

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

#### 8.1 Conclusions

The blending of polyolefins (LDPE) with engineering plastics (PA6) offers an interesting route to achieve new materials with promising property combinations. However, the major problem is the lack of compatibility between the blended polymers, giving poor interfacial adhesion, and hence poor mechanical properties of the polymer blend. One strategy to improve the interfacial properties in PA6 blends is to react them with terminal primary amines and/or chemical interchange reactions involving the amide linkage. As a result, an increase in stress transfer between the two phases can be achieved, thus improving the morphological, thermal, and mechanical properties of the blend. One compatibilizer used for the PA6/LDPE blends is ethylene-acid copolymers, either with or without partial acid neutralization with a metal cation. In introducing the hydrogen bonding and ionic interaction in polymer blends, the compatibility of the PA6/LDPE blends is improved. Compared with previous studies [Leewajankul *et al.* and Lahor *et al.*], we found that the zinc ionomer provides a stronger interaction than sodium ionomer in PA6 high content, and lithium ionomer provides the strongest interaction in LDPE high content. Therefore, using zinc for PA6 high content and lithium ionomer for LDPE high content, the melting temperature of the blends shifted to high temperature and shear/elongational viscosity was the highest. These results were opposite from the previous studies.

Chapter IV deals with the morphological, thermal, mechanical properties, and crystallization of the PA6/LDPE blends with EMAA or ionomers of different neutralization levels and different cations. The morphological, thermal, and mechanical properties were improved with the addition of the compatibilizers to the blend. There was a decrease in the dispersed phase size, the increase in the melting temperature and an increase in Young's modulus, stress, and % strain at break. Acid copolymer improved properties less than the ionomers. Sodium, zinc, and lithium cations show some differences in the efficiency as measured by the mechanical

properties, dispersed phase size, and thermomechanical properties. However, the differences were not consistent with respect to the neutralization level. In other words, there were no clear differences between the three metal cations. The neutralization of 33% at 1.5 phr is enough to achieve the maximum compatibilization effect.

Chapter V deals with the rheological properties of PA6/LDPE blends with or without compatibilizers. The effect of compatibilizers on the melt rheological properties (i.e. shear viscosity, elongational viscosity, and power law index) were studied. Four types of compatibilizers, EMAA and its ionomers (Li-EMAA, Na-EMAA, and Zn-EMAA) with different valences, sizes, and neutralization levels were used. The blends improved shear/elongational viscosity by the ionomers over EMAA, revealing a stronger interaction of the counter ions to PA6 than the carboxylic groups in EMAA. The change in shear viscosity due to the addition of an ionomer was larger at low shear rates. Both shear and elongational viscosities of the blends increased with compatibilizer amount and neutralization level. The effect of counter ion type ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ) on the melt rheological properties of the blends was less significant than the amount of compatibilizer and neutralization level. Zn-EMAA gave the largest shear and elongational viscosities for the PA6-rich blend, while Li-EMAA gave the largest viscosities for the LDPE-rich blend.

Chapter VI describes the die swell of PA6/LDPE blends at PA6 20: LDPE 80 with EMAA and 33% neutralization level of lithium ionomer. The use of compatibilizer increased the apparent shear viscosity of the PA6/LDPE blends. The increase in shear viscosity was more evident at low shear rates and depended on the amount and type of compatibilizer. From the phase morphology, introducing only 1.5 phr of EMAA or Li-EMAA was sufficient to produce the maximum reduction in dispersed phase size. The dispersed phase size was not different using the ionomer or acid copolymer, except at 0.5 phr, where blends containing Li-EMAA had significantly smaller sizes. With an increase in compatibilizer loading to 5 phr, the flow activation energy increased. Further increases in compatibilizer decreased the flow activation energy. At higher compatibilizer levels, the characteristics of the polyethylene phase were affected because ionomer consists of 91 wt% polyethylene and polyethylene has low flow activation energy. Using the Li-EMAA compatibilizer

resulted in higher flow activation energy and lower die swell than with the EMAA compatibilizer. Extrudate die swell increased with increasing shear rate and shear stress for the blends with and without compatibilizers. Additionally, extrudate die swell decreased with a decreasing size of the dispersed phase. Using EMAA compatibilizer resulted in higher extrudate swell than Li-EMAA compatibilizer.

Another application of a compatibilizer was in its use in nanocomposites to achieve fine dispersion of the organoclay in the polymer matrix. Polypropylene is a thermoplastic polymer used in a variety of applications, including food packaging and textiles. However, polypropylene presents some drawbacks on dye-ability due to the non-polar aliphatic structure and high crystallinity. In this dissertation, dye-able polypropylene fibers were prepared by adding organoclay into the polymer to act as a dye sorption agent. Sodium ionomer was used to improve the compatibility between the PP and the organo-modified clay. The reason for using the sodium ionomer was that at high shear rate, for LDPE high content, the viscosity of PA6/LDPE blends with sodium ionomer is equal to PA6/LDPE blends with lithium ionomer.

Chapter VII deals with the effect of draw ratio (9.1–28.3) on the thermal properties, mechanical properties, and dye-ability of neat PP fibers and organo-modified PP nanocomposite fibers was studied. The addition of sodium ionomer into the organo-modified clay nanocomposite PP improved the dispersion and distribution of organo-modified clay in the PP matrix. Additionally, by adding the organo-modified clay into the PP matrix, organo-modified clay does not affect the structure of the PP. Moreover the change in the draw ratio caused the improvement of crystallinity, the melting and the decomposition temperatures, and the mechanical properties and dyeability of fibers. However, increasing the draw ratio brought about lower strain at break. By introducing organo-modified clay into the PP fibers, it is clear that all properties were improved, except the crystallinity, which was decreased. Among the three dye types, the acid dyes showed the highest adsorption on neat PP and organo-modified PP nanocomposite fibers. At a draw ratio of 15.3, the organo-modified PP nanocomposite fibers had the lowest dye-ability due to highest level of crystallinity. The highest dyeability was found at a draw ratio of 28.3 because, at this level, the cross section appears to be the thinnest. The thinner cross

section of fibers allows greater chance for the organoclay to be exposed to the dye and, hence, greater dye absorption was observed.

The addition of interactions between the ionomer and the polyamide 6, which are hydrogen bonding and ionic interaction, can improve the compatibility of these blends, resulting in an improvement of mechanical, thermal, and rheological properties of the PA/LDPE blends. The acid copolymer improved properties less than ionomers. The different improvements in the polymer blends are the result of using different metal ion size in ionomer. The Zn-EMAA gave the largest shear and elongational viscosities for the PA6-rich blend (this is further discussed in Recommendations), while Li-EMAA gave the largest viscosities for the LDPE-rich blend. This is because in the case of ion-dipole interaction involving small molecules (e.g. alkali halides) the strong ion-dipole interaction increased with the decrease in metal ion size. The zinc metal ion size is bigger than sodium and lithium metal ion.

The effect of more neutralization and content level was limited by the functional group of PA6. Thus it was found that the optimum condition of blends with ionomer was 33% metal ion neutralized ethylene-co-methacrylic acid 1.5 phr compatibilizer levels. Increasing neutralization or content levels more than the optimum conditions did not improve the compatibility of the blends. The effect of cation type on the PA6/LDPE blend properties is less significant than the effect of content and neutralization level. This is further discussed in the Recommendation section.

PA6 20:LDPE 80 blends with lithium ionomer show a smaller die swell than the acid copolymer because the interaction between the ionomer and PA6 ; i.e. hydrogen and ionic bonding are stronger than the interaction between acid copolymer and PA6, which only has hydrogen bonding. Therefore, the blend with ionomer needs more energy to break the hydrogen and ionic bonding to allow polymer to flow, causing less die swell. Finally, the sodium ionomer was used as a compatibilizer for PP and organomodified clay nanocomposite because at high shear rate, for LDPE high content, the viscosity of the PA6/LDPE blends with the sodium ionomer is equal to the PA6/LDPE blends with the lithium ionomer. SEM-EDX mapping result showed improved dispersion of organo-modified clay nanocomposite in the PP matrix.

## 8.2 Recommendations

Based on what has been discovered in this study, the following recommendations are suggested:

1) For the system PA6-rich blend, the matrix is a polar polymer. The concept of polyelectrolyte can be used to explain the effect of ionomer on the compatibility of the PA6/LDPE blends. From the Debye length, the screen effect decreased as the valent ion charge increased. The monovalent ions have stronger screen effect than divalent ions; thus, the zinc ionomer can more effectively interactions with polyamide 6 than the sodium and lithium ionomers.

2) Results from the mechanical, morphological, thermal, and rheological properties showed that increasing neutralization and content levels better improve the blends properties than using different cation types. This is because the size of the metal cations used in this experiment was not significantly different so that other types of metal ions should be investigated, i.e.  $K^+$ ,  $Cs^+$ ,  $Mg^{2+}$ .

3) Other types of ethylene methacrylic acid should be studied to determine the effect of carboxylic acid content and polymer molecular weight.

4) PP organo-modified clay nanocomposite fiber should use varying amounts of EMAA ionomer.

5) Dye uptake of binary PP blends with EMAA ionomer should be investigated.