

## Melt Rheology of Low-Density Polyethylene/Polyamide 6 using Ionomer as a Compatibilizer

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### Summary

Rheology of blends of polyamide 6 with low-density polyethylene compatibilized with sodium-, zinc-, and lithium-neutralized ethylene-methacrylic acid ionomers were investigated at 11, 33 and 55% neutralization of ionomer. Blends of polyamide 6 with low-density polyethylene without compatibilizer had lower shear viscosities than a mixing rule would predict. After adding compatibilizer, the shear viscosity of the blend is increased, presumably due to the formation of graft copolymer from the reaction of the primary amine with free acid groups. The increase of shear and elongational viscosity properties is less with EMAA than with the ionomers; which is consistent with mechanical property and dispersed phase size results presented in an earlier publication. For high polyamide 6 content blends, zinc-neutralized compatibilizers yielded the highest shear and elongational viscosities; while for low polyamide 6 contents, lithium-neutralized compatibilizers yielded the highest viscosities.

### Introduction

Polyamide-6 (PA-6) and low density polyethylene (LDPE) are large volume commercial polymers which have complimentary attributes: PA-6 exhibits a high crystalline melting point, good resistance to hydrocarbon solvents, and high mechanical properties, while LDPE has excellent low temperature flexibility and good resistance to moisture permeation[1]. However, PA-6 and LDPE form thermodynamically immiscible blends and hence the blend shows low deformation capacity and poor ultimate properties. Frequently, when a polymer mixture is subjected to stress, the stress concentrate at the interface, which, for incompatible polymer pairs, is weak and unable to transfer the stress between the two phases. One strategy to improve interface properties in PA-6 blends is to react with the terminal primary amines[2] and/or a chemical interchange reactions involving the amide linkage[3]. Hence polyamides have been extensively studied as blend components. Of course, LDPE has no functional groups that will react with either moiety; hence,

introducing a third component, a compatibilizer, can improve interfacial properties. As a result, an increase in stress transfer between the two phases is produced improving the mechanical properties of the blend[4]. One compatibilizer for PA-6/LDPE blends are ethylene-acid copolymers, either with or without partial neutralization with a metal cation. In this work, we use a copolymer of ethylene and methacrylic acid partially neutralized by sodium, zinc and lithium. Such materials are termed ionomers, and are important commercial materials as pure polymers. Prior to our previous paper on the subject that detailed mechanical and morphological studies[5], no studies had been published comparing compatibilizer performance for ionomeric compatibilizers neutralized with three different cations using identically matched copolymers. This paper discusses the effect these compatibilizers have on rheological properties.

## Experiments

### *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<sup>3</sup>), was also an injection molding grade polymer graciously supplied by Thai Polyethylene Co.,Ltd. Poly(ethylene-co-methacrylic acid) (EMAA) marketed under the trademark Nucrel<sup>®</sup> 0903 (density 0.93 g/cm<sup>3</sup>) was supplied by DuPont (Thailand). The amount of acid monomer on the copolymer was 3.7 mol % (9 wt %) as determined by titration.

### *Neutralization of EMMA*

EMAA (20 g.) was dissolved at 140°C in 200 ml of solution that contained toluene and n-butanol (3:1). Either sodium or lithium hydroxide (25 ml; the concentration of hydroxide was adjusted based 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. This method is followed by Vanhoorne et al.[6]

For zinc-neutralized materials, an appropriate amount of zinc acetate was mixed with 400g of EMMA by 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 confirm the neutralization level of the ionomers, the carboxyl contents of ethylene methacrylic acid were determined by a titration method[6], 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 EMMA was also titrated to determine the starting carboxyl content of the material. Neutralization levels were 11, 33, and 55% (+/- 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 and EMAA-compatibilized blends were made in a 2-step process; first the ionomer/EMAA and LDPE were extruded together as a 50/50 master batch, then the LDPE, PA6, and an appropriate amount of the 50/50 master batch mix was extruded together.

### Rheological measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer was used to investigate the melt rheology of the as-prepared blends. The inner diameter and the length of the barrel used were 9.95 and 300 mm, respectively, with capillary diameter of 1 mm ( $L/D = 0.5$  and 20) and all measurements were made at 230°C. The apparent shear stress  $\tau_{app}$  is defined as

$$\tau_{app} = \frac{R\Delta P}{2L} \quad (1)$$

where  $R$  is the radius of the die,  $\Delta P$  the pressure drop across the die, and  $L$  is the length of the die; and the apparent shear rate  $\dot{\gamma}_{app}$  is defined as

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \quad (2)$$

where  $Q$  is the volumetric flow rate. These quantities were corrected using the procedures of Bagley [7,8] and Rabinowitsch [7,8] respectively. According to these corrections, the actual shear stress is defined as

$$\tau_{actual} = \frac{R\Delta P}{2(L+nR)} = \frac{\Delta P}{2(L/R+n)} \quad (3)$$

where  $n$  is a multiplication factor according to the Bagley correction; and the actual shear rate  $\dot{\gamma}_{actual}$  is defined as

$$\dot{\gamma}_{actual} = \frac{3n'+1}{4n'} \dot{\gamma}_{app} \quad (4)$$

where  $n'$  is the slope from a plot (in a double logarithmic scale) between the apparent shear stress and the apparent shear rate that was fitted to the Rabinowitsch correction. According to these values, the actual shear viscosity  $\eta_{actual}$  is then defined as

$$\eta_{actual} = \frac{\tau_{actual}}{\dot{\gamma}_{actual}} \quad (5)$$

The elongational contribution during the flow of the polymeric melt through a restricted die (i.e., converging flow) can also be evaluated using a well-known theory of Cogswell [8-10], according to which the important quantities can be summarized as follows:

$$N = \frac{\dot{\gamma}_{app}}{4\dot{\gamma}_{real} - 3\dot{\gamma}_{app}} \quad (6)$$

$$P_e = (\tau_{app} - \tau_{real}) \cdot \frac{4L}{D} \quad (7)$$

where  $N$  denotes an empirical constant,  $P_e$  an entry pressure, and  $D$  the inner diameter of the die. The quantities in Eqs. 6 and 7 reduce to

$$\dot{\epsilon} = \frac{4\tau_{app}}{3(N+1)P_e} \dot{\gamma}_{app} \quad (8)$$

where  $\dot{\epsilon}$  is the elongational rate, and the elongational stress  $\sigma$  can be expressed as

$$\sigma = \frac{3(N+1)P_e}{8} \quad (9)$$

Finally, according to Eqs. 8 and 9, the elongational viscosity  $\eta_e$  is defined as

$$\eta_e = \frac{\sigma}{\dot{\epsilon}} \quad (10)$$

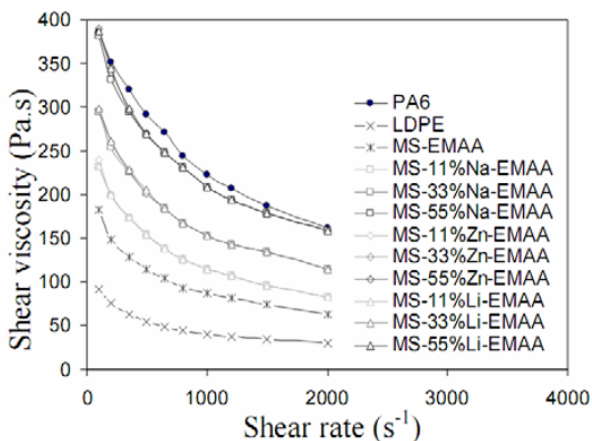
## Results and Discussion

### *Pure Materials and Masterbatches*

Figure 1 shows plots of shear viscosity versus shear rate for raw materials from the 20 mm die after the corrections have been applied. PA6 has the highest viscosity while the lowest is LDPE. There is little difference between the shear viscosity vs. shear rate behavior of the 50/50 masterbatches made with different cations at equivalent degrees of neutralization. For the pure ionomers, previous studies have shown that the viscosity at low shear rate (i.e. 1-10 s<sup>-1</sup>) are significantly different [12-16]; however at high shear rate (i.e. 100s<sup>-1</sup>) effect of counter ion of the ionomer become minimized. Their shear viscosity are quite closed. However this effect can be revealed later as it influences on compatibilization of PA6/LDPE blends. The discussion will be involved with power law index and elongational viscosity. A difference in shear viscosity is seen with changes in neutralization level; at 11%, 33% and 55% neutralization, the shear viscosity is increased approximately 1.3, 1.6 and 2.1 times from EMAA. The Ostwald-de Waele law, or “the power law” [11] was used to fit the data:

$$\tau_w = K \dot{\gamma}^n \quad (11)$$

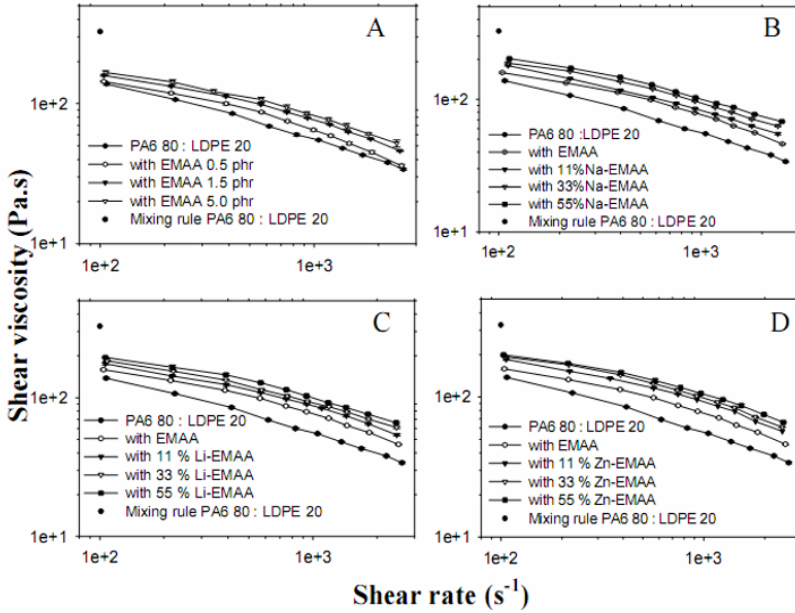
where  $\tau$  is shear stress,  $\dot{\gamma}$  is shear rate,  $K$  is a viscosity related constant and  $n$  is the power law index. For a Newtonian fluid,  $n=1$ ; for a dilatant fluid  $n > 1$ ; and for a pseudoplastic fluid,  $n < 1$ . As with the viscosity, PA6 has the highest  $n$ ; i.e. it is the least shear thinning fluid. The value of  $n$  for 55% neutralization is the highest for all compatibilizers as well.



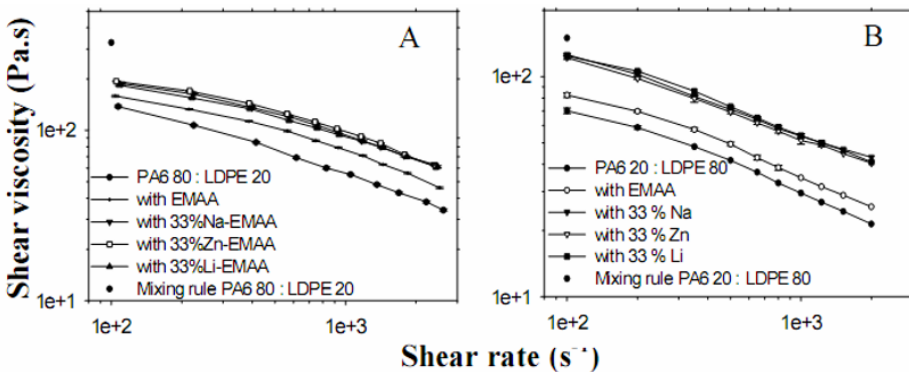
**Figure1** show shear viscosity vs shear rate of raw materials (PA6 & LDPE) and 50%wt master batch compatibilizers (i.e. EMAA, Na-EMAA, Zn-EMAA and Li-EMAA)

### *Shear viscosity of blends*

Adding 20% LDPE to PA-6 dropped the shear viscosity by a factor of  $\sim 0.37$  which is outside of the mixing rule as shown in Figure 2. Adding EMAA, i.e. making the blend more compatible, caused an increase in shear viscosity by 1.04, 1.15 and 1.21 times using compatibilizer amounts of 0.5, 1.5 and 5.0 phr respectively. Using sodium, zinc or lithium compatibilizers caused a much higher increase as shown in Figure 2; consistent with the improvements in compatibilization seen in our earlier study[5]. The increase in shear viscosity was larger for more added compatibilizer. Adding 20% PA-6 to LDPE dropped the shear viscosity by a factor of  $\sim 0.77$ ; which is clearly counter to a mixing rule since PA-6 has a higher viscosity than LDPE. Similar trends with respect to EMAA and the ionomers were found as with the high amide content blend. An increase in the neutralization level causes the shear viscosity to increase as shown in Figures 2 for both 80:20 and 20:80 blends. The increase is more abrupt at 11% and 33% vs. 55%. For the high content polyamide blends as shown in Figure 3; Zn-EMAA shows the highest increases while Na-EMAA and Li-EMAA are approximately equivalent. Due to the zinc ionomer provides stronger bonding than sodium ionomer resulting in the highest shear viscosity[17]. For the low content polyamide blends, Li-EMAA causes the largest increase in viscosity followed by Na- and Zn-EMAA because in non-polar polymers, the interaction is increased in the order of  $\text{Li} > \text{Na} > \text{K}$ , as stated by Hara A and Eisenberg A [18-19], which is inversely proportional to the size of the counterions. It is well-known that in the case of ion-dipole complexes involving small molecules the stability of the complex increases with decreasing ionic radius.



**Figure 2** show shear viscosity vs shear rate of blend PA6 80 : LDPE 20 with compatibilizers e.g. A) E-MAA , B) Na-EMAA at 1.5 phr, C) Zn-EMAA at 1.5 phr, D) Li-EMAA at 1.5 phr

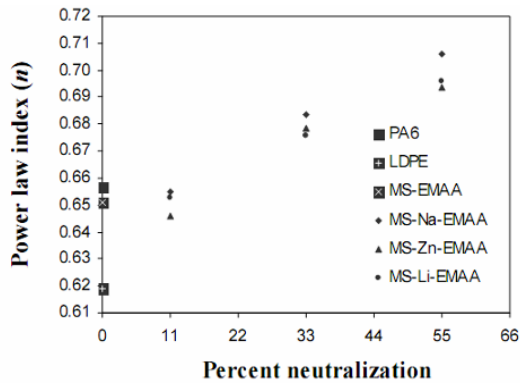


**Figure 3** show shear viscosity vs shear rate of blend A) PA6 80 : 20 LDPE compare all compatibilizers at 1.5 phr B) PA6 20 : 80 LDPE compare all compatibilizers at 1.5 phr

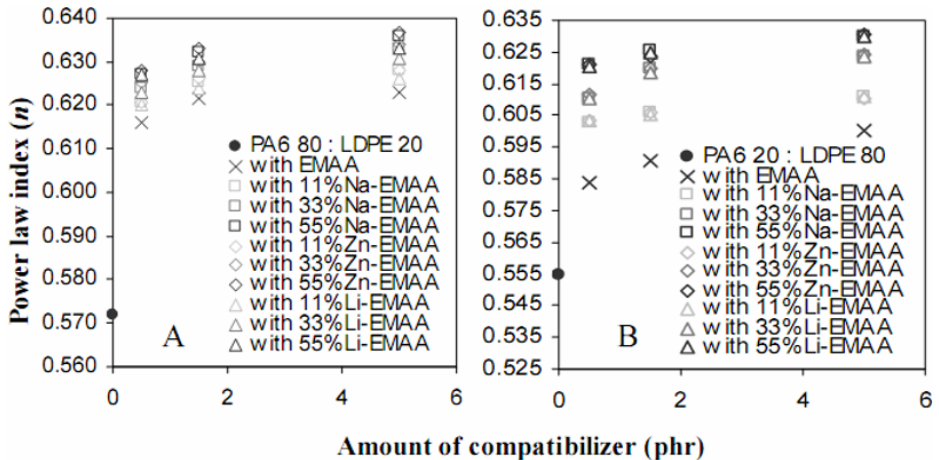
#### Power law index ( $n$ ) of blends

$n$  values shown in Figures 4 and 5 were all less than 1, implying that these melts were pseudoplastic.  $n$  values of the compatibilized blends increase with increasing the amount of compatibilizer; i.e. the material becomes more Newtonian. This result can be explained; an increase in the compatibilizer would be expected to make the polymer more viscous due to more interaction. It should be noted that, in Figure 5, the binary blends are found to be incompatible and they show a large drop in  $n$  values. However, the blends with compatibilizers exhibit high power law indexes closed to that of their major phase. This suggests that the compatibilizers function properly to

enhance compatibility between two polymeric components such that the flow behavior of the major component can be restored; i.e. the compatibilization recovers more entanglement and thus makes molecular orientation more difficult. In other words, for the compatible blends,  $n$  should increase to be closed that of PA6 in high PA6 content and that of LDPE in high LDPE content. The increase in  $n$  matches that of viscosity with respect to cation type, i.e.  $n$  is the largest for Zn-EMAA followed by Na-, Li-EMAA for the high polyamide content materials, and the highest for Li-EMAA for the low polyamide content materials. The behavior with respect to neutralization level is also similar to the shear viscosity, the power law index increases more abruptly at neutralization levels of 11% and 33%.



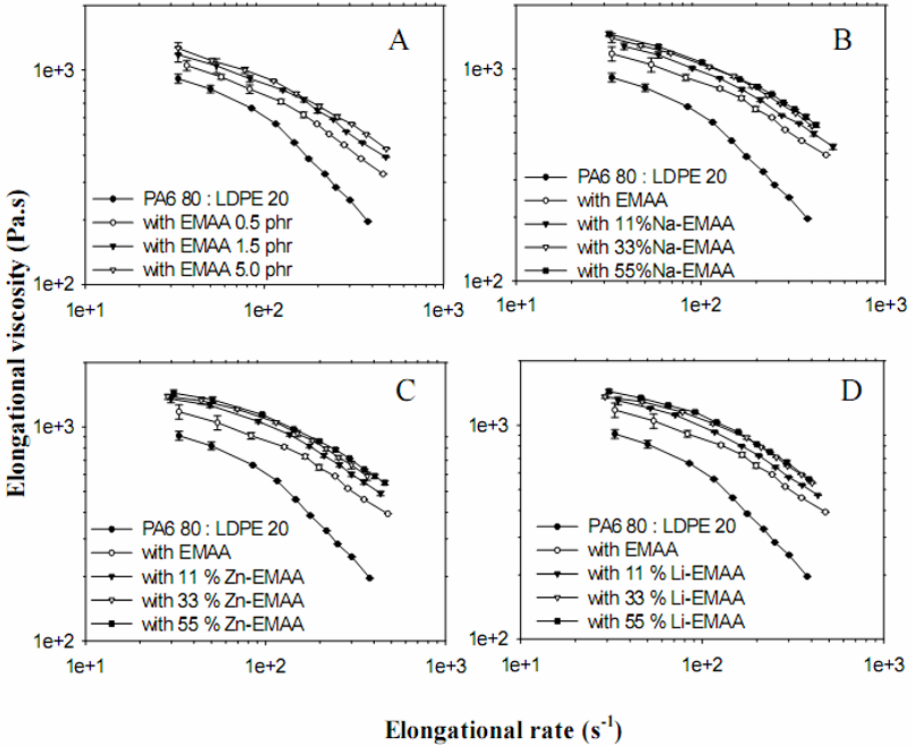
**Figure 4** show the plot of power law index vs percent neutralization of raw material and master batch



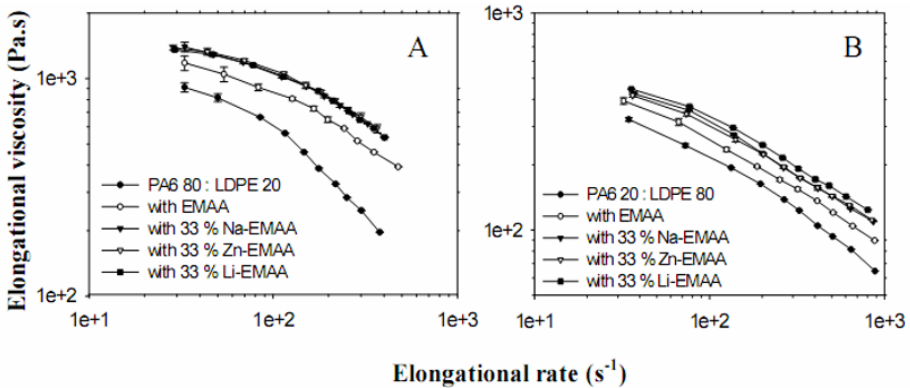
**Figure 5** show the plot of power law index vs amount of compatibilizer e.g. A) PA6 80 : LDPE 20 B) PA6 20 : LDPE 80

#### *Elongational viscosity of blends*

Elongational viscosities are shown in Figures 6 and 7. A drop in elongational viscosity with increasing elongational rate occurs, as it does with shear measurements. Both



**Figure 6** show elongation viscosity vs elongation rate of blend PA6 80 : LDPE 20 with compatibilizer e.g. A) E-MAA , B) Na-EMAA at 1.5 phr, C) Zn-EMAA at 1.5 phr, D) Li-EMAA at 1.5 phr



**Figure 7** show elongation viscosity vs elongation rate of blend A) PA6 80 : LDPE 20 compare all compatibilizers at 1.5 phr B) PA6 20 : LDPE 80 compare all compatibilizers at 1.5 phr

effects are due to chain alignment in the flow direction, and a reduction in entanglements. Introduction of compatibilizer in the blends makes the blends more compatible; as a result, LDPE branches can be expanded in the matrix (for 80/20 PA6/LDPE blends) making more entanglement; i.e. branches of LDPE make the



alignment more difficult resulting in an increase of elongational viscosity. The same type of effects occur with respect to cation type; with high polyamide content materials zinc is the most effective cation at increasing the elongational viscosity while lithium is most effective for the high olefin content materials. Unneutralized EMAA is clearly the most ineffective material; but there is an increase as compared to the blend without any compatibilizer. Finally, as with shear viscosity, the increase in viscosity at identical compatibilizer amounts increases with increasing neutralization level, and the increase is much larger for 0 to 11% and 11% to 33% as opposed to 33% to 55%.

## Conclusions

The effect of compatibilizers on melt rheological properties, i.e. shear viscosity, elongational viscosity, and power law index, of PA6/LDPE blends were studied. Four types of compatibilizers, EMAA and its ionomers (Li-EMAA, Na-EMAA, Zn-EMAA) with different valence, size and neutralization level were used. The blends show improved melt properties by the ionomers over EMAA revealing the stronger interaction of the counter ions to PA6 than the carboxylic groups in EMAA. It is found that the change in shear viscosity due to the ionomers was more obvious in the low shear rates than in the high ones. Both shear and elongational viscosities of the blends increase obviously with amount of compatibilizers and neutralization level, respectively. Nevertheless, the effect of counter ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ) in the ionomers on the melt rheological properties of the blends is less significant than amount of compatibilizer and neutralization level. However, it is found that Zn-EMAA gives the largest shear and elongational viscosities for the PA6-rich blend while Li-EMAA gives the largest viscosities for the LDPE-rich blend. Power law index of the blends are lower than unity suggesting the blends are pseudoplastic but the indices increase from 0.57 (for 80/20 PA6/LDPE) and 0.55 (20/80 PA6/LDPE) to 0.64 and 0.63, respectively, as the amount of compatibilizer and neutralization level increase. This reveals strong interactions of ionomers and PA6 as well as ionomers and LDPE to retard the shear thinning effect.

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