins' mechanical properties. Tan and Chow reported higher plasticizing effect to the network structure with higher EPO content (Tan and Chow, 2010). Sarwono et al. reported the increase of water uptake of the cured resin with the introduction of EPO (Sarwono, 2009). Another key observation is that oil-modified resins are best cured at elevated temperatures. Jin and Park (Jin and Park, 2008) used curing temperatures ranging from 120°C to 200°C over a period of 4 hours. Similarly, Tan and Chow (Tan and Chow, 2010) was based on curing at 130°C for 3 hours whereas Sarwono et al. (Sarwono, 2009) on 60°C for 1 hour followed by 130°C for 3 hours. Epoxidized *Mesua ferrea* L seed oil-modified epoxy coating was cured at 100°C (Das and Karak, 2009). Based on the preliminary study, it was found that the highest possible EPO concentration in the resin is 30% and the best method of cure is oven-curing. This study aims to investigate the mechanical properties of an EPO-epoxy coating. Results of adhesion and impact tests on the coating cured at 100°C, 130°C and 150°C for 90 minutes\_were reported and analyzed in this paper.

## EXPERIMENTAL

### *Raw materials*

Epoxidized palm olein was procured from Malaysian Palm Oil Board (MPOB), Bangi, Selangor. Commercial epoxy resin (DER 331), the curing agent (cycloaliphatic amine adduct) and the pigment (titanium dioxide) were supplied by Suka Chemicals Sdn. Bhd., Selangor.

### *Binder formulation*

EPO and DER331 were measured to 3:7 (EPO: DER331) ratio and then mechanically mixed at approximately 300 rpm until no phase separation was observed. Titanium dioxide (TiO<sub>2</sub>) was added to the mixture at a ratio of 2:1 (binder weight : pigment weight). Mixer speed was then increased to 1050 rpm. Mixing was done for approximately 1 hour. For control, similar formulations were prepared using only DER331.

### *Preparation and testing of coatings*

Commercially available mild steel plates (150mm x 150mm x 3mm and 100mm x 100mm x 1.2mm) were previously sandblasted to Sa 2.5 standard<sup>1</sup>. In the laboratory, the metal plates were abraded using sandpaper No. 80 and wiped with acetone. Coatings were applied using roller. The coated plates were heated to the predetermined temperature and kept at that temperature for 90 minutes before they were allowed to cool down to room temperature. The plates were then left at room temperature for 7 days

<sup>1</sup> International Standard ISO 8501-1(1998)

before testing to allow sufficient time for residual curing to take place. Dry film thickness was measured by Quanix 8500. Average thickness was found to be 80  $\mu\text{m}$ . Plates of dimensions 150mm x 150mm x 3mm were used for adhesion test whereas plates of dimensions 100mm x 100mm x 1.2 mm were used for impact test. Adhesion tests were done using Elcometer 108, using standard testing method as per ASTM D454. Adhesive strength was measured as the greatest perpendicular force that the coating can bear before a plug is detached. Impact resistance tests were carried out using a weight dropped from a known distance. The distance was gradually increased until the point where failure occurred was determined. Failures were detected visually in forms of crack or peeling. The impact strength is calculated using Equation 1.

$$\text{Impact strength (Joule)} = w.g.h \quad [1]$$

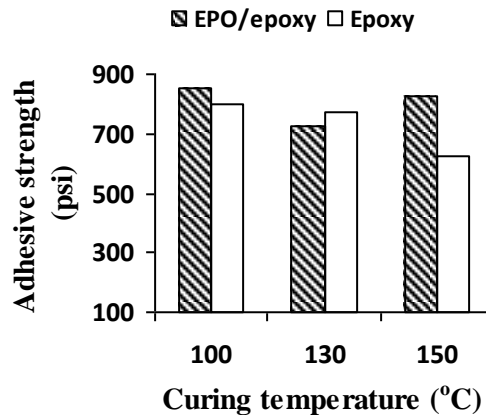
where  $w$  = weight of load (kg)  
 $g$  = gravity ( $\text{ms}^{-2}$ )  
 $h$  = height of load (m)

## RESULTS AND DISCUSSION

### *Adhesion Tests*

The results of pull-off adhesion test performed on coated specimens cured at 100°C, 130°C and 150°C are shown in Figure 3.

Figure 3: Adhesive strength of EPO/epoxy and epoxy coatings

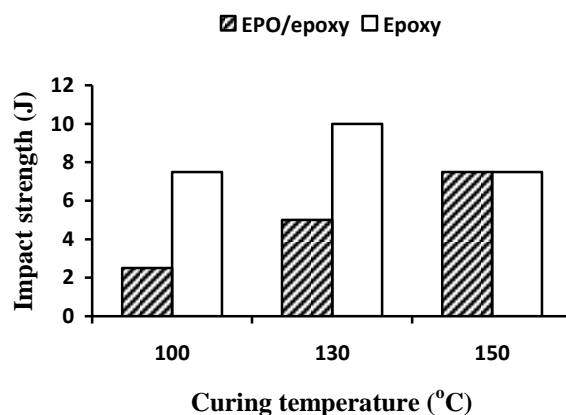


Adhesion test results show an improvement in tensile strength of EPO/epoxy coatings as curing temperature was increased from 130 to 150°C. This finding can be explained by increased crosslinking activities at higher temperatures, at which it has been hypothesized that crosslinking reaction is favored over phase separation (Brostow, Dutta, and Rusek, 2010). As a result, more hydroxyl groups were formed, resulting in better adhesive properties in the coating. On the contrary, it was found that the adhesive strength of epoxy coatings decreased with increasing curing temperature. This trend could be caused by the highly crosslinked network being too rigid and having significantly higher internal stress. In general, it was observed that all results exceeded industry's requirement for protective coating for external application, which is 500 psi (PETRONAS, 2008). Therefore, it was shown that the introduction of EPO to the coating formulation did not cause a loss in adhesion.

### Impact Tests

The calculated impact strengths are shown in Figure 4. For EPO/epoxy coatings, it is apparent that impact strength was lowest for the coating cured at 100°C. Low impact strength has been attributed to chain ends generated by unreacted EPO and epoxy resin (Sarwono, 2009). The chain ends lead to the formation of weak points that nucleate under stress. Consequently, higher temperature curing leads to less unreacted EPO and epoxy resin and better impact strength. The best result was achieved when the coating was cured at 150°C. In fact, this curing temperature produced similar impact resistance in EPO/epoxy and epoxy coatings.

Figure 4: Impact strength of EPO/epoxy and epoxy coatings



EPO/epoxy coatings may outperform epoxy coatings in terms of impact strength if cured at higher temperatures. Jin and Park reported a significant improvement in the impact strength of epoxidized soybean oil/epoxy blends cured at 120 °C for 1 hour, then 160°C for 2 hours and finally 200°C for 1 hour (Jin and Park, 2008).

### CONCLUSION

Based on the experimental data, it is proven that an EPO-epoxy formulation produces the best combination of adhesive and impact strengths when cured at 150 °C for 90 minutes. Utilization of EPO could reduce petrochemical contents in epoxy coating formulations and simultaneously produce more environmentally-friendly final products.

### ACKNOWLEDGMENT

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