CHAPTER VII
CONCLUSIONS AND RECOMMENDATIONS

The success of this work is the production and development of thermoplastic vulcanizate (TPV) made from natural rubber, fluoroplastic and biodegradable polymer via dynamic vulcanization. DBPH used as peroxide curing agents to provide higher mechanical and oil swelling properties. Organoclay used as filler to improve oil barrier properties and NBR used as benchmark in this research. The results showed that mechanical and oil swelling properties increased with ENR and DBPH contents. Dynamic vulcanization gave better properties than ternary blend. The best formula that gave the best properties was the ENR/PVDF/PLA (DBPH) ratio of 50/50/0 (5 phr) which gave the tensile strength of 9.28 MPa and Young's modulus of 250.4 MPa. The maximum percent elongation at break belonged to the ENR-cured system (DBPH 3 phr) which reported 137 %. The vulcanized ENR/PVDF gave better properties than vulcanized ENR/PVDF/PLA due to the poor interfacial adhesion and immiscibility between PVDF and PLA which were supported by FE-SEM morphology and DMA results. So, it can be concluded that the addition of PLA affected to the embrittlement of the materials. The effects of organoclay helped to decrease the rate of oil uptake and reinforce in vulcanized ENR/PVDF/PLA by increasing the tensile strength until maximum point at 3 phr of organoclay. Then further organoclay loading, the tensile strength dropped due to the agglomerations which were supported by FE-SEM morphology. The vulcanized NBR/PVDF gave better mechanical and oil swelling properties than vulcanized ENR/PVDF.

The ranges of swelling index of the blends at ENR/plastic 50/50 ratio and DBPH 5 phr were shown here. Table 7.1 reported the ranges of swelling index within 4 oil types of the blends at room temperature for 24 hours. It can be seen that the ENR/PVDF blend gave the lowest swelling index and percent swelling. The percent swelling of ENR-cured system, Ternary blend and ENR/PVDF/PLA were higher than that of ENR/PVDF around 138.5 %, 77.5 % and 5.4 %, respectively. The percent swelling of ENR/PVDF was higher than that of NBR/PVDF around 16 %. The percent swelling of ENR/PVDF/NBR was higher than that of NBR/PVDF/PLA around 6.6 %.

Table 7.1 The ranges of swelling index and percent swelling of the blends ratio of ENR/plastic 50/50 and DBPH 5 phr within 4 oil types at room temperature for 24 hours.

Materials	Ranges of swelling index	Ranges of swelling (%)
ENR-cured system	1.26 – 2.66	26.4 – 165.7
Ternary blend	1.17 – 2.40	17.4 – 104.7
ENR/PVDF/PLA	1.11 – 1.37	11.6 – 32.6
ENR/PVDF	1.07 – 1.28	6.5 – 27.2
ENR/PVDF/PLA + Organoclay 10 phr	1.07 – 1.35	7.5 – 34.8
ENR/PVDF + Organoclay 10 phr	1.11 – 1.35	11 – 35.1
NBR/PVDF/PLA	1.06 – 1.17	5.9 – 16.7
NBR/PVDF	1.06 – 1.20	6.1 – 20.6

Table 7.2 The ranges of percent swelling of the blends ratio of ENR/plastic 50/50 and DBPH 5 phr within 4 oil types at room temperature comparing between 24 hours and 7 days.

Materials	Ranges of swelling (%) for 24 hours	Range of swelling (%) for 7 days
ENR/PVDF/PLA	11.6 – 32.6	12 – 42.6
ENR/PVDF	6.5 – 27.2	11.3 – 30.7
ENR/PVDF/PLA + Organoclay 10 phr	7.5 – 34.8	10.8 – 35.4
ENR/PVDF + Organoclay 10 phr	11 – 35.1	12.6 – 36.3

As seen from table 7.2, the effect of organoclay insignificantly improved the oil swelling resistance in immersion for 24 hours. Considering the longer period of immersion, the effect of organoclay helped to stable the oil uptake. The percent swelling of ENR/PVDF/PLA increased 31 % after immersion for 7 days but in case of ENR/PVDF/PLA with organoclay 10 phr increased only 2 %. The percent swelling of ENR/PVDF increased 13 % after immersion for 7 days but in case of ENR/PVDF with organoclay 10 phr increased only 4 %.

However, the co-continuous morphology was obtained from this work in the blend ratio of ENR/plastic 50/50 whereas the blend ratio of ENR/plastic 70/30 showed the main component of ENR instead of the ideal morphology of dynamic vulcanization which show dispersion of rubber particles in thermoplastic matrix. The possible obstacles are;

- ✓ Too high viscosity of thermoplastic phases. So the melted thermoplastic could not flow and cover the rubber particles properly.
- ✓ The existence of crosslink formation in PVDF and PLA phases.
- ✓ Too active of peroxide curing system. So the rubber phases were fully cured before going to be separated by the shear force.

So the recommendations for obtaining dispersion morphology are;

- ✓ Changing the PVDF grade to lower viscosity or changing the thermoplastic types.
- ✓ Changing the curing agent from peroxide type to other types such as sulfur. Because the peroxide can crosslink in both of rubber and thermoplastic phases in contrast to sulfur.
- ✓ Lower the efficiency or acceleration of curing reaction i.e., lately adding the curing agent by using side feeder to lower the curing time.
- ✓ Adding some compatibilizer into the TPV system.

Another problem was agglomeration of organoclay, then resulted in not much improve of mechanical and oil swelling properties. So, it can be assumed that the intercalation and exfoliation of organoclay layers were not occurred. Therefore, the recommended solution is changing the method of mixing to provide higher shear force or lower the organoclay contents. Focusing on the cost of raw materials for providing the best properties of TPV in this work (the 50/40/10 ENR/PVDF/PLA ratio), it has lower cost than the commercial one (Fluoroelastomer, FKM). Table 7.3 showed the comparison of the costs.

Table 7.3 Comparison of the costs between the TPV and commercial rubber.

Raw materials	Cost (Bath)		
	Per 1 kg	TPV	Commercial rubber
ENR25	250	125	-
PVDF, Z100	500	200	-
PLA, 2002D	100	10	-
FKM, Viton GF600S	2,300	-	2,300
Total		335	2,300

It can be seen that the raw materials cost of TPV is much more lower than FKM. So, it is reasonable to substitute the very expensive FKM with dynamically vulcanized ENR/PVDF/PLA.