CHAPTER IV

BLENDS OF POLYAMIDE 6 WITH LOW-DENSITY POLYETHYLENE COMPATIBILIZED WITH ETHYLNE-METHACRYLIC ACID BASED COPOLYMER IONOMERS: EFFECT OF NEUTRALIZING CATION

4.1 Abstract

Blends of polyamide 6 with low-density polyethylene compatibilized with sodium-, zinc-, and lithium-neutralized ethylene-methacrylic acid ionomers were investigated at 11, 33, 55 wt% neutralization of ionomer. Blends of polyamide 6 with low-density polyethylene without compatibilizer had poor properties characteristic of incompatible polymer-polymer blends. After adding compatibilizer, tensile properties improved, the modulus drop associated with melting increased to higher temperatures and the dispersed phase size decreased. The improvement of mechanical properties and thermomechanical properties is less with EMAA than with ionomers. Overall, ionomers neutralized with among sodium, zinc or lithium show little difference in their compatibilization efficiency.

4.2 Introduction

Blending of polyolefins with engineering plastics offers an interesting route to achieve new materials with promising property combinations. Blends of polyolefins with polyamides, e.g. polyamide 6, have been extensively studied in view of their practical interest. Polyolefins are easy to process, insensitive to moisture, exhibit good flexibility, and are relatively inexpensive. Polyamides are rigid, more thermally stable, and possess good barrier properties to oxygen and organic solvents. Therefore, the addition of a small amount of polyolefin to a polyamide can improve the impact properties, while a polyamide dispersed in a polyolefin may enhance the oxygen resistance and hydrocarbon permeation of polyolefin, or act as a reinforcing agent.[1]

However, polyamide 6 (PA6) and polyolefins form thermodynamically immiscible blends and hence blends show poor ultimate properties. Frequently, when an immiscible blend is subjected to a stress, the stress concentrates at the polymer-polymer interface, which, for incompatible polymer pairs, is weak and unable to

transfer the stress between the continuous and dispersed phases. One strategy to reduce the negative effects of immiscibility in PA6/polyolefin blends is to introduce acid groups onto the polyolefin in order to react with terminal primary amines[2] as well as introducing the possibility of chemical interchange reactions involving the amide linkage.[3] Another strategy is to introduce a third component, a compatibilizer, to improve interfacial properties between the PA6 and the polyolefin. As a result, an increase in stress transfer between the continuous and dispersed phases is produced improving the mechanical properties of the blend.[4] Compatibilization of polyamide/polyolefin blends has been achieved through use of various polymers including ethylene-methacrylic acid copolymers[5], ethylene-acrylic acid copolymers[2], ethylene-vinyl alcohol copolymers[6] or ethylene homo- or copolymers with grafted maleic anhydride (MAH).[7] The reaction between the terminal amine group of polyamide 6 results graft copolymer formation during extrusion, which has been theorized to significantly strengthen the interface.[5]

Copolymers of ethylene with monomers containing acid groups are important commercial products. These materials are sold commercially with either hydrogen or a metal cation as the neutralizing agent for the acid group. The latter are termed ionomers, and typically the amount of acid groups neutralized with a metal cation is less than stoichiometric, i.e. some of the acid groups are neutralized with a metal cation while others are neutralized by hydrogen. One commercial ionomer is a copolymer of ethylene and methacrylic acid marketed by DuPont under the trademark Surlyn™. Three of the most common neutralizing cations are lithium (Li^+), sodium (Na^+) and zinc (Zn^{2+}). The properties of the alkali-neutralized materials and zinc-neutralized are different; for example sodium or lithium ionomers absorb significantly more water and tend to have higher fractional crystallinities than zinc ionomers.

Zinc-neutralized and sodium-neutralized ionomers have been extensively studied in previous work as blend compatibilizers for the polyamide-PE system.[8-12] The addition of compatibilizer has been shown repeatedly to increase compatibility between the two components, including improvements in mechanical properties,[13] barrier properties,[9] as well as smaller dispersed domain sizes.[11, 13, 14]

The purpose of this study is to compare the effects of sodium, zinc and lithium-neutralized ethylene-co-methacrylic acid as a compatibilizer for PA6/LDPE blends and also to study the effect of the percent neutralization level on PA6/LDPE blends. This study expands significantly what was done in previous studies because (1) different neutralization levels are compared using the same starting copolymer resins and (2) a direct comparison between three different cations is made using the same starting copolymer resin.

4.3 Experiment

Materials

The polyamide 6 employed in this study was an injection molding grade, 1013B, supplied by UBE Polyamide (Thailand). The supplier reports a molecular weight of this material of 12,000 g/mol and is reported to have approximately equal numbers of amine and carboxylic acid end groups. Low-density polyethylene LD 1450J (density 0.914 g/cm^3), was also an injection molding grade polymer graciously supplied by Thai Polyethylene Co.,Ltd.. Poly(ethylene-co-methacrylic acid) marketed under the trademark Nucrel$^®$ 0903 (density 0.93 g/cm^3) was supplied by DuPont (Thailand).

Neutralization of EMAA

A 20 g. amount of EMAA was dissolved at 140°C in a 200 ml solution that contained toluene and n-butanol (3:1). A 25 ml amount of either sodium or lithium hydroxide (the concentration of the hydroxide was adjusted. depending on the neutralization level desired) was added, and the system was refluxed at 140°C for 3 hours. The solvent was evaporated, and then 150 ml of fresh solvent was added and evaporated and then the fresh solvent addition and evaporation step was repeated two more times. The total time of the four evaporation steps and three addition steps was approximately 1 hour, i.e. the polymer was in contact with solvent for approximately 4 hours. The ionomer was dried overnight at 60°C.

For the zinc-neutralized materials, the appropriate amount of zinc acetate was mixed with 400g of EMAA by a tumble mixer for 10 minutes. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 35 rpm, corresponding to a residence time of approximately 1 minute in the extruder.

To determine the neutralization level of the ionomers, the carboxyl contents of ethylene methacrylic acid were determined by a titration method[15] which involves the titration of a hot n-butanol and toluene solution containing polymer by 0.1N sodium hydroxide in aqueous solution with phenolphthalein as the indicator. Pure E-MAA was also titrated to determine the starting carboxyl content of the material. The amount of acid monomer on the copolymer was 3.08 mol % (9 wt %) as determined by titration. Neutralization levels are 11, 33 and 55 wt% (+/- 0.5%) for the three cations.

Blend Preparation

Pellets were mixed in a tumble mixer for 10 minutes followed by drying under vacuum at 60°C for 24 hours. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 35 rpm. Blends were extruded through a single strand die; the extrudates were cooled in a water bath, dried at ambient temperature and then pelletized. The pellets were dried and kept in sealed plastic bags prior to compression molding to minimize moisture absorption. Ionomer compatibilized blends were made in a 2-step process; first the ionomer and LDPE were extruded together as a 50/50 master batch, then the LDPE, PA6 and the appropriate amount of the 50/50 master batch mix was extruded together. EMAA compatibilized blends were made in one shot, i.e. the LDPE, PA6 and EMAA were extruded together.

Specimen Preparation

Test specimens were prepared using a Wabash V 50 H 50 ton compression molding machine. The pellets were placed in a picture frame mold and the mold was preheated at 240°C for 3 minutes in the press without application of pressure. The mold was then compressed under a force of 10 tons for a further 3 minutes, after which the mold is cooled to 40°C under a pressure of 10 tons. Test specimens were cut from the molded sheets using a die cutter.

Scanning Electron Microscopy (SEM)

A Scanning electron microscope (SEM), JEOL 5200-2AE (MP152001), was used to study phase morphologies of the blends. The specimens were fractured in liquid nitrogen and etched using (i) hot decalin (for LDPE minor phase blends) and (ii) formic acid (for PA6 minor phase blends). The specimens were then coated with gold under vacuum. All SEM images were obtained using a magnification of 1000x at 15 kV.

Dynamic Mechanical Analysis (DMA)

A Solids Analyzer RSA II (Rheometric Scientific) was used to measure the storage and loss moduli as a function of temperature. Film geometry was used with 4°C temperature steps. Samples were molded to a thickness of around 0.5 mm. All experiments were performed with a 1 Hz frequency, 0.03% strain, and with static force tracking dynamic force.

Tensile Testing

A D1708 microtensile die was used to cut the samples for tensile testing, and an Instron universal testing machine was used to measure tensile strength using a crosshead speed of 1.30 mm/min. Samples were molded to a thickness of approximately 0.5 mm. At least 5 samples were used for each composition to determine an average and standard deviation.

Differential Scanning Calorimetry (DSC)

A TA Instruments Q1000 differential scanning calorimeter with liquid nitrogen cooling was used for this study, and was routinely calibrated with four different standards (cyclopentane, biphenyl, indium and tin) at a 10°C/minute heating rate. Polymer samples were cut from the same sheet used to cut samples for tensile testing, placed in aluminum DSC pans, and was scanned at a rate of 10°C/min. The melting characteristics of the two components were determined during this initial scan, while the glass transition temperature were determined during a second scan after the material was held at 250°C for 5 minutes and rapidly cooled to -100°C to assure good sample-pan contact and eliminate complicating enthalpy relaxation

effects. The fractional crystallinity was determined by integrating the area under the respective melting exotherms, and converting these enthalpies to fractional crystallinities using a melting enthalpy of 282 J/g for polyethylene and 190 J/g for polyamide.[16] Crystallinities were calculated by using Equation 1

$$\chi_c = \frac{\Delta H \times 100\%}{\Delta H_f \times wt.fraction} \qquad \text{(Equation 1)}$$

where χ_c is % wt. fraction crystallinity

ΔH is melting enthalpy of the components present in the blend

ΔH_f is heat of fusion for 100% crystallinity of the pure component, (190 J/g for PA6, and 282 J/g for LDPE)

Dynamic Stress Rheometer

A Dynamic Stress Rheometer SR 5000 (Rheometric Scientific) was used to measure the steady shear viscosity η as a function of shear rate γ. Steady-state conditions were known to occur because the viscosity was measured as a function of time and only when the viscosity was constant were measurements recorded. Cone and plate geometry (cone angle=0.0393 rad) was used with this experiment. Samples were molded to a thickness of around 0.5 mm and plate diameter 40 mm, then melted in the instrument and the two plates were brought to the proper height as determined by the manufacturer. The condition for nylon and LDPE is 230°C while the EMAA and ionomer masterbatches (50 LDPE:50 ionomer) were measured at 140°C because the materials were unstable at 230°C for the long periods of time required to measure the viscosity. Masterbatches of ionomers were used rather than pure ionomers because all of the ionomer was converted into masterbatches.

4.4 Results and Discussion

Figure 4.1A and 4.1B show micrographs of the blends PA6 80:LDPE 20 and PA6 20:LDPE 80 and indicate predominantly spherical droplets imbedded in a matrix. As expected, adhesion between the PA6 phase and the LDPE phase is poor in the uncompatiblized blends ((a) of both figures), as confirmed both by the large size of the phases as well as by the smoothness of hole surfaces. After introducing compatiblizer, the size of the dispersed phase becomes much smaller. This reduction in size suggests that drop coalescence in the extruder is being reduced. Figure 2 shows the effect of compatibilizer concentration and neutralization level on the size of the dispersed phase. As shown in Figure 4.2, only 1.5 phr of Na-EMAA , Zn-EMAA or Li-EMAA is sufficient to produce the maximum reduction in dispersed phase size. In all cases, the reduction is significantly better for the ionomer than for the acid copolymer.

For blends PA6 80:LDPE 20 with ionomers at 0.5 phr, dispersed phase size tends to decrease with increasing neutralization level for Li-EMAA. With Zn-EMAA, the dispersed phase size tends to increase with increasing neutralizing level. For Na-EMAA the dispersed phase size is independent of neutralizing level. At higher neutralization levels, the dispersed phase size does not seem to depend on neutralization level. In terms of cation, the efficiency goes as Zn> Na> Li as measured by the dispersed phase for the 0.5 phr sample; at higher compatibilizer levels there seems to be no difference. For the high LDPE content materials, Li>Zn>Na for the 0.5 phr sample, for higher levels the Li=Na>Zn. Our hope was that one cation would clearly be better than another in promoting compatibilization; however the results clearly are inconsistent with respect to dispersed phase size at least. However, it is well-known that the viscosity of ionomers depends on the neutralizing cation, and perhaps the relative viscosities of the three components might help explain the results.
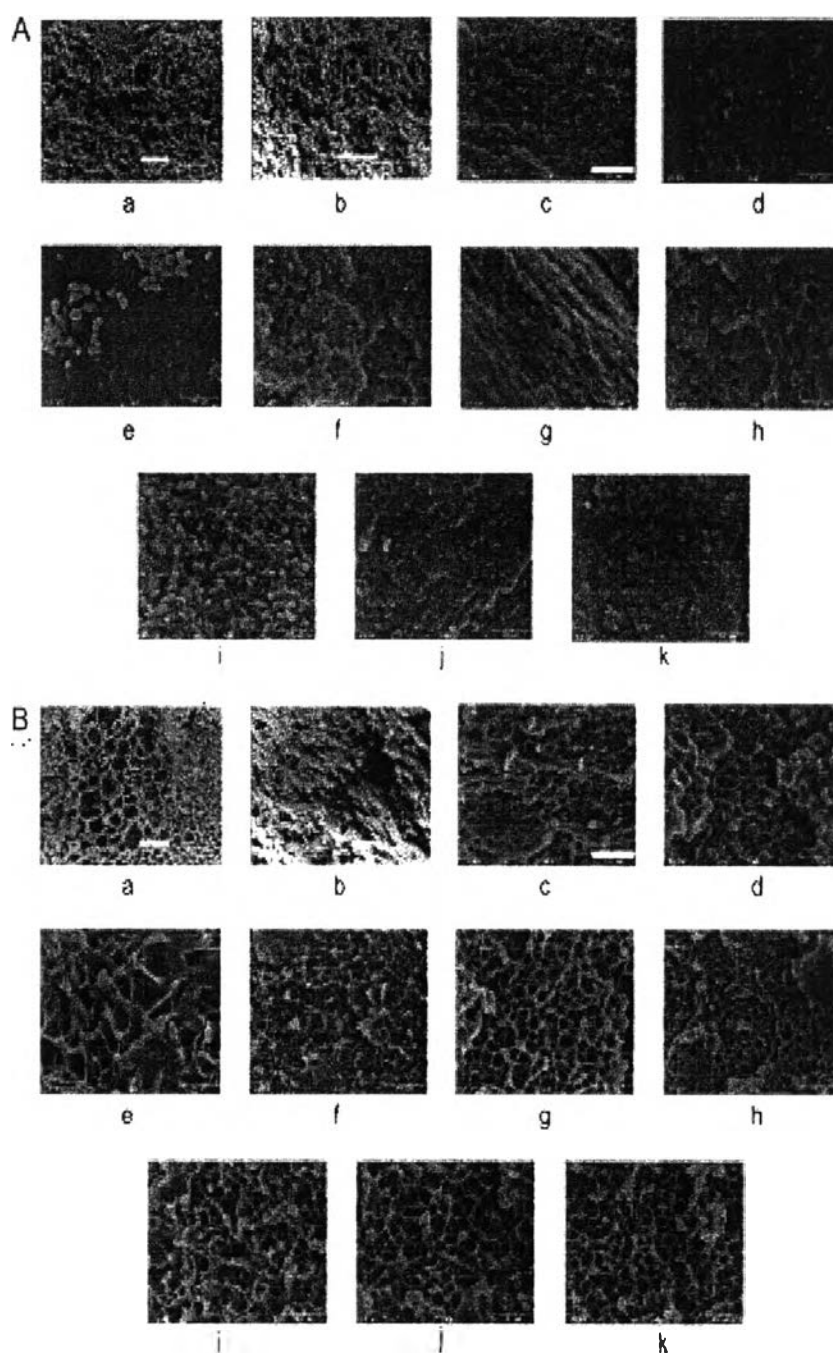
Figure 4.1 (A) SEM micrographs of PA6 80: LDPE 20 blends(a) no compatibilizer (b) EMAA 1.5 phr (c) 11%Na-EMAA 1.5 phr (d) 33%Na-EMAA 1.5 phr (e) 55%Na-EMAA 1.5 phr (f) 11%Zn-EMAA 1.5 phr (g) 33%Zn-EMAA 1.5 phr (h) 55%Zn-EMAA 1.5 phr (i) 11%L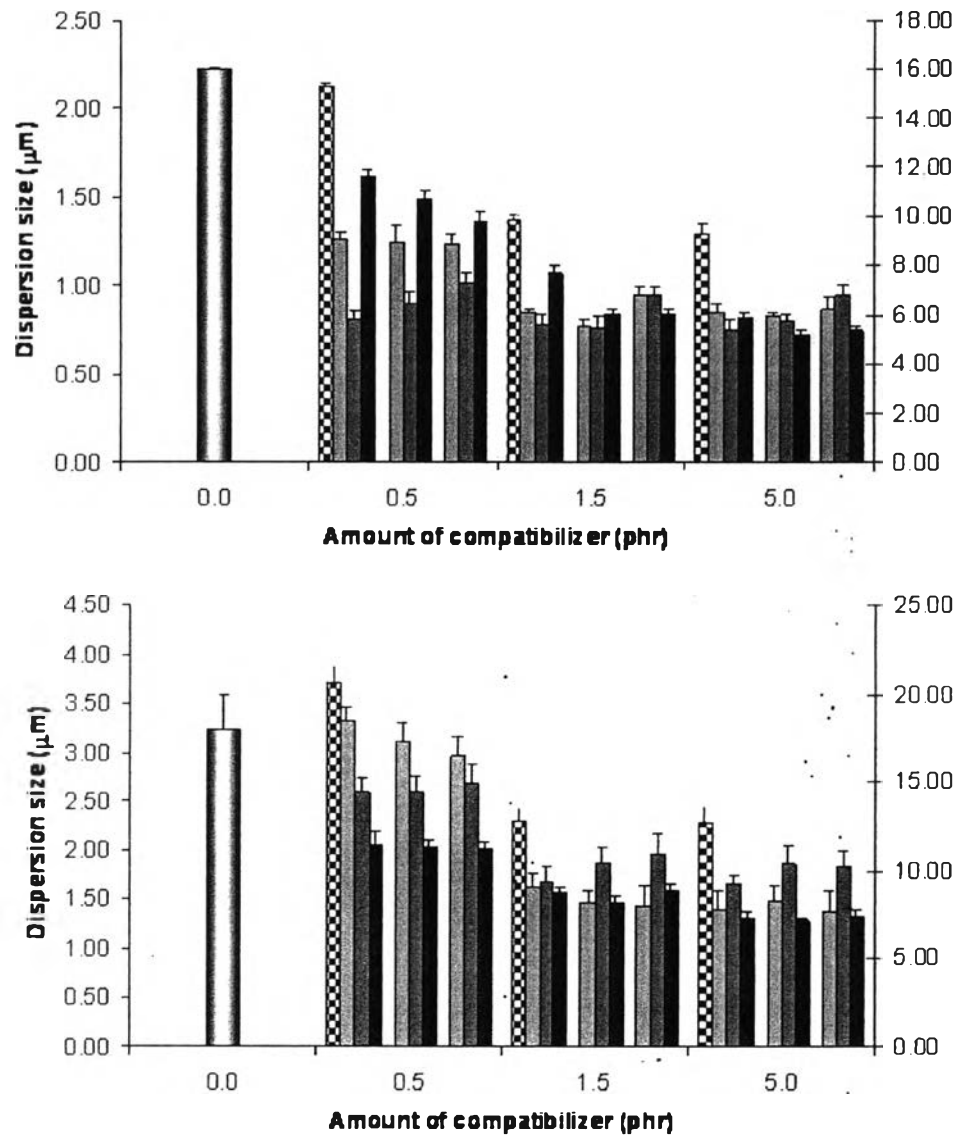i-EMAA 1.5 phr (j) 33%Li-EMAA 1.5 phr (k) 55%Li-EMAA 1.5 phr (B) SEM micrographs of PA6 20: LDPE 80 blends (a) no compatibilizer (b) EMAA 1.5 phr (c) 11%Na-EMAA 1.5 phr (d) 33%Na-EMAA 1.5 phr (e) 55%Na-EMAA 1.5 phr (f) 11%Zn-EMAA 1.5 phr (g) 33%Zn-EMAA 1.5 phr (h) 55%Zn-EMAA 1.5 phr (i) 11%Li-EMAA 1.5 phr (j) 33%Li-EMAA 1.5 phr (k) 55%li-EMAA 1.5 phr.

Figure 4.2 Dispersion size of PA6 80: LDPE 20 and PA6 20: LDPE 80 blends with 11%-55%wt Na-EMAA and Zn-EMAA and Li-EMAA (upper) and 20/80 PA6/LDPE blends with 11%-55%wt Na-EMAA and Zn-EMAA and Li-EMAA (lower). Checkerboard represents EMAA, light grey represents Na-EMAA, dark grey represents Zn-EMAA, and black represents Li-EMAA.

Figure 4.3 shows steady shear viscosities for the indicated materials and masterbatches. Neutralization of the acid has been shown to increase the viscosity of ionomers, and the viscosity continues to increase as the neutralization level increases.[17, 18] This behavior is shown in graphs (b,c,d) although the increase is not

uniform at all shear rates; for example at shear rates>1 s^{-1} the 11% Zn-neutralized sample has higher viscosity than the 33% sample. Looking only at zero-shear viscosities; the increase with neutralization is very non-linear (even in a log sense) for a given cation. Although the range of cation levels studied was very different and pure ionomers were used previously, such non-linearity is not unique.[15] However, what is unique is that the zero-shear viscosities is only slight larger for Zn vs. Na; a factor of four was seen in an earlier study that used pure ionomers.[15] The fact that the viscosity is relatively inconsistent with respect to neutralizing cation supports the inconsistency noticed in Figure 4.2. A more quantitative assessment is not possible because the relevant shear rate where such a comparison should take place is not clear.
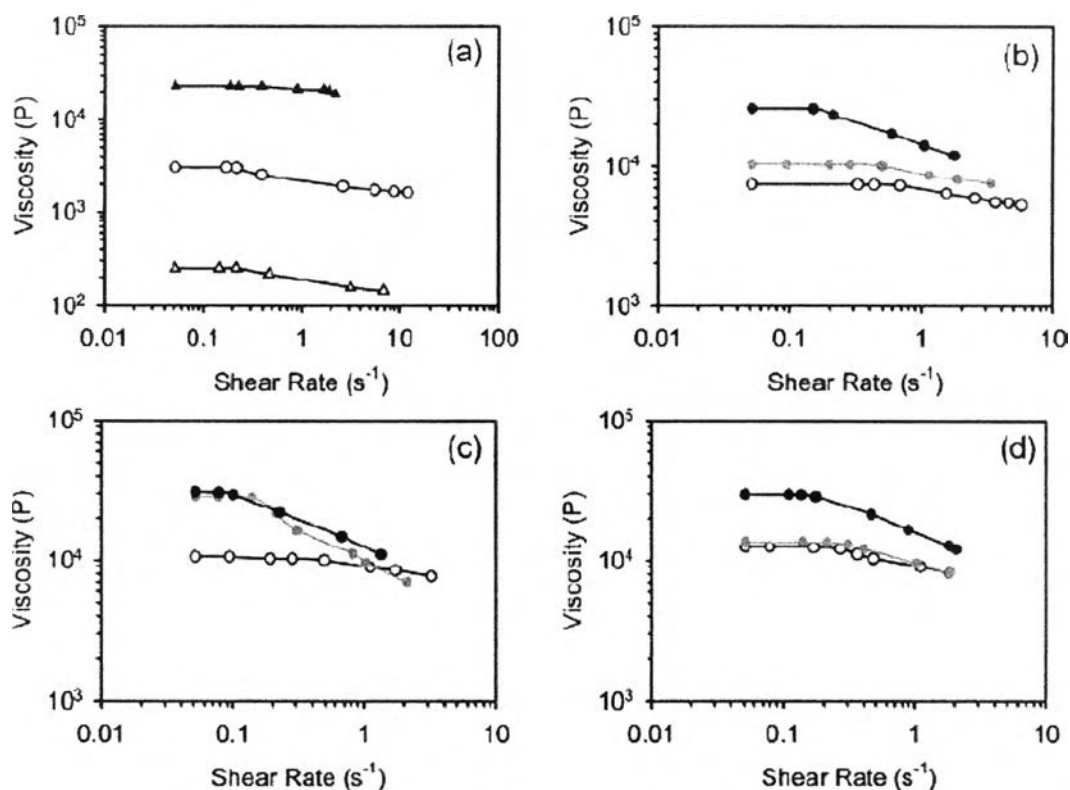

Figure 4.3 Shear viscosity vs shear rate at steady-state. (a) LDPE at 230 °C (triangle circle), PA6 at 230 °C (circle), EMAA at 140°C (black triagle) (b) 50%master batch Na-EMAA. (c) 50%master batch Zn-EMAA. (d) 50%master batch Li-EMAA. Note : white represent neutralized 11%wt, grey represent neutralized 33%wt and black represent neutralized 55% wt.

The addition of compatibilizer had no effect on the T_m as measured by DSC for any samples; the melting temperature of the polyethylene was $107.1\pm0.7°C$, while that for the polyamide 6 was $221.3\pm1.1°C$. Figure 4.4 shows the percent crystallinity for each blend. The addition of compatibilizer had effect on the percent crystallinity of nylon in the high and low nylon content blends. In the low content LDPE material, LDPE crystallinity increases with the addition of metal-neutralized compatibilizer at low compatibilizer amounts vs. EMAA compatibilizer, with Li-EMAA having the highest increase. This effect is difficult to rationalize; compatibilization should reduce chain mobility which in turn should reduce crystallization. Perhaps the metal cation is nucleating crystallinity which in turn outweighs the small reduction in chain mobility that occurs when going from 0.5 phr to 1.5 phr. Consistent with previous work that has shown that crystallinity decreases with an increase in ionomeric compatibilizer,[10, 11] the crystallinity decreases at 5.0 phr vs. 1.5 phr when considering both compatibilizer and LDPE, since the weight fraction used in the fractional crystallinity calculation uses LDPE only. In the high content LDPE material, LDPE crystallinity is retarded by EMAA, and Na or Zn-EMAA increases LDPE crystallinity respectively. There is no consistent crystallinity increase or decrease with respect to the other two cations across compatibilizer amounts/neutralization levels.
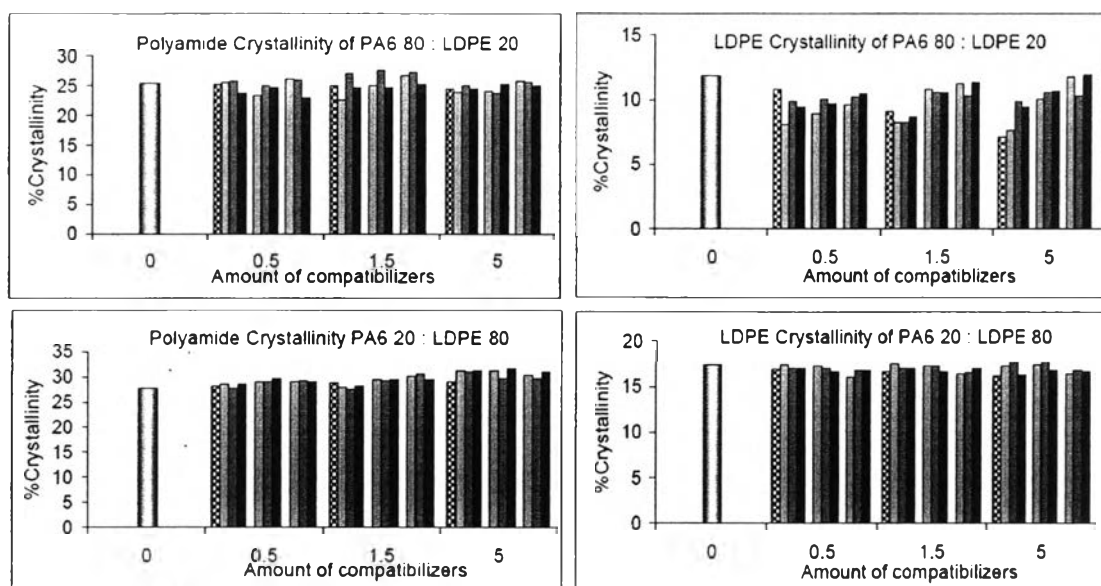
Figure 4.4 Percent crystallinity of PA6 80: LDPE 20 and PA6 20: LDPE 80 blends from DSC. Checkerboard represents EMAA, light grey represents Na-EMAA, dark grey represents Zn-EMAA, and black represents Li-EMAA.

Mechanical properties of the blends were tested and the tensile strength, elongation at break and modulus are shown in Figure 4.5. For the low content LDPE materials, ionomers significantly outperform the EMAA as a compatibilizer with respect to failure stress and failure strain, while the difference among the zinc-neutralized, sodium-neutralized and lithium-neutralized materials is not outside the range of experimental error, except the failure strain at 5% compatibilizer content. The behavior at this high content seems to be quite random, suggesting perhaps that the nature of the LDPE phase is changing (since the ionomer should be 25% of the dispersed phase). In agreement with SEM data, 1.5% compatibilizer content seems to be sufficient for optimal performance. Surprisingly, the modulus for the materials with metal-neutralized compatibilizer seems to be higher than that of the uncompatibilized or EMAA compatibilized blends, even though PA6 crystallinity (which should be the most important factor with respect to the modulus in these high PA6 content materials) is independent of these factors.

The benefits of adding compatibilizer are extremely small, if present at all, for the high content LDPE blends. There might be a small increase in failure stress and

failure strain with the addition of metal-neutralized compatibilizer but the increases are marginal. No consistent effects are found in the modulus, which does not match the higher LDPE crystallinity for the material compabilized with Li-EMAA.
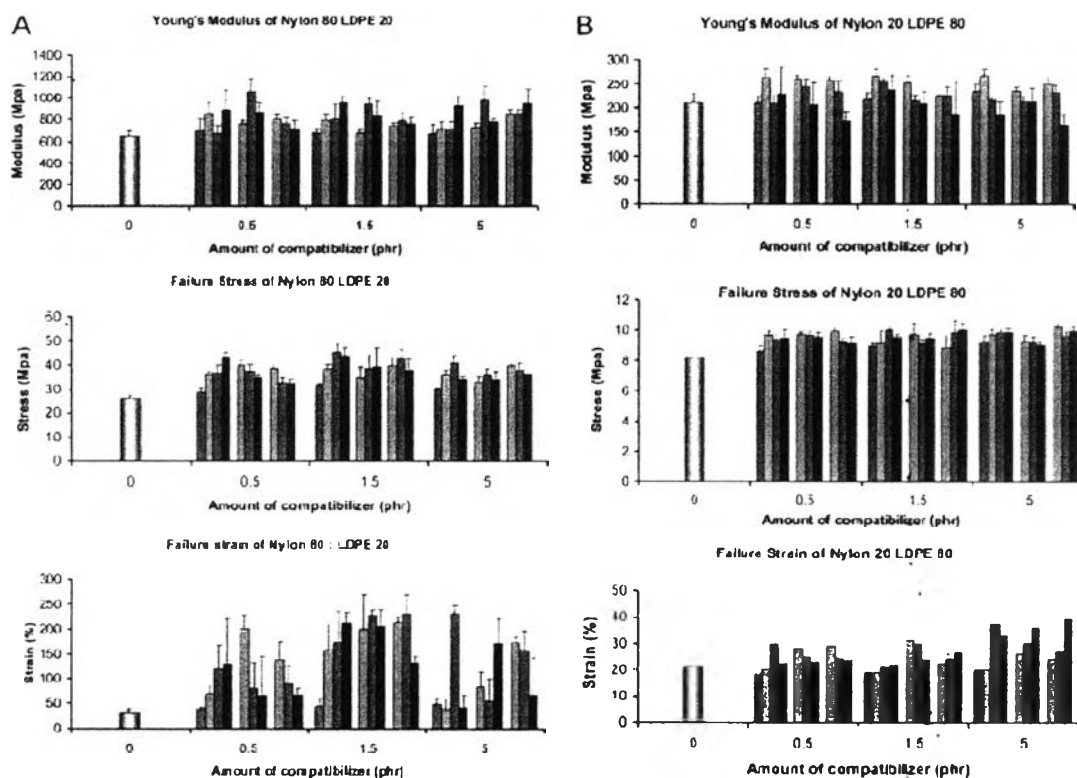

Figure 4.5 Tensile results for (a) PA6 80: LDPE 20 blends and (b) PA6 20: LDPE 80 blends. Checkerboard represents EMAA, light grey represents Na-EMAA, dark grey represents Zn-EMAA, and black represents Li-EMAA.

DMA spectra for ternary blends are shown in Figure 4.6. The addition of EMAA, Na-EMAA, Zn-EMAA or Li-EMAA leads to samples that have mechanical stability at much higher temperatures for both blend compositions, i.e. the E' drop off corresponding to the melting transition is shifted to a higher temperature as compatibilizer is added. Figure 4.7 shows the melting temperature, corresponding to a storage modulus of 10^7 dyn/cm^2, as measured by DMA. The melting temperature of PA6 80: LDPE 20 blend is lower than using EMAA or no compatibilizer vs Na-EMAA, Zn-EMAA and Li-EMAA as compatibilizer. There also seems to be no

consistent difference at the various neutralization levels regarding which cation is better able to provide mechanical stability at elevated temperatures.

There is essentially universal agreement in the literature that the mechanism of compatibilization is a reaction involving carboxylic acids. Yet, as this work shows (and other work has before[19-21], it seems quite unusual that decreasing the concentration of one of the reactants (i.e. the carboxylic acid) increases compatibilization performance. Two possibilities could explain this observation. The first is that the substantially higher viscosity of the ionomer causes improved compatibilization. However, if increased compatibilizer viscosity were the only reason, then the performance at 55% neutralization should have been better than the performance at 11% neutralization; which was not found. The other possibility is that the phase separation that the metal cation induces, or the fact that the metal cation itself is present in the sample (e.g. a catalytic effect), somehow enhances the number of covalent bonds at the PA6/LDPE interface.
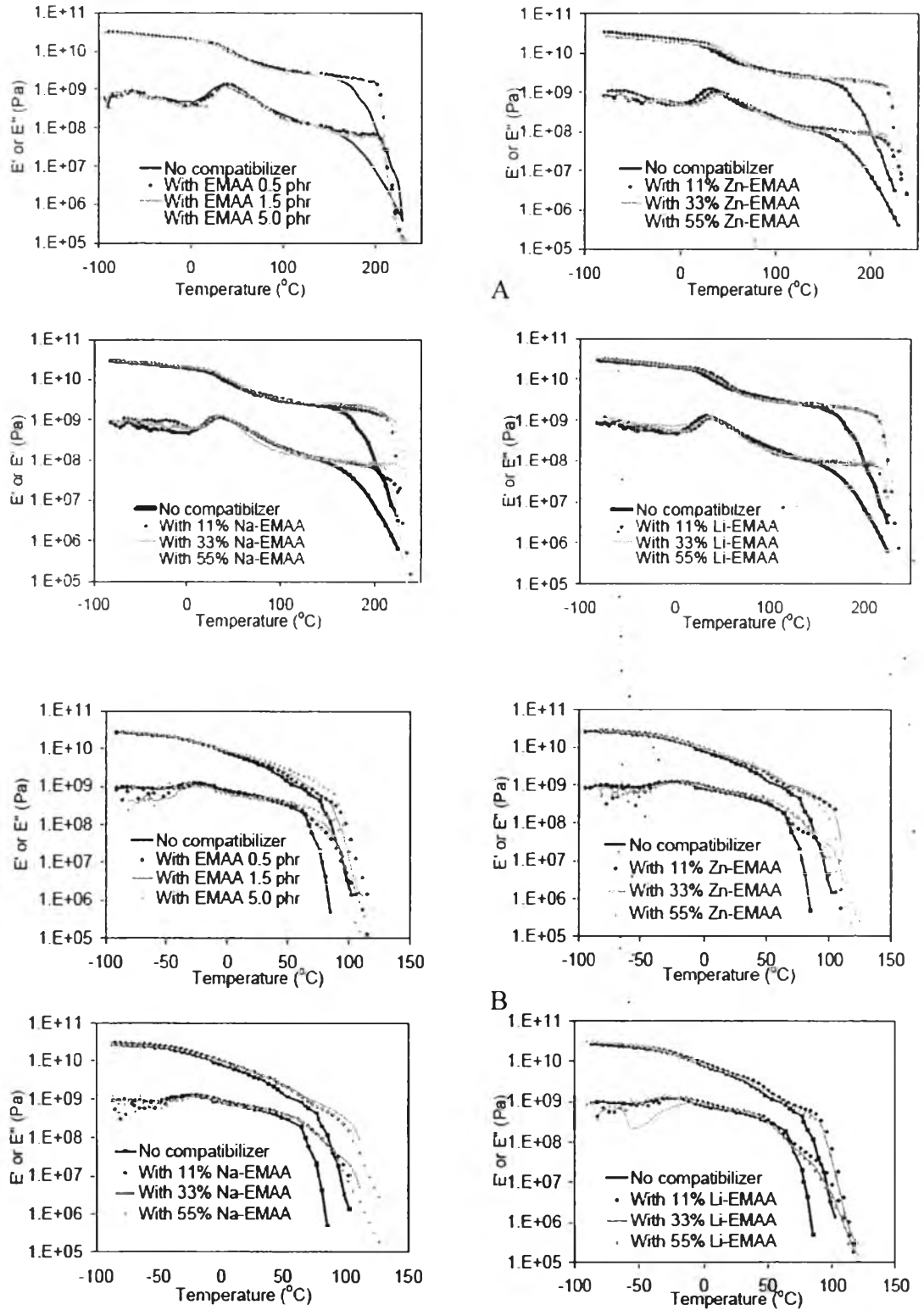
Figure 4.6 DMA results (A) PA6 80: LDPE 20 blends (B) PA6 20: LDPE 80 blends.

Melting Temperature of PA6 80: LDPE 20 by DMA

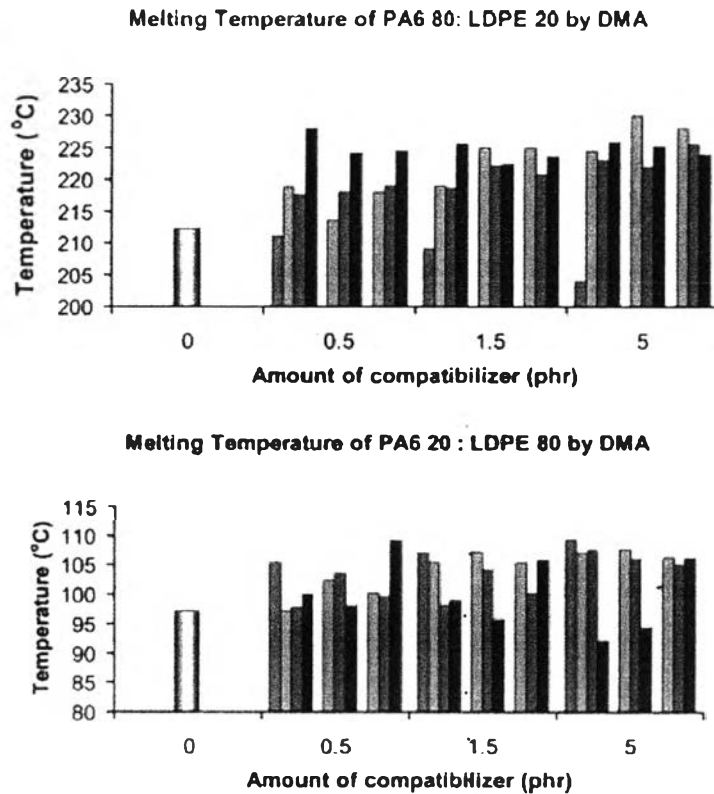**Melting Temperature of PA6 20 : LDPE 80 by DMA**

Figure 4.7 Melting temperature (determined by when storage modulus was 10^7 Pa) of PA6 80: LDPE 20 and PA6 20: LDPE 80 blends from DMA. Checkerboard represents EMAA, light grey represents Na-EMAA, dark grey represents Zn-EMAA, and black represents Li-EMAA.

4.5 Conclusions

Adding an ionomeric compatibilizer improves blend properties in polyamide 6/LDPE blends. Comparing the efficiency among sodium, zinc and lithium shows some differences in the efficiency as measured by mechanical properties, dispersed phase size and thermomechanical properties; however the differences are not consistent with respect to neutralization level or compatibilizer amount. It is possible that this inconsistency might be due to the inconsistency in viscosity; although direct comparison is not possible because of shear rate dependencies of viscosity. As compatibilizers for polyamide 6/LDPE blends, the data clearly shows however that all metal-cation neutralized materials are, on the average, better than the unneutralized acid-form.

4.6 Acknowledgement

4.7 References

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