CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

In this research, high molecular weight polybenzoxazine precursors can be synthesized via a newly developed quasi-solventless method, which could be confirmed by the spectra of FTIR and NMR. Marl filled polybenzoxazine composites exhibited lower curing temperature and higher thermal stability than pure polybenzoxazine. This effect was attributed to the acid catalyst effect by silica in marl filler. The results from SEM revealed the good dispersion of marl in the polybenzoxazine, but poor interfacial adhesion arose from the difference in polarity between the marl and the polybenzoxazine matrix. The improved interfacial adhesion was achieved by using silane and steraic acid coupling agents as the surface-modifying agent, which resulted in the better mechanical proproties of the composite i.e. at 20 wt% marl loading, the flexural modulus of the surface modified marl composites increased significantly over that of untreated marl filled polybenzoxazine composites and higher than that of pure polybenzoxazine. Similar to flexuaral properties, the impact strength of polybenzoxazine was improved after blending with the marl filler and modified-surface marl–polybenzoxazine showed the sligthly higher value. In addition, from DMA results, the glass-transition temperature of the polybenzoxazine–marl composite was higher in comparison with pure synthesized polybenzoxazine and at 20 wt% of marl content, the modified surface marl showed the higher glass transition temperature. In summary, unmodified and modified-surface marl caused an increase in the rigidity and improved the properties of polybenzoxazine.

The graft copolymer of silk sericin protein and polylactide was synthesized by in-situ catalytic bulk polymerization in the presence of marl and stannous octoate by melt mixing. The obtained marl filled graft copolymer was further blended with benzoxazine precursor and cured in step to obtain a biocomposite hardened by polybenzoxazine. The successes of grafting-from structure was investigated by FTIR, NMR, and thermal analysis. From DSC curves and XRD patterns, the graft copolymer showed no crystal structure. It meant that high efficiency of grafting obstructed the crystallization. The thermal and mechanical behavior of the

biocomposites obtained from modified-surface marl filled graft copolymer blended with polybenzoxazine are similar to polybenzoxazine–marl composites, namely, it had the lower curing temperature and the higher thermal stability than that of pure polybenzoxazine. The improved mechanical properties after introducing the graft copolymer into polybenzoxazine matrix with high loading of graft copolymer (30–50 wt %) were found to exhibited greatly improved flexural strength and modulus. The overall impact strength of the biocomposites was higher than that of the pure polybenzoxazine since the incorporated graft copolymer can absorb the loaded strength. Among the five ratios of the biocomposite done in this reserch, the 20/80 wt% of graft copolymer filled with amino silane treated-surface marl biocomposite/polybenzoxazine exhibited the optimum values of the flexural strain and the impact strength. Moreover, the DMA results showed that each glass-transition temperature of the biocomposite was comparable or higher in comparison with pure synthesized polybenzoxazine. It can be concluded that the improved toughness and flexural biocomposite material obtained from the modified-surface marl in graft copolymer embedded in a hard polybenzoxazine matrix is a promising candidate as a material to be used in a soft splint application in the future.

However, there are some recommendations for working on this thesis report;

1. The variation of mechanical values came from air bubbles that generated in the compression process. As the solvent, 1,4-Dioxane, used in the polybenzoxazine synthesis has a high boiling point (101°C) and can form the hydrogen bonding with the synthesized crosslink network, causing difficulty in solvent evaporation. Tetrahydrofuran (THF) and acetone are considered alternative solvents.

2. The amount of solvent and temperature used in the polybenzoxazine synthesizing process should be controlled because they can affect reaction time and viscosity of the obtained thermosetting.

3. It is difficult to fabricate the polybenzoxazine–marl composite and the biocomposites by compression molding technique because they were brittle and easily broken when released from mold.

4. Another choice to fabricate and cure the polybenzoxazine composites is to do it stepwise, which may help to reduce air bubbles in the specimen, by using a 3 mm silicon rubber spacer clamped between two glass plated with a silicon-based release agent and heated under vacuum to remove any air entrapped during the filling process and eliminate any trace solvent. Upon completion curing, the samples should be allowed to freely cool to room temperature to prevent the cracking (Allen and Ishida, 2006).

5. In the graft copolymer synthesis, it is recommended to use polylactone instead of polylactide because its low glass transition tempearature will reduce the brittleness of the final product after blending with polybenzoxazine.

6. Due to a large particle size of marl, it can not be suspended in highly viscous polybenzoxazine. To solve this problem, the homogenizer was used to stir marl or graft copolymer in 1,4-dioxane solution before blending it with polybenzoxazine. The compression press was then used to fabricate composite to achieve the well dispersed filler with controlled thickness of sample.

7. In the polybenzoxazine synthesis, aluminum foil is needed to use instead of beaker because it will give the better heat dispersion than beaker glass, which can avoid the agglomeration of reactants.

Moreover, there are some recommended further works to complete this research;

1. For using as a soft splint, this polybenzoxazine biocomposite materials needs the other testing for example; hardness properties, tensile properties, moisture absorption, and etc.

2. Due to the biodegradability properties of the graft copolymer, therefore this material should be tested for determination life time before used as a splint material.

3. If the soft splint is shaped with human organ, the curing temperature of polybenzoxazine should be decreased more either by excess phenol or acid catalyst. Espinosa *et al.*, 2003 reported the polybenzoxazine synthesis reaction which took place in the presence of *p*-Nitrophenol or 1,12-Dodecanedicarboxylic acid or Lewis acid catalyst such as BF_3·MEA, the maximum curing temperature was reduced. Because those substances including phenols, carboxylic acids, and Lewis acids can

act as catalyst to donate proton for initiation the benzoxazine ring-opening polymerization, so the reaction temperature will shift to the lower one.

4. Because of voids which generated during the compression process, resulted to the mechanical and dynamic mechanical properties of the composites, so the left solvent should be removed at reduced pressure or vacuum oven at the low temperature to avoid self-curing before the fabrication process.