

## CHAPTER 6: CONCLUSION AND SCOPE FOR FURTHER RESEARCH

### 6.1 Conclusion

The research studies presented in this thesis was on copolymerization of methyl methacrylate with palm oleic acid-based macromer. The macromers were synthesized by polyesterification reaction of palm oleic acid, PA and glycerol. The molecular structure of the macromers had been varied by different percentages of oleic acid content in macromers. Oleic acid, as a flexible side chains, was incorporated in the macromer structure with percentages of 28, 40 and 65 and labeled as AlkOA28, AlkOA40 and AlkOA65 respectively. The functional groups present in the macromers were characterized by FTIR and  $^1\text{H-NMR}$ . Extent of reaction at the end of the polycondensation for all three macromers was more than 95%. The second-order rate constants,  $k$ , before formation of crosslinking in the polycondensation reactions were calculated. Sample AlkOA65 showed the largest  $k$ , with value of  $18 \times 10^{-5} \text{ g (mg KOH)}^{-1} \text{ min}^{-1}$ .

Results from TGA prove that AlkOA28 has relatively higher thermal stability followed by AlkOA40 and AlkOA65. From Kissinger method, the activation energies for the macromers, AlkOA28, AlkOA40 and AlkOA65, were found to be 229.0, 183.0 and 134.0  $\text{kJ mol}^{-1}$  respectively. Ozawa, Flynn and Wall (OFW) method, used to clarify relationship between activation energy and degree of conversion ( $\alpha$ ) in the decomposition reactions, revealed more complexity in the degradation reactions with decrease in the molecular weight and increase in oleic acid content of the macromers.

Copolymerization of MMA was carried out with free  $\text{C}=\text{C}$  groups in macromers in presence of BPO as initiator at 95-100°C. The rate of copolymerization was dependent on

macromer content. The higher the macromer content, the lower is the conversion (%). Short oil length macromer also showed higher conversion (%) in the copolymerization reaction. From  $^1\text{H-NMR}$  spectra of macromer and copolymer, it was found that ratio of peak areas of vinyl group to terminal methyl group of oleate branches had decreased, providing evidence that the double bonds of the oleate moiety had reacted. Moreover  $-\text{OCH}_3$  group from MMA in  $^1\text{H-NMR}$  spectra of the copolymers could be recognized. From DSC results the copolymers exhibited only a single  $T_g$ . Increasing the MMA ratio in copolymer composition led to higher  $T_g$  and molecular weight of the copolymers. TGA analysis revealed that thermal stability of copolymers increased significantly with increase in macromer ratio. Viscoelasticity of MMC samples, as studied using dynamic mechanical analysis, showed that increment of the macromer content causes decrease in  $T_g$  at loss modulus and consequently increased elasticity.

Some of the properties of the MMC copolymers could be modified by introducing butyl acrylate (BA) monomer to replace part of MMA. The results showed that regardless on the type of macromer used, polymerization rate increased when the amount of macromer decreased (the same trend with the copolymerization rate of macromers with MMA). In addition, conversion (%) was greater compared with the conversion when acrylate monomer employed was only MMA. The presence of BA in the copolymer was proved by  $^1\text{H-NMR}$  spectrum. From DSC analysis, modified copolymers showed smaller  $T_g$  value than that of copolymer synthesized without BA monomer.  $T_g$  from DMA showed lower loss modulus at maximum peak and consequently higher elasticity compared to MMC samples. In addition, most of the samples showed  $\beta$  transitions between  $-50^\circ\text{C}$  and room temperature. The incorporation of BA into the copolymers had increased the molecular weight and thermal stability.

Another aspect of the research was directed towards evaluating of the resulting copolymers as coatings materials. The low molecular weight macromers are unable to air drying. Incorporation of MMA has resulted that the physico-mechanical and chemical resistance of the coatings were improved with increment of the MMA content. The MMA units served to speed up physical drying time as well as protecting the ester groups toward hydrolysis but adhesion has decreased. Overall, the best results for coating performances were observed after incorporation of 5% BA in copolymers synthesized from the short oil length macromer, AlkOA28. This series demonstrated the best adhesion, scratch hardness, water and salt resistances. Copolymer modified with BA had a longer drying time compared to the unmodified copolymers. For this series of modified copolymers (macromer/acrylate ratio = 0.25), conversion and solid content were 90.7% and 31.1% respectively.

## **6.2 Suggestions for further research**

This research has presented the groundwork for preparing acrylic alkyd resin based coatings from palm oleic acid with high solid content as environmentally friendly coatings. There are much work remain to be completed and many reaction possibilities that can be used in improving this research. Due to the compatibility of the alkyd resins with a number of polymers such as epoxy resins, acrylic resins, polyurethane resins and so on, this makes them very versatile polymers to produce a broad range of coating materials. There are number of research works that can be presented as suggested below.

1. In recent years, beside the high solid coatings, many activities have been carried out to achieve more environmentally friendly coatings and that designing alkyd emulsions are one of those activities. Alkyd emulsions reduce the organic solvent content in the

coating formulation compared to other environmentally friendly systems. One of the aspects to consider for further work is to synthesize palm oleic acid-based coatings by using emulsion method.

2. It would also be interesting to choose hyper branch polyols such as pentaerithritol, as a crosslinker agent to achieve the alkyd resin based coatings and besides using different metal oxides as anti corrosion operative.

3. Another aspect to consider in future work is to synthesize palm oleic acid alkyd resin-based polyurethane acrylic coatings.